CHEMISTRY 273

DEGENERACIES IN ABELIAN GROUPS

"THE EXCEPTION THAT EDIFIES THE RULE"

I. We have shown that

(a) If a set of operators (say $\hat{\mathcal{H}}$ and the symmetry operations of a point group) mutually commute, then they can be simultaneously diagonalized; i.e., there will be a set of eigenfunctions such that each operation takes every function into a constant times itself.

(b) Each of these functions necessarily forms the basis for a one-dimensional irreducible representation, whose characters are just the eigenvalues of the function under the group operations.

(c) Since each symmetry operation takes the function into a constant times itself (i.e., one-dimensional representations) there is (almost) no compelling reason to expect any degeneracies in the energies (the eigenvalues of $\hat{\mathcal{H}}$). Of course, this would not be true if the symmetry operations took the wavefunctions into linear combinations of themselves (i.e., non-Abelian groups with two- or three-dimensional irreducible representations), in which case several sets of functions will be eigenfunctions of $\hat{\mathcal{H}}$ (the various sets corresponding to arbitrary combinations of degenerate eigenfunctions).

II. Suppose that we have a set of real operators ($\hat{\mathcal{H}}$ and the symmetry operations of a point group) which all mutually commute and thus have one one-dimensional irreducible representations. Can we ever expect the eigenvalues of the hamiltonian to be degenerate?

(a) Suppose that the i^{th} and j^{th} irreducible representations are distinct but are complex conjugates of one another:

$$\Gamma_i(\Re) = (\Gamma_j(\Re))^*$$

Since $\hat{\Re}\psi_i = \Gamma_i(\Re)\psi_i$ and $\hat{\Re}\psi_j = \Gamma_j(\Re)\psi_j = (\Gamma_i(\Re))^*\psi_j$ and $\hat{\Re} = \hat{\Re}^*$ (operators real) then $\psi_i^* = \psi_j$ [since $\hat{\Re}\psi_i^* = \Gamma_j(\Re)\psi_i^*$], i.e., ψ_i and ψ_i^* each form the basis for a distinct one-dimensional representation (note ψ_i and ψ_i^* are distinct eigenfunctions if $\psi_i^* \neq$ (const.) ψ_i).

However $\hat{\mathcal{H}}$ is a hermetian operator which means that its eigenvalues must be real so that

$$\hat{\mathcal{H}}\,\psi_i = E_i\,\psi_i$$

$$\hat{\mathcal{H}}^*\psi_i^* = E_i^*\psi_i^* = E_i\psi_i^* \qquad \text{(since } E_i \text{ is real)}$$

$$\hat{\mathcal{H}}\,\psi_j = E_j\psi_j$$

$$\hat{\mathcal{H}}\ \psi_j = \hat{\mathcal{H}}^*\psi_i^* \qquad \text{(since } \psi_i^* = \psi_j \text{ and if } \hat{\mathcal{H}} \text{ is real)}$$

$$E_j\psi_j = E_i\,\psi_i^*$$

$$E_j\psi_j = E_i\psi_j$$

$$E_j = E_i \text{ (degenerate!!)}$$

thus $E_i = E_i^* = E_j$ since E_i and E_j are real, and we do expect degeneracies in this case.

(b) Note that the groups C_n, C_{nh}, and S_n ($n \geq 3$) are of this type.

(c) The hamiltonian in the Schrödinger equation fits the above requirements whenever it contains no imaginary terms (this will generally be the case when there are no magnetic fields present).

(d) Thus if we have an Abelian group (only one-dimensional irreducible representations) and do not expect degeneracies due to having irreducible representations which are complex conjugates of one another, then any degeneracy is accidental by edict!