<u>Basic Elements of Group Theory</u>

1. The molecular point groups consist of all symmetry operations that leave the rigid body made up by the molecular equilibrium conformation invariant (only lead to a permutation of equivalent nuclei). The symmetry operations act on the “dynamic variables”, that is, electronic coordinates and nuclear displacements.

2. The molecular Hamiltonian commutes with all symmetry operations $\mathcal{R}$ or, equivalently, remains invariant under all $\mathcal{R}$, i.e. $\mathcal{R}\,\hat{\mathbf{H}}\,\mathcal{R}^{-1} = \hat{\mathbf{H}}$ (transforms totally symmetric).

3. The eigenfunctions Ψ of $\hat{\mathbf{H}}$ transform in a symmetry-adapted manner, i.e. $\mathcal{R}\Psi = \pm\Psi$ in the absence of degeneracy. For degenerate eigenvalues the corresponding eigenfunctions transform only within the “degenerate set”.

4. The transformation matrices are the subject of representation theory and are called representation matrices (irreducible for a given eigenvalue of $\hat{\mathbf{H}}$). The eigenfunctions “form the basis of” (or “span”) the representation. In the non-degenerate case the matrices are 1 x 1 matrices and equal to their character (= trace of matrix).

5. Products of wavefunctions (or wavefunctions and operators) span the “direct product” of the individual representations.

6. The representation spanned by the integrand of a matrix element has to contain the totally symmetric irreducible representation at least once, if the integral is not to vanish by symmetry.