Theory of Group for Physics Applications
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Lecture – 23
Character tables & molecular Applications – I

So, now we continue with the things we were doing last time, some of it let us restate the abstract things and then these two lectures are quite nice. So, I hope to rely on them ok.

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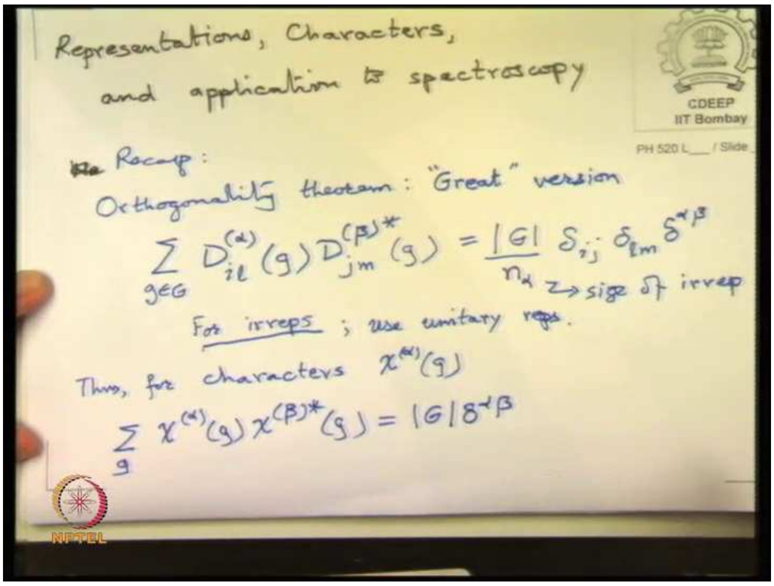

So, now the title for today's lecture is representations, characters and applications to spectroscopy. So, to just recap slide somewhat what we were doing last time, we have the orthogonality theorem.

Let us write once the orthogonality theorem in its most general form based on which because of for deriving which Schur's proved his lemma. So,

$$\sum_g D^{(\alpha)}_{il}(g)\, D^{(\beta)*}_{mj}(g) = \delta_{ij}\,\delta_{ml}\,\delta^{\alpha\beta}\frac{|G|}{n_\alpha}$$

So, this is the Great one indeed it deserves that name. So, this is size of irreps. So, this is for irreps α. So, the theorem of course, applies to irreducible representations and then the derived once from this and we use unitary reps and from this we derived the related the relation for characters, $\chi^{(\alpha)}$(g); we have the relation sum over g but then we can we know that the characters are same for all the elements in a class and we have already discuss the geometric meaning of a class, there essentially elements that do the same thing, but are their starting points are different that is all.

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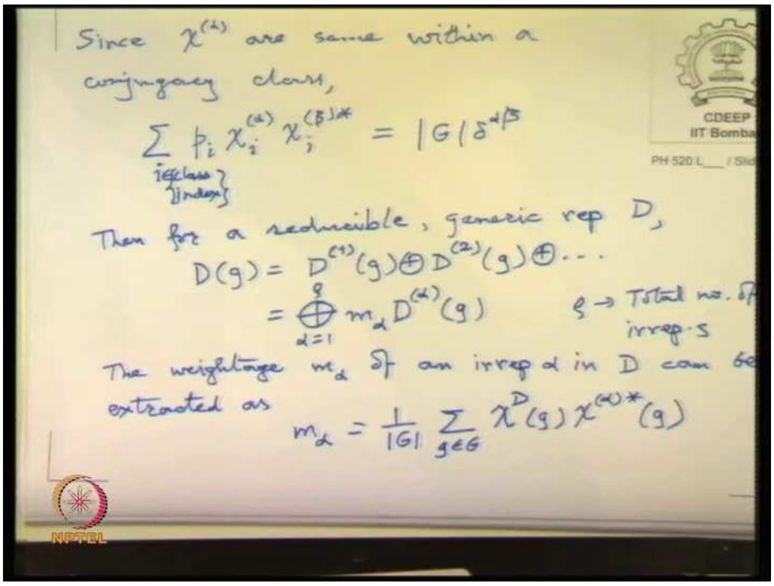

So, since $\chi^{(\alpha)}$(g) are same within a conjugacy class, we can also write this out as p_i, where this is the number of members in the class i and now we do not sum over g anymore.

So, this summation was over g, but now we simply sum over classes, i index is the class actually. Then we learn from this that for a reducible representation which we just called D, such that D is direct sum in linear algebra sense of some standard way of listing irreducible representations, which we sometimes write symbolically as $\sum_{\alpha=1}^{\rho} m_\alpha D^{(\alpha)}(g)$ and ρ is total number of irreps distinct irreps of course, right. So, from this we can deduce that the weightage, m_α of an irrep alpha in D can be extracted by using the orthogonality. Take the characters in the representation D whatever it is and then multiplied by χ^*, project it out onto the representation α and sum over all g that gives the weightage of the representation α in it.

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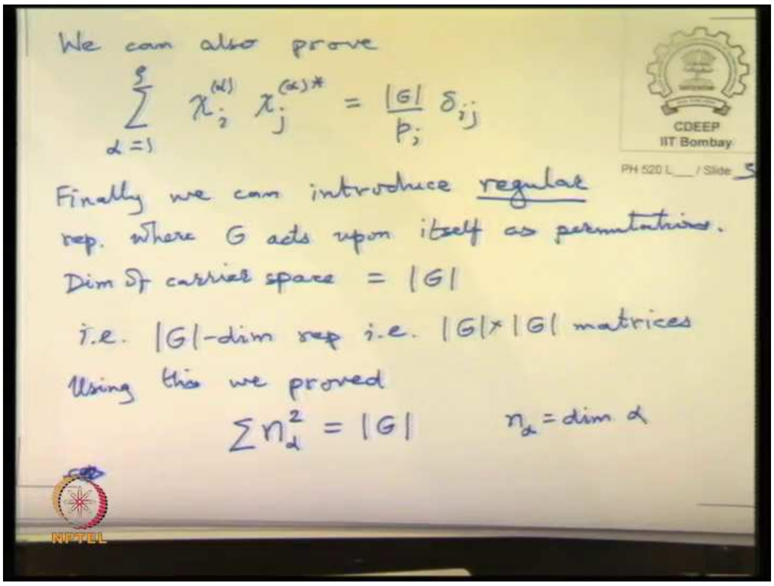

We also had proved that there is another kind of orthogonality relation,

$$\sum_{\alpha=1}^{\rho} \chi^{(\alpha)}(g)\chi^{(\beta)*}(g) = \frac{|G|}{p_i}\delta^{\alpha\beta}$$

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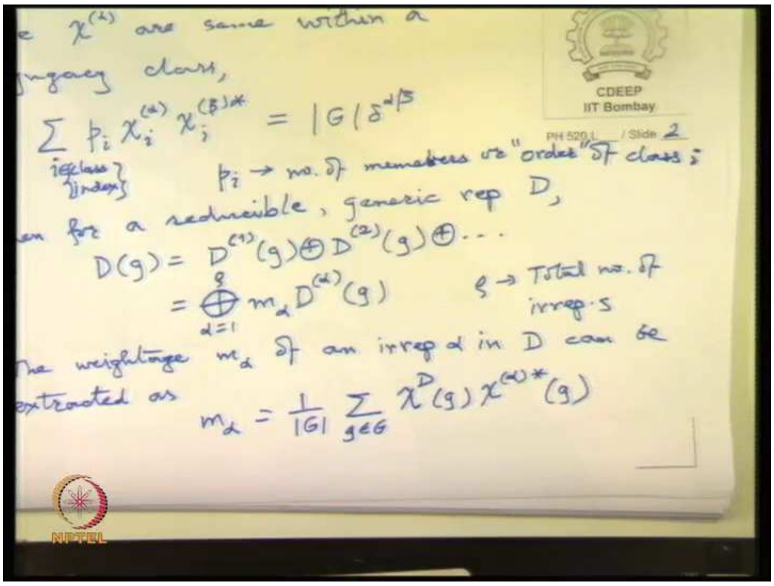

It is called order of the class, the order of class i is p_i then we have another kind of orthogonality where we also get this. The up short of all this is that we have very strong constraints on the number of classes we can have an the number of irreps we can have. And then there is a clever construct called the regular representation where G acts upon itself as permutations. So, dimension of the carrier space, what is the carrier space? So, the carrier space on which g is realized is g itself. So, it is obviously, a G dimensional representation.

So, G dim representation i.e. again I want to emphasize |G|×|G| matrices. When somebody says irrep of size n it means n×n size matrices. Now one thing we learnt was that in the regular representation identity is the only one that as non zero characters and so I will not repeat all this, but using this once can prove we proved that $\sum_{\alpha} n_{\alpha}^{2} = |G|$, where n_α is the dimension of the irrep α.

So, some square of the dimensions has to add up to G. So, this is going to restrict number of classes and number of representations, not only that we had seen that the number of times a particular representation is contained in this regular representation is exactly equal to the size of that representation. So, you can see last times lecture and we had proved all this.

Now today I want to take up uses of this in chemistry and I could have done this myself, but I find some really nice slides on the internet. So, this is actually some introductory course in chemistry.

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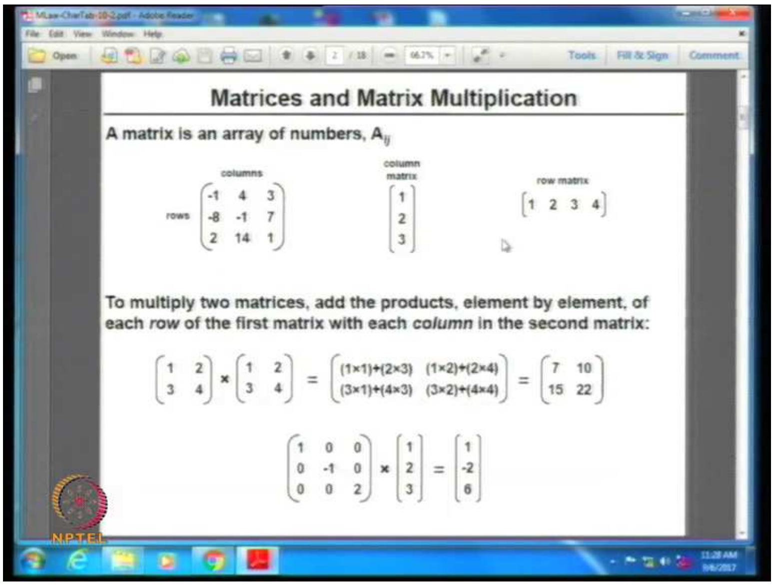

So, of course, the slide starts nicely by telling you what is the matrix, that is nice.

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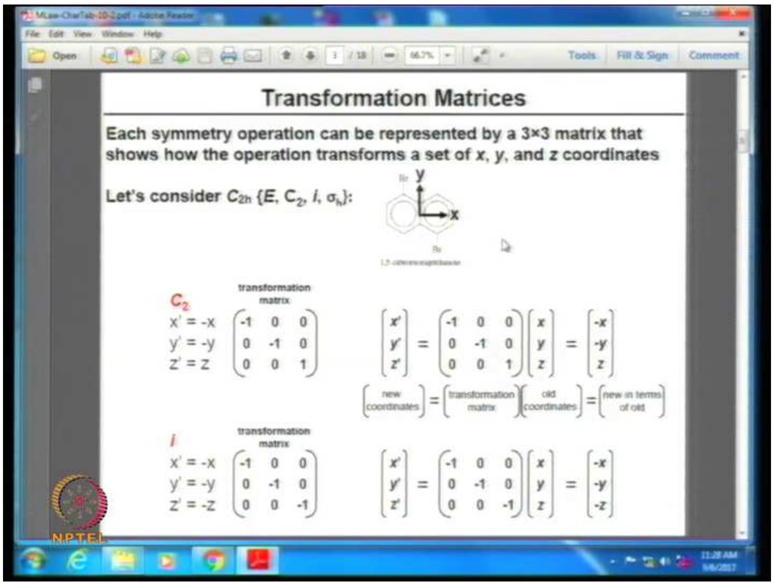

But then it quickly goes into complexity saying that, if you have a molecule like this. He is going to consider 3 dimensional case. So, in the quiz we just gave this ellipse in the plane and just worried about its transformations within the plane, but once you have a molecule although the molecule is planar; there is the z direction because the atoms are not actually points. So, if you just make an idealized figure, which is planar then it is fine, such molecules are called planar, but indeed you can flip the z axis and it has a meaning because the atoms are some fluffy things which go upside down.

So, for this these elements are identified; E which is identity, C_2 is just because their bromine singing here you can only do a 180 rotation, then there is a full space in version which is or sending x→-x, y→-y, z→-z and finally, there is σ_h this is what we would not consider if we have an idealized planner figure, but here if you ran the plane in the plane of the molecule, there is a reflection symmetry about that. So, there is a z→-z is a separate symmetry. Using this C 2 is identified; so, this is x, y and z axis. So, the C_2 is just 180 rotation so, it is -1, -1, this is 1 and the this is inversion a (-), (-), (-).

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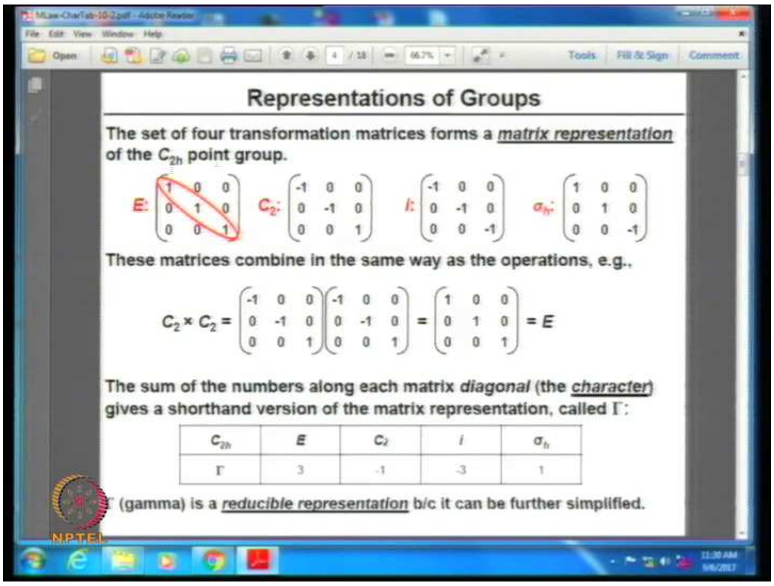

Now, points out what are characters and that there is a the Obey group law, but let us look at the bottom table. Here we should read this row carefully; here is a particular representation that is being presented identities of course, $\begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix}$, C_2 is where x and y are exchange, because it is a 180 rotation then there is full space in version and then there is a z axis reflection the σ_h plane ok.

These together form a group and you can check because $C^2 = I$, $\sigma_h^2 = I$ and so on. So, for this particular 3×3 representation if you begin to write the characters, then for the identity we will write 3. For the C_2 we will get a -1 because it is trace of this, for the inversion we get -3 and for the reflection plane we get 1 ok. Now this gamma is reducible and one of the ways of seeing it is that after all it is just $\begin{bmatrix} [1] & 0 & 0 \\ 0 & [1] & 0 \\ 0 & 0 & [1] \end{bmatrix}$ dimensional. So, it is block diagonal with each block just containing one element.

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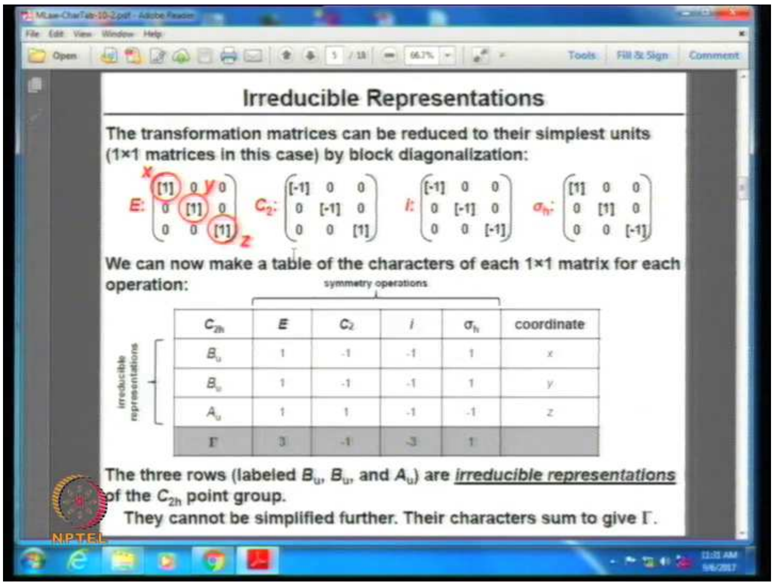

So, this is clearly a reducible representation and that is what is identified essentially if the each of the axis is treated more or less independently. So this square bracket identify the single representation in this, and we can write out the character table of this. Now there is a notation of these B, B and A which will be explained soon. This is actually guess work and we are going back and forth a little bit. Just to repeat we know that this is an abelian group. So, every element is in it is own conjugacy class right and so, there are four conjugacy classes, correspondingly we know there should be four independent irreps right, there has many conjugacy classes as the irreps. But the way we are breaking up this representation, we are getting only 3 of them, but whatever they are we are writing them down.

So, 1, -1, -1, 1, 1, -1, -1, 1 then the second row is 1, -1, -1, 1 etcetera. So, these are just writing this out and showing how the reducible rep is just composed of this. Each of these occurs once in it, the m_α that we were deriving is only one in this case. Mind you this is a very very simple example, but do not be fooled by it because it gets complicated very quickly.

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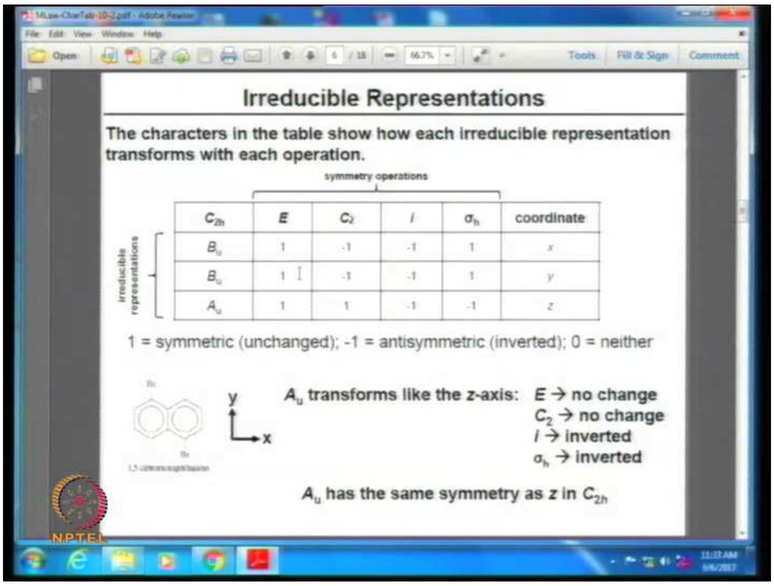

So, this is written out character show each irrep and how it transforms and points out that, this is the other thing from chemistry and from physical point of view; this row essentially captures property of x coordinate, this row captures property of y coordinate. And the other thing is that if this particular axis x, what is its fate under each of the elements that you have to see. And if nothing happens to it then we get a character 1 and if it gets flipped then we get a character -1.

And if it is neither then we get actually 0 ok. If it is not a definite that is the rule about characters. So, you will see how chemist work this out they are not going to worry about Schur's lemma ok. So, they will just figure out from here that oh you just assign character 0, if nothing happens to it. Now in this case each of the elements of course, does touch these symmetrically or anti symmetrically. So, this is what happens for and now he has introduced one more representation. So, here it is explain the A_u transforms like the lowest one, transforms essentially like z axis. So, the things that do not change, we get 1, the things get flipped we get -1, if actually it neither was symmetric nor anti symmetric then we would have to put entry 0.

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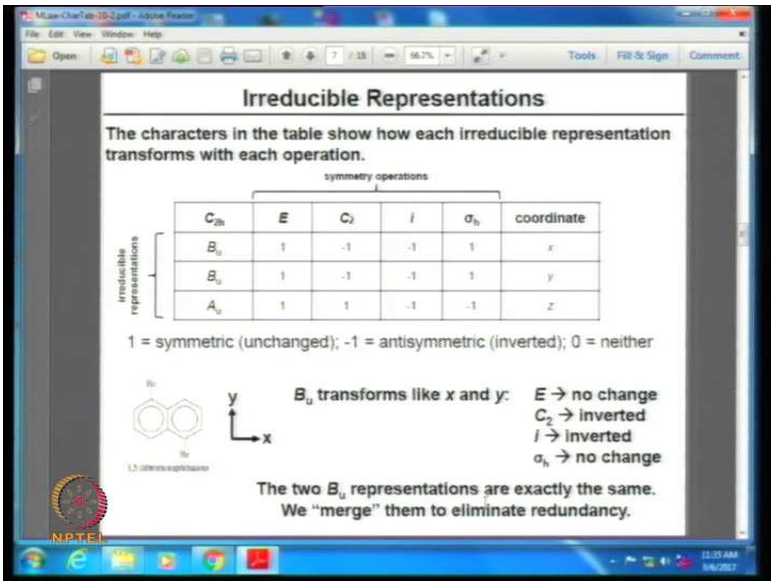

Now, so A_u has the same symmetry as z in C_{2h} and the 2 B_u representations are exactly the same and we can quote merge them. So, they actually reduced only one particular representation, this is because the 2 are in the same conjugacy class. So, they are not giving anything new.

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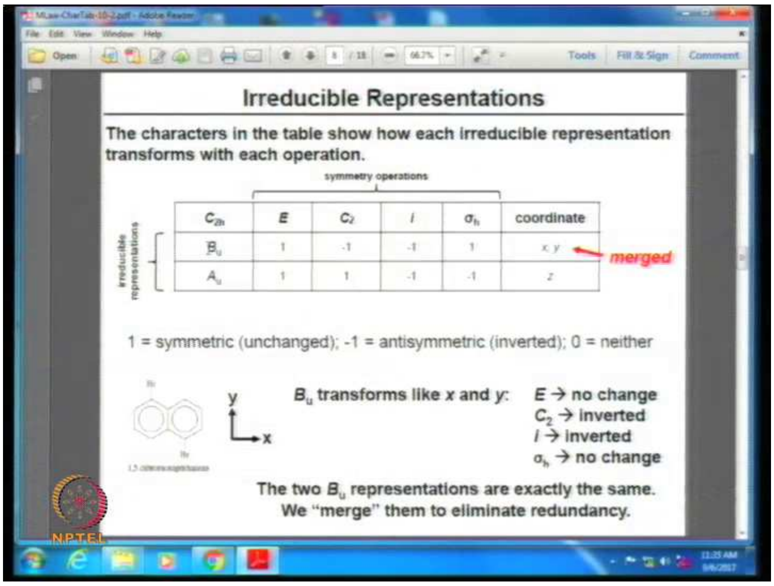

So, x and y these are merged. So, this is called B_u and this is the z one is called A_u. This terminology is A, B and E and we are not going to really worry about it, but you will see it listed all the time. What is interesting to worry about is the fate of which coordinates are covered by this particular representation and fate of this is captured by this representation. Now, but we know that we do not need two more rows here and list of complete irreps.

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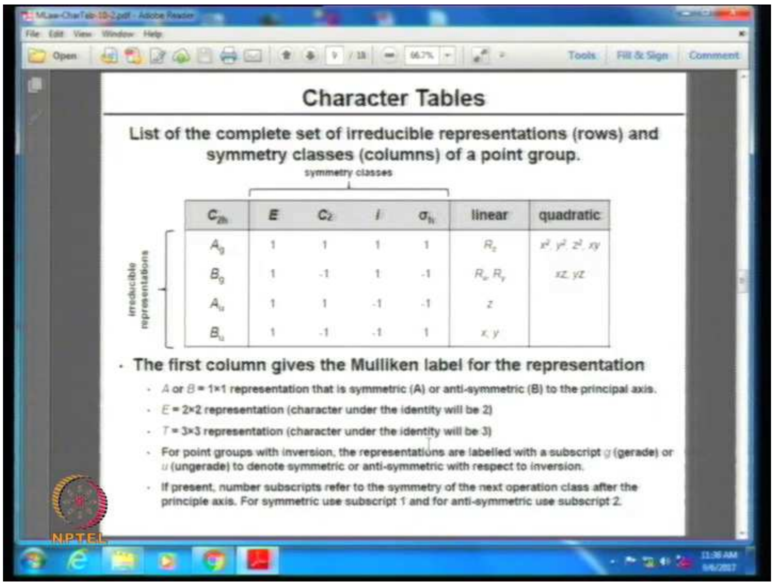

So, here in addition to A_u and B_u, 2 new things are added A_g and B_g. The A_g is the trivial representation everything is represented by just 1. Remember that the trivial rep is always one of the irreps that is the very important thing to remember and then this you may ask where the hell did B_g come from and even if you knew know geometry or visualization, we can get it by orthogonality, because I know there are 4 classes I have 3 representations in hand already, I have to guess the fourth one. Well it has to be a choice of +1's and -1's such that it is orthogonal which each of the other 3. So, automatically we get these signs because right if you just work it out it will come out like that.

So, this point number 4, this subscript u and g as essentially German word origin. For point groups with inversion, the representations are labeled with a subscript g, which means gerade or u which means ungerade, to denote symmetric or antisymmetric with respect to inversion. So, whatever that is I will not elaborate on it further, but that is the way of that is the nomenclature used.

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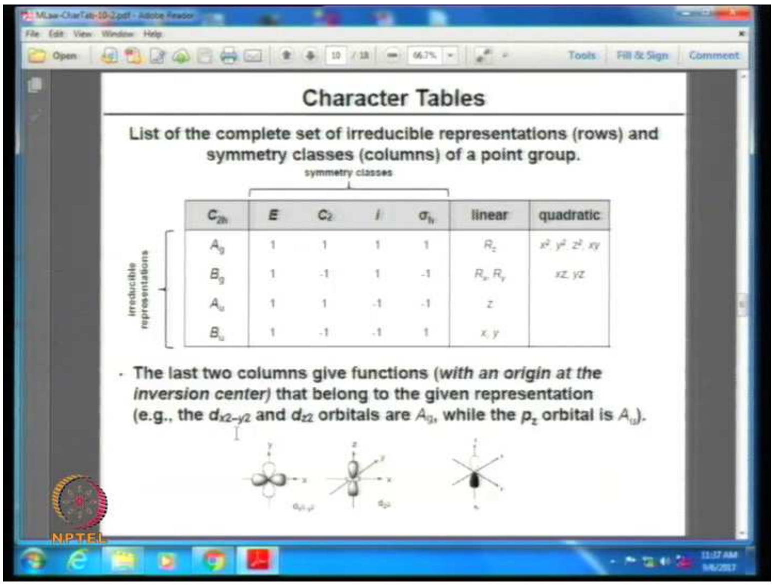

So, now the more important thing from chemistry or physics point of view are that he has added these 2 columns. So, first one was we already had this A_u and B_u and they were properties of z, x and y but these 2 are also properties of rotations R_z and R_x R_y.

So, identity the trivial representation is property of rotations about z axis whereas, rotations about R_x and R_y themselves get affected by this element B. So, they are here, they share essentially what happens to the xz plane and to the yz plane. So, R_x if you rotate about x axis, you rotate y and z so, that is this z or you rotate about y axis, which means you rotate x into z. So, this new classes that we got, the new irreps we got were such that, they have specific property with respect to the quadratic things. Particularly the trivial one leaves x^2, y^2, z^2 and the product xy individually invariant whereas, the xy plane, yz plane is left invariant by this second class of irrep.

And there is a direct correspondence of R_z then you get x y z, x y, x y z and y z x this will be important a little bit later. So, and this is how they simply read of chemist just read of by looking at a molecule, what the character table is in by guess work and by orthogonality figure out the whole table. So, the last 2 columns give functions, with origins at the inversion centre that belong to the given representation. So, for example, this is some typo actually it means d_x^2, d_y^2 or this is the d orbital x, x^2, y^2 and d_z^2 orbitals are A_g, in the p_z orbital belongs to A_u. So, this is p and these are high level there are d.

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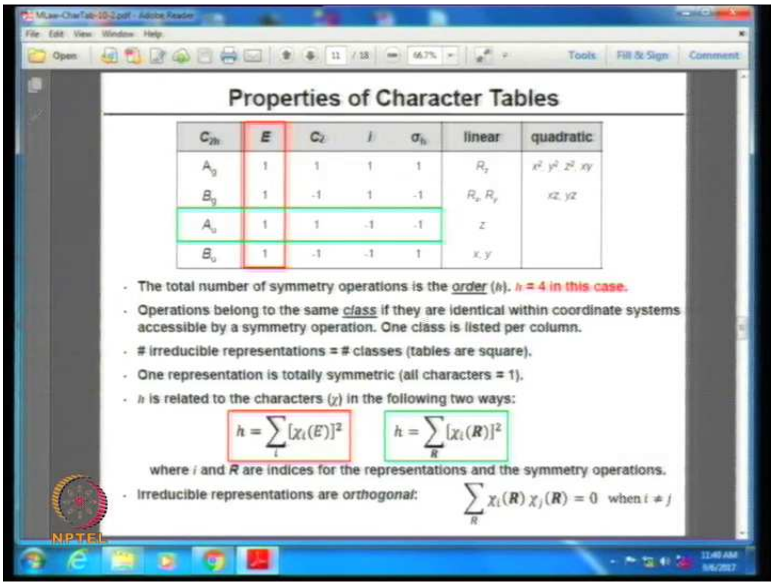

Now, is coming back to actually emphasize what we just did, the tricks we played and also yeah is just checking without proof the results we have proved and we have proved this, $\sum_i |\chi_i(E)|^2 = h$, but there is also another interesting result which is that sum over R. We proved a preliminary version of this, but not this particular result, we did proved that sum over all α gives you δ_{ij}. So, if you take square of that then you will actually get this result.

Here h is the order of the whole group ok. So, he is just verifying that if you take any particular. So, χ(E) =1, χ^2 sum of these has to be equal 1 and sum over for a particular i fixed value of the, it is what which way is it running. So, there is a i labels irreps and so, that orthogonality properties basically verified here and he also points out which we already noted.

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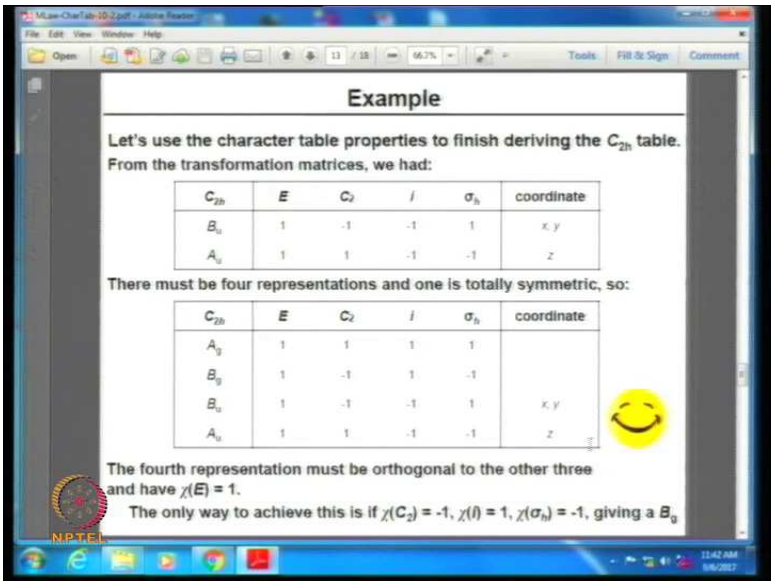

So, the bottom 2 are already guessed first, I mean occurred naturally you wrote a 3D representation and these 2 occurred there.

We already know that the trivial one has to be there and he is asking how do you get the middle ones and you get them by orthogonality. So, that is what is he is proving and happy that it can be done good.

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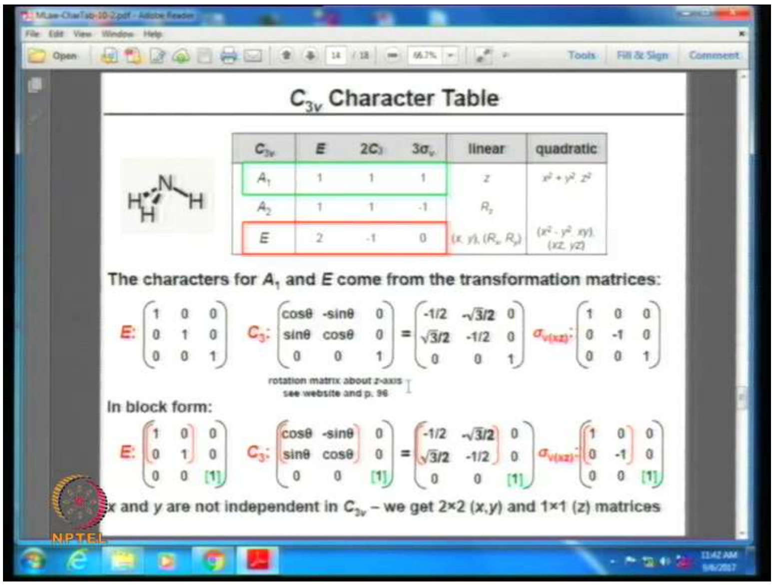

So, now we come to a more interesting example, the previous one simply had only 1D represents, but now we also have a 2D representation. So, is just one degree more complicated and this is going to be C_{3v}. C_{3v} means 3 fold rotations and vertical planes. So, the v are the planes that contain the axis of rotation. So, v plane that contains the nitrogen and one of the hydrogens at a time you have a reflection symmetry.

Now, in this case again you can begin with the quote organic representation that you would think of by writing a 3×3 matrix. You would have the C_3, there will be 2 C_3 elements because 120 and 240 degree rotation. So, they would have this form cos$\boldsymbol{\theta}$, sin$\boldsymbol{\theta}$, which 420 just boils down to this matrix, and then we also have the vertical axis let us say which contains the x and z plane then it changes the sign only of y ok. So, these are firstly noted as properties of specific elements. So, there are 2 different rotations about the z axis, but they both belong to same conjugacy class, because each of them is a scaring out of 120 rotation relative to the previous thing.

So, they can be related by a conjugacy relation, they would belong to the same class. Similarly the 3 reflection planes are all doing geometrically the same thing is just there it is this plane or that plane and in fact, a rotation the z axis rotation can rotate the planes into each other. So, they all belong to the same class. So, we write the class name by this geometric suggestive thing and the number of elements in it C_3 is the threefold rotation 2 $\pi/3$ rotation but there are 2 of those. So, we just bothered to list only the classes and not the whole group. The whole group will have 6 elements, but we write only the classes directly and here he has taken only one member of the representative; identity this C_3 rotation we took only that 120 not the 240 and the character is 0 and this one will have character this one will have character +1 ok.

We have to come back to this. So, by the way there is a slight ambiguity, E to denote the identity element, but E is also used by chemist in the old German notation the G and U there is also a thing called E. So, the irrep is also called E for some reason ok. But now he points out that this generic 3D representation that we could think of is; obviously, reducible right because it has 2×2 blocks and it has a 1×1 block of the z axis. So, it is a reducible representation. Is it clear? And so, here shown by drawing this red matrix delimiters around the upper matrix and then green thing lower. But the 2×2 cannot be reduced any further because the operations are mixing x and y axis. So, there is no way to reduce it any further.

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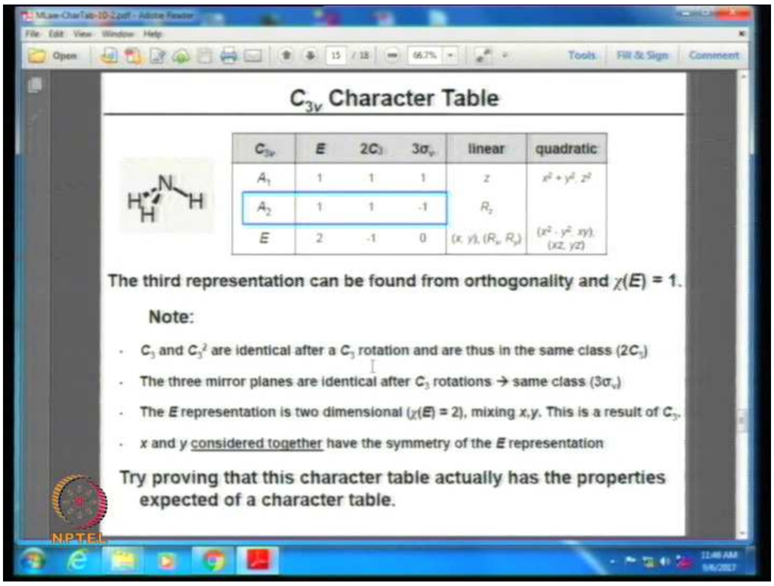

And therefore, draws up the character table, the third representation we find by orthogonality. So, these 2 A_1 and E are over here already. A_1 is the green box basically is the lower one that split off and it was actually trivial nothing happens to the z axis. So, it is 1 1 1 1 1 and this one will be called A_1, but there are only 3 conjugacy classes. So, there is a middle row to be filled, you can get it by orthogonality because you just have to multiply this with this way.

So, you will get 3 relations, which will determine the 3 coordinates. So, that is what he says here the third representation can be found by orthogonality and the fact that the χ(E) =1 that it is a one dimensional representation ok. So, additionally says try proving that this character table actually as the properties expected of a character table, but that property is actually orthogonality, but you can check the column wise orthogonality as well.

But what is important to note also is that, the class A_1 and A_2, under A_1 the property of z and property of x^2, y^2, z^2 is captured. Under A_2 which we have to introduce by hand essentially captures the R_z, which I would think captures the xy plane, but that is not true. So, the E, third one where the character of identity is 2 and this is the character of this rotations (-1/2)+(-1/2) = -1 and 3 is 0 because as you remember if the element that you are considering has a definite property that we get a minus sign, if the element being considered as no definite property then we get 0.

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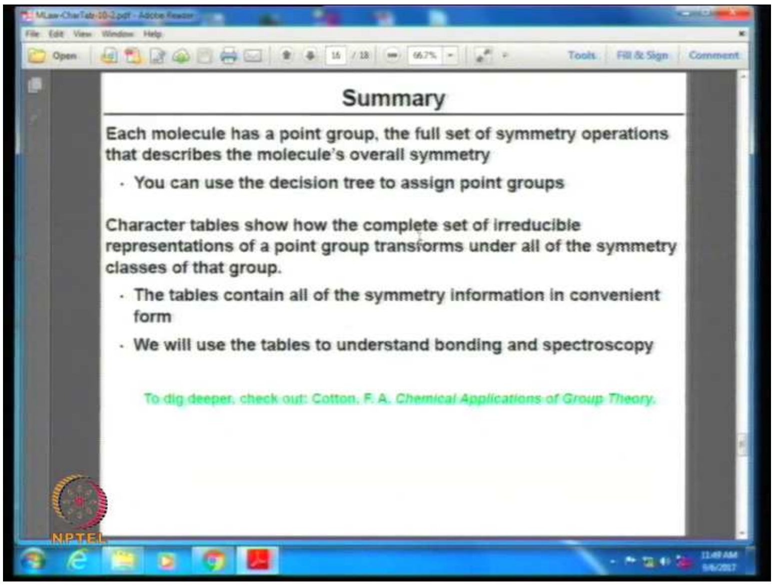

So, each molecule has a point group and you can go down decision tree, the tree is there in that K Horns thing and first part there for is to identify character tables ok.

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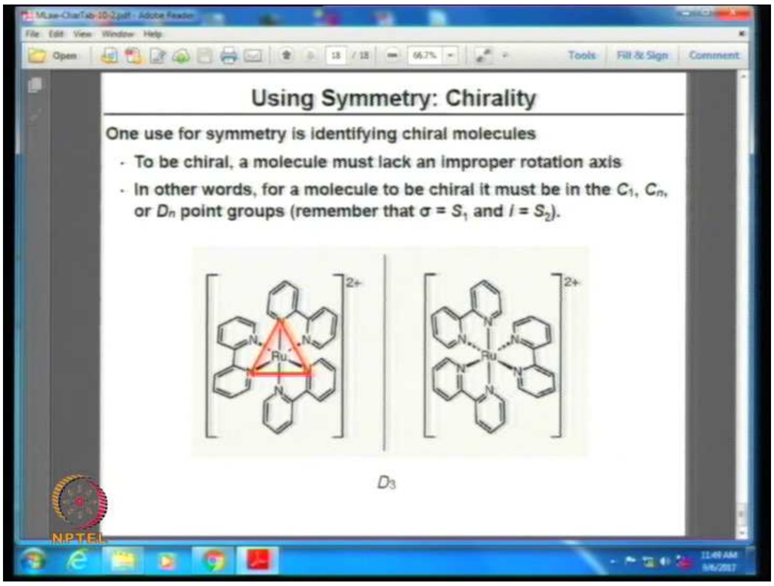

So, this is end of this part, which is quick and rough way of building up character tables.