

21 Group Theory Basics

1. Reference: "Group Theory and Quantum Mechanics" by Michael Tinkham.
2. We said earlier that we will go looking for the set of operators that commute with the molecular Hamiltonian. We had earlier encountered the angular momentum operators that commute with the full Hamiltonian. We will encounter a new family of operators: molecular symmetry operators that also commute with the Hamiltonian.
3. Why is that so? Because if you exchange any two atoms that are identical the molecule does not change. The probability has to be unchanged with respect to such exchanges *or symmetry operators as they are called* and all observables should be the same with respect to interchange of atoms. Hence the Hamiltonian has to be *invariant* with respect to such operations. **But the wavefunction may not be invariant, since only observables are required to be invariant under the action of symmetry operations and in fact the wavefunction is not an observable!!**
4. We say in such a case that the Hamiltonian commutes with the operations that leave the molecule invariant.
5. Kinds of symmetry operations that we look for in a molecule are
 - (a) n-fold rotation axis.
 - (b) mirror planes or reflection planes.
 - (c) inversion center.
 - (d) rotation-reflection axis.
 - (e) identity (means do nothing).
6. Consider for example the case of ammonia.
7. It has the following symmetry operations that leave the molecule invariant: E, C₃, C₃², σ_v, σ'_v, σ''_v

8. Like all the other operators that commute with the Hamiltonian, the symmetry operators also make things easier by providing additional information on the nature of the eigenfunctions. This is similar to the additional information we had due to commuting operators like the angular momentum operators (where we had quantum numbers). The symmetry operators that commute with the Hamiltonian also provide additional quantum numbers but these are now called by a different name; **irreducible representations** as they are called have this additional information. We will see more on this.
9. But before we get that far some examples where symmetry can make our life easier without doing any work:
 - (a) Consider a molecule that has an inversion center. Clearly, the probability density of the electrons has to be symmetric about this inversion center. The nuclei also have to be symmetrically arranged about this point and hence charge has to be symmetric about this point. Hence a molecule that has an inversion center *cannot have a dipole moment*. Considered staggered ethane as an example.
 - (b) Optical activity: Any molecule that has an inversion center, or a reflection plane or a rotation-reflection axis cannot be optically active, or in other words cannot be chiral.
10. So we can obtain such powerful information without doing any work.

11. So how do we characterize the symmetry operations for a given molecule? Here we define what are known as *point groups*. The complete collection of operations that leave a molecule invariant form what is known as a point group. (More on this later but for now let us see how we can find out what the point group of a given molecule is).

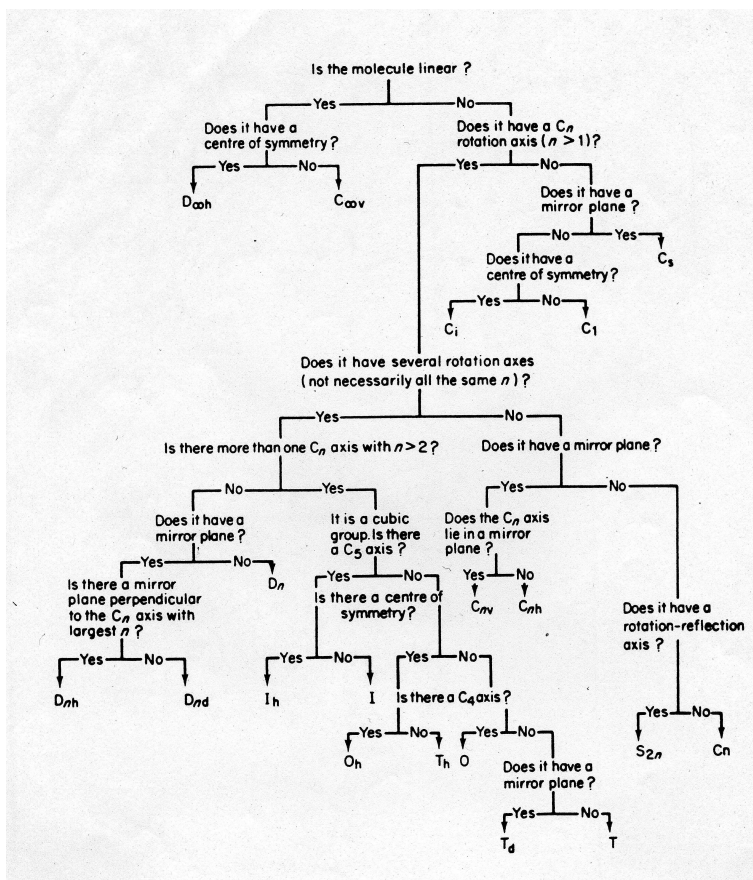


Figure 19: The Point Group table

12. So why are these called point groups? because we are essentially permuting fixed points in space.
13. So how is all this useful to us? Let \mathcal{O}_R be a symmetry operation that commutes with the Hamiltonian (that is leaves the molecule invariant). Let $\{s_i\}$ be the eigenvalues of \mathcal{O}_R and let its corresponding eigenvectors be $\{\psi_i\}$. In that case the matrix elements of the Hamiltonian with respect to $\{\psi_i\}$ are

$$\begin{aligned}\langle \psi_i | H | \psi_j \rangle &= \frac{1}{s_j} \langle \psi_i | H s_j | \psi_j \rangle \\ &= \frac{1}{s_j} \langle \psi_i | H \mathcal{O}_R | \psi_j \rangle \\ &= \frac{1}{s_j} \langle \psi_i | \mathcal{O}_R H | \psi_j \rangle \\ &= \frac{1}{s_j} \langle \psi_i | s_i H | \psi_j \rangle \\ &= \frac{s_i}{s_j} \langle \psi_i | H | \psi_j \rangle\end{aligned}\tag{21.1}$$

which basically says:

$$(s_j - s_i) H_{i,j} = 0\tag{21.2}$$

If ψ_j and ψ_i do not have the same eigenvalue with respect to \mathcal{O}_R , then $H_{i,j} = 0$.

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14. This is a very powerful relation. **Which basically says that the eigenvectors of the symmetry operators \mathcal{O}_R block-diagonalize the Hamiltonian matrix.**
15. This is a very powerful property because the computation time for diagonalization of a matrix (which is what is required to obtain its eigenvalues and eigenvectors) scales as N^3 with the size of the matrix N . (What is meant by the statement is that if you double the size of a matrix from an $N \times N$ to a $2N \times 2N$ matrix, then what happens to the computation time required for diagonalizing the new matrix is, it changes from $C \times N^3$ for the old matrix to $C \times (2N)^3 \equiv [8 \times (C \times N^3)]$. That is diagonalizing the new matrix is 8 times more expensive than diagonalizing the old one, even though the new one is only twice as large as the old matrix.

16. OK. So how does it help us if we have a block-diagonal matrix. We can diagonalize each block separately. So consider a 10×10 matrix. The computation time required to diagonalize this would be $C \times 10^3$. Say we block diagonalize this to a 5×5 , a 3×3 and 2×2 . Then the time required to diagonalize the new matrix is $[C \times 5^3 + C \times 3^3 + C \times 2^3 = C \times 160 \ll C \times 10^3]$. So already in this small case we have a big difference in computation time. Normal calculations are much more expensive than the example we considered so the savings would be enormous.
17. Remember we said earlier that we look for a commuting set of operators to simplify the problem? Here is one more case where that is true.
18. **That and we have a new quantum number based on s_i the eigenvalue of the symmetry operator \mathcal{O}_R to label our eigenstates.** (Note in spherical harmonics we had l , etc to label our eigenstates which were themselves related to eigenvalues of the angular momentum operator that commuted with the Hamiltonian.)

19. Having now seen one more reason why we should learn group theory (that is it makes computation easier), lets now look at another reason why group theory is important to learn.
20. We have stated earlier that if a molecule obeys a certain symmetry then it means that the Hamiltonian corresponding to that molecule commutes with the relevant symmetry operation. We used this in Eq. (21.1) where we assumed that $\mathcal{O}_R H = H \mathcal{O}_R$.
21. In that case let us assume that the function $|\phi_n\rangle$ is an eigenstate of the Hamiltonian H with eigenvalue E_n and let us assume that this eigenvalue has many degenerate states, say l_n is the degeneracy. In that case:

$$\begin{aligned}\mathcal{O}_R H |\phi_n\rangle &= \mathcal{O}_R E_n |\phi_n\rangle \\ H [\mathcal{O}_R |\phi_n\rangle] &= E_n [\mathcal{O}_R |\phi_n\rangle]\end{aligned}\tag{21.3}$$

Therefore $[\mathcal{O}_R |\phi_n\rangle]$ is also an eigenstate of H with eigenvalue E_n . **In fact, this way we can get all the degenerate eigenstates of H with eigenvalue E_n .** (This last statement is not entirely true. If you can get all the degenerate eigenstates of H in this fashion, then the degeneracy is called a *normal degeneracy*. If not it is called an *accidental degeneracy*. For example the $2s, 2p$ degeneracy in hydrogen atom is an accidental degeneracy. In the case of *accidental degeneracy* it generally implies some underlying deeper symmetry that hasn't been accounted for or the symmetry is not an exact one. For the $2s, 2p$ case it was shown by Fock in 1935, that there exists a deeper symmetry that makes these degenerate.)

22. A few important remarks:

- We did notice for the case of $\{L^2, L_z, L_x, L_y\}$ that although L^2 commutes independently with each of L_x, L_y, L_z , independently, the fact that each of L_x, L_y, L_z do not commute with each other has an important bearing on the eigenstate structure of L^2 (\rightarrow degeneracy).
- Similarly here if there exists a family of symmetry operators $\{\mathcal{O}_R^i\}$ that do not commute with each other but commute with H , the Hamiltonian, we will have degeneracy for the same reasons that we found for the case of angular momentum!!
 - In this case we can pick one of the operations inside a manifold of non-commuting operators as special (like we picked L_z as special as opposed to picking L_x or L_y) and the other operators in that manifold can be used to switch between the degenerate eigenstates.
 - Note: This is exactly what happened for angular momentum. We picked the L_z operators as special and the L_x and L_y help convert between the eigenstates of L_z . (See the exam problem on spin.)
 - This point leads to an important concept in group theory (2- and 3-dimensional irreducible representations) as we will see later.
- This brings in two important family of groups:
 - *Abelian Groups*: Where all molecular symmetry operations commute with each other.
 - *Non-abelian Groups*: Where all molecular symmetry operations do not commute with each other.

23. To proceed further and to learn how to use group theory we will need to learn a few concepts.
24. The first concept is *what is a group?* A group has the following properties:
- (a) A group is closed. Which means that the product of any two elements in the group also belongs to the group. For example consider the C_{3v} group that ammonia belongs to with group elements $E, C_3, C_3^2, \sigma_v, \sigma'_v, \sigma''_v$. The product of any two elements belongs to group. We will see more on this later.
 - (b) The group has an identity which does nothing. E is used to represent the identity.
 - (c) Every element of the group has an inverse and the inverse element is also a part of the group.
 - (d) The group operations are associative. $(AB)C = A(BC)$.

25. To illustrate this definition we introduce the group multiplication table. For example for the C_{3v} group that ammonia belongs to with group elements $E, C_3, C_3^2, \sigma_v, \sigma'_v, \sigma''_v$, the group multiplication table looks as follows:

26. **Homework:** For water, write down its point group using the Point Group table provided in Fig. (11). Write down all the symmetry elements of water and also write down the group multiplication table.

27. The operations that we have included in the symmetry group are basically rotation, reflection, inversion center, rotation-reflection and identity operations. These are operations that act on some point in three dimensional space and move it to another point in three dimensional space. Hence we should be able to write down matrix representations for these operations. (A matrix acting on a vector, which represents the position of a point in space, gives a vector which is the position of the new point.)
28. To obtain such matrix representations it is useful to keep the following definition for a rotation matrix that rotates something by an angle θ in the x-y plane.

$$\begin{bmatrix} \cos \theta & \sin \theta \\ -\sin \theta & \cos \theta \end{bmatrix} \quad (21.4)$$

and a reflection about a plane that is at an angle θ from the horizontal is given by

$$\begin{bmatrix} \cos 2\theta & \sin 2\theta \\ \sin 2\theta & -\cos 2\theta \end{bmatrix} \quad (21.5)$$

29. Using these we can write down *representations* for the C_{3v} group as:

34. So its clear that there are many ways of representing these symmetry operations. Some are more complex than others. But clearly the three-dimensional representations we had in the previous page are *reducible* to the 1 and 2 dimensional representations.
35. So there are some representations that are *reducible* and some that are *irreducible*. It is the irreducible representations that we need. These are the ones that bear serious value to quantum chemistry.
36. Example of irreducible representations and the character table:
37. A few examples we can see now, but we will see the reasons why these are useful in a more rigorous fashion. Perhaps the single most important usage of these character tables and irreducible representations is in creating what are known as “symmetry adapted linear combinations” of orbitals, thats is energy levels that obey a certain symmetry. This makes our life easier and it gives us greater insight into the physics of our problem. This we will see in greater detail next time.

38. We saw what a group is. We also saw what a group representation is. A representation is a collection of objects (in our case rotation, reflection, matrices or simply determinants of these) that mimic the characteristics (think group multiplication table) of a group.
39. We saw what a homomorphic representation is. For example the determinant of the matrices we derived for the operations in C_{3v} are a homomorphic representation. Since these “numbers” *do not include all the details of the group, only some*. For example the one-dimensional representation in the previous page does not differentiate between the mirror planes, but it does give the same group multiplication table.
40. The two-dimensional representation we saw earlier is “isomorphic” since it does differentiate between all the elements and still has the same group multiplication table.
41. We then saw we could combine such representations to get higher dimensional representations. And those would still have the characteristics of the group (in that these higher dimensional representations would still obey the group multiplication table). If we construct a 3-dimensional representation from the one and two-dimensional reps, as we did in the previous page, the three-dimensional representations also obey the group multiplication table.
42. So where do we stop. How many representations can we have.

43. There is a theorem that says we stop when the sum of the square of the dimensionality of each representation should add up to the total number of elements in the group.
44. The irreducible representations (irreps) in the C_{3v} case are then either 1 or two dimensional. We saw two dimensional matrices last time that can be used to represent the operations of the C_{3v} group. We also saw that determinants can be used to do the same (although homomorphically!). There is one more element that can be used to represent the operations in C_{3v} and that is the number 1. If we were to use the number 1 to represent all the objects of the group, the group multiplication table would be satisfied in a trivial (homomorphic) manner.
45. And $1^2 + 1^2 + 2^2 = 6$, the number of elements in the group.

46. So how do we in general derive the irreps? We will only discuss this in detail if we have the time. But basically, it is not difficult for a general case. We first write down a “regular representation”. Each irrep occurs in the regular representation a number of times that is equal to the dimensionality of the representation. This way we have the irreps.
47. We use the irreps to write the character table.
48. In the character table you see rows labeling the representations and under each column the various representations for an operation are written down. For example look at the C_{3v} character table and you will find the one and two dimensional representations that we had earlier.
49. Now, in the character table, we might find either the full two dimensional representation that we had earlier or just trace of the relevant matrix. The trace is called the character. (Less information than the two-dimensional representation, but easier to handle.)
50. For example, the irreps in C_{3v} are labeled A_1 (one-dimensional and from just putting 1 for all operations), A_2 (one-dimensional and using the determinants from previous) and E (the two-dimensional irreps).

51. Important property of the character table:

- (a) The sum of the squares across the rows is equal to the dimensionality of the group. (Remember that there are more elements in the group than the number of columns in the character table generally. For example in C_{3v} there are two C_2 and three mirrors.)
- (b) Each row is orthogonal to the others.
- (c) These two are together called the *great orthogonality theorem*.

52. Hence the irreps form an orthogonal vector space. **And it is a projection onto the irrep vector spaces that block diagonalizes the Hamiltonian.**

53. So we introduce projection operators and transfer operators that will and transfer functions onto the “subspace” or direction of the irrep. Lets start with the projection operators since these are easier to see.

$$\mathcal{P}_{\lambda\lambda}^{(i)} = \frac{l_i}{h} \sum_R \Gamma^{(i)}(R)_{\lambda\lambda}^* P_R \quad (21.6)$$

where $\mathcal{P}_{\lambda\lambda}^{(i)}$ is the projection operator that projects a function onto the λ -th column of the (i) -th irrep. (If you think characters then λ is always 1.) h is the total number of elements in the group (that is 6 for C_{3v}). l_i is the dimensionality of the irrep. We are summing over all the elements of the group and P_R is the corresponding operation that acts on a function (while R acts on a point in space, P_R acts on a function).

54. The transfer operator is a generalization of the projection operator and one you obtained the λ -th column of the (i) -th irrep, you can get the κ -th column of the (i) -th irrep by applying the transfer operator on the λ -th column of the (i) -th irrep:

$$\mathcal{P}_{\lambda\kappa}^{(i)} = \frac{l_i}{h} \sum_R \Gamma^{(i)}(R)_{\lambda\kappa}^* P_R \quad (21.7)$$

55. All this is a little abstract. We will do an example to see how all this is used. That example will teach us how to use the character table. Three important usages of the character table:
- (a) We can write down projection operators from above, and using the character table. These projection operators when applied to some initial function, will provide us with “Symmetry Adapted linear combinations” (SALC). These SALCs can be used to block-diagonalize the Hamiltonian. In addition if our guess functions are atomic orbitals (that is orbitals on atoms), we obtain “Symmetry Adapted linear combination of atomic orbitals” (SALC-AO). These SALC-AOs are actually pretty decent qualitative guesses for the molecular orbitals that one would get after solving the Schrödinger Equation. Note: The SALC-AOs will not contain *all* the information you need from solving the Schrödinger Equation. Only some information, based entirely on symmetry and in many cases these can give good qualitative ideas. For example the Woodward-Hoffman rules are derived from here. We will take an example later and show how the SALC-AOs are derived.
 - (b) The character tables also tell us what kind of linear, quadratic and cubic (in some versions of character tables) functions transform according to which irrep.
 - (c) Based on these character tables can be used to predict spectra, which you will learn next semester in Parmenter’s course.
56. So let's now embark into a couple examples to see how these uses of the character table come about. All this will be done on the board: I will do on the board first an illustration of how a projection operator can be used, then the SALC for water. (So you should write these down. :-))

57. Lets return to water and consider all possible atomic orbitals on the oxygen. Consider now the eigenvalue problem:

$$\mathcal{R}\psi = \gamma\psi \tag{21.8}$$

where \mathcal{R} is a symmetry operation from the point group of water.

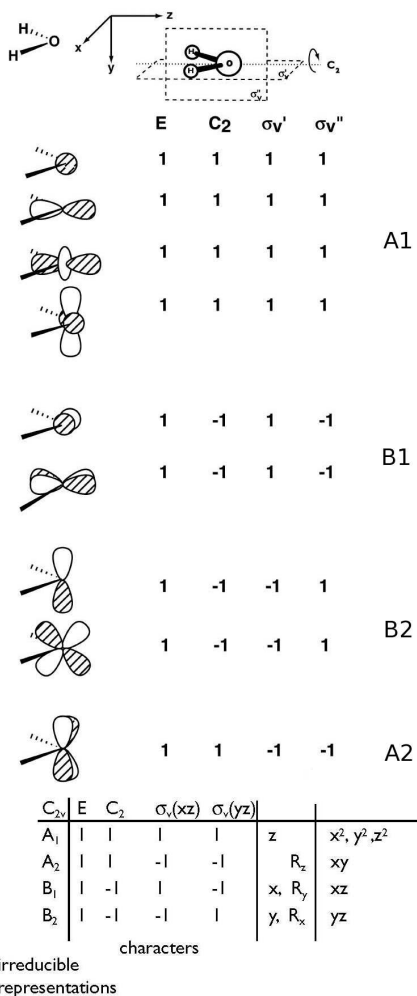


Figure 20: How the AOs transform according the symmetry operations

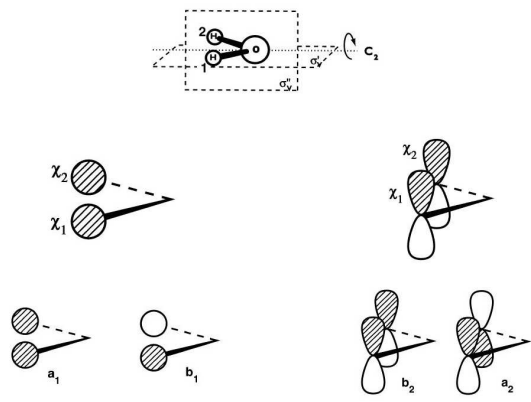


Figure 21: SALC-AO for H₂O from the 2s and 2p_y orbitals on the hydrogens