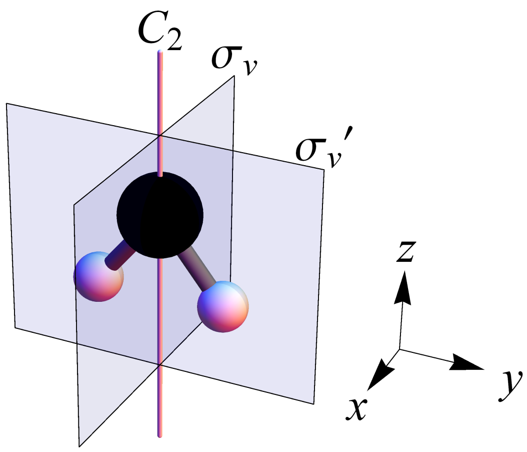
**Quantum Chemistry Supplementary Subject**
**GROUP THEORY PROBLEMS 2**

1. Determine the point groups of the following: (a) a maple leaf; (b) the symbol on the Isle of Man flag; (c) a snowflake; (d) a tennis ball (with seam); (e) a hexagonal pencil (sharpened at one or both ends).

2. What are the point groups of the following molecules: (a) the chair form of cyclohexane (ignoring hydrogens); (b) the boat form of cyclohexane (ignoring hydrogens); (c) the staggered configuration of ferrocene; (d) the eclipsed configuration of ferrocene; (e) buckminsterfullerene.

3. Construct the group multiplication table of $C_{2v}$. (You may find it helpful to think of the water molecule pictured below as an example of something with $C_{2v}$ symmetry.)




4. Form a basis for the valence orbitals of water, comprising the $2s$ and $2p$ orbitals of the oxygen atom and the two $1s$ orbitals of the hydrogen atoms. Find the matrix representatives of the $C_{2v}$ group operations in this basis.

   Hints: the basis is $\{O2s, O2p_x, O2p_y, O2p_z, H_1 1s, H_2 1s\}$. The matrices are six-dimensional, and there are four of them to determine. For example, you should find that

$$\mathbf{D}(C_2) = \begin{pmatrix} 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 & 0 & 0 \\ 0 & 0 & -1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 \\ 0 & 0 & 0 & 0 & 1 & 0 \end{pmatrix}$$

   Verify that your matrices satisfy the second row of your group multiplication table obtained in Q3.

5. Taking the matrix

$$\mathbf{U} = \begin{pmatrix} 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 1/\sqrt{2} & 1/\sqrt{2} \\ 0 & 0 & 0 & 0 & -1/\sqrt{2} & 1/\sqrt{2} \end{pmatrix}$$

show that the similarity transformation $\mathbf{U}^{-1}\mathbf{D}(R)\mathbf{U}$ reduces your representation of Q4 into the direct sum of six one-dimensional representations (holding for all four elements $R$ of the group).

Hints: you may find it useful to recall two results shown last year in the maths course. First, note that $\mathbf{U}$ is orthogonal and hence $\mathbf{U}^{-1} = \tilde{\mathbf{U}}$. Second, remember that matrices with the same block diagonal structure can be multiplied 'block by block'.

6. Since the representations in the direct sum of Q5 are all one-dimensional, they must be irreducible representations. Obtain the characters of the representations and hence (using the $C_{2v}$ character table) identify which irreducible representations they are.

7. What are the orbitals in the transformed basis of Q5?

8. Explain why the 'trivial' representation $\mathbf{D}(R) = 1$ (for all elements $R$) is a representation of every point group. Is it a faithful representation?

9. Show that if $\mathbf{D}(R)$ and $\mathbf{D}(S)$ are matrix representatives of the symmetry elements $R$ and $S$ respectively, then $\mathbf{D}(RS) = \mathbf{D}(R)\mathbf{D}(S)$. (In other words, show that the matrices obey the same multiplication rules as the symmetry elements themselves.)

10. Show that a similarity transformation of a representation preserves its multiplication rules.