Chapter 2
The Nature of the Covalent Bond

2.1
Atomic Orbitals and Hybridization
Valence Electrons and the Electronic Configuration of Carbon

- atomic orbitals filled with electrons starting from low to high energy states (Aufbau principle)

- electronic configuration of carbon in the ground state is \(1s^2\ 2s^2\ 2p^2\)
- only the valence shell, that is, 2s and 2p orbitals relevant for bonding
- carbon is tetravalent, can accommodate a maximum of 8 electrons in 4 pairs; electron octet rule
• atoms in real molecules have different coordination geometries, depending on the number of neighbors

Valence Shell Electron Pair Repulsion (VSEPR) Model qualitatively describes coordination geometries:

- **tetrahedral** for 4; **trigonal-planar** for 3; **linear** for 2 neighboring atoms (or electron pairs)
• linear combinations of sets of atomic orbitals are also allowed stationary states

- two regular atomic orbitals
- linear combination by vector addition
- two “new” 2sp hybrid orbitals

- hybrid orbitals are obtained by linear combination of atomic orbitals (vector addition)
- the total number and the total energy of the orbitals must be preserved
Hybridization of Atomic Orbitals (by Linear Combination)

- Valence Shell Electron Pair Repulsion (VSEPR) gives (electrostatic) explanation for geometries
- tetrahedral for 4 (→ sp3); trigonal planar for 3 (→ sp2); and linear for 2 (→ sp) connected atoms
Hybridization of Atomic Orbitals by Linear Combination

- The total number and the total energy of the orbitals must be preserved.

- Sp² and sp hybridized carbon atoms have additional one or two 2p orbitals available.

- Hybridization is an ad hoc explanation to reconcile atomic orbitals with observed “real” geometries.

- However, true energy minimization of real systems results in “mixing of states”, with same result.
2.2
Formation of Single Bonds
**Formation of Single Bonds (Valence Bond Model)**

- according to valence bond model, covalent bonds are formed by pairing electrons of atomic orbitals

![Diagram showing the formation of single bonds through in-phase combination of atomic orbitals](image)

- in-phase combination of atomic orbitals
- single bonds are $\sigma$-bonds (rotational symmetry) between sp$^3$, sp$^2$, sp, or s orbitals
- due to rotational symmetry of the $\sigma$-orbital, rotation is free without breaking the bond
• upon decreasing the distance between atoms, atomic orbitals start to interact and split energetically
• number of orbitals conserved, LCAO with one combination “in phase” and another one “out of phase”
Molecular Orbitals Energy Diagrams

- schematic molecular orbital energy diagram for a symmetric diatomic molecule (such as H₂)

- energy splitting increases with atomic orbital overlap
- number of orbitals preserved but sum of all orbital energies increases (electron density increases)
- bond energy is stabilization of filled bonding orbital $\sigma$ (due to electron delocalization)
- antibonding orbital $\sigma^*$ is energetically destabilized but remains empty
Molecular Orbital View of the Covalent Bond in Multiatom Molecules

- simplified and schematic molecular orbital energy diagram of the methane molecule

![](image)

- linear combination of atomic orbitals to obtain molecular orbitals may start from LCAO hybrid orbitals
- interactions between orbitals or orbital sets of matching symmetry
Molecular Orbital View of the Covalent Bond in Multiatom Molecules

- simplified and schematic molecular orbital energy diagram of the methane molecule

\[ \frac{1}{4} 2s(C) + \frac{3}{4} 2p(C) - 1s(H) \]
\[ \frac{1}{4} 2s(C) + \frac{3}{4} 2p(C) + 1s(H) \]

- a more correct approach would start from atomic orbitals instead of hybrid orbitals
- result will be (almost) the same due to “mixing” of orbitals
- VSEPR model and hybridization are useful and valid simplifications
Polarization of Covalent Bonds

unpolarized σ-bond

\[ \text{A} \quad \text{A} \]

polarized σ-bond

\[ \delta^+ \quad \delta^- \quad \text{A} \quad \text{X} \]

ionic bond

\[ \oplus \quad \text{A} \quad \text{X} \]

increasing electronegativity (of X and Y)

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<th>IB</th>
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<th>IIIA</th>
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negative inductive Effect (−I effect)

\[ \delta^- \quad \text{H} \quad \text{F} \quad \text{C} \quad \text{R} \quad \text{H} \quad \delta^{+++} \quad \delta^- \quad \text{H} \quad \text{O} \quad \text{C} \quad \text{CH}_3 \quad \text{H} \quad \delta^{++} \quad \delta^- \quad \text{H} \quad \text{N} \quad \text{C} \quad \text{R} \quad \text{H} \quad \delta^+ \]

\[ \delta^- \quad \text{H} \quad \text{F} \quad \text{C} \quad \text{R} \quad \text{H} \quad \delta^{+++} \quad \delta^- \quad \text{H} \quad \text{Cl} \quad \text{C} \quad \text{R} \quad \text{H} \quad \delta^{++} \quad \delta^- \quad \text{H} \quad \text{Br} \quad \text{C} \quad \text{R} \quad \text{H} \quad \delta^+ \]

\[ \delta^- \quad \text{H} \quad \text{F} \quad \text{C} \quad \text{R} \quad \text{H} \quad \delta^{+++} \quad \delta^- \quad \text{H} \quad \text{F} \quad \text{C} \quad \text{CH}_2 \quad \text{CH}_2 \quad \text{R} \quad \delta^{+++} \quad \delta^+ \]

\[ \delta^- \quad \text{H} \quad \text{F} \quad \text{C} \quad \text{R} \quad \text{H} \quad \delta^{+++} \quad \delta^- \quad \text{H} \quad \text{F} \quad \text{C} \quad \text{CH}_2 \quad \text{CH}_2 \quad \text{R} \quad \delta^{+++} \quad \delta^+ \]

\[ \delta^- \quad \text{H} \quad \text{F} \quad \text{C} \quad \text{R} \quad \text{H} \quad \delta^{+++} \quad \delta^- \quad \text{H} \quad \text{F} \quad \text{C} \quad \text{CH}_2 \quad \text{CH}_2 \quad \text{R} \quad \delta^{+++} \quad \delta^+ \]
• simplified and schematic molecular orbital diagrams of the C–C and the C–F bond

• atomic and hybrid orbitals of more electronegative elements lower in energy (higher electron affinity)
• increasing energy difference between bonding partners implies less electronic interaction
• bonding MO are closer in energy to and “look more like” AO from more electronegative element
• antibonding MO are closer in energy to and “look more like” AO from less electronegative element
2.3
Formation of Multiple Bonds
Formation of Carbon-Carbon Multiple Bonds

- double or triple bonds are one σ bond plus one or two π-bonds, respectively
- π bonds formed between residual p orbitals, node plane along bond, no rotational symmetry
- rotation around π-bonds requires breaking them (energetically costly, impossible at room temperature)

<table>
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<th>Bond Type</th>
<th>Bond Length (Å)</th>
<th>Bond Energy (kJ/mol)</th>
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<td>Ethene</td>
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<td>Ethyne</td>
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Molecular Orbital View of the Carbon-Carbon Double Bond

- simplified and schematic molecular orbital energy diagram of the ethene molecule

- only orbitals of matching symmetry & orientation interact, hence sp² with sp², and pz with pz
- distinct σ bond (from two sp²) and π bond (from two pz) with different bond energies, symmetries
- chemistry dominated by highest occupied, lowest unoccupied molecular orbitals (HOMO, LUMO)
- typically π HOMO and π* LUMO between σ and σ* because pz overlap much smaller
Rotation Around a Double Bond

- $\sigma$ bond has rotational symmetry with respect to carbon-carbon bond axis, but $\pi$ bond does not.

- Rotating the $\pi$ orbitals by $90^\circ$ equates to breaking the $\pi$ bond ($\approx 260$ kJ/mol), energetically disfavorable.
- simplified and schematic molecular orbital energy diagram of the ethyne molecule

- only orbitals of matching symmetry & orientation interact, hence sp\(^2\) with sp\(^2\), p\(_z\) with p\(_z\), and p\(_y\) with p\(_y\)
- distinct σ-bond (from two sp\(^2\)) and two independent π-bonds (from the two p\(_z\) and p\(_y\), respectively)
- the two π-bonds are identical in energy, symmetry, just different in orientation
- chemistry dominated π HOMO and π* LUMO, hence reactivity of ethyne similar to ethene
Molecular Orbital View of the Carbon-Oxygen Double Bond in the Carbonyl Group

- simplified and schematic molecular orbital energy diagram of the carbon-oxygen double bond

- again $\sigma$ bond from $sp^2(C)$ with $sp^2(O)$ and $\pi$- bond from $p_z(C)$ with $p_z(O)$ with different bond energies
- oxygen hybrid orbitals lower in energy due to electronegativity difference of carbon and oxygen
- bonding $\sigma$ orbital and, in particular, bonding $\pi$ orbital “look like” oxygen orbitals
- $\sigma$ bond and, in particular, more polarizable $\pi$ bond polarized towards oxygen (higher electron density)
2.4
Electron Delocalization, Aromaticity, and Resonance Structures
Molecules with Several Multiple Bonds

- bond lengths for single and double bonds, energy barriers for rotation for single bonds in dienes/trienes

- dienes and trienes with alternating double and single bonds are called conjugated double bonds
- conjugated double bonds longer than normal, single bonds shorter, with a high rotation barrier

\[
\begin{align*}
\text{1.33 Å} & & \text{1.33 Å} & & \text{1.33 Å} & & \text{1.54 Å} \quad \bigcirc \; 3 \text{ kJ/mol} \\
\text{H} & \text{C}=\text{C} & \text{H} & & \text{H} & \text{C}=\text{C} & \text{H} & & \text{H} & \text{C}=\text{C} & \text{H} & & \text{H} \\
\text{1.34 Å} & & \text{1.34 Å} & & \text{1.34 Å} & & \text{1.45 Å (all bonds)} \\
\text{H} & \text{C}=\text{C} & \text{C}=\text{C} & & \text{H} & \text{C}=\text{C} & \text{C}=\text{C} & & \text{H} & \text{C}=\text{C} & \text{C}=\text{C} & & \text{H} \\
\text{1.47 Å} \quad \bigcirc \; 30 \text{ kJ/mol} & & \text{1.46 Å} & & 1.46 \text{ Å} \quad \bigcirc \; 30 \text{ kJ/mol} & & \text{ }}
\]
Valence Bond Model of Molecules with Cumulated and Isolated Double Bonds

- “cumulated double bonds” in direct vicinity are in orthogonal planes, do not interact electronically

1,3-propadiene

1,5-pentadiene

- “isolated double bonds” separated by one or more spy carbons are in arbitrary planes, do not interact

- neither cumulated nor isolated multiple bonds “communicate”, i.e., interact electronically
Valence Bond Model of Molecules with Cumulated and Isolated Double Bonds

- “conjugated double bonds” are in the same plane and $p_z$ orbitals are in direct contact

\[
\text{1,3-butadiene}
\]

- “conjugated triple bonds” are in the same planes, $p_z$ and $p_y$ orbitals are in direct contact

\[
\text{1,3-butadiyne}
\]

- alternating multiple (double or triple) and single bonds are called “conjugated multiple bonds”
- conjugated multiple bonds interact with each other electronically, and electrons are delocalized
“Electron in a 1D Box” Model for a Linear π-Conjugated Systems

- “electron in 1D Box with infinite potential well” is a simple model for linear π-conjugated systems

- Linear combination of 4 2p<sub>z</sub> orbitals results in a set of four molecular orbitals
- Resulting molecular π-orbitals are delocalized over all four carbon atoms
- Energy successively increases with number of node planes in the π-system
Frontier Orbitals and Bond Orders in 1,3-Butadiene

- simplified and schematic MO energy diagram of the frontier orbitals of 1,3-butadiene

- double bonds have bond order <2, central single bond bond order >1, restricted rotation (30 kJ/mol)
- HOMO is less stabilized, HOMO-LUMO gap smaller compared to ethene, butadiene is more reactive
• delocalization of $\pi$-electrons: HOMO/LUMO gap decreases, bond order of central bonds converges to 1.5
Electron Delocalization in Cyclic $\pi$-Conjugated Multiple Bonds

- electron delocalization particularly pronounced for the $\pi$-electrons in “cyclic conjugated double bonds”

- molecules with cyclic conjugated double bonds can be represented by (neutral) “canonical formulae”
- all bonds are symmetrically equivalent, equal bond length 1.45 Å, bond order 1.5
- compounds with $2n+1$ cyclic conjugated double bonds are particularly stable, called “aromatic”
“Electron in a 1D Box” Model for Cyclic π-Conjugated Systems

- “electron in a box with steady boundary condition” is a simple model for cyclic π-conjugated systems

- All π-orbitals, including HOMO extend over all six carbons, “do not look like” double bond MO
- Two degenerate HOMO better stabilized than the one in ethene; aromatic π-system particularly stable
“Electron in a 1D Box” Model for Cyclic $\pi$-Conjugated Systems

- “electron in a box with steady boundary condition” is a simple model for linear $\pi$-conjugated systems

- two degenerate HOMO better stabilized than the one in ethene; aromatic $\pi$-system particularly stable
- all six carbon bonds are equal, bond order 1.5; no bond length alternation, no double bonds
A General Approximation for the MO Energy Diagrams of Cyclic

- **Hückel rule for “aromaticity”:** monocyclic conjugated systems with \(4n+2\) electrons, are highly stable.
“aromaticity” is a historically derived concept for the unusual chemical stability of some double bonds.

- Only benzene strictly fulfills Hückel definition of aromaticity (all-carbon, monocyclic, $4n + 2$ π electrons).
- In a broader sense, all compounds with cyclic conjugated π-systems are called “aromatic compounds”.
- This includes compounds with heteroatoms and examples with $4n$ π electrons (although less stable).
Representing Delocalization with Resonance Structures

- delocalization of cyclic $\pi$-conjugated systems can be represented by neutral resonance structures

\[
\begin{array}{c}
\begin{array}{c}
\text{H} \\
\text{H} \\
\text{H} \\
\text{H} \\
\text{H} \\
\text{H} \\
\text{H} \\
\text{H}
\end{array}
\quad \leftrightarrow \quad \\
\begin{array}{c}
\text{H} \\
\text{H} \\
\text{H} \\
\text{H} \\
\text{H} \\
\text{H} \\
\text{H} \\
\text{H}
\end{array}
\end{array}
\]

- drawing the neutral resonance structures of cyclic $\pi$-conjugated systems:
  - draw $\sigma$ bond framework of $sp^2$-hybridized carbons/heteroatoms (and attached atoms)
  - draw the $\pi$ electron pairs of the double bonds (ideally in another color)
  - indicate with arrows how to move $\pi$ electron pairs from a multiple bond to an adjacent single bond
  - only $\pi$ electron pairs can be moved; never change $\sigma$ bond framework
  - respect the valency rules; carbon atoms must never become pentavalent
  - enclose resonance structures in square brackets and link with double arrows

- resonance structures are representations of delocalization; $\pi$ electrons do not really move/resonate
Representing Delocalization with Resonance Structures

- representing delocalization in linear $\pi$-conjugated systems requires zwitterionic resonance structures

\[
\begin{array}{c}
\text{H} & \text{C} & \text{H} \\
\text{H} & \text{C} & \text{H} \\
\text{H} & \text{C} & \text{H} \\
\end{array}
\]

- drawing the zwitterionic resonance structures of linear $\pi$-conjugated systems:
  - draw $\sigma$ bond framework, then $\pi$ electron pairs of the double bonds (ideally in another color)
  - indicate with arrows how to move $\pi$ electron pairs from a multiple bond to an adjacent single bond
  - alternatively, move $\pi$ electron pair to adjacent carbon atom where it becomes a free electron pair
  - only move $\pi$ electron pairs; never change $\sigma$ bond framework
  - respect the valency rules; add formal charges to indicate missing/excess electrons on carbons
  - enclose resonance structures in square brackets and link with double arrows

- resonance structures are representations of delocalization; $\pi$ electrons do not really move/resonate
• zwitterionic resonance structures comprise positive/negative formal charges

- Carbanion:
  - Trivalent (3 electrons)
  - 5 electrons
  - Negative formal charge
  - 3 bonds, 1 electron pair
  - Octet rule fulfilled

- Double-bonded carbon:
  - Tetravalent (4 electrons)
  - 4 bonds
  - Neutral
  - Octet rule fulfilled

- Carbocation:
  - Trivalent (3 electrons)
  - 3 bonds
  - Positive formal charge
  - Electron sextet (deficient)

- Formal charges are determined by homolytic bond cleavage and counting electrons
- Valency is determined by counting electron pairs involved in covalent bonds to neighbouring atoms
- Stable carbon is always tetravalent, never pentavalent; reactive states/intermediates can be trivalent
- Octet rule is always fulfilled (maximum 4 electron pairs); electron sextet possible but electron deficient
Using Resonance Structures to Compare Delocalization and Determine Bond Orders

- degree of delocalization can be estimated from total number of resonance structures

**Benzene**

two neutral resonance structures

**Naphthalene**

three neutral resonance structures

- degree of delocalization increases with number of neutral resonance structures in cyclic π systems
Using Resonance Structures to Compare Delocalization and Determine Bond Orders

- degree of delocalization and bond orders can be estimated from total number of resonance structures

1,3-butadiene

one neutral (major), six zwitterionic (minor) resonance structures

1,3,5-hexatriene

one neutral (major), twelve zwitterionic (minor) resonance structures

- degree of delocalization increases with number of zwitterionic resonance structures in linear π systems
Using Resonance Structures to Compare Delocalization and Determine Bond Orders

- degree of delocalization and bond orders can be estimated from total number of resonance structures

Benzene

two neutral (major), eighteen zwitterionic (minor) resonance structures

1,3,5-hexatriene

one neutral (major), twelve zwitterionic (minor) resonance structures

- a system with more neutral resonance is always more delocalised than one with only zwitterionic ones
multiple bonds to electronegative atoms (O, N, S) that are part of the pi system are $\text{M}$ substituents

- Resonance structures involving electron-withdrawing groups

- Resonance structures with negative formal charge on those atoms significantly better stabilized

- Contrary to all-carbon systems, this results in molecule with strong dipole moment
• –M substituents determine electron density and reactivity patterns in π-conjugated systems

• every other carbon in the π-conjugated system carries positive formal charge in resonance structures
• in reality, every other carbon in the delocalized π system is electron deficient (positive partial charge δ−)
Resonance Structures Involving Electron-Donating Groups

- atoms with free electron pairs (O, N, S, Hal) single-bonded to the $\pi$ system are $+M$ substituents

\[
\text{ethene} \\
\begin{array}{c}
\text{H}^+ \text{C} & \text{H} \\
\text{H} & \text{C} & \text{H} \\
\end{array} \quad \leftrightarrow \quad \begin{array}{c}
\text{H}^+ \text{C} & \text{H} \\
\text{H} & \text{C} & \text{H} \\
\end{array} \quad \leftrightarrow \quad \begin{array}{c}
\text{H}^+ \text{C} & \text{H} \\
\text{H} & \text{C} & \text{H} \\
\end{array} \\
\text{minor} \quad \text{neutral} \quad \text{minor}
\]

\[
\text{alkoxy ethene} \\
\begin{array}{c}
\text{H}^+ \text{C} & \text{O} & \text{R} \\
\text{H} & \text{C} & \text{H} \\
\end{array} \quad \leftrightarrow \quad \begin{array}{c}
\text{H}^+ \text{C} & \text{O} & \text{R} \\
\text{H} & \text{C} & \text{H} \\
\end{array} \quad \leftrightarrow \quad \begin{array}{c}
\text{H}^+ \text{C} & \text{O} & \text{R} \\
\text{H} & \text{C} & \text{H} \\
\end{array} \quad \leftrightarrow \quad \begin{array}{c}
\text{H}^+ \text{C} & \text{O} & \text{R} \\
\text{H} & \text{C} & \text{H} \\
\end{array} \\
\text{major} \quad \text{minor} \quad \text{major} \quad \text{minor}
\]

- resonance structures with positive formal charge on those atoms avoids highly deficient electron sextet
- contrary to all-carbon systems, this results in molecule with strong dipole moment
+M substituents determine electron density and reactivity patterns in \( \pi \)-conjugated systems.

- Every other carbon in the \( \pi \)-conjugated system carries negative formal charge in resonance structures.
- In reality, every other carbon in the delocalized \( \pi \) system is electron-rich (negative partial charge \( \delta^- \)).
• the ensemble of all relevant resonance structures can be used as an approximation for bond orders

- determine all relevant resonance structures and individual bond orders in each structure
- overall bond order of a given bond can be estimated from its average over all resonance structures