Symmetry and Group Theory
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Lecture – 31
Practice Session: Review of Some Questions and Solutions

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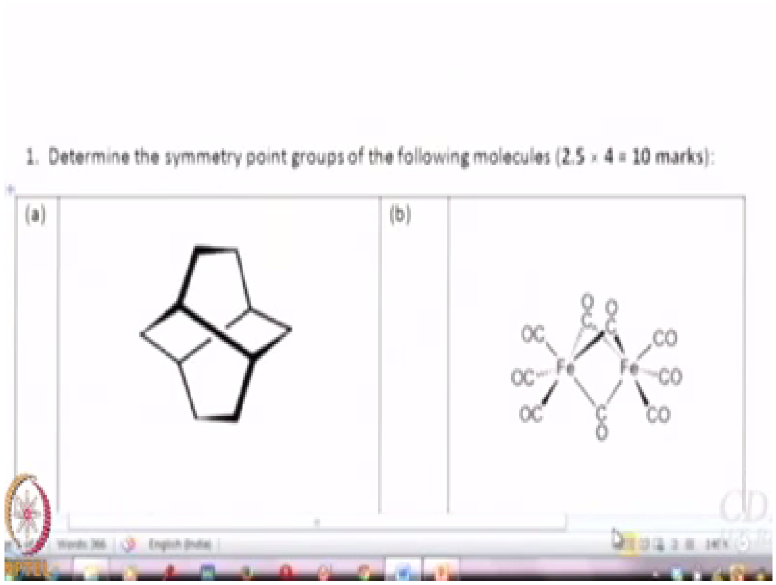

In the last few classes, I might have given the equation that itself a mathematics course, it is not, it is definitely a chemistry course, symmetry course so, let us use a little bit of that, okay and then we will come back but before anything, I like to go through the mid some questions, in the first question, I have not corrected the answers sheets yet but the first question is convinced me that we need more practice in this point group business.

So, I am going to give you one more assignment on point groups, please work them out and one day beyond these regular class days, we can have a tutorial session as Vishnu as suggested and we can just discuss those answers but you really need more practice in this that is what I thought that this is easy, but you need to work out may be 50, 60 more point groups then you will be masters.

Let us discuss what we had, what is the first one, what is this, tell me? Cd2, right, where is the C2 axis, this is one C2 axis and joining these two; is there is C2 axis, what is the C2 axis? So, what is the position of the perpendicular C2, that is what I am asking, the vertical C2 is quite obvious in between; through which plane; perpendicular to the plane of the slide means, you are saying joining these 2, right.

Is that C2? This symbol is looking like an x, if I join the front with the back, is there a C2 axis or not, so what are you joining then, and we joining the midpoints of the bonds, right, so if you join the midpoints of these bonds, this one and this one, will there also work? No, this one and this one, will it work, what are you join, there is no atom here, this is the midpoint that is what I am asking, you should join the atoms.

If you join the atoms, is there a C2 axis, sure, what is this molecule called by the way, do you know, is called twist end, so you can see the twist, right full of twists, yes, it is a twist end, all right, so these are 2 C2 axis, any other symmetry operations; symmetry element, no, right, okay, so how many marks for this; 2and 1/2, right, so the way we are going to grade is; if you identify all the symmetry elements correctly and do not write anything extra.

And get the point group correct, then you get 2 and 1/2, if you write the correct symmetry elements and get the point group correct but innovative enough to identify more symmetry elements that other mortars cannot see, then you get 2, okay and if you do not get the symmetry point group correct but I have got at least some correct symmetry operations, so you might have whether you get extra symmetry operations or not, then you get 1.

It is very difficult to get 0 out of 2 and 1/2 okay, right. Second one; it is d3h, the second one d3h, do you see the C3 axis, where is the C3 axis, joining the 2 E ends ends, is that C3, check, CO, CO, CO and this is CO, CO, CO, then again, in the middle here, CO, CO, CO; C3 axis, all right, now believe me, okay, do you have perpendicular C2 axis, where are they? Passing through 2 carbons, then I will get C2, is that right.

(()) (04:59) infinite number carbons, is not it better to say joining the O and the C, so it is allowing the CO bond, is not it, allow the beijing CO bond that is a very specific way of saying it, is not it, allowing the CO bonds; allow the beijing CO bonds, so there are 3 such, so those are the C2 axis, all right, Anup, you see C2, very good, plane of symmetry, all planes will be like that, which one, where is the plane of symmetry and define the plane, 3 points make up a plane that is a 3 beijing carbons.

Or if you want to make it more interesting, the 3 Beijing oxygen; 3 oxygen in the Beijing carbonyl groups, whatever you want to say, the 3 CO bonds that is sigma. Is there any other sigma, where are those sigma's, there is sigma d, right, where are those sigma d; but do they matter in the nomenclature, they do not, right. So, you have C3 principle axis, we have 3 perpendicular C2 axis and you have a horizontal plane, it is d3h.

So, if you have written all these and nothing else you get 2 and1/2, if you have written all these and you have also discover some more C2 axis or some more sigma and all you get 2. In fact, if you have not written sigma d, I will give you 2 and 1/2, if you have got d3h correct, that is why you wanted, right. **"Professor – student conversation starts"** no, you have written what, sigma d, it is not a problem, it is a correct, right, so why you will be analyse for that.

But if you miss sigma d, I do not mind because after all finding symmetry point group was the question, okay, what about this, this one.

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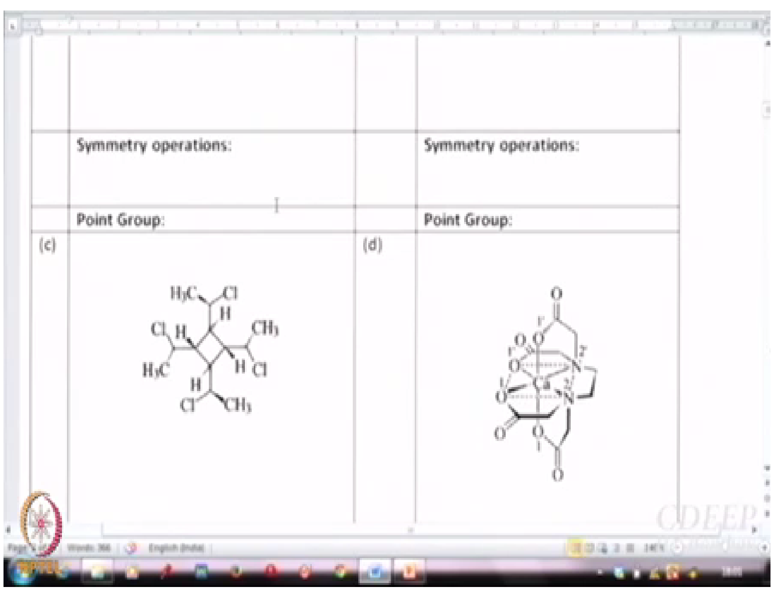

What is the name, does anybody know the name? I do not but which symmetry point you visit, looking at a first glance, I thought it is C4 because it has a square, is there a C4 axis, no, why not? You have after all this chlorine goes to chlorine, this chlorine goes to that chlorine, that chlorine goes to this chlorine, so why is this sort of C4 axis? The problem is with hydrogen and methyl groups.

So, if this not a C4 axis, what can it be? Is it a C2 axis, see this C; CCH3 is above the plane, this CCH3 is below the plane, so if you take the axis that is perpendicular to the square, then it does not give you a C2, sorry, what is that, that is C4 operation, so you turn it around CH3 goes to CH3, fine, this CH3 goes to this CH3 that also is fine, what about these H, this H is above the plane, this H is also above the plane, that is okay, this is below the plane that is below the plane, that is fine.

And what else this CH, okay fine, so which axis is it? Looks like it is a C2 axis right, is there any other axis or plane or anything, do I put 2 power into the C2's, where? Mid points of the opposite bonds, let us see, you are saying there are going to be C2's right, are they C2's, they are not C2's, they would have been C2, if the chlorine was here and if it was on the plane understand, so this is not a C2, understand what happens, if I perform a C2 about this.

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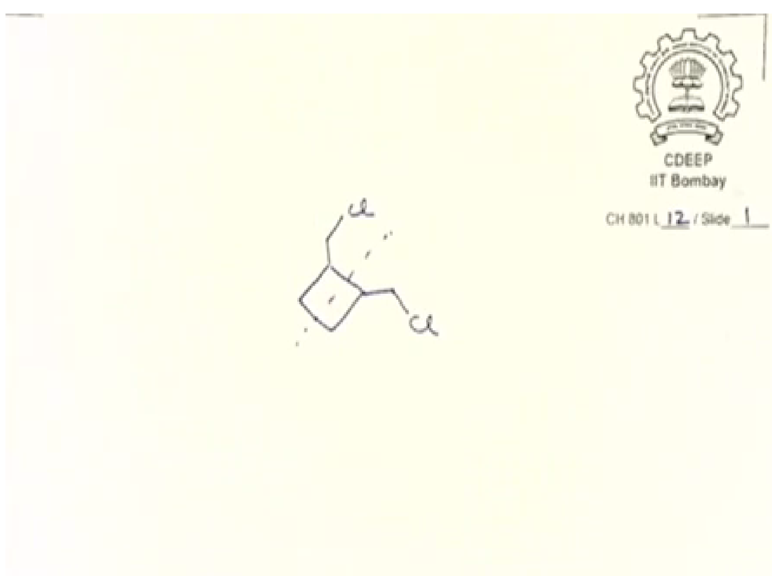

(()) (10:04) this, what you are saying is; you are saying this is a C2, while perform a C2 operation is not a symmetry operation, right, which lecture is in exam last time, 11 or 10, 12, all right, you agree that there is not a symmetry operation, that is not the symmetry operation then the other one will also not be the symmetry operation, so what will be have, we have C2, is there any plane, no plane, so you have C2, so which one we visit, okay, is there C2 as well as an S4.

And if you remember the algorithm, we have said that the algorithm comes handy only when you have nothing other than CN axis which also doubles as S2N axis, then the point may be is not CN, it is S2N, right, so which point we visit, S4. Now, this one, I put (()) (11:13) is 1, 1 dash, 2, 2 dash is be enough you can see, can you see, now tell me what is that, yeah, I took so much of trouble making it big an make it small again anyway, where is a C2 axis, through calcium of course and bisecting the OO bond and bisecting the C bond also.

Okay, bisecting the OO line, all right, and now I think you see it better because you see this, what is this, this thing as developed mind of its own, hmmm, okay, so see this is 1, this is 1 dash, this is 2, this is 2 dash, the problem is this is also 1, that is 1 dashed unfortunately that should have been 3, 3 dash, that would have been easier you understand, right, 2 and 2 dash will exchange place, this 1; equatorial 1 and equatorial 1 dash will exchange places, when you apply C2. **"Professor – student conversation ends."**

Is there anything else, any other symmetry operations, any other symmetry element, sigma H is not there, what about sigma v, this ONNO containing calcium the equatorial plane, is that a sigma plane, is that a plane of symmetry, no, right because this breach is from this nitrogen, this breach is from this nitrogen, it is not a sigma plane, is there; so what you find, you found a C2 axis, is there an S axis, S4 axis, No, so this C2, okay.

So, complicated molecules are simple point groups all right, you cannot imagine what kind of (()) (13:59) while photocopying the question papers, the colleague from organic chemistry came and said, what is this, why are you teaching organic chemistry, another colleague from inorganic chemistry, why are you dealing with all molecules, now what is; all molecules are physical molecules, there is no unphysical molecule.

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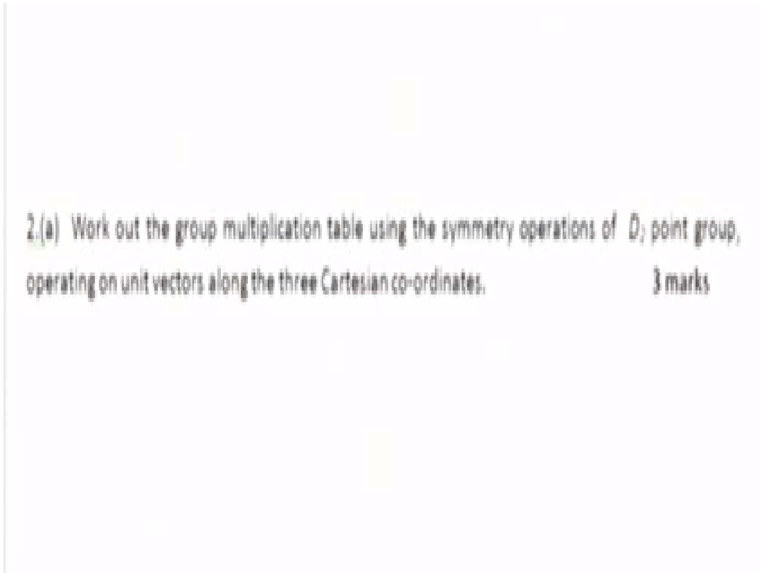

This was easy, work out the group multiplication tables using the symmetry operations of D2 point group operating on unit vectors along 3 Cartesians coordinates that was easy I hope, right. I do not need to go through this, you can work this out, actually, go about this question into 3 parts or 4 parts, second part was the sub groups.

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Identify the sub groups present, how will you identify sub groups, how many sub groups were there, what were the sub groups? So, you have to have distinct groups among the groups, there should be nothing outside the sub groups in the collection that you take, okay they have to be interrelated among each other, okay.

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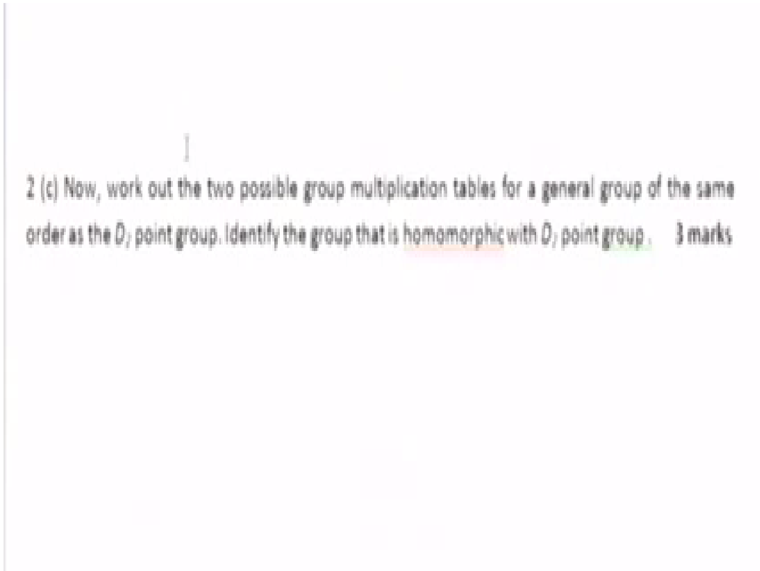

Now, that was the typo that I corrected here, D2, now work out the 2 possible group multiplication table for a general group of the same order as the D2 point group, what is the order of D2 point group? 4 and this is something we have done in class, right, so when you have 2 subgroups, one is a cyclic and the other is not, is not it, for H = 4, so that is all that you have to do and then homomorphism means exactly the same multiplication table.

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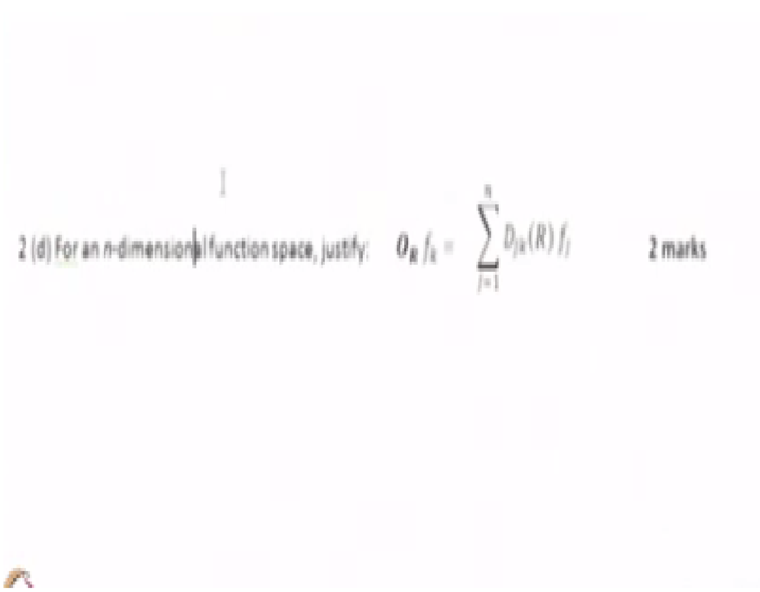

So, you have to compare this with that and do it and this is perhaps the easiest question, what was the next one? So, here for in dimensional functional space justify, OR fk = this, many people have written many things, all I have wanted was, I wanted you tell that this djkr is the transformation matrix operating on coordinates and the reason why I am using djk and not dkj is that when I write OR we are working with orthonormal function.

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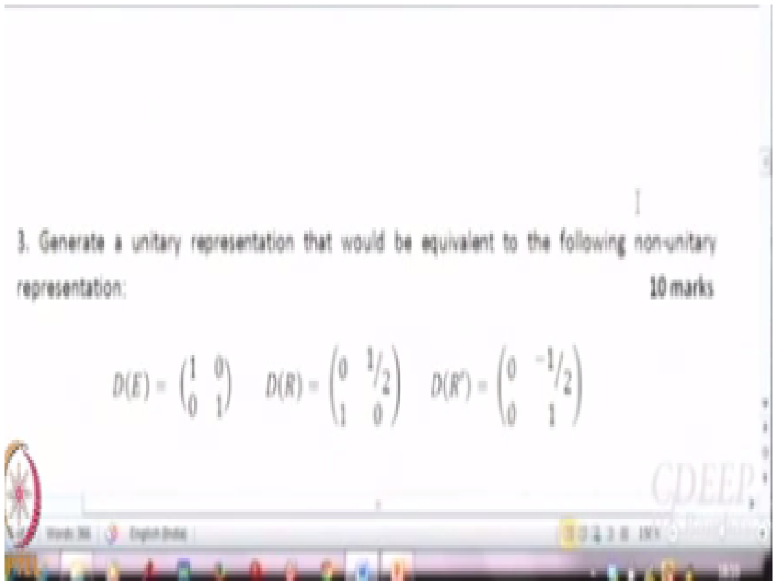

If you wrote that then I am happy, if you wrote something else that also makes sense then also I am happy, make sense in this context of course. Then, we had yeah this was the toughest question but there is a reason why I wanted to ask this and whoever is attempted this as actually made a smart choice, I think everybody is understood what I wanted from this, I have written down this recipe in the class before last hour in the last class, I wanted; class before last.

So, I wanted you to take this matrices, put the value in the recipe and go as far as you could, actually you can go all the way, who went, Anup, did you go, it is just that you get ugly numbers, you have any 0.44 square root of something like that but then, one thing to remember in case you go along in the middle, what is that you are dealing with the Hermitian matrix, so you could never get an imaginary number.

If you got imaginary number that means you went wrong somewhere, so whoever could go up to that and wrote and whoever is written after that that is the way I should proceed afterwards get full mark, no issue, okay. Now the reason why I wanted to ask you this question, after all your examination does not that is also a learning process, so what I wanted you to understand is 2 things.

First of all, we can actually plug in numbers and work these things out, point number 1. Point number 2 is that it is not necessary that you will always get very simple nice numbers, you do get ugly numbers, if you have to do things numerically that is why we do not want to do things numerically, all right that is why we want to still to develop the theory further, so that it will reach a situation where we will not get ugly numbers anymore.

See, now that we are working with character tables, you will see that things are very simplified, today, we will encounter as situation, where it is not all that simple with character tables. But even that is better than the square roots and all that you are getting, right, so this is the difference between the doing something numerically and doing something theoretically, many of you are going to do stimulations.

So, what you do not realise is that the computer does for you what you try to do in the mid some exam there, the computer consists all kinds of ugly numbers that you do not like okay, you want to do deal with numerically, you have to deal with these ugly numbers, okay, fine. Now, that was 3, 4; what is no 4, doing.

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This is what little disappointed that some people who had so much of difficulty because the point is I have told you what are there and that more or less we will write correctly but after that you should have been able to work out the character table. I told you to practice, right, so you will work out 2 more characters' tables today which are much smaller than TD but which have complex numbers.

So, I think everybody knows now to use these 5 rules to work out character tables. Now, here there are 6 marks, so even if you have not been able to work out the character table completely, you can get full marks, provided you have shown that you know how to you know the rules and how to use them and you write down the headings correctly and you have gone and you have got the mulliken nomenclature correct.

What are the mulliken nomenclatures for these symmetry species that you got? So here we encounter a 3 dimensional representation, 3 dimensional irreducible representations, there if you have got confused, I do not mind, because the thing is this 1, 2 is very well defined for one dimensional representations, for E and T, it is a little more, it is not impossible to figure out, you still look at the characters.

But there if you are getting T1 instead of T2 I am fine. Yeah that also has bases like your A1 and A2 but that is not something that we will discuss in very detail, so it is a little more complicated, okay, so and fine if you write T2 instead of T1, okay but that is also form the characters.

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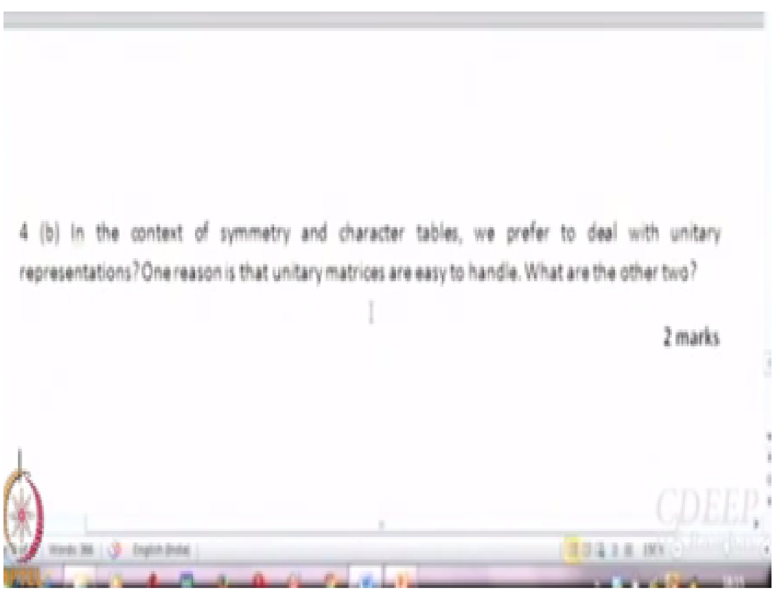

Now, 4b; in the context of symmetry and character tables, you prefer to do deal with unitary representation and what I must have said in the class at least 25 times is that one reason for doing that is that they are easy to handle, I wanted to know what are the other 2. So, you tell me what are the other 2 reasons? **“Professor – student conversation starts”** They deal with orthonormal bases sets, so yes, so it applies to orthogonality theorem.

What else, first of all; both answers came from orthogonality, first answer I expecting is this that then you can use the orthogonality theorem, the second answer is expecting is that yeah okay, you can expand a little bit on that we can always fix bases and go to orthonormal, that is right but I was actually expecting something else and that would come if you inspect the character tables little carefully.

What do we have in the character tables, what is written on the right hand side, x, y, z, Rx, Ry, Rz, right so on and so forth, so these are all orthonormal, these all from orthonormal bases, generally why is that we are studying all these, eventually you will see, we are going to walk with bases which are orthonormal in nature, even if you work with orbitals, orthonormal right, so that is the answer I was looking for the second one. **“Professor – student conversation ends.”**

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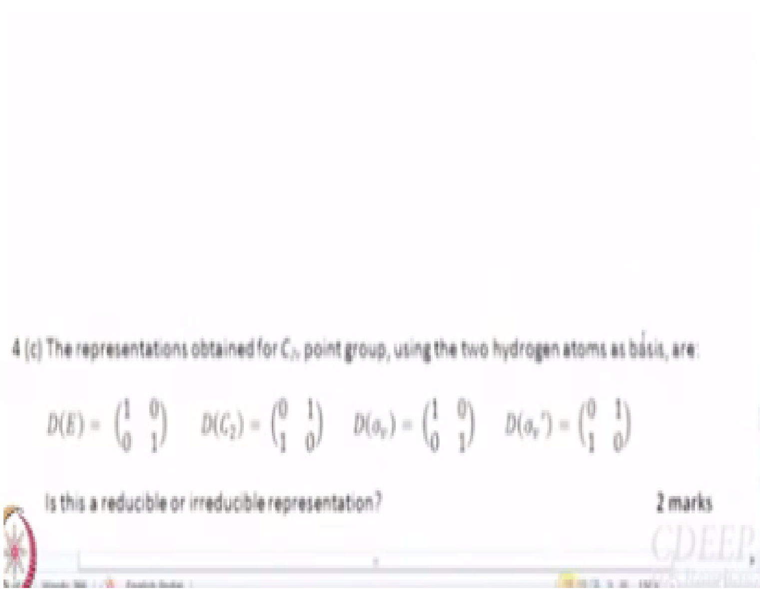

But if you have given a reasonable different answer you get marks, no issue, marks have not really the issue. This is the last question, 4c; the representation obtained for C2v point group using the 2 hydrogen atoms as bases are, D, DC2, D sigma v, D sigma v dashes, what is the answer, are they reducible? Or are they I mean this is reducible representation or this is an irreducible representation.

Now, you tell me why you have written, has anybody written irreducible, there is no harm in you know owning up, you have written, so now I want to know your logic, there is a reason why I am asking the question, why you have written it is irreducible? Actually, I can defend that it is a reducible is not just to make sure that blood pressure does not go up, it is a reducible representation, it is correct.

But I could in a way argue that it is irreducible from what I have studied so far, you want to say something, so I could say that this is not block factorised and I have studied that reducible representations must be block factorisable, so that is the point, so it is not block factorised, block factorisable yeah, right, so this is reducible it is not. Now, you tell this is reducible, sorry, so why does this have to be reducible. **“Professor – student conversation starts.”**

Well, the answer I was expecting is that we have worked out C2v character tables in this class, right, so the answer I was expecting is that for C2v, we know that you can only have 4 one dimensional representations, you cannot have a 2 dimensional irreducible representation, so you are saying the same thing but as usual you can think of a more complicated explanation than I can.

What is there? What do you know? What do you work out? You know that sum over li square = h, what he is saying, so which implies that is how we did it right, some question are knowing, we have to know the 5 rules that you cannot go without, you have to know something right end of the day, so but what I wanted was application of that it is fine, what are you saying is also correct. **“Professor – student conversation ends.”**

What I was said in class is that 4 square members are = the sum of 4 square numbers = 4 and if that to be integers as positive numbers, every l has to be 1, it is not possible to have to that should be the logic.