

2

The Nature of the Covalent Bond

Table of Contents

1. Introduction (2 h)

- 1.1. Organic Chemistry and Soft Matter Research
- 1.2. Carbon as the Basis of Organic Chemistry

2. The Nature of the Covalent Bond (6 h)

- 2.1. Atomic Orbitals and Hybridisation
- 2.2. Formation of Single Bonds
- 2.3. Formation of Multiple Bonds
- 2.4. Electron Delocalization & Resonance Structures

3. Molecular Structure and Nomenclature (4 h)

- 3.1. Basic Rules of Nomenclature
- 3.2. Isomerism

4. Mechanisms of Organic Reactions (10 h)

- 4.1. Reaction Thermodynamics & Kinetics
- 4.2. Reaction Types and Intermediates
- 4.3. Nucleophilic Substitutions
- 4.4. Nucleophilic Reactions on Carbonyl Carbons

4.5. Electrophilic Additions

4.6. Electrophilic Substitutions

4.7. Elimination Reactions

4.8. Radical Reactions

4.9. Orbital-Controlled Reactions

5. Polymer Chemistry (6 h)

- 5.1. Introduction to Polymer Science
- 5.2. Step-Growth Polyreactions
- 5.3. Chain-Growth Polymerizations
- 5.4. Living and Controlled Polymerizations

6. Organic and Polymer Materials (2 h)

- 6.1. Thermoplastic Polymers
- 6.2. Elastomers
- 6.3. Surfactants
- 6.4. Organic Dyes and Semiconductors

Learning Goals and Reading Recommendations

- allowed stationary states ψ are solutions to the Schrödinger equation
- atomic orbitals $|\psi|^2$ represent space of non-zero probability for an electron
- covalent bond described by linear combination of atomic or hybrid orbitals
- bond energy is stabilization of filled bonding orbital σ
- antibonding orbital σ^* energetically destabilized but remains empty
- multiple bonds can be described as distinct σ bond plus one or two π bonds
- conjugated multiple bonds interact, and electrons are delocalized
- electron delocalization particularly pronounced for “aromatic” cyclic systems
- delocalization can be represented by resonance structures

2.1 Atomic Orbitals and Hybridization

Reading Recommendations

- Clayden, Greeves, Warren, *Organic Chemistry*, Oxford University Press, 2nd ed., **2012**, pp 80–83, 99–105.
- Jamart, Bodiguel, Brosse, *Les cours de Paul Arnaud - Cours de chimie organique*, Dunod, 19th ed., **2015**, pp 73–82.

The Time-Independent Schrödinger Equation

- electrons (waves) around a nucleus, have to fulfill the time-independent Schrödinger equation

$$\hat{H}\psi = E\psi$$

- Schrödinger equation is a **differential equation** that describes the **allowed states** (stationary state wave functions ψ) of an electron in the field of an atomic nucleus:

“If the Hamilton operator $\hat{H}$ acts on a wave function ψ and the result is proportional to ψ , then ψ is an allowed stationary state and the proportionality constant (Eigenvalue) is its energy E .”

- in one dimension:

$$\hat{H}\psi(x) = -\frac{h^2}{8\pi^2} \frac{d^2\psi(x)}{dx^2} + V(x)\psi(x) = E\psi(x)$$

- in three dimensions:

$$\hat{H}\psi(r) = -\frac{h^2}{8\pi^2} \nabla^2\psi(r) + V(r)\psi(r) = -\frac{h^2}{8\pi^2} \left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right) \psi(r) + V(r)\psi(r) = E\psi(r)$$

where ∇^2 is the Laplace operator, $V(r)$ is potential energy, m is electron mass, h is the Planck constant

Quantum Numbers and Exclusion Principle

- the allowed states are described by unique combinations of quantum numbers and can be decomposed as the product of a **spatial function** ψ_{nlm} and a **spin function** ξ
- atomic orbitals are described by the spin-independent term ψ_{nlm} of the wavefunctions**

Name	principal QN n	azimuthal QN ℓ	magnetic QN m_ℓ	spin QN m_s	electrons
1s	1	0	0	$+\frac{1}{2}, -\frac{1}{2}$	2
2s	2	0	0	$+\frac{1}{2}, -\frac{1}{2}$	2
2p	2	1	+1, 0, -1	$+\frac{1}{2}, -\frac{1}{2}$	6
3s	3	0	0	$+\frac{1}{2}, -\frac{1}{2}$	2
3p	3	1	+1, 0, -1	$+\frac{1}{2}, -\frac{1}{2}$	6
3d	3	2	+2, +1, 0, -1, -2	$+\frac{1}{2}, -\frac{1}{2}$	10

- atomic orbital described by set of quantum numbers n (1 ...), ℓ (0 ... $n-1$), and m ($-\ell$... $+\ell$)
- n, ℓ, m correspond to electron energy, angular momentum, momentum vector component
- Pauli exclusion principle:** each electron in a quantum system must have a **unique set of quantum numbers**; hence, **orbitals filled with up to two electrons with different spin QN m_s**

Quantum Numbers and Exclusion Principle

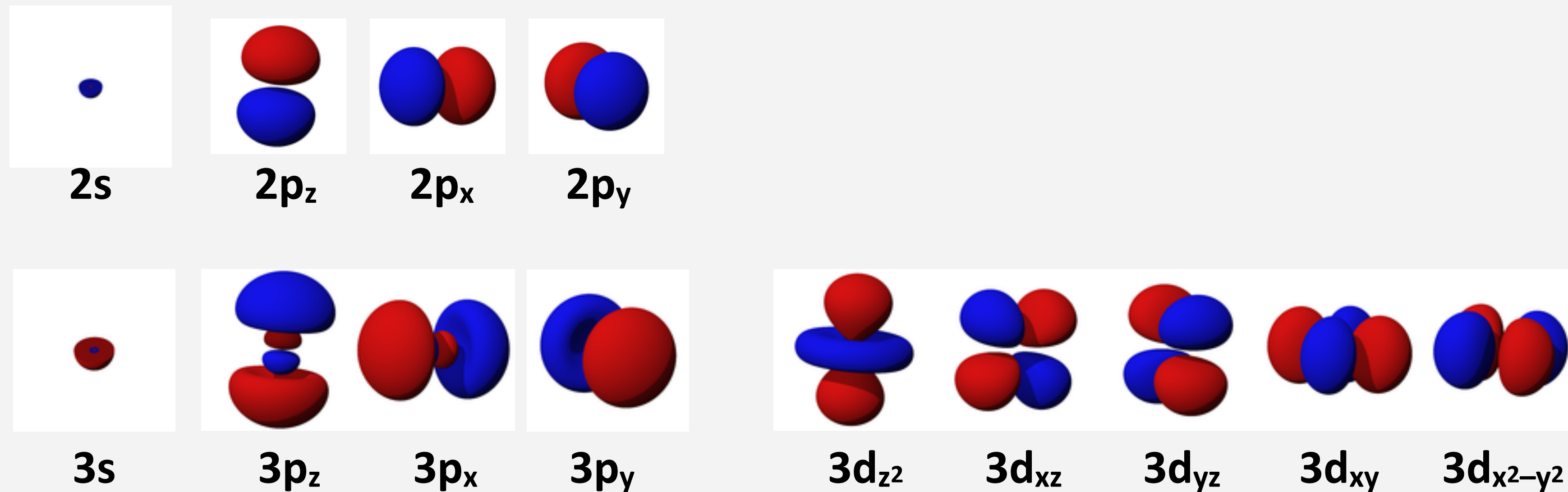
- atomic orbitals are described by the spin-independent term of the wavefunctions
- allowed stationary states ψ described by unique combinations of quantum numbers

name	principal QN n	azimuthal QN ℓ	magnetic QN m	spin QN s	electrons
1s	1	0	0	$+\frac{1}{2}, -\frac{1}{2}$	2
2s	2	0	0	$+\frac{1}{2}, -\frac{1}{2}$	2
2p	2	1	+1, 0, -1	$+\frac{1}{2}, -\frac{1}{2}$	6
3s	3	0	0	$+\frac{1}{2}, -\frac{1}{2}$	2
3p	3	1	+1, 0, -1	$+\frac{1}{2}, -\frac{1}{2}$	6
3d	3	2	+2, +1, 0, -1, -2	$+\frac{1}{2}, -\frac{1}{2}$	10

- atomic orbital described by set of quantum numbers n (1 ...), ℓ (0 ... $n-1$), and m ($-\ell$... $+\ell$)
- n, ℓ, m correspond to electron energy, angular momentum, momentum vector component

Pictorial Representations of Atomic Orbitals

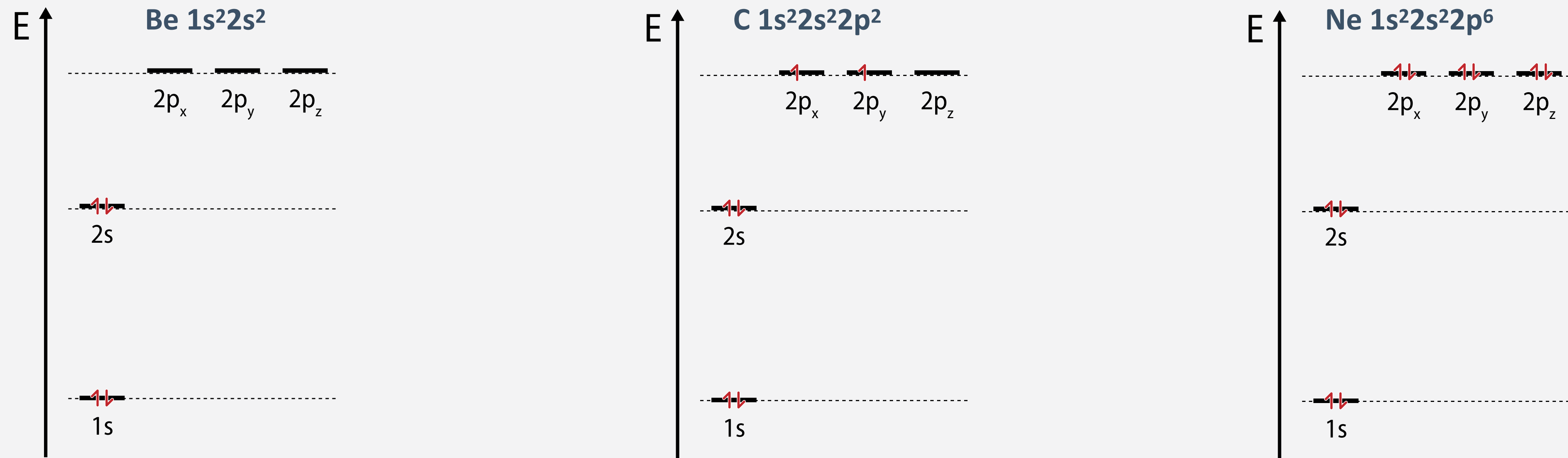
- spatial shape of atomic orbitals often graphically represented using the probability density $|\psi|^2$
- contour surfaces are probability isosurfaces of $|\psi|^2 = \text{const.}$ (e.g., 0.95)



- representations use **color coding** to show **phase (sign)** of the **probability amplitude ψ** itself
- **node planes** are **hypersurfaces of zero-probability** to observe the electrons $|\psi|^2 = 0$

Electronic Configuration and Valence Electrons

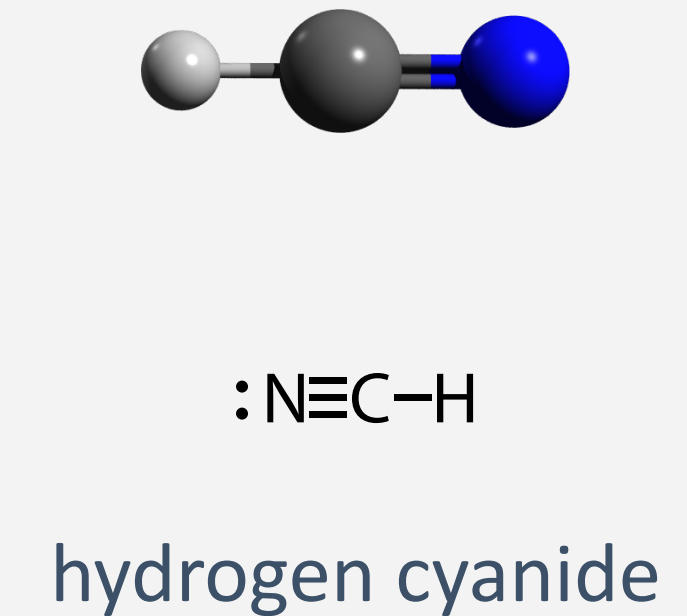
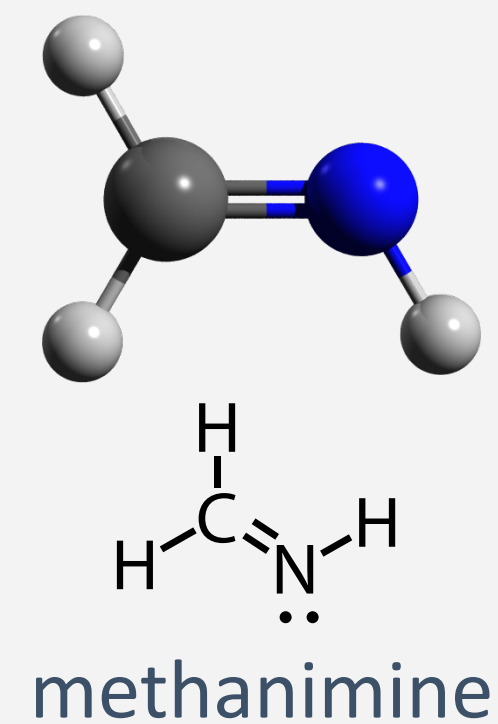
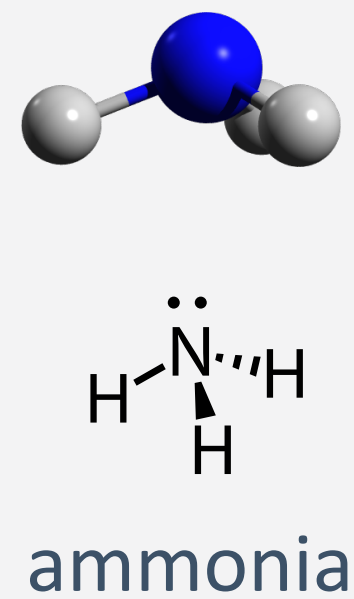
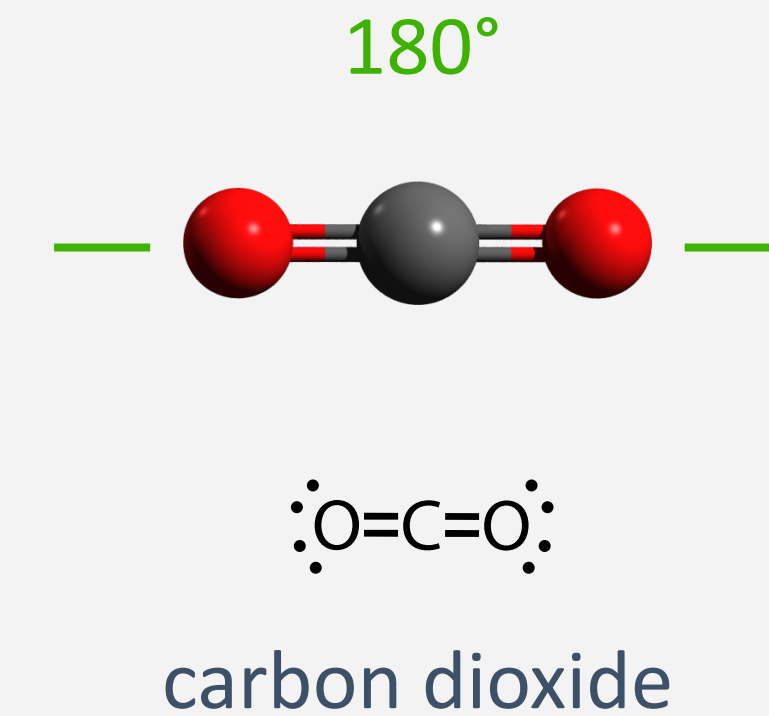
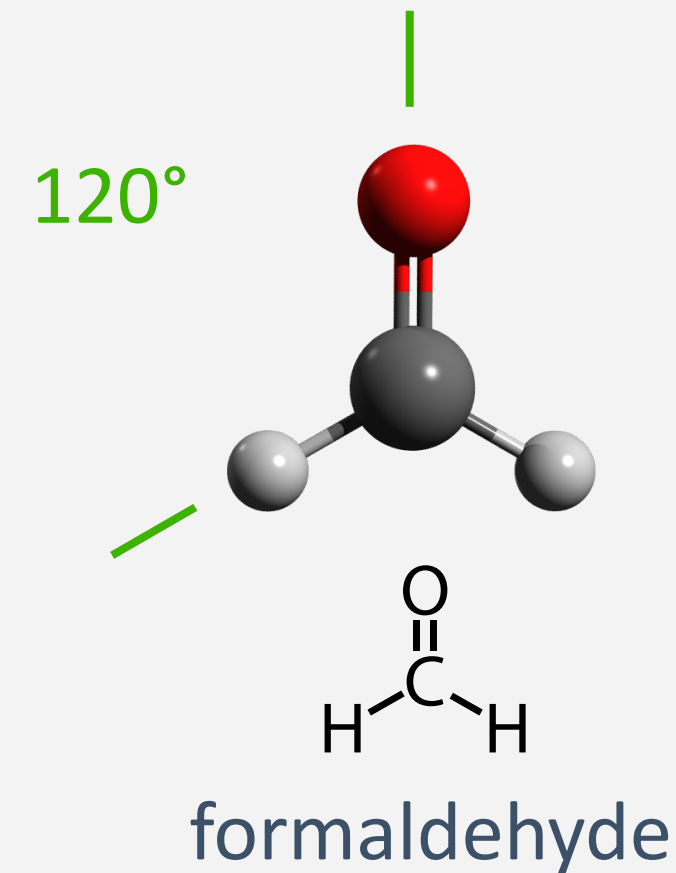
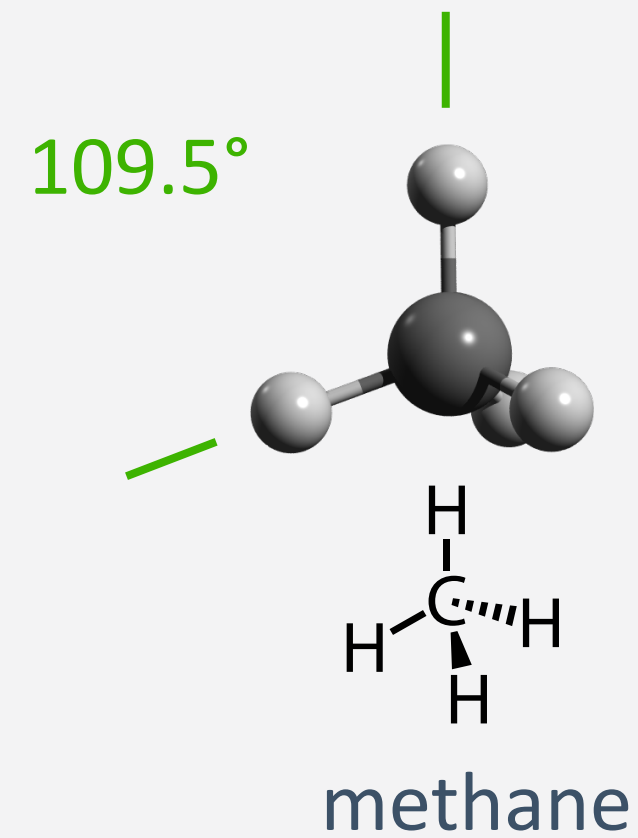
- **electronic configuration** is the repartition of the electrons over the available atomic orbitals:



- **Aufbau principle (Klechkovski rule)** demands to fill the orbitals from lower energies up, obeying the **Pauli exclusion principle** and **Hund's maximum multiplicity rule**
- only **valence shell** (outer-most, highest-energy shell containing electrons, highest QN n) and **valence electrons** relevant for chemical bonding and reactions
- electronic configuration of **carbon in the ground state is 1s² 2s² 2p²**; can accept up to four electrons (from up to four bonding partners), carbon is tetravalent

Valence Shell Electron Pair Repulsion (VSEPR) Model

- atoms in molecules have coordination geometries depending on the number of neighbors



- VSEPR model qualitatively describes coordination geometry
- tetrahedral** for 4; **trigonal-planar** for 3, **linear** for 2 neighboring atoms (or electron pairs)

Hybridization of Atomic Orbitals by Linear Combination

- linear combinations of sets of atomic orbitals are also allowed stationary states

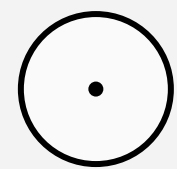
two regular
atomic orbitals



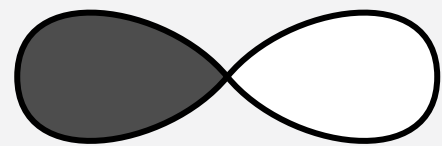
linear combination
by vector addition



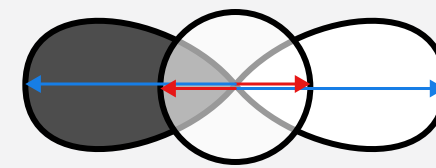
two “new” 2sp
hybrid orbitals



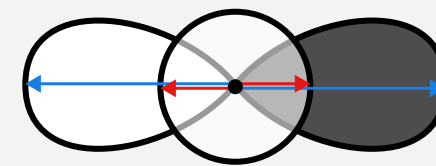
$2s$



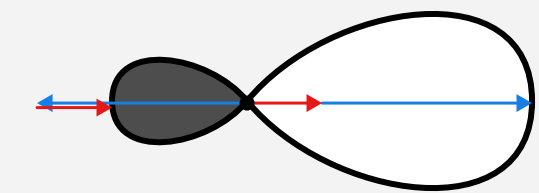
$2p_x$



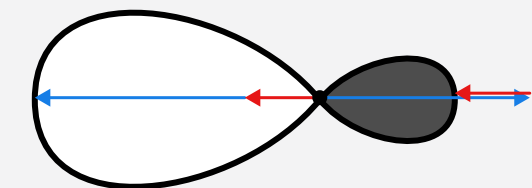
$2s+2p_x$



$2s-2p_x$



$2sp_1$



$2sp_2$

- 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
- solutions are linearly independent

Valence Bond Theory and Hybridization

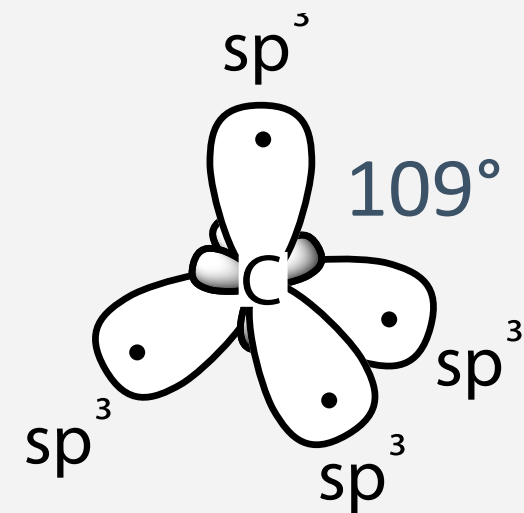
- Hermiticity: from a set of n solutions (an orthonormal basis), one can find a new set of n orthonormal solutions by linear combination

$$\Psi_1 = \frac{1}{2}(s + p_x + p_y + p_z)$$

$$\Psi_2 = \frac{1}{2}(s + p_x - p_y - p_z)$$

$$\Psi_3 = \frac{1}{2}(s - p_x + p_y - p_z)$$

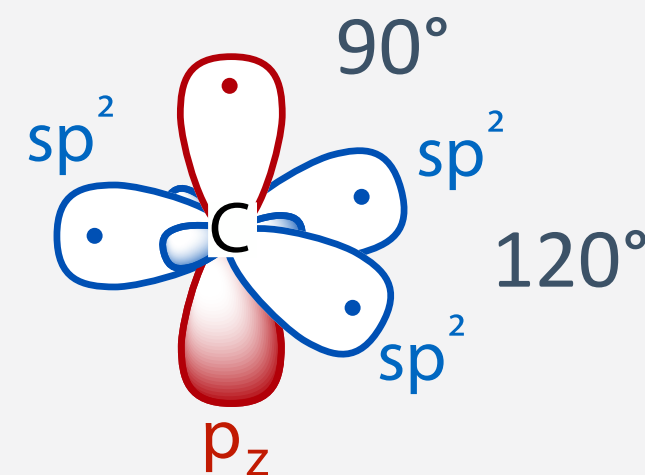
$$\Psi_4 = \frac{1}{2}(s - p_x - p_y + p_z)$$



$$\Psi_1 = \frac{1}{\sqrt{3}}s + \sqrt{\frac{2}{3}}p_x$$

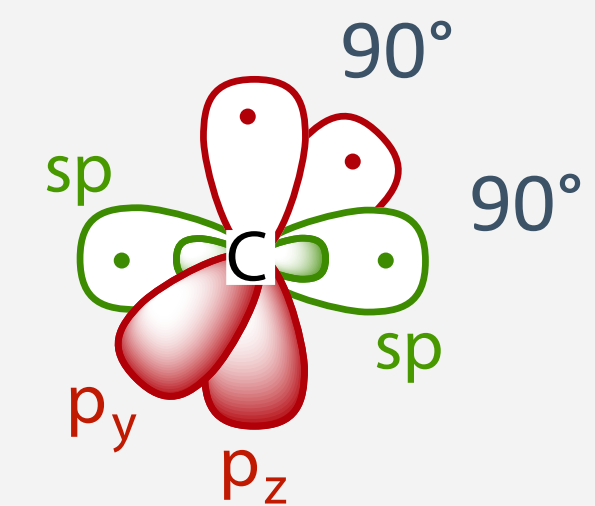
$$\Psi_2 = \frac{1}{\sqrt{3}}s - \frac{1}{\sqrt{6}}p_x + \frac{1}{\sqrt{2}}p_y$$

$$\Psi_3 = \frac{1}{\sqrt{3}}s - \frac{1}{\sqrt{6}}p_x - \frac{1}{\sqrt{2}}p_y$$



$$\Psi_1 = \frac{1}{\sqrt{2}}s + \frac{1}{\sqrt{2}}p_x$$

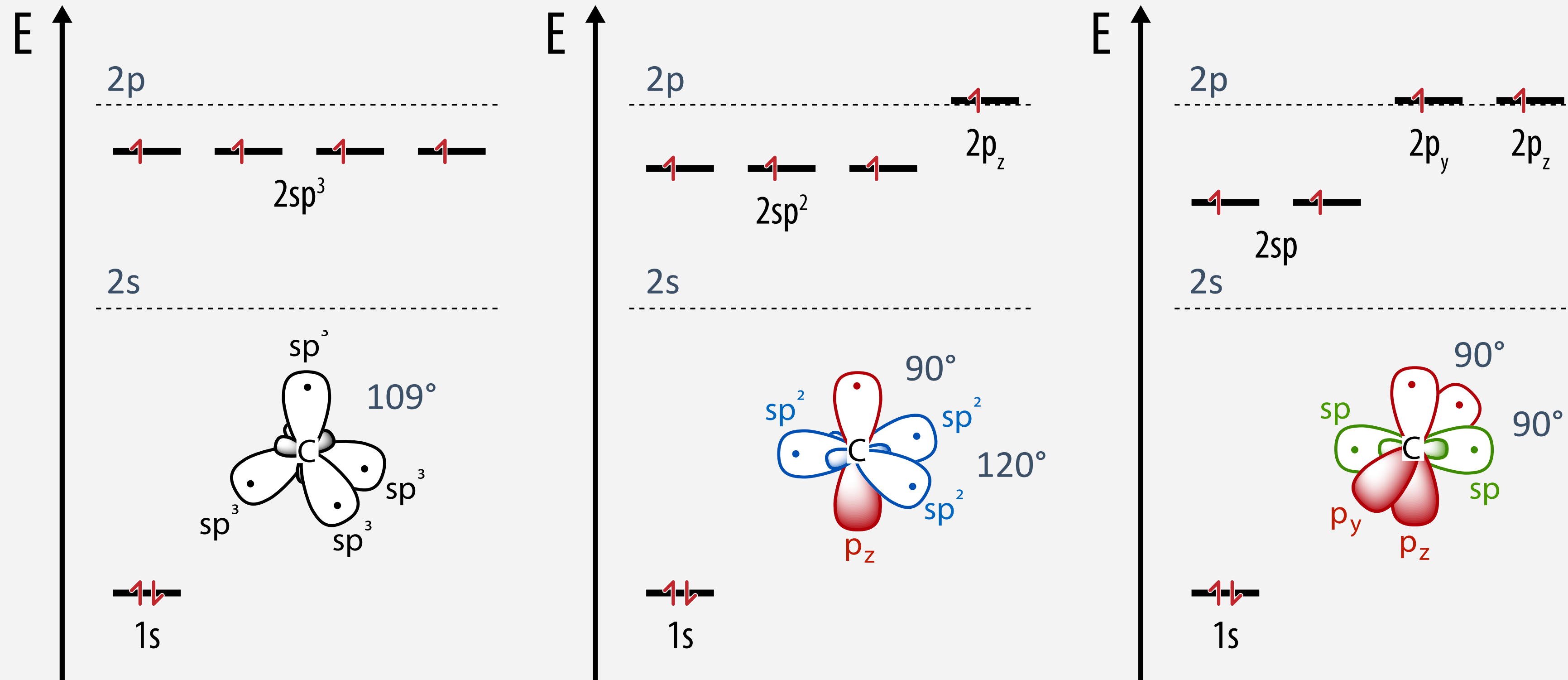
$$\Psi_2 = \frac{1}{\sqrt{2}}s - \frac{1}{\sqrt{2}}p_x$$



- hybrid orbitals (mixed states) by linear combination of atomic orbitals (pure states)
- hybridization reconciles molecular geometries with available valence shell orbitals

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 “real” geometries

Learning Outcomes

- **allowed stationary states ψ are solutions to the Schrödinger equation**
- **atomic orbitals represent space of finite probability to observe an electron**
- **valence shell is outer-most, highest-energy shell filled with electrons**
- **VSEPR model qualitatively describes coordination geometry**
- **hybridization is a concept to reconcile atomic orbitals with geometry**
 - linear combination of atomic orbitals results in hybrid orbitals
 - total number and total energy of the orbitals must be preserved