Introduction:

The shape of the molecules

Lewis’ Theory states the following rules about the molecular structures: i) Electrons (e-), especially those of the outer most (Valence) electronic shell, play a fundamental role in chemical bonding, ii) e- transfer leads to ionic bonds, iii) Sharing of e- leads to covalent bonds, and iv) e- are transferred of shared to give each atom a noble gas configuration, one with eighth outer-shell e-, or the octet.

Lewis structure can be built based on the following rules:

- All valence e- of the atom in a Lewis structure must appear in the structure.
- Usually, all e- in a Lewis structure are paired.
- Sometimes, multiple covalent bonds are needed for C, N, O, P and S atoms.
- H atoms are always terminal atoms.
- Central atoms are generally those with lowest electronegativity.
- C atoms are always central atoms.
- Except for the very large number of chainlike organic molecules, molecules and polyatomic ion generally have compact, symmetrical structure.

The following stategies should be applied to write Lewis structure:

1. Determine the total number of valence e- that must appear in the structure.
2. Identify the central atom(s) and terminal atoms.
3. Write the plausible skeletal structure. Join the atoms in the skeletal structure by single covalent bonds.
4. For each bond in the skeletal structure, substract two e- from the total number of valence e-.
5. With the valence e- remaining, first complete the octets of the terminal atoms, then, to the extent possible, complete the the octets of the central atom(s).
6. If one or more central atoms is left with an incomplete octet after Step 5, move lone-pair e- from terminal atoms to form multiple covalent bonds to central atom(s).

The shape of a molecule is established by experiment or by a quantum mechanical calculation confirmed by experiment. The results of these experiments and calculations are usually agreed with the valence-shell electron-pair repulsion theory (VSEPR). It is also called the geometric distribution of e- groups as the electron-group geometry and the geometric arrangement of the atomic nuclei as the molecular geometry. The most expected situations in which central atoms have two, three, four, five, or six e- groups distributed around them. Then, their electron-group geometries would be one of the followings: i) Two e- groups: linear, ii) Three e- groups: trigonal planar, iii) Four e- groups: tetrahedral, iv) Five e- groups: trigonal-bipyramidal, and v) Six e- groups: octahedral

To apply the VSEPR Theory the following step would be followed:

1. Draw the possible Lewis structure of the species (molecule or polyatomic ion).
2. Determine the number of e- groups around the central atom, and identify them as being either bond e- groups or lone pair of e-.
3. Establish electron-group geometry around the central atom.
4. Determine the molecular geometry from the positions around the central atom occupied by the other atomic nuclei.

The electronegativity differences between central and terminal atoms determine whether the bond dipoles exist in a molecule and the molecular shape determines whether bond dipoles cancel (nonpolar molecules) or combine to produce a resultant dipole moment (polar molecules).

The symmetry of the molecules

Symmetry operations are actions that leave the molecule apparently unchanged and each symmetry operation is associated with a symmetry element. The notations and explanations for the symmetry operations are as follows:

• \( E \) = The identity transformation (\( E \) coming from the German Einheit, meaning unity).

• \( C_n \) = Rotation (anticlockwise) through an angle of \( 2/n \) radians, where \( n \) is an integer. The axis for which \( n \) is greatest is termed the principle axis.

• \( C_n^k \) = Rotation (clockwise) through an angle of \( 2k/n \) radians. Both \( n \) and \( k \) are integers.

• \( S_n \) = An improper rotation (clockwise) through an angle of \( 2/n \) radians. Improper rotations are regular rotations followed by a reflection in the plane perpendicular to the axis of rotation. Also known as alternating axis of symmetry and rotationreflection axis.

• \( i \) = The inversion operator (the same as \( S_2 \)). In Cartesian coordinates, \((x, y, z) \rightarrow (-x, -y, -z)\). Irreducible representations that are even under this symmetry operation are usually denoted with the subscript \( g \) for gerade (german=even), and those that are odd are denoted with the subscript \( u \) for ungerade (german=odd).

• \( \sigma \) = Mirror plane (from the German word for mirror - Spiegel).

• \( \sigma_h \) = Horizontal reflection plane - passing through the origin and perpendicular to the axis with the 'highest' symmetry.

• \( \sigma_v \) = Vertical reflection plane - passing through the origin and the axis with the 'highest' symmetry.

• \( \sigma_d \) = Diagonal or dihedral reflection in a plane through the origin and the axis with the 'highest' symmetry, but also bisecting the angle between the twofold axes perpendicular to the symmetry axis.

The point group of a molecule is identified by noting its symmetry elements and comparing these elements that define each group. The assignment of the point groups of molecules depends on the identifying symmetry elements and the following strategies in Figure 1.
The crystal structures

In a crystal the repeating unit is three-dimensional; its contents consist of atoms, molecules, or ions. The smallest unit of volume of a crystal that shows all the characteristics of the crystal’s pattern is a unit cell. It should be noted that the unit cell is just the fundamental box that describes the arrangement. The unit cell is described by the lengths of its edges— a, b, c (which are related to the spacings between layers, d)— and the angles between the edges, α, β, and γ. Unit cells are stacked in three dimensions to build a lattice, the three-dimensional arrangement corresponding to the crystal.

In a simple, or primitive, lattice, (Figure 2) only the eight corners of the unit cell are equivalent. In other types of crystals, objects equivalent to those forming the outline of the unit cell may occupy extra positions within the unit cell. A body-centered lattice has equivalent points at the eight unit cell corners and at the center of the unit cell. Iron, chromium, and many other metals crystallize in a body-centered cubic (bcc) arrangement.
(Figure 2). The unit cell of such a metal contains one atom at the corners of the cell plus one atom at the center of the cell (and therefore entirely in this cell); this makes a total of two atoms per unit cell. A face-centered cubic (fcc) structure (Figure 2) involves the eight points at the corners and six more equivalent points, one in the middle of each of the six square faces of the cell. A metal (calcium and silver are cubic examples) that crystallizes in this arrangement has one atom at the corners plus three more in the faces, for a total of four atoms per unit cell. In more complicated crystals, each lattice site may represent several atoms or an entire molecule.

Nearly all metals crystallize in one of three types of lattices: body-centered cubic (bcc), face-centered cubic (fcc; also called cubic close-packed), and hexagonal close-packed. The latter two types are called close-packed structures because the particles (in this case metal atoms) are packed together as closely as possible. The differences between the two close-packed structures are illustrated in Figure 3. Let spheres of equal size represent identical metal atoms, or any other particles, that form close-packed structures. Consider a layer of spheres packed in a plane, A, as closely as possible (Figure 3). An identical plane of spheres, B, is placed in the depressions of plane A. If the third plane is placed with its spheres directly above those in plane A, the ABA arrangement results. This is the hexagonal close-packed (hcp) structure (Figure 3). The extended pattern of arrangement of planes is ABABAB . . . . If the third layer is placed in the alternate set of depressions in the second layer so that spheres in the first and third layers are not directly above and below each other, the cubic close-packed (ccp) structure, ABCABCABC . . . , results (Figure 3). In close-packed structures each sphere has a coordination number of 12, that is, 12 nearest neighbors. In ideal close-packed structures 74% of a given volume is due to spheres and 26% is empty space. The body-centered cubic structure is less efficient in packing; each sphere has only eight nearest neighbors, and there is more empty space.

Figure 3. Packing types
Experiment 1.

Procedure Part I: Constructing Molecular Models

For the following molecules:

\[
\begin{array}{cccccc}
\text{H}_2\text{S} & \text{CO}_3^{2-} & \text{AsCl}_6 & \text{PCl}_5 & \text{I}_3 \\
\text{NH}_3 & \text{SO}_4^{2-} & [\text{GaF}_3]^{2-} & \text{XeF}_4 & \text{XeO}_3 \\
\end{array}
\]

1) Write down the correct Lewis structure
2) Find the electron pair geometry (EPG) around the central atom
3) Find the molecular geometry (MG) using Valence Shell Electron Repulsion Theory (VSEPR)
4) Write down the VSEPR notation
5) Using 3-D molecular models construct the above molecules
6) Draw these 3-D molecules in your notebook
7) Write down the bond angles
8) Write down the hybridization of central atom
9) State if the molecule has a dipole moment
Procedure Part II: Determining Symmetry Elements

For the following molecules:
\( \text{NH}_3 \quad \text{SiF}_4 \quad \text{PF}_5 \quad \text{NHF}_2 \quad \text{CO}_2 \quad \text{IOF}_4 \quad \text{IO}_2\text{F}_2 \)

1) Write down the correct Lewis structure
2) Find the electron pair geometry (EPG) around the central atom
3) Find the molecular geometry (MG) using Valence Shell Electron Repulsion Theory (VSEPR)
4) Draw these 3-D molecules in your notebook
5) Write down the bond angles
6) State if the molecule has a dipole moment
7) List all the symmetry elements the molecule has (e.g. \( E, C_n, \sigma_h, \sigma_v, i, S_n \))
8) Assign the point group
Procedure Part III: Determining Crystal Structures

For the followings crystal structures:

<table>
<thead>
<tr>
<th>Simple cubic</th>
<th>Body Centered Cubic (bcc)</th>
<th>Face Centered Cubic (fcc)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Diamond</td>
<td>Graphite</td>
<td></td>
</tr>
<tr>
<td>Wurtzite (ZnS)</td>
<td>Rock Salt (NaCl)</td>
<td>Calcite (CaCO₃)</td>
</tr>
</tbody>
</table>

1) Examine crystal structures
2) Draw these 3-D crystal structures in your notebook
3) Calculate the number of each atom in a lattice and show molecular formulae calculation
4) Find the coordination numbers for each atom
5) Find the number of octahedral and tetrahedral holes, if there is any.
6) Calculate packing factor for simple cubic, body centered cubic (bcc), and face centered cubic (fcc) structures