• Expanded valence shells (extended octets) – more than 8e\(^-\) around a central atom
  – Extended octets are formed only by atoms with vacant d-orbitals in the valence shell (p-elements from the third or later periods)
  – Extended octets form when:
    • There are too many electrons (\(n_{\text{need}} < n_{\text{rem}}\)) or more than 4 atoms are bonded to the central atom
      – electron-rich structures \(\Rightarrow\) 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 XeF\(_4\).
\[n_{\text{tot}} = 8(\text{Xe}) + 4 \times 7(\text{F}) = 36\]
\[n_{\text{rem}} = 36 - 8 = 28\]
\[n_{\text{need}} = 0(\text{Xe}) + 4 \times 6(\text{F}) = 24\]
\[n_{\text{need}} < n_{\text{rem}}\]
4 extra e\(^-\) \(\Rightarrow\) add 2 lone pairs at Xe

\[
\begin{align*}
  \text{F} & \quad : \text{F}: \\
  \text{F} - \text{Xe} - \text{F} & \quad : \text{F} - \text{Xe} - \text{F} : \\
  \text{F} & \quad : \text{F}:
\end{align*}
\]

Example: Write the Lewis structure of I\(_3^\text{−}\).
\[n_{\text{tot}} = 3 \times 7(\text{I}) + 1(\text{charge}) = 22\]
\[n_{\text{rem}} = 22 - 4 = 18\]
\[n_{\text{need}} = 4(\text{I}) + 2 \times 6(\text{I}) = 16\]
\[n_{\text{need}} < n_{\text{rem}}\]
2 extra e\(^-\)
\(\Rightarrow\) add 1 extra lone pair at the central I atom after completing the octets for all atoms

\[
\begin{align*}
  \text{I} & \quad \text{I} \quad \text{I} \\
  \text{I} & \quad \text{I} \quad \text{I} \\
  \text{I} & \quad \text{I} \quad \text{I}
\end{align*}
\]

Example: Select the favored resonance structure of the PO\(_4^3\text{−}\) anion.
\[\text{Formal charges:}\]
(a) O \(\rightarrow\) 6-(6+1)=-1 \quad P \rightarrow 5-(0+4)=+1
(b) O\(^−\) \(\rightarrow\) 6-(6+1)=-1 \quad P \rightarrow 5-(0+5)=0
O= \(\rightarrow\) 6-(4+2)=0
– Structure (b) has an extended octet (10 e\textsuperscript{-}) at the P atom
– Structure (b) is more favored (contributes more to the resonance hybrid) due to the lower formal charges

\[ \Delta H_{r}^{\circ} = \Delta H_{B}^{(\text{broken})} - \Delta H_{B}^{(\text{formed})} \]

\[ \Delta H_{r}^{\circ} = \text{Energy is absorbed (+) to break the bonds of the reactants and emitted (-) during forming the bonds of the products} \]

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 \( \text{CH}_4(g) + 2\text{F}_2(g) \rightarrow \text{CH}_2\text{F}_2(g) + 2\text{HF}(g) \)

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

\[ \Delta H_{r}^{\circ} = \Delta H_{B}^{(\text{broken})} - \Delta H_{B}^{(\text{formed})} = [4 \times 412 + 2 \times 158] - [2 \times 412 + 2 \times 484 + 2 \times 565] = -958 \text{ kJ} \]

(this value is only an estimate, the exact value can be calculated using $\Delta H_{f}^{\circ}$ 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:

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

```
<table>
<thead>
<tr>
<th>Arrangement</th>
<th>Characteristic Angles</th>
</tr>
</thead>
<tbody>
<tr>
<td>Linear</td>
<td>180°</td>
</tr>
<tr>
<td>Trigonal Planar</td>
<td>120°</td>
</tr>
<tr>
<td>Tetrahedral</td>
<td>109.5°</td>
</tr>
<tr>
<td>Trigonal Bipyramidal</td>
<td>90°, 120°</td>
</tr>
<tr>
<td>Octahedral</td>
<td>90°, 120°</td>
</tr>
</tbody>
</table>
```

- **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 nonbonding groups (lone pairs) and \(m\) is the number of bonding groups (atoms attached to the central atom)
• 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:

$$\begin{array}{c|c}
\text{Class} & \text{Shape} \\
\hline
AX_2 & \text{Linear} \\
AX_3 & \text{Trigonal planar} \\
AX_4 & \text{Tetrahedral} \\
AX_5 & \text{Trigonal bipyramidal} \\
AX_6 & \text{Octahedral}
\end{array}$$

Examples:

- $\text{Cl} \text{ -- Be -- Cl}$: Linear shape, bond angle of $180^\circ$

- $\text{F} \text{ -- B -- F}$: Trigonal planar shape, bond angles of $120^\circ$

• The VSEPR model treats multiple bonds in the same way as single bonds (a single bonding electron-group)

Example: $\text{CO}_3^{2-}$

$$\begin{array}{c}
\text{C} \\
\text{O} \\
\text{O} \\
\end{array}$$

→ **Three** atoms attached to a central atom ($AX_3$) → **Trigonal planar shape**, bond angles of $120^\circ$
→ 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

⇒ $\angle \text{Cl}-\text{C}-\text{Cl} < 120^\circ$

$\angle \text{Cl}-\text{C}-\text{O} > 120^\circ$