Superimposable Mirror Images

Chiral molecules have the property that they are not superimposable on their mirror image. Molecules that are not superimposable on their mirror image are termed "dissymmetric", a term that is preferred over "asymmetric" because the latter term means literally "without symmetry". It is said that molecules lacking a mirror plane or center of inversion are dissymmetric, but this can be generalized as follows: a molecule lacking an improper axis of rotation S_n is dissymmetric (recall that S_1 is a mirror plane, and S_2 is an inversion center).

Introduction to Point Group Character Tables

If we are going to analyze a molecule with respect to its electronic structure, or with regard to vibrational behavior, or concerning some other property, a good place to start is to (*i*) assign the molecule to its correct point group, and then to (*ii*) look up the character table corresponding to that point group. For example, we find that the water molecule belongs to the point group C_{2v}, the character table for which is displayed below.

C_{2v}	E	C_2	$\sigma_v(xz)$	$\sigma_v'(yz)$		
A_1	1	1	1	1	z	x^2, y^2, z^2
A_2	1	1	-1	-1	R_z	xy
B_1	1	-1	1	-1	x, R_y	xz
B_2	1	-1	-1	1	y, R_x	yz

First off, let's look at the different regions of the character table.

- Top left corner: this gives the Schönflies symbol for the point group, in this case, C_{2v}.
- Top row, center: a complete listing of the symmetry operations, here E, C_2, $\sigma_v(xz)$, $\sigma_v'(yz)$. In the character table, the symmetry operations are grouped into classes. For the case of C_{2v}, each operation is in its own class.
- Leftmost column: these are the Mulliken symbols that are used to label each of the *irreducible representations* of the point group. There are always the same number of irreducible representations as there are classes of operations in the point group. The Mulliken symbols come from Robert S. Mulliken, the father of molecular orbital theory and an MIT undergraduate (B.Sc., 1917).
- Center rows: these are the the characters of the irreducible representations. This language comes from the fact that the symmetry operations can be represented as matrices, and the character of a matrix (also called the *trace*) is the sum of its diagonal elements. The irreducible representation having all characters equal to 1 is termed the *totally symmetric representation*.
- Right side: to the right of the characters is a listing of some functions. The characters of an irreducible representation summarize the behavior of those functions upon carrying out the group operations. This will be illustrated using atomic orbitals as representative functions.

Character Tables with Multiply Degenerate Irreducible Representations

In the case of the C_{2v} character table, all of the irreducible representations were singly degenerate. For this reason, individual functions (such as atomic orbitals) were sufficient to serve as a basis for each of the irreducible representations. If in a character table listed under the E operation you see the number 2, then you know that this irreducible representation is *doubly degenerate*; that is, two functions together are required to serve as a basis for the representation. This happens because the functions are "mixed" upon carring out the group operations. This will be illustrated for the group C_{3v}. In general, the presence of three-fold or higher order principal rotation axes gives rise to degenerate irreducible representations.

C_{3v}	E	$2C_3$	$3\sigma_v$		
A_1	1	1	1	z	x^2+y^2, z^2
A_2	1	1	-1	R_z	
E	2	-1	0	$(x,y)(R_x,R_y)$	$(x^2-y^2,xy)(xz,yz)$

In the point group C_{3v}, there is a doubly degenerate irreducible representation given the Mulliken symbol E, not to be confused with the E operation.

C_{3v} is a group with order six, this being the number of operations present. There are three classes of operations, and three irreducible representations, one of which is doubly degenerate. It is interesting to note that none of the nine atomic orbitals (s, p, d) serve as a basis for the A_2 irreducible representation. In fact, we have to go all the way to the f manifold of atomic orbitals to find a six-lobed orbital that serves as a basis for the A_2 irreducible representation.

Rotations about the x, y, and z axes also constitute functions often listed at the right-hand side of the character table. In the case of the C_{3v} point group, it is seen that R_z serves as a basis for the A_2 irreducible representation (counter-clockwise rotation becomes clockwise upon reflection through a σ_v plane).