B7 Symmetry 2009-10: Questions

1. Using the definition of a group, prove the Rearrangement Theorem, that the set of h products RS obtained for a fixed element S, when R ranges over the h elements of the group, comprises each element of the group exactly once.

2. Find the equivalence classes of the point group D_{4h} by collecting together symmetry operations that are related by symmetry. How many distinct classes of C_2 operation are there?

3. Show that the representation matrices generated by

$$\hat{R}\varphi_i = \sum_j \varphi_j D_{ji}(R)$$

satisfy $D(R)D(S) = D(RS)$. Demonstrate that these matrices form a group.

Consider secondly the alternative definition

$$\hat{R}\varphi_i = \sum_j D_{ij}(R)\varphi_j$$

and show that matrices generated in this way do not satisfy $D(R)D(S) = D(RS)$.

4. Use the Great Orthogonality Theorem to show that, if Γ is irreducible, then

$$\frac{1}{h}\sum_c h_c |\chi^{\Gamma}(c)|^2 = 1 \ .$$

What is the result when Γ is a reducible representation

$$\Gamma = m_1\Gamma_1 \oplus m_2\Gamma_2 \oplus \ldots \ ?$$

5. The cyclic group of order h has elements $\{A, A^2, A^3, \ldots, A^h\}$, where $A^h = E$.

(a) How many irreducible representations are there, and what are their dimensions?

(b) Find the irreducible representations and verify the orthogonality theorem for their characters. [Hint: Note that the homomorphism requires that $D(A)^h = D(A^h)$.]

6. Write down the first and second orthogonality theorems for characters, and interpret them in terms of the orthogonality of the rows and columns, respectively, of the character table. Use these theorems to show that the number of irreducible representations is equal to the number of classes.

7. The regular representation Γ^{reg} for a group with elements R_k is defined so that

$$D^{reg}_{ij}(R_k)=1 \quad \text{if } R_i^{-1} R_j = R_k \ ;$$
$$D^{reg}_{ij}(R_k)=0 \quad \text{if } R_i^{-1} R_j \neq R_k \ .$$

Show that $\chi^{reg}(E) = h$, the order of the group, and that $\chi^{reg}(R) = 0$ for $R \neq E$. Hence show that

$$\Gamma^{reg} = \sum_s n_s \Gamma_s$$

where n_s is the dimension of the s^{th} irreducible representation Γ^s. Show also that

$$\sum_s (n_s)^2 = h \, .$$

8. Find the irreducible representations spanned by a set of *d* orbitals on an atom located at the origin for the following point group symmetries:

(i) C_{2v}; (ii) C_{4v}; (iii) T_d; (iv) O_h.

9. Find the irreducible representations spanned by the *f* orbitals of a rare earth ion in an octahedral complex of O_h symmetry. [You may find it helpful to note that O_h is the direct product of the groups O and C_i and that therefore the irreducible representations of O_h are those of O with an additional *g* or *u* label.]

10. Use symmetry to determine which of the molecules H_2O, CH_4, CFHO and CHFBrCl may have dipole moments. What can you say, on symmetry grounds, about the direction of the dipole moment in each case?

11. The charge and dipole, quadrupole & octopole moments *etc*. of a molecule (the multipole moments of rank 0, 1, 2, 3, … , *n*, …) have respectively 1, 3, 5, 7, … , *2n+1*, … components which transform like the spherical harmonics of rank 0, 1, 2, 3, … , *n*, … Determine which is the lowest-rank non-vanishing multipole moment for the following molecules: H_2O, BF_3, CF_4, CO_2, SF_6.

12. (a) Show that by symmetry arguments any molecule may carry a non-zero charge.

(b) Does symmetry allow a non-zero dipole moment for CO? Discuss briefly its likely magnitude relative to other molecular dipole moments and its expected sign.

The (correct) answer to (b) illustrates the following principle. *If symmetry arguments tell us that the dipole moment may be non-zero, we expect that it will indeed be non-zero.*

(c) This principle applies to dipole moments, but, as part (a) and the existence of many neutral molecules together indicate, not to charges. Why does this principle not apply to charges?

13. Consider electric dipole transitions from the non-bonding molecular orbitals of the water molecule (whose symmetries are a_1 and b_1) to the antibonding ones (a_1 and b_2). In each case, determine whether the transition is allowed and, if so, in what polarization.

14. Using the equation derived in the notes,

$$\chi^{(J)}(\alpha)=\frac{\sin(J+\frac{1}{2})\alpha}{\sin\frac{1}{2}\alpha} ,$$

show that in the Full Rotation Group

$$\chi^{(j_1)}(\alpha)\chi^{(j_2)}(\alpha)=\sum_{J=|j_1-j_2|}^{j_1+j_2}\chi^{(J)}(\alpha) ,$$

and hence that

$$\Gamma^{(j_1)}\otimes\Gamma^{(j_2)}=\Gamma^{(j_1+j_2)}\oplus\Gamma^{(j_1+j_2-1)}\oplus\cdots\oplus\Gamma^{(|j_1-j_2|)} .$$

[Multiply the RHS by $\sin\frac{1}{2}\alpha$ top and bottom, then use: *2 sin A sin B = cos (A–B) – cos (A+B)*. Terms should cancel out pairwise.]

15. How many components are there of the doubly excited (v = 2) state of a T_{1u} vibration of an octahedral molecule of O_h symmetry, and what are their symmetries?

16. (a) In the full rotation group *SO(3)* the symmetrized and antisymmetrized squares of $\Gamma^{(J)}$ are

$$[\Gamma^{(J)}\otimes\Gamma^{(J)}]_+=\Gamma^{(2J)}\oplus\Gamma^{(2J-2)}\oplus\cdots\oplus\Gamma^{(0)} ,$$

$$[\Gamma^{(J)}\otimes\Gamma^{(J)}]_-=\Gamma^{(2J-1)}\oplus\Gamma^{(2J-3)}\oplus\cdots\oplus\Gamma^{(1)} .$$

Use this result to find the allowed terms for a d^2 atomic configuration. For these terms, you should use the usual labels S, P, D *etc.*, where S ≡ $\Gamma^{(0)}$, P ≡ $\Gamma^{(1)}$, D ≡ $\Gamma^{(2)}$ and so on; include also the spin multiplicity of each term, as in ^{1}S for example.

(b) Determine the terms arising from the configurations e_g^2, e_gt_{2g} and t_{2g}^2 in symmetry O_h. Which are singlets and which triplets?

(c) Construct a correlation diagram connecting the free-atom terms with those in a strong octahedral crystal field for (i) a d^2 ion and (ii) a d^8 ion.

[One way of doing this is to put the free atom terms on the left hand side of the diagram. For both d^2 and d^8, assume the ordering ^{3}F < ^{1}D < ^{3}P < ^{1}G < ^{1}S, though in fact ^{1}D ≈ ^{3}P. On the right hand side, put the three strong field terms e_g^2, e_gt_{2g} and t_{2g}^2 in the appropriate energy order. Now derive the relevant states from the free atom terms on the left – for instance ^1D splits into ^1E_g and $^1T_{2g}$ – and from the free atom configurations on the right. All the states are *g*, not *u*, in this problem. Correlate the lowest energy available states of each symmetry from each side of the diagram.]

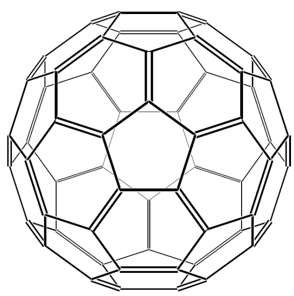
17. The quadrupole–quadrupole polarizability $C_{\alpha\beta,\gamma\delta}$ transforms according to the symmetrized square of Γ_Θ, where Γ_Θ is the representation spanned by the components of Θ, the quadrupole moment. Θ transforms in the same way as the spherical harmonics Y_{2M} (*i.e.,* like *d* orbitals). What is the number of independent non-zero components of $C_{\alpha\beta,\gamma\delta}$ for a molecule whose symmetry is:
(i) I_h ; (ii) O_h ?

18. Show that, whatever the symmetry Γ of the electronic state in a linear molecule may be, there is no non-symmetric vibrational mode (of symmetry Γ_Q) that satisfies the Jahn–Teller condition $(\Gamma \otimes \Gamma)_+ \ni \Gamma_Q$.

19. Show that infra-red and Raman spectroscopy can be used to distinguish planar D_{3h} from pyramidal C_{3v} structures of AX_3 molecules. [Use descent in symmetry tables to find the vibrational symmetries for C_{3v} from those for D_{3h}.]

20. In the infra-red spectrum of BF_3, the A_2'' fundamental ν_2 and its second overtone $3\nu_2$ are seen, but not the first overtone $2\nu_2$. Why is this? What would you expect to see in the region of the first overtone of the E' mode ν_4?

21. Consider the vibrations of buckminsterfullerene, C_{60}, taking axes on each C atom so that *z* describes its outward displacement. Verify that all the (x,y) displacements form a basis for the regular representation of I_h. Hence determine the symmetries of all the normal modes of C_{60}. Which of these modes are infra-red active and which are Raman active? Describe the form of the modes that are responsible for the two most intense Raman bands.



Tripos Questions (Typical of Paper 2)

22. Show that the character of the representation spanned by a set of spherical harmonics of angular momentum j for a rotation through α about any axis is

$$\chi^j(\alpha) = \frac{\sin(j+\frac{1}{2})\alpha}{\sin\frac{1}{2}\alpha}$$

Explain what is meant by the direct product of two irreducible representations Γ_a and Γ_b. What is the condition for the direct product to contain the symmetric representation Γ_1?

The dipole-quadrupole polarizability $A_{\alpha,\beta\gamma}$ (α, β, $\gamma = x$, y or z) describes the quadrupole moment induced by an external field or the dipole moment induced by an external field gradient. It has 15 independent components, which transform in the same way as the set of products of one *d* function with one *p* function. How many of these independent components may be non-zero for a molecule of symmetry (i) $C_{\infty v}$, (ii) T_d?

23. The symmetrized cube of a representation Γ has character

$$\chi^{\Gamma^3_+}(R) = \tfrac{1}{6}\{[\chi^\Gamma(R)]^3 + 3\chi^\Gamma(R)\chi^\Gamma(R^2) + 2\chi^\Gamma(R^3)\}.$$

(a) The states of an oscillator of symmetry Γ with three quanta of vibration transform according to the symmetrized cube of Γ. Show that there are always four such states for a doubly degenerate vibration. What are the symmetries of these states in (i) C_{3v} and (ii) T_d symmetry?

(b) The first hyperpolarizability β_{ijk} (where each of i, j and k may take the values x, y or z) has 27 components, but the independent components are fewer in number and transform according to the symmetrized cube of the symmetry species of the dipole operator $\hat{\mu}$. Show that the hyperpolarizability of a molecule of C_{3v} symmetry has 3 independent non-vanishing components. How many independent non-vanishing components are there for a molecule of T_d symmetry?

Other Tripos questions: 2000-34, 2001-36, 2002-36, 2003-22, 2004-28, 2005-27, 2006-28, 2007-27, 2008-28.

Shorter Tripos questions (Paper 4): 2004-73, 2006-71, 2007-71.