Groups and Symmetries

Problem Sheet 6

1. The octahedral group O is the group of symmetries of a cube or octahedron. Its classes and irreducible representations have the same structure as those of the tetrahedral group (see Q4.4): its character table is

O	$\{e\}$	$\{3C_2 = 3C_4^2\}$	$\{8C_3\}$	$\{6C_2\}$	$\{6C_4\}$
A_1	1	1	1	1	1
A_2	1	1	1	-1	-1
E	2	2	-1	0	0
T_1	3	-1	0	-1	1
T_2	3	-1	0	1	-1

where A_1, A_2, E, T_1, T_2 are simply conventional names for the irreducible representations.

Consider an ion in a crystal at a site where it is surrounded by a regular octahedron of negative ions. Deduce the splitting of the $2L + 1$ degenerate electron energy levels for $L = 1, 2, 3, 4, \ldots$ due to the octahedral crystal field.

The octahedron of negative ions is now distorted by tiny elongation along one of the threefold axes of rotation, thereby reducing the symmetry group to D_3 (the $3C_2$ of D_3 being in the same class as the $6C_2$ of O). Deduce the further splitting of the electron energy levels.

2. An ion is located in a hexagonal crystal of point group $D_6 \cong D_3 \otimes Z_2$. Calculate how the $L = 1, 2, 3, 4, \ldots$ electron energy levels are split by the crystal field. [The character table for D_6 may be deduced from those of Z_2 and D_3: its six classes are $\{e\}$, $\{2C_6\}$, $\{2C_6^2\}$, $\{C_6^3\}$, $\{3C_2\}$, $\{3C_2'\}$.]

The hexagonal symmetry is further broken, by a trigonal distortion, down to the subgroup D_3. Does this produce any further splitting?

Finally, the introduction of a magnetic field along the original sixfold axis reduces the symmetry to C_3. Without further calculation state how the previous degeneracy is affected.

3. Deduce selection rules for dipole transitions between the states formed in Q6.1, both before and after the distortion of the octahedron of negative ions. In the latter case consider both an external field along the direction of the crystal distortion, and perpendicular to it.

4. (a) Show explicitly, by operating with all the group elements, that the functions xy and $x^2 - y^2$ generate 1-dimensional irreducible representations of C_{4v} and identify them.

   (b) Generate representations of C_{4v} starting from the functions (i) z (ii) x^2 (iii) x^3 and (iv) $\exp(ix)$. In those cases where the representation is reducible, reduce it and find suitable combinations of functions which generate the constituent irreducible representations.

   (c) Show that the representation of C_{4v} which is generated by starting from the function $f(ax + by)$, where a, b are non-zero real constants, is equivalent to the regular representation.

   (d) Use projection operators methods to construct general basis functions which transform according to the irreducible representations of C_{4v}.

5. The functions xe^{-r^2}, ye^{-r^2} and ze^{-r^2} are degenerate energy eigenfunctions for a particle moving in a spherically-symmetric harmonic oscillator potential. If a perturbation with C_{3v} symmetry is applied, deduce how this three-fold degeneracy will be split.

6. (a) The six functions $(x^2, y^2, z^2, xy, xz, yz)$ form a basis for the direct sum of the $L = 0$ and $L = 2$ representations of the full rotation group. By restricting to the octahedral group of Q6.1, deduce that $x^2 + y^2 + z^2$, $(x^2 - y^2, x^2 + y^2 - 2z^2)$ and (xy, xz, yz) must form bases for the A_1, E and T_2 representations, respectively.

   (b) In Raman scattering photons are scattered inelastically off atoms, the difference in energy of the incident and scattered photons being accounted by for by an atomic electron jumping energy levels. The rate may be computed by evaluating transition matrix elements of the form

$$\langle b|\mathbf{rr}|\mathbf{a}\rangle = \sum_{\mathbf{c}} \langle \mathbf{b}|\mathbf{r}|\mathbf{c}\rangle \langle \mathbf{c}|\mathbf{r}|\mathbf{a}\rangle$$

   for the electron transition $a \to b$ through some indeterminate intermediate state c. Deduce selection rules for Raman scattering from a crystal with octahedral symmetry. Distinguish between the situation where the incoming and outgoing photons are polarized along parallel directions and that in which they are polarized in perpendicular directions.