# Chemical Applications of Symmetry and Group Theory
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## Lecture – 39

Hello and welcome. We have reached almost the end of this course. In the last class we looked at the electronic states of naphthalene molecule. So, what we did? We took the SALCs that are formed out of the P Pi orbitals on the carbon atoms of naphthalene molecule and filled it up with the electrons using Hund's Rule and using Pauli's exclusion principle and we found symmetries of the individual electrons in this molecular orbitals and then we formed the different excited states by putting or electron taking from one of the filter orbital to one of the vacant orbital.

So, we learnt how to form the, find the symmetry of the electronics states. So, what he got? We formed 3 different excited states. So, they were.

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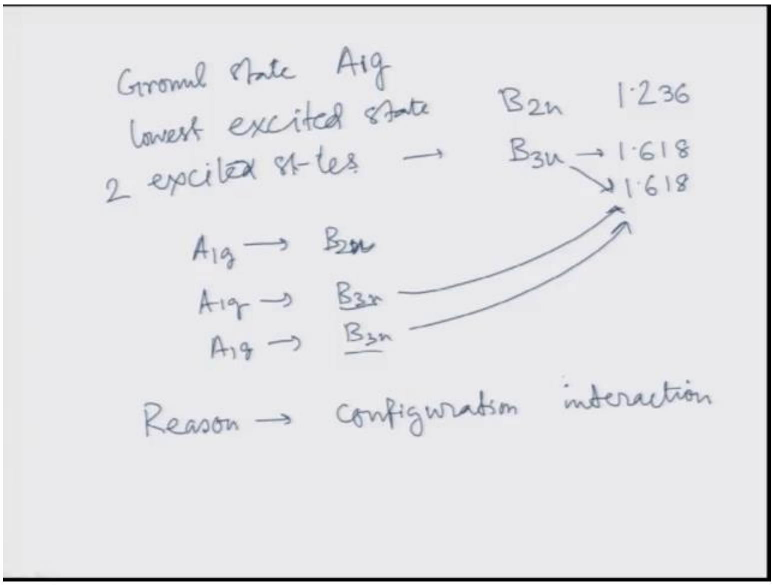

Ground state $A_{1g}$
lowest excited state $B_{2u}$ 1.236
2 excited states → $B_{3u}$ → 1.618
↘ 1.618

$A_{1g} \rightarrow B_{2u}$
$A_{1g} \rightarrow B_{3u}$
$A_{1g} \rightarrow B_{3u}$

Reason → configuration interaction

The ground state was totally symmetric it heat transforms has the totally symmetric irreducible presentation. While the lowest excited state that was B 2u symmetry. So, and also there are, we looked at 2 other excited states both of that. So, 2 excited states both of which had B 3u symmetry and we also looked at their energy side. So, for B 3u state we found the energy to be 1.236 in unit of (Refer Time: 02:28) and for the other 2 excited states which had B 3u symmetry, we found the energy to be 1.618. So, for both the B 3u, we had 2 excited state having B 3u symmetry and both of them we calculated, we found this energy by using Huckels Approximation and solving the secular determinant, secular equations we found this energies. Now, one important part in this case that we will be talking about today, though this is the value that we are getting by calculation and we also got the electric selection rules for the transitions from the ground state A 1g to B 2u and this to B 3u states and found whether the condition was allowed or disallowed.

Now, when someone looks at the energies of this states, these 3 states surprisingly it is found that this, there are two different energies actually for this 2 states having B 3u symmetries. So, there is something else going on. So, like I have A 1g to B 2u and A 1g to B 3u, A 1g to B 3u and this both of this should have the same energy of transition, but experimentally one finds the they have actually different energies and (Refer Time: 04:20) fact the energies of B 2u is actually in between the energies of two B 3u states that is quite surprising. So, why is it so? That is what we will look at. So, in a nutshell if I tell the reason, the reason is known as configuration interaction. So, reason is configuration interaction.

So, what is that? That we will look at, whenever we wanted to find out the energies of any given state, what we did? We looked at the energy integral.

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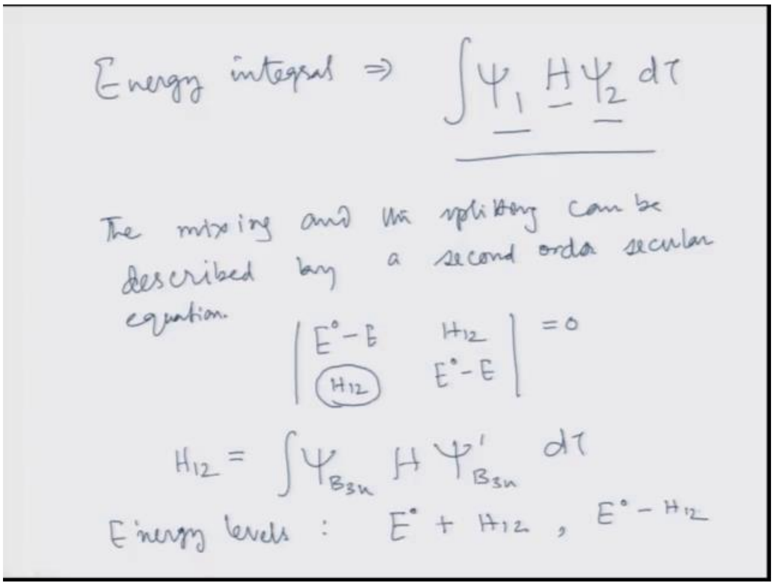

Energy integral ⇒ $\underline{\int \underline{\Psi_1}\, \underline{H}\, \underline{\Psi_2}\, d\tau}$

The mixing and the splitting can be described by a second order secular equation.

$$\begin{vmatrix} E^\circ - E & H_{12} \\ \boxed{H_{12}} & E^\circ - E \end{vmatrix} = 0$$

$$H_{12} = \int \Psi_{B_{3u}}\, H\, \Psi'_{B_{3u}}\, d\tau$$

Energy levels : $E^\circ + H_{12}$ , $E^\circ - H_{12}$

So, the energy integral that we looked at was something like this. So, the Hamiltonian and this and what we said about the value of this integral? So, far we have been talking about that, this particular integral may have a non zero value if this Psi 1 and Psi 2 have the same symmetry; that means, if Psi 1 and Psi 2 belongs to the same irreducible presentation of the point group because this Hamiltonian being the energy operator, it is totally symmetry. We transform as the totally symmetry irreducible presentation.

Therefore, this Psi 1 and Psi 2 must be having same symmetry, otherwise there will be 0. Now what we have in the present case? That 2 excited state belonging to the same symmetry B 3u, so can I have some this particular situation, we can say that even though 2 states belonging to the same energy, they may leave this integral to have a zero value. So, this is a special case. So, this is something like which is kind of accidental.

Now, what may happen here is that 2 states having same symmetry that is B 3u they may interact with each other and while interacting, after interaction they get split up. So, when you get these new states. So, you have two B 3u states they are at the same energy. Calculated, we found that they are of same energy and they are of same symmetry. Now there is some interaction is going on and after that they are forming 2 different states which are different in their energies and this energy gap is quiet substantial. So, that this other energy step B 2u that lies somewhere in between. So, if we, in this case actually the resultant new steps they cannot be expressed as the purely one of the B 3u energy state. None of these new stages can be expressed as the pure B 3u stage.

So, there you know, therefore, we have to assume that there is some kind of mixing and due to this mixing you get a splitting. So, in that case we can describe this mixing and splitting by second order secular equation. So, mixing and the following splitting can be described by a second order secular equation. We have seen this secular earlier and we solved them and found the energies for the very same naphthalene molecule.

So, how will this look like? It will look like; it is very similar to the other secular equation that we have formed. Now here this each 1, 2 is of particular interest because (Refer Time: 09:43) element they give you the interaction terms right. So, this H 12, I can now express in this following way. So, if I say I take Psi B 3u and the Hamiltonian and then I get a new Psi B 3u, I call it as Psi B 3u prime integration over d term.

So, in such a case what we have is 2 different states with 2 different energies and what are their energies. So energy levels that have like E 0 plus H 12 and you have E 0 minus H 12 that we have to have. So, this entire situation is pretty much analogues to the occurrence of a 2 by 2 determinantal equation right, for the energies of 2 individual orbitals of same symmetry. Now actually in practice it is bit different, it is difficult to compute the magnitude of this H 1 to this particular integral because it involves actually the electron repulsion and which is always difficult to you measure.

So, if I want to show how actually this you takes of same symmetry and same energy they mix and spilt diagrammatically. Then I can show it like following way.

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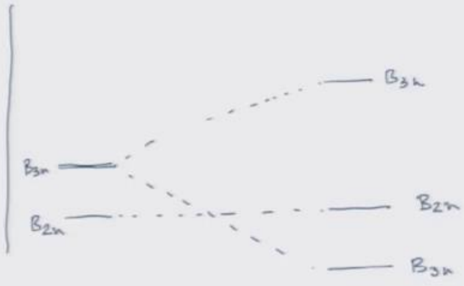

In case of vibrational transitions
configuration interaction →
Fermi resonance

So, I had to start with say this is may - B 2u symmetry and then I have 2 steps with B 3u both of them have B 3u symmetry. So, this means that they have same energies. So, just for clarity we are drawing in such way that are slightly separated, but if remember both of them have same energy start with. So, this B 2u this take is not interacting with any others step. So therefore, that remains as such. Why? This guy both of them will mix and they will form states, which are having energies completely different from the original energies of individual B 3u states. So, this is my new picture after this interaction and mixing and splitting.

So, in most general form this configuration interaction it involves 2 states having same symmetry. Now always if you have this kind of situation, what you have ended up? What you have is you have a split it in (Refer Time: 13:18) and it can not only happen in case of electronic state. You can have the same situation in case of Vibrational transition also involving original steps. Now this is not, we are not going to talk about these things in details, but I will just mention that in case of Vibrational transition involving original steps such mixing or rather if I say configuration interaction, that leads to very exotic phenomena this is called Fermi Resonance.

And because of this kind of configuration interaction in case of Vibrational transitions, very unique thing happens that even a very mode which is very weak such as like combination mold, we mentioned about that our term, this combination or over turn bands can actually become much more intense by borrowing intensity or oscillator strength from an allowed transition or rather I should say from a pure fundamental transitions.

So, here whatever we talked here so far is to tell you that we use this energy integrals to say and find out whatever the energies of this any given particular state and also we use this type of integral and use the symmetry impose the symmetry conditions in such a way that we said always that 2 states which are involved in having condition between then must belong through the same symmetry has that of the operated correct. So, in this particular when you looked at today, this opposite like in certain cases when you have the same symmetries of this 2 states and you should have an allowed transition in such is I mean like you should have integral that should not vanished.

Now, there in some cases you may end up actually getting a complete different picture because of the interaction of the states having same symmetry and same energy. This interaction you known has configuration interaction which is very much valid in case of electronic and other like Vibrational energy states and one important aspect is you use this (Refer Time: 16:35) theory in while talking about molecular resonance and all this things and you use this you resonance energy. So, by which you talk about the stabilization in integral resonance stabilization. So, that actually uses this configuration interaction in a particular way. So with this we will conclude this session.

So, I hope we could complete the basic notion of the symmetry aspects of various different types of transitions in a given molecule vibration and electronic and we learned how to find out the symmetries of these various states (Refer Time: 17:33) end the case of normal mode of vibration or being the electronic states of in a given molecule and then we found out the symmetry selection rules and also in today’s class we learnt about the case a special cases when even having you know 2 states with same symmetry may end up giving a different result because of the mixing of the 2 states.

So in the next class we will come with summary of the total the course that we had so far. So, we will try to summarize whatever we learnt and try to give you recapitulation of whatever the relations that we had so far.

Thank you very much.