1. Find all the possible symmetry operations for 1,2-propadiene:

![image](C=CC=C)

**Solution:**

The operations are: $E, C_2, C_2', C_{2''}, S_4, S_4', \sigma_v, \sigma_v'.

The $C_2$ axis is along $C = C = C$. The $C_2'$ and $C_{2''}$ axes are perpendicular to the $C_2$ axis and are located along the plane of the paper and perpendicular to the plane.

2. Derive the $C_{2v}$ multiplication table by applying two successive symmetry operations and identifying the resulting operation. Note that $C_{2v}$ point group is Abelian.

**Note that you need to construct a multiplication table not a direct product table.**

**Solution:**

The group is Abelian, which means that the order of multiplication does not matter, which simplifies the problem. The products can be worked out as follows:

Multiplication by $OE$ (the identity operation) always yields $O$ as the result (where $O$ is one of the symmetry operations in $C_{2v}$). Also operations such as $OO$ give $E$ (rotation and reflection). The only remaining operations are between $C_2, \sigma_v(xz)$ and $\sigma_v'(yz)$. The molecule is taken to reside in $yz$ plane. Let’s consider $C_2\sigma_v$ as an example. To visualize what is happening, think about NO$_2$ molecule and place $p_x$ atomic orbitals on the oxygen atoms. Note that the $x$ direction is out of the paper plane. $C_2$ will exchange the two oxygens and at the same time flip the $p_x$ orbitals around. Then $\sigma_v$ reflection just exchanges the oxygens again but without flipping the $p_x$ orbitals. The
net effect was to get flip the \( p_x \) orbitals. This same effect may be obtained by \( \sigma_v' \) operation and therefore \( C_2\sigma_v = \sigma_v' \). The same method can be used to go over all the remaineng elements in the product table.

3. What are the symmetry elements and point groups for the following molecules:

\[
\begin{align*}
\text{a) CH}_2\text{FCl} & \quad \text{d) HI} \\
\text{b) Sb} & = \text{O} & \text{e) TeCl}_4^- \\
\text{c) O = C = C = C = C = O} & \quad \text{f) cyclopropene:}
\end{align*}
\]

Solution:

In a) and b) only \( C_s \) symmetry element. The point group is \( C_s \).
In c) the symmetry elements are: \( C_\infty \) axis, \( \infty \) number of perpendicular \( C_2 \) axes and \( \sigma_v \) planes and \( \sigma_h \) plane. The poing group is \( D_{\infty h} \).
In d) the symmetry elements are: \( C_\infty \) axis and \( \infty \) many \( \sigma_v \) planes. The point group is \( C_{\infty v} \).
In both e) and f) the symmetry elements are: \( C_2 \) axis and two \( \sigma_v \) planes. The point group is \( C_{2v} \).

4. What are the irreps for \( s, p \) and \( d \) atomic orbitals in \( D_{6h} \) point group?

Solution:

From the character table we can see that both \( x \) and \( y \) correspond with the \( E_{1u} \) irrep. The \( p_x \) and \( p_y \) orbitals behave the same way and belong to \( E_{1u} \) as well. By using the same logic, \( p_z \) is \( A_{2u} \). \( s \) orbitals are always spherically symmetric and hence this is \( A_{1g} \). The Cartesian components of \( d \) orbitals are: \( d_{xz}, d_{yz}, d_{x^2-y^2}, d_{xy}, d_{z^2} \). These behave spatially exactly like the spatial operations (subscripts). As such, we immediately identify these as: \( E_{1g} \).
5. The following are the normal vibration modes of water molecule:

![Normal vibration modes of water molecule](image)

Apply the $C_{2v}$ symmetry operations for these modes and determine their irreducible representations (consider the directionality of the vectors shown).

**Solution:**

Mode 1 is unchanged under any symmetry operation in $C_{2v}$ and hence it has $A_1$ symmetry. The mode would be labelled as $a_1$.

Mode 2 is unchanged under any symmetry operation and hence the label is $a_1$.

The arrows correspond demonstrate the direction of atomic motion in molecular vibration.

Mode 3 is unchanged with $E$ and $\sigma'_v(yz)$ and the directions of the arrows get reversed ($-1$) with $C_2$ and $\sigma_v(xz)$. Thus the mode is labelled as $b_2$.

6. Consider $\text{H}_2\text{O}$ molecule residing in $yz$ plane (symmetry $C_{2v}$). Let $H_1$ and $H_2$ denote their 1$s$ orbitals. What are the irreps for the following linear combinations: $S_1 = H_1 + H_2$ and $S_2 = H_1 - H_2$? Which oxygen atom valence orbitals may form molecular orbitals with $S_1$ and $S_2$?

**Solution:**

The orbitals $S_1$ and $S_2$ can be visualized as shown below (the first figure).

From this we can see that $S_1$ corresponds to $A_1$ (all operations give 1) and $S_2$ to $B_2$ (characters $1 -1 -1 1$). The symmetry labels for the orbitals are therefore $a_1$ and $b_2$, respectively. The oxygen atom orbitals are shown in the second figure below. The 2$s$ O orbital is clearly $A_1$ (totally symmetric). According to the above picture, 2$p_z$ is also $A_1$. $p_y$ appears to be $B_2$ and $p_x$. 

7. Function $f_1$ exhibits symmetry corresponding to irrep $E_2$ and function $f_2$ irrep $A_1$ in $C_{6v}$ point group. Show that integral $\int f_1(x)f_2 d\tau = 0$ ($x$ represents multiplication by $x$ coordinate).

**Solution:**

Operator $x$ belongs to $E_1$ in $D_{6h}$ (the operator column). Thus the product we need to look at is $A_1 \times E_1 \times E_2$. The product table tells us that this is equal to $B_1 + B_2 + E_1$ (a sum of three characters). Since $A_1$ is not present in this sum, the integral is zero.

8. The ground state electronic wavefunction in $\text{H}_2\text{O}$ has $A_1$ symmetry in $C_{2v}$ point group. What are the symmetries of the excited states that can absorb
Linearly polarized light in a) $x$, b) $y$ and c) $z$ directions?

Solution:

The $C_2$ axis is along the $z$ axis and the molecule is in the $yz$ plane. The operator $x$ belongs to $B_1$. The ground state is $A_1$ and by looking at the product table, we can see that the excited state must have $B_1$ symmetry ($B_1 \times B_1 = A_1$). For $y$ ($B_2$) and $z$ ($A_1$) the corresponding excited state symmetries must be $B_2$ and $A_1$, respectively.