INDIAN INSTITUTE OF TECHNOLOGY BOMBAY

NPTEL

NPTEL ONLINE CERTIFICATION COURSE

Molecular Spectroscopy – A Physical Chemist's perspective

Lecture-31

Symmetry Operations Transformation Matrices

With

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We have taken a small holiday from spectroscopy to discuss something that many of us already to some extent and that is symmetry of molecules and at this point, I cannot blame you if you are surprised and if you think what's going on, why is it that in our course spectroscopy, all of a sudden we have started talking about symmetry point groups and staff that we have studied in organic chemistry or inorganic chemistry.

The reason why we are doing this is as you are going to see in the next couple of months, symmetry plays a very important role in spectroscopy. So what is the recurring question of the discussion we are having. The recurring question is we have two wavefunctions, two state characterized by two wavefunctions. Can we or can we not get a transition between the two?

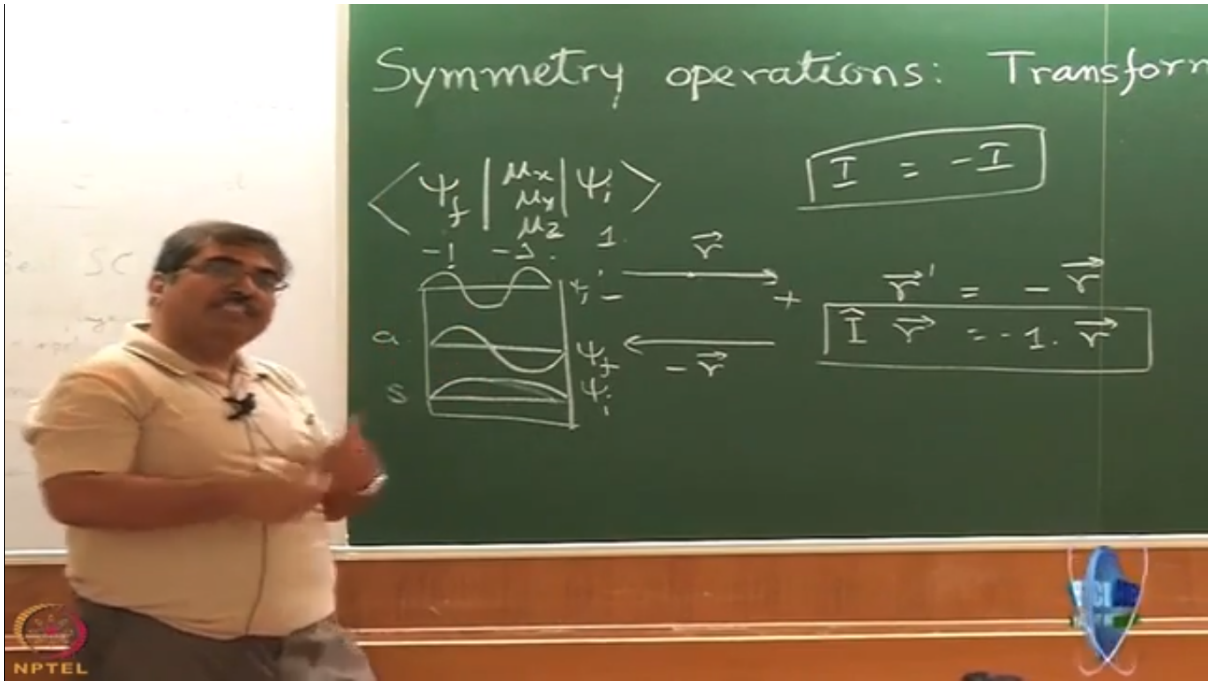
That is the theme of the course. If you have to summarize the entire course in one sentence then that would be it. Now, as far as diatomic molecules are concerned, we can do exact calculations and we can get the answer to the this question exactly. When we go to polyatomic molecules, even when we go to electronic spectroscopy of diatomic molecules, it becomes apparent that the situation is such that if you ignore symmetry, then you cannot go that far and also there are problems that become simpler if you consider symmetry.

In fact, that is not the case only for spectroscopy, even in quantum mechanics of molecules that you have studied, you have studied things like Hartee-Fock theory and all that, maybe you have studied, many of you Huckel approximation, Huckel approximation remember. So you understand, I mean suppose I want to work out the energy levels and spectra of something like, say, naphthalene.

In Huckel theory, what have you learnt? You get something, well you get a determinant, don't you? What does that determinant called? Secular determinant. In case of Huckel, how big will that determinant be? So what I am saying? In case of naphthalene, how big will it be under Huckel approximation or any approximation?

Right, 10x10, ten this side, tend this side. You want to work with the determinant? I don't. That's too big for me. So what you can do is using symmetry you can break down such determinants into smaller determinants, 2x2, maximum 3x3, and you can work with that. So symmetry helps you simplify complicated quantum mechanical problems in general.

In this course, what we'll do is we'll focus on how symmetry plays a role in determining whether a transition takes place or not. So even though we learn how to derive character tables, we will not ask questions of that but we will ask questions and that is a part we'll hear. We will ask questions on using character tables and also other concepts of symmetry that we develop now. That is the point.



So essentially, what is it that determines whether a transition takes place or not. By now you have I hope been convinced sufficient that it is transition moment integral being non-zero. So when I have a transition moment integral. I can actually write it as a sum of three. I'll write the components of dipole moment, μ_x or μ_y or μ_z, work with one of them at a time. Ψ_i integrated over all space. This integral has to be non-vanishing. This has to be non-zero.

Now see, let us think of some wavefunctions, some easy wavefunctions that we know. Let us talk about let us say your old friend, particle in a 1-D box wavefunctions. I see that particle in a 1-D box brings smiles to some faces. We know we have studied in several different courses. So you know the wavefunction. This is the first one, this is second one and you know how it goes.

Now particle in a box as you know is a model works to certain extent like conjugated polyenes. So actually it is a model that can be used in real chemical systems to some extent, not to a very large extent. Now see, suppose I want to say that I have a particle in a box. This is my level 1, this is my level 2. Will the transition work or not work? Let us look at the symmetries of this? Do you see that there is an -- what is it, odd function or even function? Even function. What is this? Odd function. That means if you change x to -x, it will change. it will change sign.

If I think in another way, think of this point, if this is a centre inversion, if I take a conjugated polyene then it will have a centre of inversion, then this is symmetric with respect to inversion. This is anti-symmetric with respect to inversion. I hope we all know the meaning of anti-symmetric, symmetric and anti-symmetric. Symmetric means does not change signs, anti-symmetric means plus becomes minus, minus become plus.

So we agree that this is symmetry, this is anti-symmetry. Suppose I consider μ_x or μ_y or μ_z, so they are like vectors along x or y or z. Are they symmetric or anti-symmetric with respect to inversion? This is your centre of inversion. This is plus, this is minus. What is inversion? Start from one point, go to the centre, go to an equal distance on the other side, you should get the same thing back. What happens if you invert this arrow? This is what happens.

So if I write this as some vector r, this is -r. Is it okay or no? So if I write it in a form of an equation, what do I get? I say r' is the transformed vector, is equal to -r. So see, this operation that I have done, an inversion, can be written in the form of an equation that is what we are going to build up on in the next couple of days.

So it is anti-symmetry. We agree? So if I write it like this is equal to -1.r. So this now becomes, to make things more interesting, I can write like this. Let us say this is my inversion operator that operates on the vector r that gives me -1.r.

Now this is a form of equation that has been deeply ingrained in our minds by now. what kinds of equation is this? It's an eigenvalue equation, isn't it? It's an eigenvalue equation, you have an operator, inversion operator, operating in some function, r, it gives you back the same function multiplied by an eigenvalue equation. Eigenvalue is -1.

So you can think like this also that if the eigenvalue is -1 then it is anti-symmetric, if the eigenvalue is 1, then it is symmetric. If the eigenvalue is something else, then it is something else. We'll come to that something else later.

So now see, what is the eigenvalue for Ψ_i if this is Ψ_i, this is Ψ_f? Eigenvalue is 1 for Ψ_i. for Ψ_f, -1, excellent. For μ_x or μ_y or μ_z, what is the eigenvalue no matter whether you take x or y or z. They will all look like these arrows. x will be like this, y will be like this, z will be like this, that all, -1. So you take the product of eigenvalues, what do you get? -1x-1x1, 1. That means the integrant does not change upon inversion. The integrant does not change sign upon inversion.

However, if I draw one more, now let us say this is Ψ_f'. What is it? Is the eigenvalue 1 or -1 for this is 1? Symmetric, anti-symmetric, symmetric. So now see, now the integrant becomes anti-symmetric. What does that mean? If you apply inversion, you take a molecule, take this conjugated polyene and invert it. Integrant becomes -1. What happens to the integral then? Should the integral change? I've just inverted a molecule, should an allowed transition become a disallowed transition? No. So what happens if you take the value of the integral the integral value cannot change.

So even though the integral value has become -i. Before inversion, let us say the value of the integral is i. After inversion of course it will become -i. So what you get is that in this case, i has to become -i. When is i=-i? Only when i=0. Is that right? Can you think of any other remember whose negative is equal to itself? No. So the point is this, when your integrant is symmetric with respect to symmetry operation then the integral survives. When it is anti-symmetric, then it does not survive.

We are going to come back to this. So in case you have questions, hold on to them and we can revisit them when we discuss this in more detail. The reason why we did it is to just show you is that symmetry can give you certain answers. So the answer that I get here is that you cannot have -- what is the lowest level? What is the quantum number, 0 or 1? 1. So 1 to 2 transition is not allowed. 1 to 3 transition can be allowed. What about 1 to 4? Not allowed. 1 to 5, maybe allowed.

You can do the same thing with harmonic oscillator wavefunction. What do you say is 0 to 1 is allowed, 0 to 2 is not allowed. So you already get $\Delta V=\pm 1$. So you see, using symmetry you can arrive at the selection rule in a little simple fashion but then of course, a simple fashion is

usually a less accurate or less rigorous fashion also. So if you just use symmetry for simple harmonic oscillator, for example, what you'll end up saying is that 0 to 1 is allowed, 0 to 3 is allowed, 0 to 5 is allowed.

You'll never be able to say that only $\Delta V=\pm 1$ is allowed. So far are we okay so if the integrant changes sign then the integral has to be 0. That means in order for the integral to survive your integral must be symmetric with respect to so far we have discussed only inversion.

Now what we are trying to say is this think of a harmonic oscillator wavefunction. From this argument we can say that this 0 to 1 transition is allowed because 0 wavefunction looks at least qualitatively like this, one wavefunction is like this. So this is symmetric, this is anti-symmetric. 2 is also qualitatively like this. So I can say that for a harmonic oscillator, 0 to 1 is allowed, 0 to 2 is not allowed.

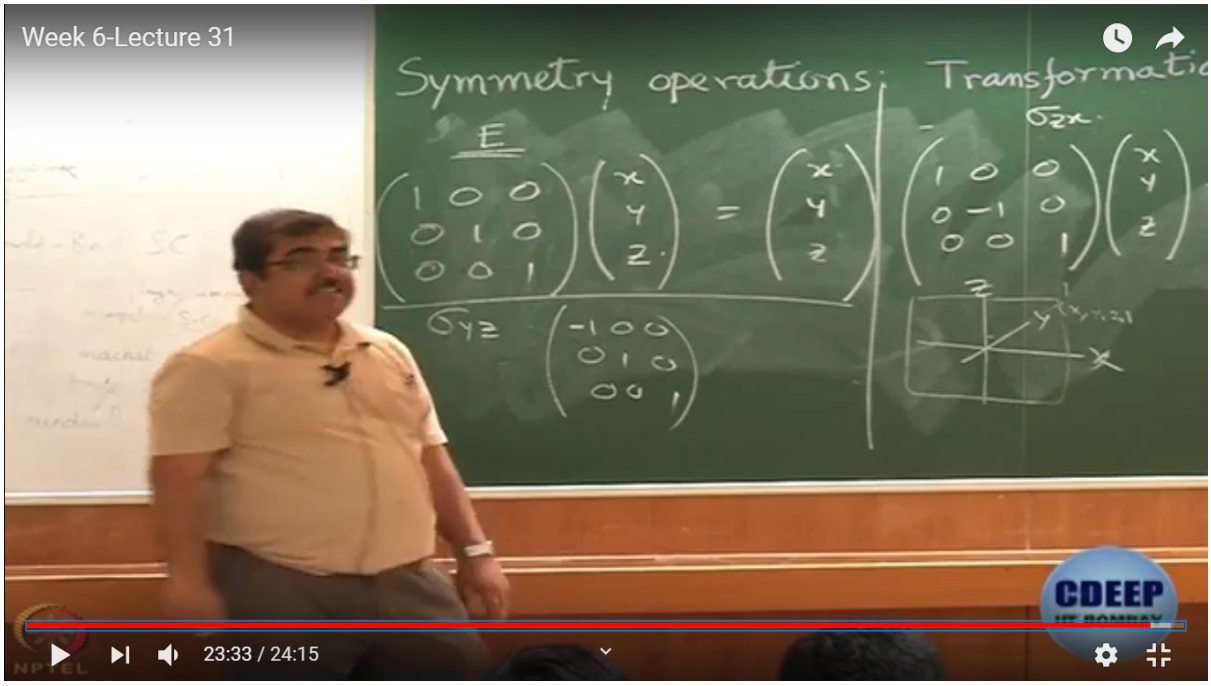
But if I use only symmetry argument I'll end up saying that 0 to 3 is also allowed. Understand what I am saying. But actually it is not. Only $\Delta V=\pm 1$ is allowed that is what we have derived already. So using symmetry you can usually get a good hint about which transitions will be allowed, but eventually you have to do the quantum mechanics also, but symmetry helps us simplify complex problems. That's it. That's why we'll study it.

So what we have to do now is this, the way we have discussed very briefly in the previous day is we introduce symmetry operations, symmetry elements, symmetry point groups and in case you need to revise a little bit about that, what you could do is you could, of course, read cotton's symmetry in chemistry book, first couple of chapters.

Now what we'll do is this, so far we have presented the problem to you as a geometry problem. But then as we have returned here, it is not very difficult to convert this problem in geometry to a problem in algebra and if you want to develop a systematic way of using symmetry to solve problems in spectroscopy or quantum mechanics, then it is going to be more convenient if you write this in the language of algebra.

Thus, finally what we want to do is when you go to big molecules and all, we don't want to do anything ourselves. It's I guess too tedious. We want to ask a computer to do it. Computer is blind and deaf; the only thing it understands is numbers and that's also in a special form. So we try to convert everything to numbers and the way in which we go from the domain of geometry to the domain of algebra is by using what are called transformation matrices.

What we'll do is we'll try and write a matrix for each and every symmetry operation. Let us try to do that, then we'll get into something called representations. So in order to do this, so here what we'd do. We tried out our symmetry operation on a vector, r. So in this case, r is called the basis. The function or set of functions on which you make your operator operate is called the basis. As we'll see, using a basis that is of relevance to us, we can try to construct the transformation matrices.



Let us try doing that. Initially, let us do some very generic examples. Then we'll get into some point groups. Let's start with simple basis, x, y, z. Let us say, I am using the basis, x, y, z. I want to see how x, y, z the coordinates transform in response to different symmetry operations. Are we clear? Are we clear what the basis is? Are we clear what is the meaning of basis and are we clear what we are trying to do? If not, this is the time to ask.

Remember, the question is explain this concept of basis once more. You take some function, ϕ. You make some symmetry operation operate on it. You get some transformed function and we are going to -- well let us say an eigenvalue equation, something like this, we get something like f.ϕ. So what we are saying is this function forms a basis for the discussion of this symmetry operation.

Sometimes one function is not enough. Like here, I want to see how the coordinates transform. I could take them separately but as you'll see a little later, for sudden functions you cannot take them separately. So then what we do is instead of taking one function, I can take an array of function, write them as a row vector or a column vector. Have we understood what basis is?

Basis is a function or set of functions on which our symmetry are being made to operate. Are we clear about that? Now, let me write, these are the transform functions, x', y', z'. Let me now select my symmetry operation. When we learned tables, what is the table we started with? Multiplication table, very easy question. When you are kids, small children, when we learn multiplication table, we started with the table of 29.32, isn't it? What was the first table we learn? 2. Actually 10 would be easier. So if you are even lesser you would start with the table of 1. 0 so everything is 0, why do you multiply.

What we'll do here is that we'll start this seemingly complicated discussion with the simplest possible multiplication, multiplication by 1. What is 1 in symmetry? Which operation is that? Identity operation, identity or you can say C1. C1 means rotating by 360^{o} or in other words, doing nothing.

So if it was addition, it would be 0; multiplication it is 1. So let us say E. So E operates on x, what is x'? x. If E operates on y, what is y'? y. When E operates on z, what is that? See, you better answer now when it is easy; later it will get complicated.

So if this is the case, then I think it is not very difficult for you to understand that instead of the operator, I might as well write a matrix. What is the matrix I'll write? Unit matrix;

$$\begin{vmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{vmatrix}$$

, very simple. So what we are saying is under the operation of E, each of the coordinates remain unchanged. So another way of putting it would be that each of these coordinates, x, y, and z are symmetric with respect to the operation E, and at this point, if you think that that the discussion that we are making is trivial, then I am with you.

I agree with you; the discussion is trivial. The only reason why we are saying it is to kind of get into the subject. Have you all understood this or is there a question? No question? Very good. Now let me try something else. Let me try something, say, σ_{zx}. x, y, z, σ_{zx} will have it own transformation matrix. That will give me x', y', z' that I am not writing now. So tell me. You want me to draw it. x, y, z. So what I am doing is I've taken some point here, coordinates or you can write x_1, y_1, z_1, if it's more comfortable for you, it doesn't matter.

How will they transform? I am reflecting with reflect to the plane, z-x that is the plane of the board. What will x become? x remains x. What will z become? Yes, z becomes zee. And what will y become? -y. what is the matrix? $\begin{vmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{vmatrix}$. So almost the same as the unit matrix with the difference that one of the coordinates is actually anti-symmetric. So what do we see? x is symmetric, z is symmetric with respect to σ_{xz}, y is anti-symmetric.

How would this matrix change if I wanted to write it for say σ_{yz}? Yes, σ_{yz} maybe I'll write it here. What are the coordinates that would change sign? What are the coordinates that would not change sign? Exchanges sign. What about y and z? same. So matrix will be what?

$$\begin{vmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{vmatrix}$$

. And if it is reflection with respect to x-y, z changes sign and x and y don't.

So it will be $\begin{vmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{vmatrix}$ where the minus(-) sign just goes down the diagonal, that is all.

Okay.