Symmetry of Molecules and Group Theory (Hagiwara)

Problem Set #4(For Chapter 5&6) 2019/11/27

1. Prove that the direct product of any two 2 x 2 matrices has a trace equal to the product of the traces of the 2 x 2 matrices.

2. In determining vibrational selection rules we shall need to determine whether integrals of the type:

$$\int \psi_v^0 f \psi_v^1 d\tau$$

are nonzero, where the function f is x, y, z, x^2, y^2, z^2, xy, yz, zx, or any combinations or sets thereof. Also, ψ_v^0 is totally symmetric and ψ_v^1 may belong to any irreducible representation. Identify the irreducible representations to which may belong in order to give nonzero integrals for molecules of symmetry C_{4v} and D_{3d}.

3. Work out the molecular orbitals of bifluoride anion (HF_2^-, $D_{\infty h}$) following the procedure below.
(1) Taking account a linear arrangements of the three atomic orbitals, s_H, p_{F1}, p_{F2}, obtain the representations of them.
(2) Construct the secular determinant for the LCAO's.
(3) Show that the energy level of bonding and antibonding orbital based on LCAO's is expressed by $[(\alpha s_H + \alpha p) \pm \{(\alpha s_H - \alpha p)^2 + 4\beta^2\}^{1/2}] / 2$, where αs_H and αp are Coulomb integrals of s orbital of hydrogen atom and p_z orbitals of fluorine atoms and β is a resonance integral for s_H and p_z orbitals.
(4) Draw the molecular orbital energy diagram and show the electron configuration.