The Shapes of Molecules

10.1 Lewis Structures of Polyatomic Species

- **Skeleton structure** – the connectivity of atoms in polyatomic species
  - Central atom(s) – usually the atom with the lower group number or higher period number (lowest EN)
    - Often written first in the formula – PCl₅, SO₃, …
    - Normally H is not a central atom
  - Polyatomic ions
    - The cation and the anion of an ionic compound are treated separately
    - Total number of valence e⁻ is adjusted for the charge of the ion

### Rules for Writing Lewis Structures

1. Write the skeleton structure by placing a single bond (e⁻ pair) between each bonded pair of atoms
2. Count the total number of valence electrons of all atoms, \( n_{tot} \) (correct for the charges of ions)
3. Count the number of remaining electrons, \( n_{rem} \) (total number of e⁻ minus e⁻ used in the skeleton structure as bonds)
4. Count the number of needed electrons, \( n_{need} \) (the e⁻ needed to complete the octet (or duplet) structures of all atoms)
5. If \( n_{need} = n_{rem} \), add the remaining e⁻ as lone pairs to complete the octets for all atoms, or
   - If \( n_{need} > n_{rem} \), add multiple bonds (1 bond for each deficient pair of e⁻) and complete the structure with lone pairs

### Example: Write the Lewis structure of \( \text{H}_2\text{O} \).
1. O is the central atom (can’t be H)
   \( \Rightarrow \text{H–O–H} \) (4 e⁻ in the skeleton structure)
2. \( n_{tot} = 1(\text{H}) + 6(\text{O}) + 1(\text{H}) = 8 \)
3. \( n_{rem} = 8 - 4 = 4 \)
4. \( n_{need} = 0(\text{H}) + 4(\text{O}) + 0(\text{H}) = 4 \)
5. \( n_{need} = n_{rem} \) \( \Rightarrow \text{H–O–H} \)

### Example: Write the Lewis structure of \( \text{SO}_4^{2-} \).
1. S is the central atom (higher period # than O)
   \( \text{(8 e⁻ in the skeleton structure)} \)
2. \( n_{tot} = 6(\text{S}) + 4\times6(\text{O}) + 2(\text{charge}) = 32 \)
3. \( n_{rem} = 32 - 8 = 24 \)
4. \( n_{need} = 0(\text{S}) + 4\times6(\text{O}) = 24 \)
5. \( n_{need} = n_{rem} \Rightarrow \text{complete structure with lone pairs} \)

### Resonance in Lewis Structures

Example: Write the Lewis structure of \( \text{NO}_3^- \).
1. N is the central atom (lower group # than O)
   \( \text{6 e⁻ in the skeleton structure} \)
2. \( n_{tot} = 5(\text{N}) + 3\times6(\text{O}) + 1(\text{charge}) = 24 \)
3. \( n_{rem} = 24 - 6 = 18 \) \( n_{need} = 2(\text{N}) + 3\times6(\text{O}) = 20 \)
4. \( n_{need} > n_{rem} \) deficiency of 2 e⁻ (2 e⁻ pairs)
   \( \Rightarrow \text{add 1 more bond between N and one of the Os and complete the structure with lone pairs} \)
– All three structures are valid Lewis structures and differ by the position of bonds and lone pairs → **Resonance structures**
– Neither of the resonance structures is realistic
– The real structure is a blend (**resonance hybrid**) of the contributing Lewis structures
– The three bonds are identical (intermediate between a single and a double bond)
– The bond order is \((2+1+1)/3 = 1.33\)

**Example:** Benzene, \(\text{C}_6\text{H}_6\).

- The two structures have **equal energies** and **contribute equally** to the hybrid
- The electrons from the double bonds are **delocalized** between all six \(\text{C}\) atoms
- The six \(\text{C}–\text{C}\) bonds are identical with bond orders of 1.5

**Formal charge (FC)** – a charge assigned to atoms in Lewis structures assuming that the shared \(e^-\) are divided equally between the bonded atoms.
- The \# of \(e^-\) assigned to an atom in a Lewis structure → all lone pair \(e^-\) (\(L\)) and half of the shared \(e^-\) (\(S\))
- The \# of valence \(e^-\) of an atom (\(V\)) → \(V = \text{group#}\)
- The \# of bonds for an atom (\(B\)) → \(B = S/2\)

\[
\text{FC} = V - \left[ L + S/2 \right] = V - \left[ L + B \right]
\]

- The FC shows the extent to which atoms have gained or lost \(e^-\) in covalent bond formation
- The sum of all FCs equals the charge of the species

**Exceptions to the Octet Rule**
- **Odd electron species** (radicals) → \(\cdot\text{CH}_3, \cdot\text{OH}, \cdot\text{NO}, \cdot\text{NO}_2, \ldots\)
  - Have an unpaired electron – paramagnetic
  - Highly reactive and short lived species
  - Significance to atmospheric chemistry (smog) and human health (antioxidants)

**Example:** Write the Lewis structure of NO. \([\text{N}–\text{O}]\)

\[
\begin{align*}
\text{n}_{\text{tot}} & = 5 + 6 + 1 = 12 \\
\text{n}_{\text{rem}} & = 16 - 4 = 12 \\
\text{n}_{\text{need}} & = 6 + 4 + 6 = 16 \\
\text{n}_{\text{need}} & > \text{n}_{\text{rem}} \quad \text{deficiency of 4} e^- \quad \Rightarrow \quad \text{add 2 more bonds}
\end{align*}
\]

- \(a) [\cdot\text{N}=\text{O}]:\)
- \(b) [\cdot\text{N}≡\text{C}–\text{O}]:\)
- \(c) [\cdot\text{N}–\text{C}≡\text{O}]:\)

\[
\begin{align*}
V & \rightarrow 5(\text{N}) \ 4(\text{C}) \ 6(\text{O}) \\
L+B & \rightarrow a) 6(\text{N}) \ 4(\text{C}) \ 6(\text{O}) \ FC \rightarrow a) -1(\text{N}) \ 0(\text{C}) \ 0(\text{O}) \\
L+B & \rightarrow b) 5(\text{N}) \ 4(\text{C}) \ 7(\text{O}) \ FC \rightarrow b) 0(\text{N}) \ 0(\text{C}) \ -1(\text{O}) \\
L+B & \rightarrow c) 7(\text{N}) \ 4(\text{C}) \ 5(\text{O}) \ FC \rightarrow c) -2(\text{N}) \ 0(\text{C}) \ +1(\text{O})
\end{align*}
\]

**Example:** Write the possible resonance structures of the \(\text{NCO}^-\) ion (N-C-O) including the formal charges of all atoms.

\[
\begin{align*}
\text{[N–C–O]}^- & = 5 + 4 + 6 + 1 = 16 \\
\text{n}_{\text{tot}} & = 16 - 4 = 12 \\
\text{n}_{\text{need}} & = 6 + 4 + 6 = 16 \\
\text{n}_{\text{need}} & > \text{n}_{\text{rem}} \quad \text{deficiency of 4} e^- \quad \Rightarrow \quad \text{add 2 more bonds}
\end{align*}
\]

- \(a) [\cdot\text{N}=\text{C}–\text{O}]:\)
- \(b) [\cdot\text{N}≡\text{O}–\text{C}]:\)
- \(c) [\cdot\text{N}–\text{C}≡\text{O}]:\)

\[
\begin{align*}
\text{V} & \rightarrow 5(\text{N}) \ 4(\text{C}) \ 6(\text{O}) \\
L+B & \rightarrow a) 6(\text{N}) \ 4(\text{C}) \ 6(\text{O}) \\
L+B & \rightarrow b) 5(\text{N}) \ 4(\text{C}) \ 7(\text{O}) \\
L+B & \rightarrow c) 7(\text{N}) \ 4(\text{C}) \ 5(\text{O})
\end{align*}
\]

<table>
<thead>
<tr>
<th>Most favored</th>
<th>Least favored</th>
</tr>
</thead>
<tbody>
<tr>
<td>{(\cdot) FC on the more EN atom}</td>
<td>(highest FCs)</td>
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</tbody>
</table>
• **Electron deficient molecules** – molecular compounds of some elements from groups 2 and 3A (Be, B and Al) form **incomplete octets** (have less than 8e- around the central atom)

**Example:** Write the Lewis structure of BeH₂.

\[ \text{H–Be–H} \]

\[ \text{n}_{\text{tot}} = 2 + 2 \times 1 = 4 \]

\[ \text{n}_{\text{rem}} = 4 - 4 = 0 \]

\[ \text{n}_{\text{need}} = 4 \]

⇒ additional bonds can not be used (no remaining e-)

\[ \text{H–Be–H} \]

⇒ the structure has an incomplete octet for the Be atom because the molecule is **electron-deficient**

**Example:** Write the Lewis structure of BF₃.

\[ \text{ntot} = 3 + 3\times7 = 24 \]

\[ \text{n}_{\text{rem}} = 24 - 6 = 18 \]

\[ \text{n}_{\text{need}} = 2 + 3\times6 = 20 \]

\[ \text{n}_{\text{need}} > \text{n}_{\text{rem}} \]

⇒ deficiency of 2 e⁻ ⇒ add 1 more bond

\[ \text{F} \]

\[ \text{BF₃} \]

\[ \text{BF₃(g)} + :\text{NH₃(g)} \rightarrow \text{NH₃BF₃(s)} \]

The second resonance structure has only 6e⁻ around B (incomplete octet), but it is the favored structure due to the lower formal charges

– Structures with incomplete octets are **electron-deficient** and tend to react with molecules that have abundance of e⁻ in the form of lone pairs

\[ \text{BF₃(g)} + :\text{NH₃(g)} \rightarrow \text{NH₃BF₃(s)} \]

– The lone pair of N is used to form the bond between B and N and completes the octet of B

\[ \text{Coordinate covalent bond} – \text{a bond in which both electrons come from the same atom} \]

**Expanded valence shells (extended octets)** – more than 8e⁻ around a central atom

– Expanded octets are formed only by atoms with vacant d-orbitals in the valence shell (p-elements from the third or later periods)

– Expanded octets form when:

  • There are too many electrons (\( \text{n}_{\text{need}} < \text{n}_{\text{rem}} \)) or more than 4 atoms are bonded to the central atom
  – electron-rich structures ⇒ place the extra electrons at the central atom

• Structures with **lower formal charges** can be achieved by forming an extended octet

**Example:** Write the Lewis structure of XeF₄.

\[ \text{ntot} = 8(\text{Xe}) + 4\times7(\text{F}) = 36 \]

\[ \text{n}_{\text{rem}} = 36 - 8 = 28 \]

\[ \text{n}_{\text{need}} = 0(\text{Xe}) + 4\times6(\text{F}) = 24 \]

\[ \text{n}_{\text{need}} < \text{n}_{\text{rem}} \]

4 extra e⁻ ⇒ add 2 lone pairs at Xe

\[ \text{F} \]

\[ \text{F–Xe–F} \]

\[ \text{F} \]

\[ \text{I₃}^- \]

\[ \text{Example:** Write the Lewis structure of I₃⁻.} \]

\[ \text{ntot} = 3\times7(\text{I}) + 1(\text{charge}) = 22 \]

\[ \text{n}_{\text{rem}} = 22 - 4 = 18 \]

\[ \text{n}_{\text{need}} = 4(\text{I}) + 2\times6(\text{I}) = 16 \]

\[ \text{n}_{\text{need}} < \text{n}_{\text{rem}} \]

2 extra e⁻ ⇒ add 1 extra lone pair at the central I atom after completing the octets for all atoms

\[ \text{I–I–I} \]

\[ \text{I} \]

\[ \text{I} \]

\[ \text{I} \]

\[ \text{I} \]

\[ \text{I} \]

\[ \text{I} \]

\[ \text{I} \]
Example: Select the favored resonance structure of the $\text{PO}_4^{3-}$ anion.

\[
\begin{array}{c}
\text{(a)} & \text{(b)} \\
\begin{array}{c}
\text{:O} & \text{:O} \\
\text{P} & \text{O} \\
\text{O} & \text{P} \\
\end{array} & \begin{array}{c}
\text{:O} & \text{:O} \\
\text{P} & \text{O} \\
\text{O} & \text{P} \\
\end{array}
\end{array}
\]

Formal charges:
(a) $\text{O} \rightarrow 6 - (6 + 1) = -1$  $\text{P} \rightarrow 5 - (0 + 4) = +1$
(b) $\text{O}^- \rightarrow 6 - (6 + 1) = -1$  $\text{P} \rightarrow 5 - (0 + 5) = 0$
$\text{O}= \rightarrow 6 - (4 + 2) = 0$

Structure (b) has an extended octet (10 e$^-$) at the $\text{P}$ atom.
Structure (b) is more favored (contributes more to the resonance hybrid) due to the lower formal charges.

9.4 Using Lewis Structures and Bond Energies to Calculate $\Delta H$ of Reaction

- Any reaction can be represented as a two step process in which:
  - All reactant bonds break to give individual atoms
  - All product bonds form from the individual atoms

Example: Estimate the standard enthalpy of the reaction $\text{CH}_4(\text{g}) + 2\text{F}_2(\text{g}) \rightarrow \text{CH}_2\text{F}_2(\text{g}) + 2\text{HF}(\text{g})$

1. Lewis structures are needed to get the bond order
2. Bonds broken (reactants):
   - 4 $\text{C} - \text{H}$ (412 kJ/mol), 2 $\text{F} - \text{F}$ (158 kJ/mol)
3. Bonds formed (products):
   - 2 $\text{C} - \text{H}$ (412 kJ/mol), 2 $\text{C} - \text{F}$ (484 kJ/mol), 2 $\text{H} - \text{F}$ (565 kJ/mol)

\[
\Delta H^\circ = \Delta H^\circ_{\text{broken}} - \Delta H^\circ_{\text{formed}} = [4 \times 412 + 2 \times 158] - [2 \times 412 + 2 \times 484 + 2 \times 565] = -958 \text{ kJ}
\]
This value is only an estimate, the exact value can be calculated using $\Delta H^\circ$ data

10.2 Molecular Shape and the Valence-Shell Electron-Pair Repulsion Model

- The chemical and physical properties of compounds are intimately related to their molecular shapes
  - Molecular shapes (geometries) depend on the three-dimensional arrangement of atoms in space
    - Bond distances, bond angles, …
  - Lewis structures do not represent the true shape of molecules
  - Molecular shapes are studied experimentally, but can be predicted using various theoretical models
**Valence-shell electron-pair repulsion (VSEPR) model** – the electron-groups around a central atom are arranged as far from one another as possible in order to minimize the repulsion between them
- **Electron-groups** are regions with high e⁻ density (lone pairs or bonds) around the central atom
- The **electron-group arrangement** that minimizes the repulsion depends on the number of electron-groups that repel each other:

  2  3  4  5  6

- **Both** bonding and nonbonding e⁻ groups are considered in the **electron-group arrangement**
- **Only** the bonding e⁻ groups are considered in the **molecular shape** since they determine the positions of the atoms (lone pairs are ignored)

**VSEPR classes** – representations in the form \( AX_mE_n \), where \( A \) is the central atom, \( X \) is an atom attached to it, and \( E \) is a nonbonding group (lone pair)

\[ n \] is the number of non-bonding groups (lone pairs) and \( m \) is the number of bonding groups (atoms attached to the central atom)

**The five most common electron-group arrangements and their characteristic angles:**

- **Linear** shape, bond angle of 180°
- **Trigonal planar** shape, bond angles of 120°
- **Tetrahedral** shape, bond angles of 109.5°

**Examples:**

- \( \text{Cl} — \text{Be} — \text{Cl} \):
  - Linear shape, bond angle of 180°
- \( \text{F} — \text{B} — \text{F} \):
  - Trigonal planar shape, bond angles of 120°

**VSEPR classes** \( AX_2, AX_3, AX_4, AX_5 \) & \( AX_6 \)
- All electron-groups surrounding the central atom are **bonding groups**
- If all surrounding atoms (\( X \)) are the same, the **bond angles** are equal to the characteristic angles of the arrangement
- The **molecular shape** and electron-group arrangement have the same name:

**Examples:**

- Tetrahedral shape, bond angles of 109.5°
- Trigonal bipyramidal shape, bond angles of 120 and 90°
• The VSEPR model treats multiple bonds in the same way as single bonds (a single bonding electron-group)

Example: \( \text{CO}_3^{2-} \)

\[ \begin{align*}
\text{O} & \quad \mid \\
\text{C} & \quad \mid \\
\text{O} & \quad 2^-
\end{align*} \]

→ Three atoms attached to a central atom (AX\(_3\)) → Trigonal planar shape, bond angles of 120°

→ Any one of the resonance structures can be used to predict the molecular shape

• The effect of double bonds on bond angles

Example: \( \text{Cl}_2\text{CO} \)

→ Three atoms attached to the central atom, no lone pairs (AX\(_3\))

⇒ Trigonal-planar shape

⇒ The bond angles deviate from the ideal values

⇒ The double bond has greater e\(^-\) density and repels the single bonds stronger

\[ \angle \text{Cl}-\text{C}-\text{Cl} < 120° \]

\[ \angle \text{Cl}-\text{C}-\text{O} > 120° \]

• Trigonal planar electron-group arrangement with one lone pair

→ Two atoms attached to the central atom + one lone pair (AX\(_2\)E) → Bent shape

→ The lone pair is bulkier and repels the bonding pairs stronger → bond angle is less than 120°

Example: \( \text{SO}_2 \)

\[ \begin{align*}
\text{O} & \quad \mid \\
\text{S} & \quad \mid \\
\text{O} & \quad \mid
\end{align*} \]

Bent shape

Bond angle of \( \sim 119° \)

• Tetrahedral electron-group arrangement with one lone pair

→ Three atoms attached to the central atom + one lone pair (AX\(_3\)E) → Trigonal pyramidal shape

→ The lone pair is bulkier and repels the bonding pairs stronger → bond angles are less than 109.5°

Example: \( \text{NH}_3 \)

\[ \begin{align*}
\text{H} & \quad \mid \\
\text{N} & \quad \mid \\
\text{H} & \quad \mid
\end{align*} \]

Trigonal pyramidal shape

Bond angle of 107.3°

• Tetrahedral electron-group arrangement with two lone pairs

→ Two atoms attached to the central atom + two lone pairs (AX\(_2\)E\(_2\)) → Bent shape

→ The two lone pairs have even greater repelling effect → bond angles are less than 109.5°

Example: \( \text{H}_2\text{O} \)

\[ \begin{align*}
\text{H} & \quad \mid \\
\text{O} & \quad \mid \\
\text{H} & \quad \mid
\end{align*} \]

Bent shape

Bond angle of 104.5° (lower than in NH\(_3\))

• Strengths of electron group repulsions

lone pair-lone pair > lone pair-bonding pair > bonding pair-bonding pair

⇒ In the electron arrangement, lone pairs occupy positions as far from one another and from bonding pairs as possible

• Trigonal bipyramidal electron-group arrangement with 1, 2 or 3 lone pairs

→ VSEPR classes AX\(_4\)E, AX\(_3\)E\(_2\) and AX\(_2\)E\(_3\)

→ The lone pairs occupy equatorial positions (provides more space for the lone pairs and minimizes the repulsion)
Octahedral electron-group arrangement with 1 or 2 lone pairs
- VSEPR classes \( AX_2E \) and \( AX_4E_2 \)
- The lone pairs occupy positions opposite to each other (provides the lowest repulsion)

Summary of molecular shapes for central atoms with lone pairs

Steps in determining molecular shapes using the VSEPR model:
- Write the Lewis structure
- Determine the electron-group arrangement, ideal bond angles and VSEPR class
- Place the surrounding atoms and lone pairs in appropriate positions around the central atom and predict any deviations from the ideal bond angles
- Name the molecular shape
- For molecules with more than one central atom, find the electron-group arrangement and corresponding shape around each central atom (one central atom at a time)

Example: Determine the electron arrangement and molecular shape of \( I_3^- \).
1. Lewis structure →
2. El-group arrangement → **trigonal bipyramidal** (2 bonded atoms + 3 lone pairs = 5), VSEPR class \( AX_2E_3 \)
3. Lone pairs in equatorial positions, atoms in axial positions (180° bond angle)
4. Molecular shape → **linear**

Example: Determine the shapes of \( SF_6 \) and \( ClF_3 \)

10.3 Charge Distribution in Molecules

**Bond Polarity and Molecular Polarity**

- **Polar covalent bonds** (due to unequal sharing of the bonding electrons) \(\rightarrow\) **bond dipoles**
- **Dipole moment** \(\mu\) – a measure of the magnitude and direction of a dipole
  - \(\mu\) increases with increasing the partial charges of the atoms \(Q\) and the bond distance \(r\) \(\rightarrow\mu = Q \cdot r\)
  - The direction of \(\mu\) is from plus to minus
  - SI units \(\rightarrow\) C\(\cdot\)m
  - Other units \(\rightarrow\) debye (D) \(1\) D = \(3.336 \times 10^{-30}\) C\(\cdot\)m

- **Molecular dipole moment** (associated with the molecule as a whole) – can be represented as a sum of the bond dipoles of all bonds
- **Nonpolar** molecules – zero dipole moment
  - Homonuclear diatomic molecules (H\(_2\), O\(_2\), F\(_2\), ...)
  - Polyatomic molecules where the bond dipoles cancel each other
  - CO\(_2\) is nonpolar – the bond dipoles of the C–O bonds cancel due to the linear shape

- **Polar** molecules – nonzero dipole moment
  - Heteronuclear diatomic molecules (HF, CO, ...)
  - Polyatomic molecules where the bond dipoles do not cancel each other

\[\text{H}_2\text{O} \text{ is a polar molecule because the} \quad \text{bond dipoles of the} \quad \text{O-H bonds do not cancel due to the bent molecular shape} \]

- **Highly symmetric molecules are normally nonpolar**
  - AX\(_n\) molecules (n=2, 3, 4, 5, 6) where X are atoms of the same element
  - Molecules with symmetrically positioned lone pairs (AX\(_2\)E\(_3\), AX\(_3\)E\(_2\))
  - Molecules with asymmetrically positioned lone pairs or different atoms attached to the central atom are normally polar
    - AX\(_2\)E, AX\(_3\)E\(_2\), AX\(_2\)E\(_2\), AX\(_3\)E, AX\(_4\)E, AX\(_5\)E, ...
    - CF\(_3\)H, CF\(_2\)H\(_2\), SO\(_2\) (bent), ...

- **Example:** Is PCl\(_2\)F\(_3\) a polar molecule?
  1. The Lewis structure is similar to PCl\(_5\) (five atoms bonded to the P atom, no lone pairs)
  2. The Cl atoms are larger and take two of the equatorial positions; the F atoms are smaller and take the two axial and one of the equatorial positions
  - The P–F dipoles are larger than the P–Cl dipoles (\(\DeltaEN\) is larger for P and F)
  - The molecule is polar – the bond dipoles don’t cancel (asymmetric arrangement)
Summary of molecular polarities for molecules having central atoms without lone pairs

- Linear (non-polar)
- Trigonal planar (non-polar)
- Tetrahedral (non-polar)
- Trigonal bipyramidal (non-polar)
- Octahedral (non-polar)

Summary of molecular polarities for molecules having central atoms with lone pairs

- Bent (polar)
- Trigonal pyramidal (polar)
- Bent (polar)
- Square pyramidal (polar)
- See-saw (polar)
- T-shaped (polar)
- Linear (non-polar)
- Square planar (non-polar)