MASSACHUSETTS INSTITUTE OF TECHNOLOGY

Applications of Group Theory to the Physics of Solids—6.734J & 8.510J

PROBLEM SET # 4

Issued: March 1, 2002 Due: March 8, 2002

1. (a) Write the (4×4) direct product matrix A formed from the (2×2) matrices B and C in accordance with $A = B \otimes C$, where

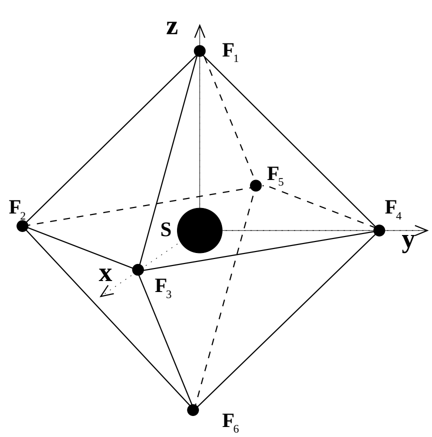
$$B = \begin{pmatrix} b_{11} & b_{12} \\ b_{21} & b_{22} \end{pmatrix} \qquad \text{and} \qquad C = \begin{pmatrix} c_{11} & c_{12} \\ c_{21} & c_{22} \end{pmatrix}.$$

   (b) Consider electric dipole transitions in a molecule with full cubic O_h symmetry for transitions between an initial state with A_{1g} symmetry (s-state) and a final state with T_{1u} symmetry (p-state), where the perturbation associated with electromagnetic interaction is $\mathcal{H}_{em} \sim \vec{p} \cdot \vec{A}$. [Note that one of these electric dipole matrix elements is proportional to a term $(1|p_x|x)$, where $|1)$ denotes the s-state and $|x)$ denotes the x partner of the p-state.] Of the 9 possible matrix elements that can be formed, how many are non-vanishing? Of those that are non-vanishing, how many are equivalent?

   (c) If the initial state has E_g symmetry (rather than A_{1g} symmetry), repeat part (a). You will find it convenient to use as basis functions for the E_g level the two partners $x^2 + \omega y^2 + \omega^2 z^2$ and $x^2 + \omega^2 y^2 + \omega z^2$ where $\omega = \exp(2\pi i/3)$.

   (d) Repeat part (a) for the case of electric dipole transitions from an s-state to a p-state in tetragonal D_{4h} symmetry. Consider the light polarized first along the z direction and then in the $x - y$ plane. Note that as the symmetry is lowered, the selection rules become less stringent.

2. Consider the SF_6 molecule with octahedral symmetry shown on p. 176 of class notes.



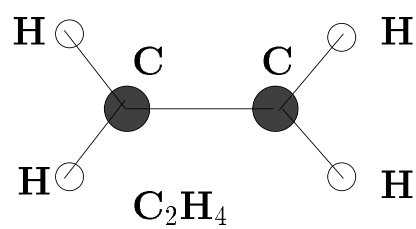
(a) Using $\chi^{\text{atom sites}}$, construct the linear combination of atomic orbitals for the six fluorine atoms which transform according to the 3 irreducible representations contained in $\chi^{\text{atom sites}}$, assuming for the moment that there are s functions on the six fluorine sites, labeled F_i, $i = 1, \ldots 6$.

(b) What are the symmetries for the six LCAO's in (a), if we now assume that we have p-functions on each of the fluorine sites?

(c) What are the irreducible representations corresponding to σ-bonds and π-bonds for the central sulfur atom to the 6 fluorine atoms? Sketch the orientation of these bonding orbitals.

(d) What are the angular momentum states required to bond the sulfur to the fluorine.

3. C_2H_4 (ethylene) is a planar molecule which has the configuration shown on the diagram below:



(a) Identify the appropriate point group for C_2H_4.

(b) Find $\chi^{\text{atom sites}}$ for the 2 carbon atoms and for the 4 hydrogen atoms.

(c) Give the block diagonal structure for the secular equation for the electronic energy levels of ethylene.

(d) How do the carbon atoms satisfy their bonding requirements? Which angular momentum states are needed to form bonding orbitals from each carbon atom?