5.62 Physical Chemistry II
Spring 2008

5.62 Lecture #13 Supplement:
Nuclear Spin and Symmetry Number

$P_{12}\Psi = \pm\Psi$ is required for all pairs of identical particles. + for boson, – for fermion. (Identical means *same* nucleus, *not same* chemical environment.)

$(P_{12})^2\Psi = \Psi$ means that there are only two classes of symmetry functions for each group of identical nuclei.

e.g. benzene   6H $I_i = 1/2$ I = 3,1 para: degeneracy   7 + 3 = 10
     4, 2, 0 ortho: degeneracy   9 + 5 + 1 = 15

         6C $I_i = 0$ only $I_{tot} = 0$

To construct Ψ with legal permutation symmetry with respect to ψ_{rot}, we need to consider superpositions of bonded networks. e.g. the C_2 symmetry operation permutes pairs of C's and pairs of H's. Yet the permutation must be even with respect to C's.

How many bonded networks are there?

$$\frac{6!6!}{2\cdot6}$$

We divide by 12 because this is the overcounting due to rotationally related identical structures. 12 is the symmetry number.

We divide q_{rot} by the symmetry number because we are correcting the number of distinct bonded networks. We normally do not include the number of bonded networks because this is merely a function of the total number of identical atoms. This permutation degeneracy is conserved as long as atoms are conserved.

But actually every rotation-vibration level of benzene is $\frac{6!6!}{12} = 43,200$ fold degenerate! But we never worry about this degeneracy because, for normal levels of internal excitation, bonds are conserved. But at high excitation, bond-breaking isomerization occurs.

This means that the appropriate symmetry group for a molecule is called "The Molecular Symmetry Group", a subgroup of the "Complete Permutation Inversion Group". The subgroup consists of all "feasible" permutations and permutation-inversions.