CHEMISTRY 273

SUMMARY OF IMPLICATIONS OF THE COMMUTATION OF SYMMETRY OPERATORS AND THE HAMILTONIAN

1. Physical picture:

equivalent points $\vec{q_1}, \vec{q_2}, \vec{q_3}, \ldots$, etc., where $\hat{\mathcal{R}}\ \vec{q_i} = \vec{q_j}$

for non-degenerate wavefunctions

$$\psi^2(\vec{q_1}) = \psi^2(\vec{q_2}) = \psi^2(\vec{q_3}) \ ..$$

$$\psi(\vec{q_1}) = \pm\psi(\vec{q_2}) = \pm\psi(\vec{q_3}) \ldots \qquad \psi(\vec{q_1}) = e^{i\alpha}\,\psi(\vec{q_2}) = e^{i\alpha}\psi(\vec{q_3}) \ldots$$

The wave function must have the same magnitude at symmetry equivalent points, but the sign relationships of ψ at these points corresponds to the symmetry classifications of the wavefunctions.

For an m-fold degenerate wavefunctions $\{\psi_1 \cdots \psi_m\}$

$$\sum_{i=1}^{m} \psi_i^2(\vec{q_1}) = \sum_{i=1}^{m} \psi_i^2(\vec{q_2}) = \sum_{i=1}^{m} \psi_i^2(\vec{q_3}) \quad \ldots$$

i.e., the relative signs and magnitudes of the ψ's at symmetry equivalent points must assure the equality of observable electron density of symmetry equivalent positions.

2. Mathematical picture:

Since $\hat{H}$ commutes with all symmetry operations of a point group (the $\hat{\Re}_k$'s).

(b) Eigenfunctions of $\hat{H}$ are also eigenfunctions of $\hat{\Re}_k$'s and the eigenvalues of $\hat{\Re}_k$'s are "good" quantum numbers.

[The set of eigenvalues E_i, r_{1i}, r_{2i}... specify the actual state corresponding to ψ_i.]

(c) If **all of the symmetry operators mutually commute**, then a single set of vectors (wavefunctions) are eigenvectors for all $\hat{\Re}$'s. In this case

$$\hat{\Re}_k \psi_i = r_{ki}\psi_i$$

and there is (almost) not reason to expect two E_i's to be the same, i.e., any degeneracy is accidental.

(d) If s**ymmetry operators do not mutually commute with one another**, there must be more than one set of eigenvectors of $\hat{H}$. This implies degeneracy in the eigenvalues and eigenvectors of $\hat{H}$!