# 11.2 Types of Covalent Bonds

- The overlap (merging) of atomic orbitals can occur in two geometric configurations
  - **End-to-end overlap** along the internuclear axis (**σ-bonding**)
  - **Side-to-side overlap** on each side of the internuclear axis (**π-bonding**)
- ➤ Overlap between two *s* orbitals or between one *s* and one *p* orbital always leads to **σ-bonds**
- ➤ Overlap between two *p* orbitals leads to either **σ-bonds** or **π-bonds**
- ➤ Overlap involving **hybrids** always leads to **σ-bonds**

## Example: Ethane ($C_2H_6$)
- ❑ The two **C** atoms are in *sp³* hybridization (tetrahedral)
- ❑ For each **C**, three of the *sp³* hybrids overlap with the **1s** orbitals of the **H** atoms to form six σ-bonds
- ❑ The remaining *sp³* hybrids of the **C** atoms overlap with each other along the internuclear axis to form a σ-bond
- ❑ The electron density increases in the overlapped regions between the nuclei along the internuclear axis
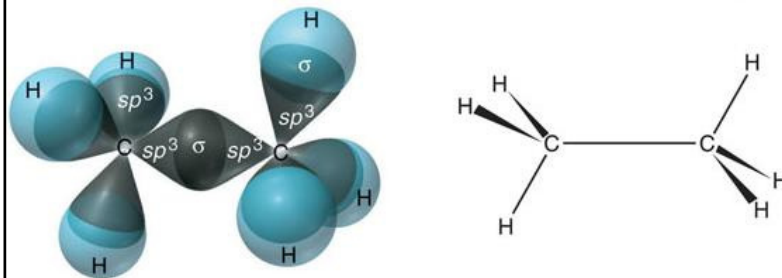


## Example: Ethylene ($C_2H_4$)
- ❑ The two **C** atoms are in *sp²* hybridization (trig. planar)
- ❑ For each **C**, two of the *sp²* hybrids overlap with the **1s** orbitals of the **H** atoms to form four σ-bonds
- ❑ The remaining *sp²* hybrids of the **C** atoms overlap with each other along the internuclear axis to form a σ-bond
- ❑ The unhybridized *p* orbitals of the **C** atoms overlap with each other side-to-side above and below the internuclear axis to form a π-bond
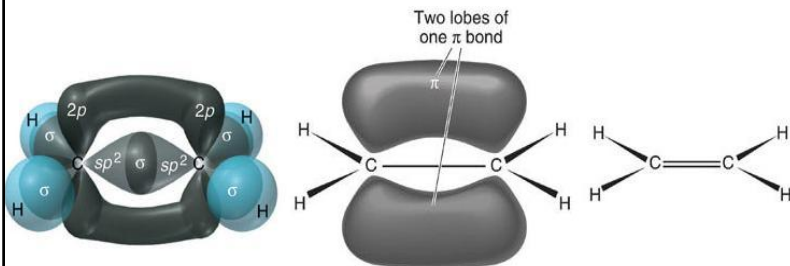


## Example: Acetylene ($C_2H_2$)
- ❑ The two **C** atoms are in *sp* hybridization (linear)
- ❑ For each **C**, one of the *sp* hybrids overlaps with the **1s** orbitals of the **H** atoms to form two σ-bonds
- ❑ The remaining *sp* hybrids of the **C** atoms overlap with each other along the internuclear axis to form a σ-bond
- ❑ The unhybridized *p* orbitals of the **C** atoms overlap with each other side-to-side above and below the internuclear axis to form two π-bonds
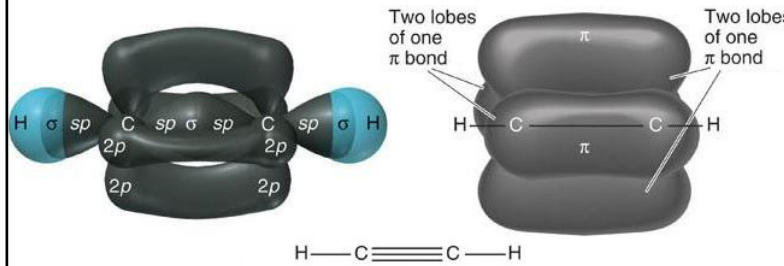
- **Single** bonds are always σ-bonds
- **Double** bonds contain one σ-bond and one π-bond
- **Triple** bonds contain one σ-bond and two π-bonds
  - π-bonds are typically weaker than σ-bonds since side-to-side overlap is less extensive than end-to-end overlap
  ⇒ Double (or triple) bonds are less than twice (or three times) stronger than single bonds

**Example: $CH_2O$** (trig. planar e-group arrangement)



**C** atom in $sp^2$ hybridization:
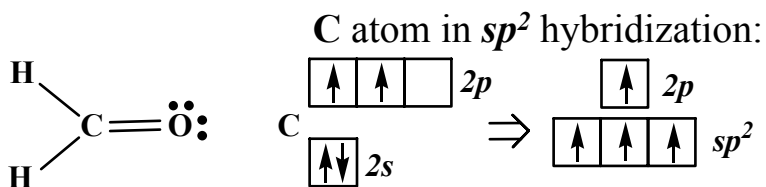
- Two of the $sp^2$-hybrids of **C** are used to form σ-**bonds** with the **H** atoms and the third one with the **O**
- The **O** atom is also in $sp^2$ hybridization; two of the $sp^2$ hybrids are used to hold the lone pairs of **O** and one to form a σ-**bond** with **C**

**σ-skeleton of $CH_2O$**



$sp^2$-**hybrids**

**π-bonding in $CH_2O$**



π-**bond**
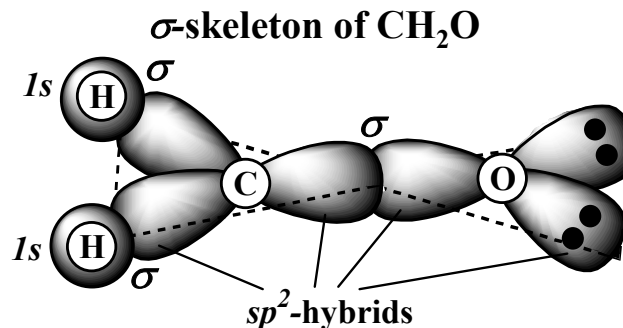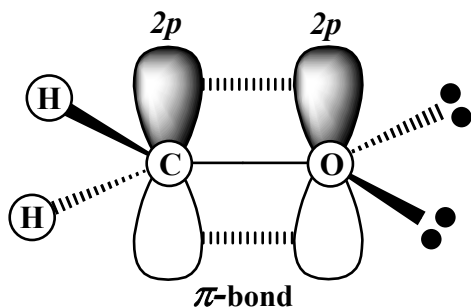
- The unhybridized $p$-orbitals of **C** and **O** are perpendicular to the σ-**skeleton** and overlap side-to-side to form a π-**bond**
- ⇒ **$CH_2O$ has 3 σ-bonds and 1 π-bond**

- **Internal rotation** in molecules
  - **Allowed** around **single bonds** (the overlap between the orbitals is preserved during rotation)
  - **Not allowed** around **double bonds** (rotation disturbs the parallel alignment of the $p$-orbitals and reduces their overlap, the π-**bond** breaks)
- ⇒ Molecules with double bonds can have *cis-trans* **isomers (Example: $C_2H_2Cl_2$)**
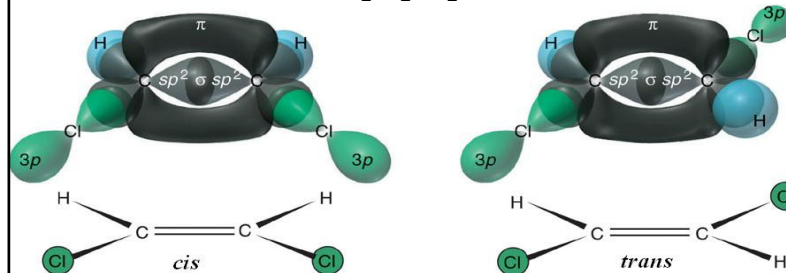
## 11.3 Molecular Orbital (MO) Theory

- Limitations of the VSEPR model and the VB theory (based on localized bonding e-pairs) – fail in describing:
  - **Electron-deficient compounds** – have too few electrons ($B_2H_6$, Diborane – must have at least **7** bonds (**14 e⁻**) to bond the **8** atoms, but has only **12** valence **e⁻**)
  - **Radicals** – odd electron species (**NO**, **11 e⁻**s)
  - **Paramagnetism** – some molecules have paramagnetic properties without having unpaired **e⁻**s in their Lewis structures ($O_2$ is paramagnetic, but has no unpaired **e⁻**s in its Lewis structure)

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- The molecular orbital theory resolves these problems by introducing **molecular orbitals**
  - Similar to the atomic orbitals, but spread throughout the whole molecule
  - Can be occupied by no more than 2 electrons with opposite spins – Pauli exclusion principle (explains the significance of **e⁻** pairs)
  - Can be occupied by single electrons (provides explanations of odd-electron species and paramagnetic properties)
- The **MO**s are solutions of the Schrödinger equation for the molecule as a whole (only approximate solutions are available)

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## Formation of MOs in $H_2$

- As two **H** atoms (*A* and *B*) approach each other, their **1s** orbitals ($1s_A$ and $1s_B$) overlap and interfere with each other
- The interference yields two **MO**s
  - Constructive interference (the amplitudes of the wavefunctions add together) → **bonding MO ($\sigma_{1s}$)**

  $$\sigma_{1s} = 1s_A + 1s_B$$

  - Destructive interference (the amplitudes of the wavefunctions subtract from each other) → **antibonding MO ($\sigma_{1s}$*)**

  $$\sigma_{1s}* = 1s_A - 1s_B$$

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- The bonding **MO** (molecular orbital) is **enhanced** between the nuclei
  - Increased electron density between the nuclei
  - **e⁻**s on $\sigma_{1s}$ have lower energy than in the isolated **H**s
- The antibonding **MO** has a **node** between the nuclei
  - Reduced electron density between the nuclei
  - **e⁻**s on $\sigma_{1s}$* have higher energy than in the isolated **H**s



Waves reinforce — Amplitudes of wave functions added

Waves cancel — Amplitudes of wave functions subtracted

- **MO**s formed by end-to-end overlap of **AO**s along the internuclear axis are labeled as $\sigma$-**orbitals** ($\sigma$-bonding)
- **MO**s formed by side-to-side overlap of **AO**s on each side of the internuclear axis are labeled as $\pi$-**orbitals** ($\pi$-bonding)

- **MO** energy level diagrams
  - Electrons occupy first the lowest energy **MO**s
  - Each **MO** can accommodate up to two electrons with opposite spins (Pauli)
  - Electrons enter degenerate **MO**s singly adopting parallel spins (Hund)
- Bond order (**BO**)
  $$BO = (B - A)/2$$
- **B** - # **e**⁻s on bonding **MO**s
- **A** - # **e**⁻s on antibonding **MO**s
- ➤ In general, the higher the **BO** the stronger the bond



$H_2$ bond order = $\frac{1}{2}(2 - 0) = 1$

- For $H_2$, the **two e**⁻s enter $\sigma_{1s} \rightarrow BO = (2-0)/2 = 1$ (the energy of the molecule is lower than that of the free atoms) $\Rightarrow$ the molecule is **stable**
- For $He_2$, the **four e**⁻s fill both $\sigma_{1s}$ and $\sigma_{1s}* \rightarrow BO = (2-2)/2 = 0$ (the bonding effects of $\sigma_{1s}$ and $\sigma_{1s}*$ cancel) $\Rightarrow$ the molecule is **unstable**
- For $He_2^+$, $BO = (2-1)/2 = 0.5 \Rightarrow$ the ion is **stable**



$He_2$ bond order = 0          $He_2^+$ bond order = $\frac{1}{2}$

- Electron configurations
  - For $H_2 \rightarrow (\sigma_{1s})^2$;  For $He_2^+ \rightarrow (\sigma_{1s})^2 (\sigma_{1s}*)^1$

**Example:** Is $H_2^-$ a stable ion?  Electr. Configuration?

Total # of valence **e**⁻s $\rightarrow$ **1(H) + 1(H) + 1(charge) = 3**

Electron configuration $\Rightarrow (\sigma_{1s})^2 (\sigma_{1s}*)^1$

$BO = (2-1)/2 = 0.5$
$\Rightarrow$ **the ion is stable**