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 – PCl_5, SO_3, …
    - 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 $\mathbf{e^-}$ is adjusted for the charge of the ion

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Rules for Writing Lewis Structures

1. Write the **skeleton structure** by placing a single bond ($\mathbf{e^-}$ pair) between each bonded pair of atoms
2. Count the total number of valence electrons of all atoms, $\mathbf{n_{tot}}$ (correct for the charges of ions)
3. Count the number of remaining electrons, $\mathbf{n_{rem}}$ (total number of $\mathbf{e^-}$ minus $\mathbf{e^-}$ used in the skeleton structure as bonds)
4. Count the number of needed electrons, $\mathbf{n_{need}}$ (the $\mathbf{e^-}$ needed to complete the octet (or duplet) structures of all atoms)

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5. If $\mathbf{n_{need}} = \mathbf{n_{rem}}$, add the remaining $\mathbf{e^-}$ as lone pairs to complete the octets for all atoms, or

   If $\mathbf{n_{need}} > \mathbf{n_{rem}}$, add multiple bonds (1 bond for each deficient pair of $\mathbf{e^-}$) and complete the structure with lone pairs

Example: Write the Lewis structure of $\mathbf{H_2O}$.

1. **O** is the central atom (can't be H)

   ⇒ **H–O–H** (**4** $\mathbf{e^-}$ in the skeleton structure)
2. $\mathbf{n_{tot} = 1(H) + 6(O) + 1(H) = 8}$
3. $\mathbf{n_{rem} = 8 - 4 = 4}$
4. $\mathbf{n_{need} = 0(H) + 4(O) + 0(H) = 4}$
5. $\mathbf{n_{need} = n_{rem}}$ ⇒ $\mathbf{H{-}\underset{\cdot\cdot}{\ddot{O}}{-}H}$

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

1. **C** is the central atom (lower group # than **N**)

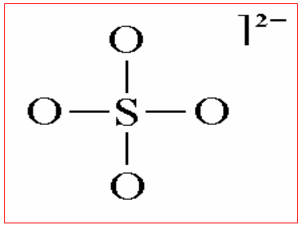
   ⇒ **H–C–N** (**4** $\mathbf{e^-}$ in the skeleton structure)
2. $\mathbf{n_{tot} = 1(H) + 4(C) + 5(N) = 10}$
3. $\mathbf{n_{rem} = 10 - 4 = 6}$
4. $\mathbf{n_{need} = 0(H) + 4(C) + 6(N) = 10}$
5. $\mathbf{n_{need} > n_{rem}}$ deficiency of **4** $\mathbf{e^-}$ (**2** $\mathbf{e^-}$ pairs)

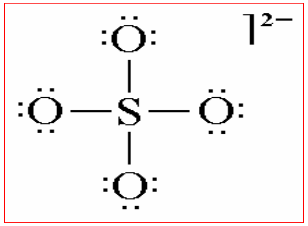
   ⇒ add **2** more bonds between **C** and **N** and complete the structure with lone pairs

   $\mathbf{H{-}C{\equiv}N{:}}$

Example: Write the Lewis structure of $\mathbf{SO_4^{2-}}$.

1. **S** is the central atom (higher period # than **O**) (**8 e⁻** in the skeleton structure)
2. $\mathbf{n_{tot} = 6(S) + 4\times6(O) + 2(charge) = 32}$
3. $\mathbf{n_{rem} = 32 - 8 = 24}$
4. $\mathbf{n_{need} = 0(S) + 4\times6(O) = 24}$
5. $\mathbf{n_{need} = n_{rem}}$ ⇒ complete structure with lone pairs



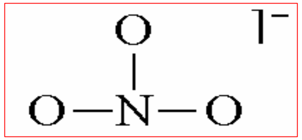


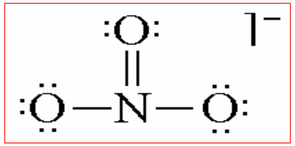
Resonance in Lewis Structures

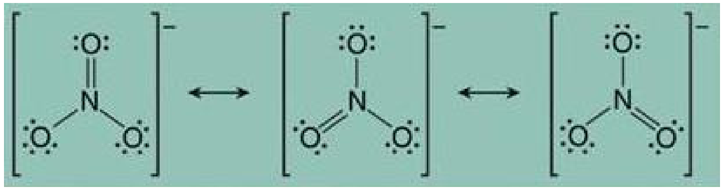
Example: Write the Lewis structure of $\mathbf{NO_3^-}$.

1. **N** is the central atom (lower group # than **O**) **6 e⁻** in the skeleton structure
2. $\mathbf{n_{tot} = 5(N) + 3\times6(O) + 1(charge) = 24}$
3. $\mathbf{n_{rem} = 24 - 6 = 18}$
4. $\mathbf{n_{need} = 2(N) + 3\times6(O) = 20}$
5. $\mathbf{n_{need} > n_{rem}}$ deficiency of **2 e⁻** (**1 e⁻** pair)

⇒ add **1** more bond between **N** and one of the **Os** and complete the structure with lone pairs

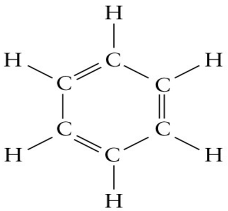


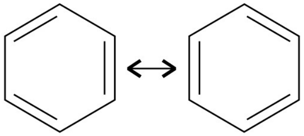




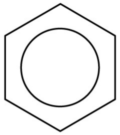
- All three structures are valid Lewis structures and differ by the position of bonds and lone pairs → **Resonance structures**
- Neither of the resonance structures is realistic
- The real structure is a blend (**resonance hybrid**) of the contributing Lewis structures
- The three bonds are identical (intermediate between a single and a double bond)
- The bond order is (2+1+1)/3 = 1.33

Example: Benzene, $\mathbf{C_6H_6}$.





- The two structures have **equal energies** and **contribute equally** to the hybrid
- The electrons from the double bonds are **delocalized** between all six **C** atoms
- The six C–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 = group#
  - The # of bonds for an atom (**B**) → B = S/2

$$\mathbf{FC = V - [L + S/2] = V - [L + B]}$$

- The **FC** shows the extent to which atoms have gained or lost **e**$^-$ in covalent bond formation
  - The sum of all **FC**s equals the charge of the species

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

$[N–C–O]^-$

$n_{tot} = 5 + 4 + 6 + 1 = 16$

$n_{rem} = 16 - 4 = 12$ $n_{need} = 6 + 4 + 6 = 16$

$n_{need} > n_{rem}$ deficiency of **4** e$^-$ ⇒ add **2** more bonds

a) $[:\ddot{N}=C=\ddot{O}:]^-$ b) $[:N\equiv C–\underset{\cdot\cdot}{\ddot{O}}:]^-$ c) $[:\underset{\cdot\cdot}{\ddot{N}}–C\equiv O:]^-$

V →	5(N)	4(C)	6(O)				
L+B → a)	6(N)	4(C)	6(O)	FC → a)	-1(N)	0(C)	0(O)
L+B → b)	5(N)	4(C)	7(O)	FC → b)	0(N)	0(C)	-1(O)
L+B → c)	7(N)	4(C)	5(O)	FC → c)	-2(N)	0(C)	+1(O)

- FCs are used to evaluate the relative importance of resonance structures
  1. Lewis structures with lower **FC**s are favored
  2. Lewis structures with like **FC**s on adjacent atoms are less favorable
  3. Lewis structures with negative **FC**s on the more electronegative atoms are favored

Example: Evaluate the importance of the three possible resonance structures of the **NCO**$^-$ ion

a) $[:\ddot{N}=C=\ddot{O}:]^-$	b) $[:N\equiv C–\underset{\cdot\cdot}{\ddot{O}}:]^-$	c) $[:\underset{\cdot\cdot}{\ddot{N}}–C\equiv O:]^-$
-1 0 0	0 0 -1	-2 0 +1

Most favored
[(-) **FC** on the more **EN** atom]

Least favored
(highest **FC**s)

Exceptions to the Octet Rule

- **Odd electron species** (radicals) → $\cdot CH_3$, $\cdot OH$, $\cdot NO$, $\cdot NO_2$, …
  - 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**.

$[N–O]$

$n_{tot} = 5 + 6 = 11$ $n_{rem} = 11 - 2 = 9$

$n_{need} = 6 + 6 = 12$ ⇒ add **1** more bond

$$\cdot\ddot{N}=\ddot{O}: \leftrightarrow :\ddot{N}=\ddot{O}\cdot$$

- **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 **BeH_2**.

H–Be–H $\quad$ $\mathbf{n_{tot} = 2 + 2\times1 = 4}$

$\mathbf{n_{rem} = 4 - 4 = 0}$ $\quad$ $\mathbf{n_{need} = 4}$

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

H–Be–H

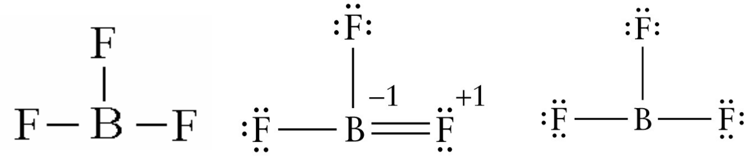
⇒ the structure has an incomplete octet for the **Be** atom because the molecule is **electron-deficient**

Example: Write the Lewis structure of **BF_3**.

$\mathbf{n_{tot} = 3 + 3\times7 = 24}$

$\mathbf{n_{rem} = 24 - 6 = 18}$ $\quad$ $\mathbf{n_{need} = 2 + 3\times6 = 20}$

$\mathbf{n_{need} > n_{rem}}$ $\quad$ deficiency of **2** **e$^-$** ⇒ add **1** more bond



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

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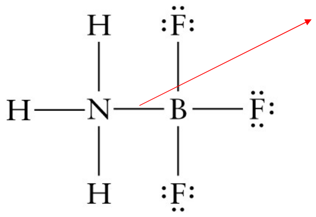
– Structures with incomplete octets are **electron-deficient** and tend to react with molecules that have abundance of **e$^-$** in the form of lone pairs

$$\mathbf{BF_3(g) + :NH_3(g) \rightarrow NH_3BF_3(s)}$$

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



Coordinate covalent bond – a bond in which both electrons come from the same atom