MASSACHUSETTS INSTITUTE OF TECHNOLOGY

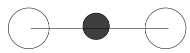
Applications of Group Theory to the Physics of Solids—6.734J & 8.510J

PROBLEM SET # 5

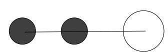
Issued: March 8, 2002 Due: April 3, 2002

1. This problem concerns molecular vibrations for the C_2H_4 molecule of Problem #3, of Problem Set #4.
   (a) Using the point group and $\chi^{\text{atom sites}}$ found in Problem 3 of Problem Set #4, find the symmetries of the allowed molecular vibrations.
   (b) Sketch the normal mode displacements for each of the allowed molecular vibrations in (a).
   (c) Which modes are infrared-active? Which are Raman-active? What are the polarization selection rules?

2. Both CO_2 and N_2O are linear molecules, but have different equilibrium arrangements:



CO_2



N_2O

   (a) What are the appropriate point groups for CO_2 and N_2O?
   (b) What are the differences in the symmetries of the normal mode vibrations for these two molecules?
   (c) Show schematically the atomic displacements for the normal mode vibrations of each molecule.
   (d) What are the expected differences in their IR vibrational spectra? Raman vibrational spectra?
   (e) What are the expected differences in the rotational spectra of these two molecules?
   (f) Which of these rotational modes can be excited by infrared or Raman spectroscopy?

3. (a) Find the molecular vibrations for the hypothetical molecule XH_{12} where the 12 hydrogen atoms are at the vertices of a regular icosahedron and the atom X is at the center of the icosahedron. Find $\chi^{\text{atom sites}}$ for XH_{12} for the icosahedral group I_h.
   (b) What are the symmetries for the normal modes? Which are infrared-active? Raman active?
   (c) What are the polarization selection rules for the infrared-active modes? for the Raman-active modes?

4. Use the following character table for the permutation group $P(5)$.

$P(5)$ or S_5	(1^5)	$10(2,1^3)$	$15(2^2,1)$	$20(3,1^2)$	$20(3,2)$	$30(4,1)$	$24(5)$
Γ_1^s	1	1	1	1	1	1	1
Γ_1^a	1	–1	1	1	–1	–1	1
Γ_4	4	2	0	1	–1	0	–1
$\Gamma_{4'}$	4	–2	0	1	1	0	–1
Γ_5	5	1	1	–1	1	–1	0
$\Gamma_{5'}$	5	–1	1	–1	–1	1	0
Γ_6	6	0	–2	0	0	0	1
$\chi_{\text{perm.}}(\psi_1\psi_1\psi_1\psi_1\psi_1)$	1	1	1	1	1	1	1
$\chi_{\text{perm.}}(\psi_1\psi_1\psi_1\psi_1\psi_2)$	5	3	1	2	0	1	0
$\chi_{\text{perm.}}(\psi_1\psi_1\psi_1\psi_2\psi_2)$	10	4	2	1	1	0	0
$\chi_{\text{perm.}}(\psi_1\psi_1\psi_1\psi_2\psi_3)$	20	6	0	2	0	0	0
$\chi_{\text{perm.}}(\psi_1\psi_1\psi_2\psi_2\psi_3)$	30	6	2	0	0	0	0
$\chi_{\text{perm.}}(\psi_1\psi_1\psi_2\psi_3\psi_4)$	60	6	0	0	0	0	0
$\chi_{\text{perm.}}(\psi_1\psi_2\psi_3\psi_4\psi_5)$	120	0	0	0	0	0	0

(a) Multiply element

$$P_i = \begin{pmatrix} 1 & 2 & 3 & 4 & 5 \\ 3 & 2 & 1 & 4 & 5 \end{pmatrix}$$

by element

$$P_j = \begin{pmatrix} 1 & 2 & 3 & 4 & 5 \\ 4 & 2 & 5 & 1 & 3 \end{pmatrix}$$

to form $P_k = P_iP_j$ and $P_{k'} = P_jP_i$. In which classes are P_k and $P_{k'}$? Are your results consistent with the character table?

(b) Show that there are 10 symmetry elements in the class $(2,1^3)$ and 20 symmetry elements in class $(3,2)$ for the permutation group $P(5)$. Give an example of a symmetry element in each class.

(c) Verify the results given in Table 10.6 for the Pauli-allowed states for p^5 by considering unfilled states (holes) in the p-shell.

(d) Referring to Table 10.6, what are the irreducible representations for the spin configuration $(\uparrow\uparrow\downarrow\downarrow\downarrow)$?

(e) Using Hund's rule, what are the total spin and orbital angular momenta values for the d^5 configuration? Explain how to find the irreducible representations for this configuration from Table 10.6. You will make use of some of the results in (e) when you work parts (h) and (i) of this problem.

(f) What are the characters for the equivalence transformation for a state where 3 of the 5 electrons are in a p-state and 2 electrons are in a d-state? Explain how you obtained your result. What irreducible representations are contained in this equivalence transformation?

(g) What are the Pauli allowed states (as would be given in Table 10.6) with the largest L value for the p^3d^2 configuration?

(h) Consider the addition of Mn^{2+} as a substitutional magnetic impurity for CdTe. Since Mn^{2+} has five $3d$ electrons, use the permutation group $P(5)$ to find the Pauli-allowed states for the Mn^{2+} ion in CdTe. Of these Pauli-allowed d^5 states, which is the ground state based on Hund's rule (see part e)?

(i) Using the electric dipole selection rule for optical transitions, find the allowed transitions from the ground state for Mn^{2+} in CdTe in (a) to Pauli-allowed states in the $3d^44p$ configuration.