2.2 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

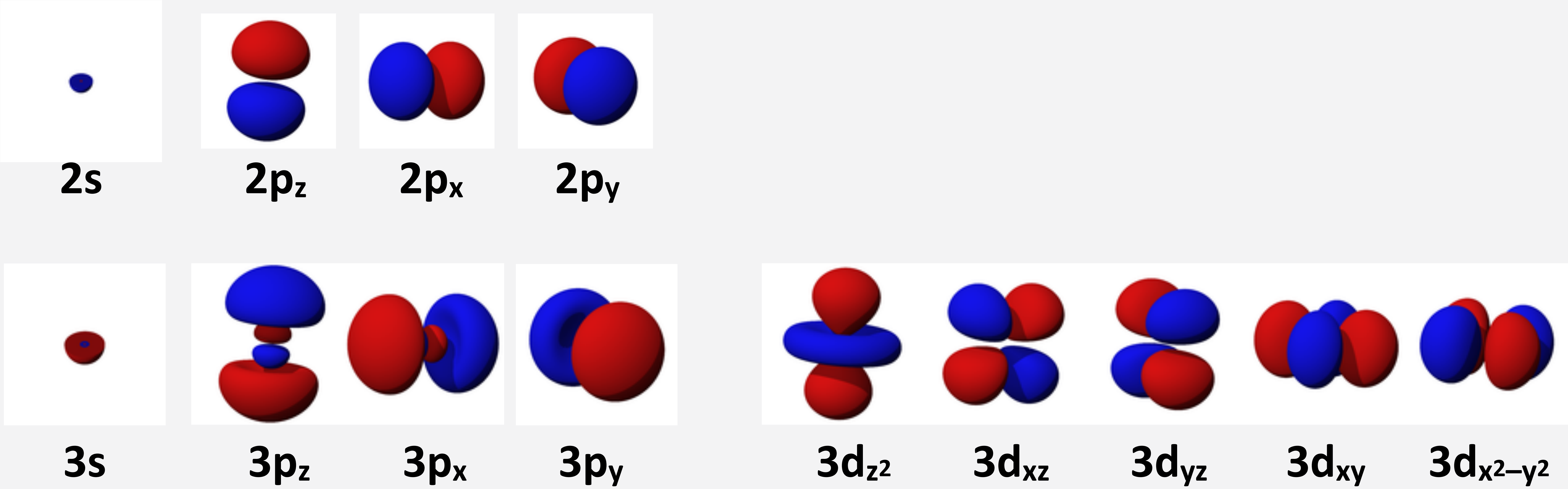
- the allowed states are described by unique combinations of quantum numbers and can be decomposed as the product of a spatial function ψ_{nlm} and a spin function ξ
- **atomic orbitals are described by the spin-independent term ψ_{nlm} of the wavefunctions**

Name	principal QN n	azimuthal QN ℓ	magnetic QN m_ℓ	spin QN m_s	electrons
1s	1	0	0	+½, –½	2
2s	2	0	0	+½, –½	2
2p	2	1	+1, 0, –1	+½, –½	6
3s	3	0	0	+½, –½	2
3p	3	1	+1, 0, –1	+½, –½	6
3d	3	2	+2, +1, 0, –1, –2	+½, –½	10

- **atomic orbital described by set of quantum numbers n (1 …), ℓ (0 … n–1), and m (–ℓ … +ℓ)**
- **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**

Pictorial Representations of Atomic Orbitals

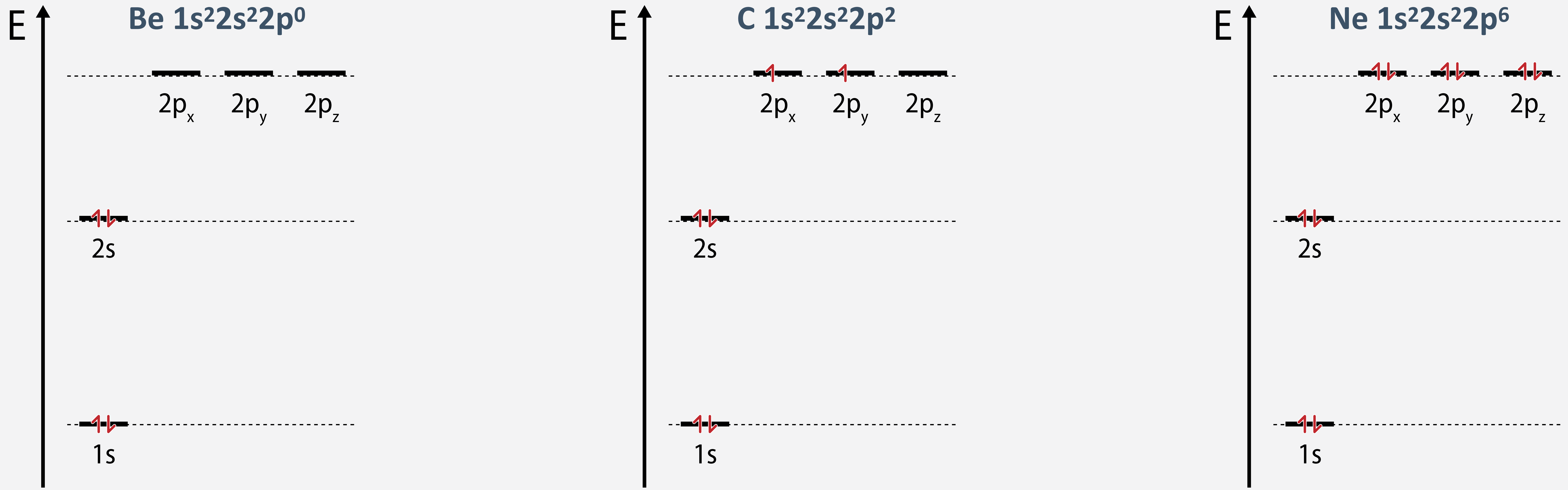
- **atomic orbitals describe the shape of the allowed stationary state ψ of an electron in space**
- shape of atomic orbitals graphically represented using the probability density $|\psi|^2$
- contour surfaces are probability isosurfaces of $|\psi|^2$ = const. (e.g., 0.95)



- **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 $|\psi|^2 = 0$**
- **important: atomic orbitals *only* describe spatial wavefunction ψ_{nlm}, ignoring spin wavefunction ξ**

Electronic Configuration and Valence Electrons

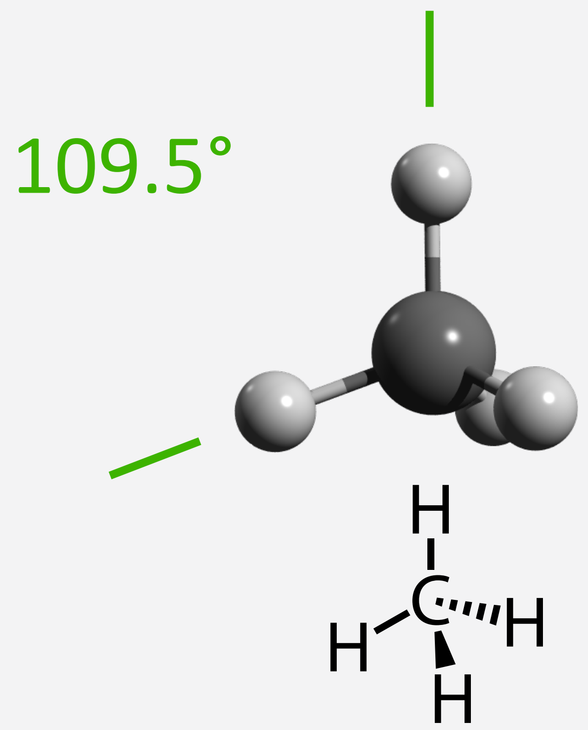
- electronic configuration is the repartition of the electrons over the available atomic orbitals:



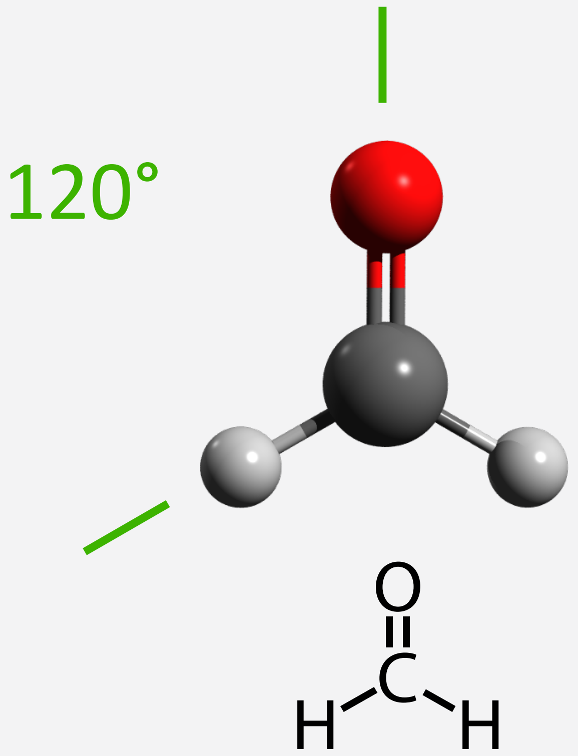
- **Aufbau principle (Klechkovski rule) demands to fill the orbitals from lower energies up, obeying the Pauli exclusion principle and Hund's maximum multiplicity rule**
- **only valence shell (outer-most, highest-energy shell containing electrons, highest QN *n*) and valence electrons relevant for chemical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

Valence Shell Electron Pair Repulsion (VSEPR) Model

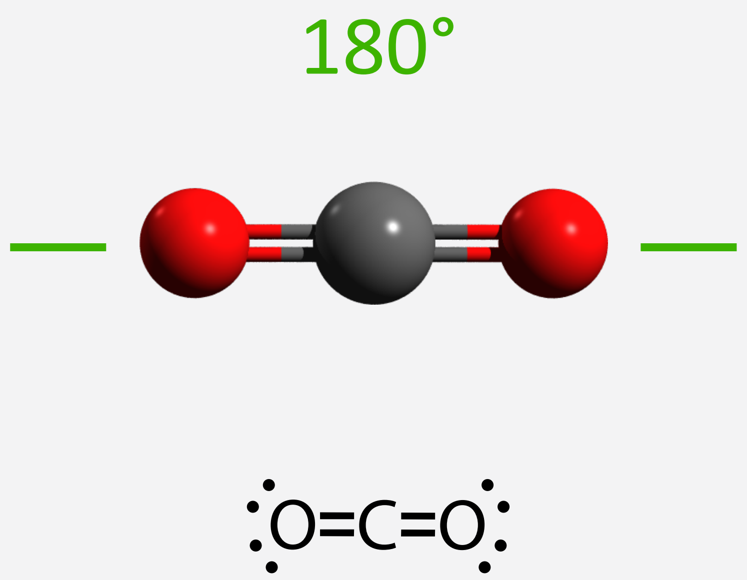
- atoms in molecules have coordination geometries depending on the number of electron pairs



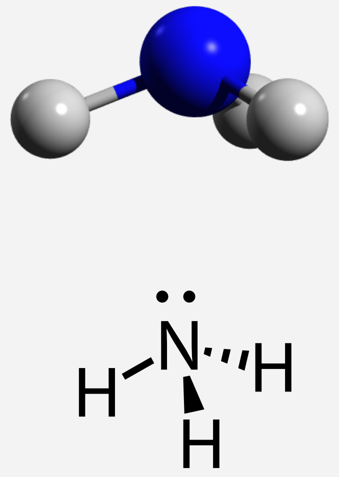
methane



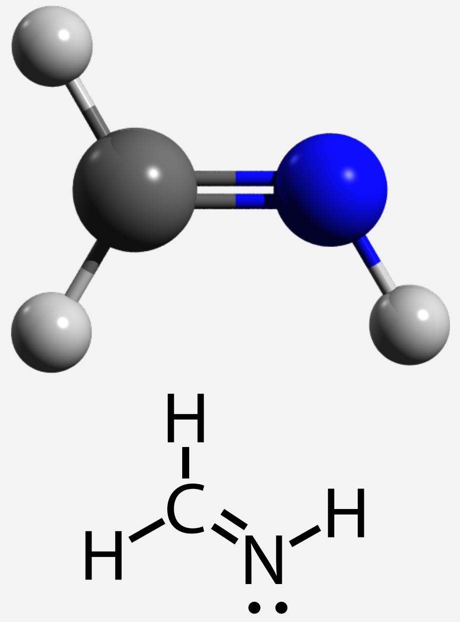
formaldehyde



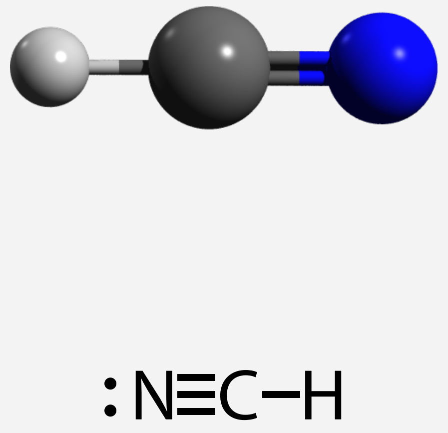
carbon dioxide



ammonia



methanimine



hydrogen cyanide

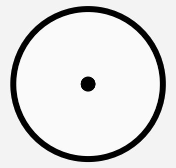
- **VSEPR model qualitatively describes coordination geometry**
- **tetrahedral for 4; trigonal-planar for 3, linear for 2 neighboring atoms (or electron pairs)**

Key Concept: See reader VSEPR Model and Hybridization

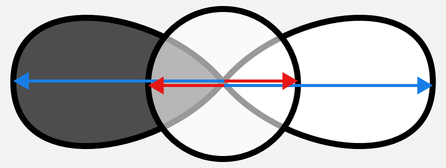
Hybridization of Atomic Orbitals by Linear Combination

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

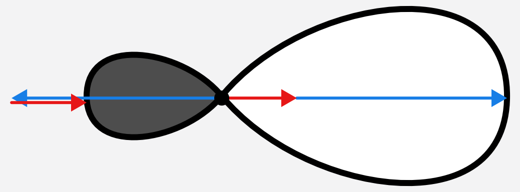
two regular atomic orbitals → linear combination by vector addition → two “new” 2sp hybrid orbitals



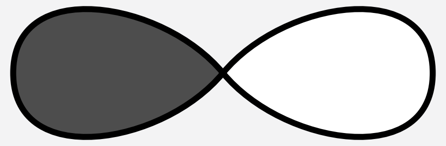
$2s$



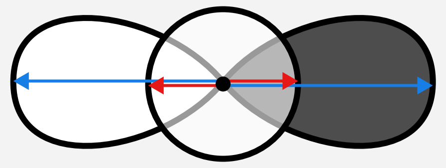
$2s+2p_x$



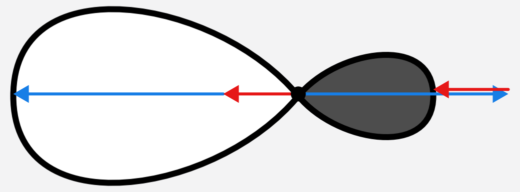
$2sp_1$



$2p_x$



$2s-2p_x$



$2sp_2$

- **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

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

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

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

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

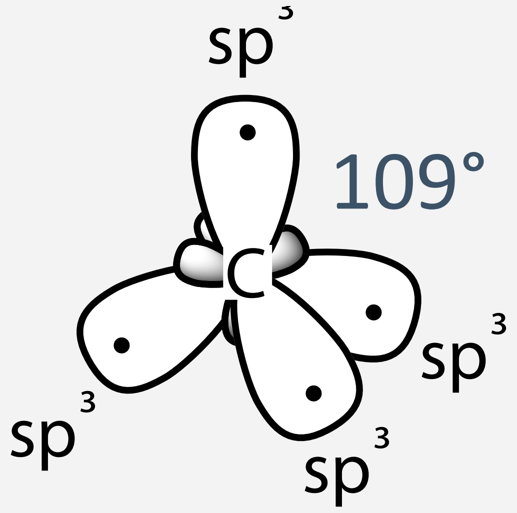
$$\Psi_1 = \frac{1}{\sqrt{3}}s + \sqrt{\frac{2}{3}}p_x$$

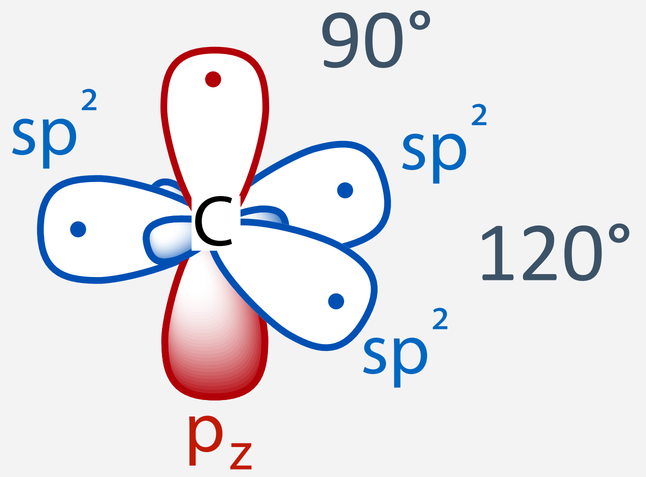
$$\Psi_2 = \frac{1}{\sqrt{3}}s - \frac{1}{\sqrt{6}}p_x + \frac{1}{\sqrt{2}}p_y$$

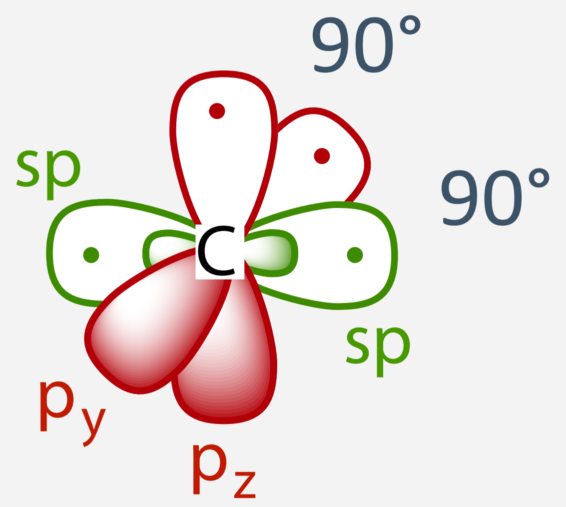
$$\Psi_3 = \frac{1}{\sqrt{3}}s - \frac{1}{\sqrt{6}}p_x - \frac{1}{\sqrt{2}}p_y$$

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

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



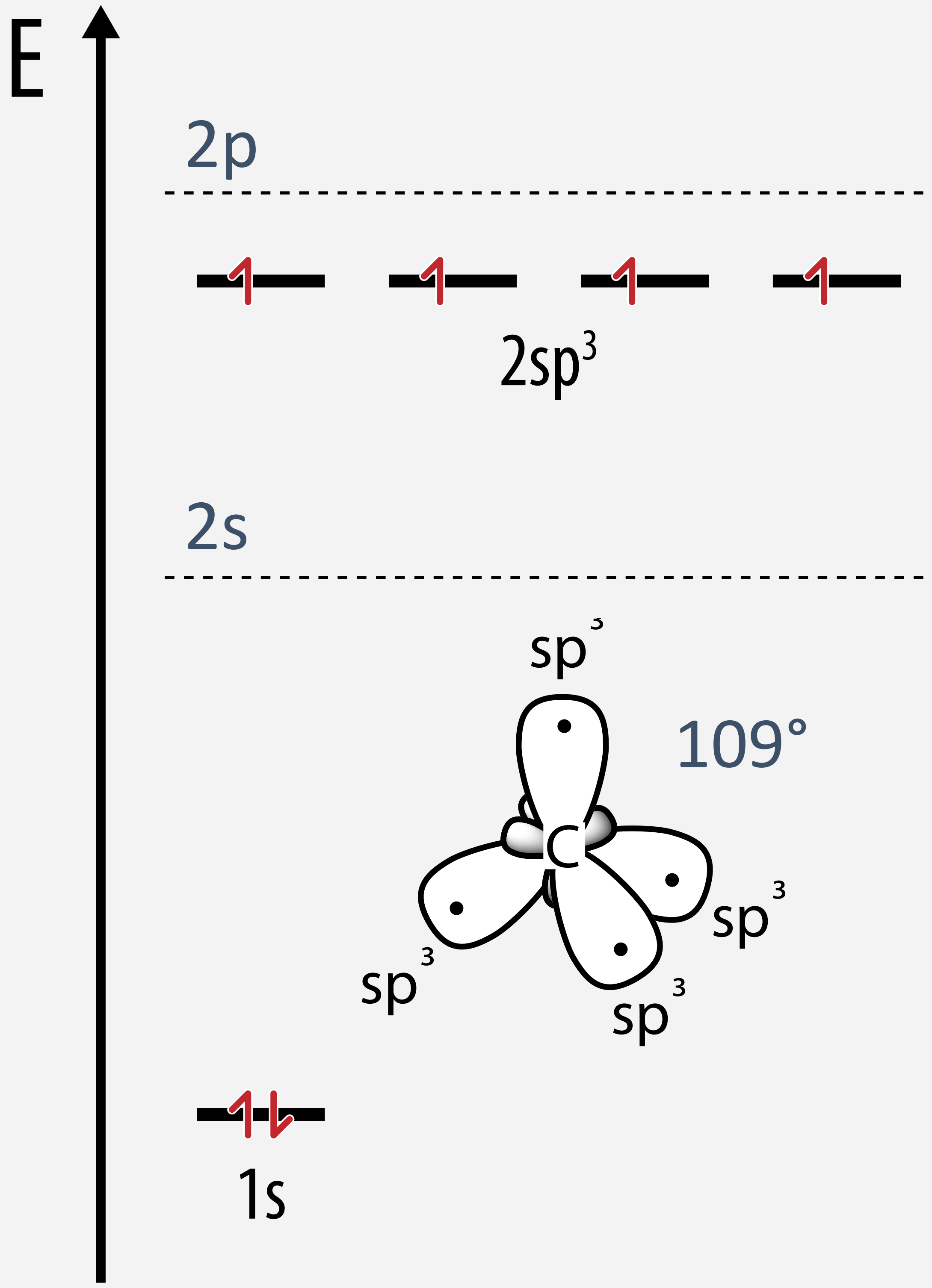


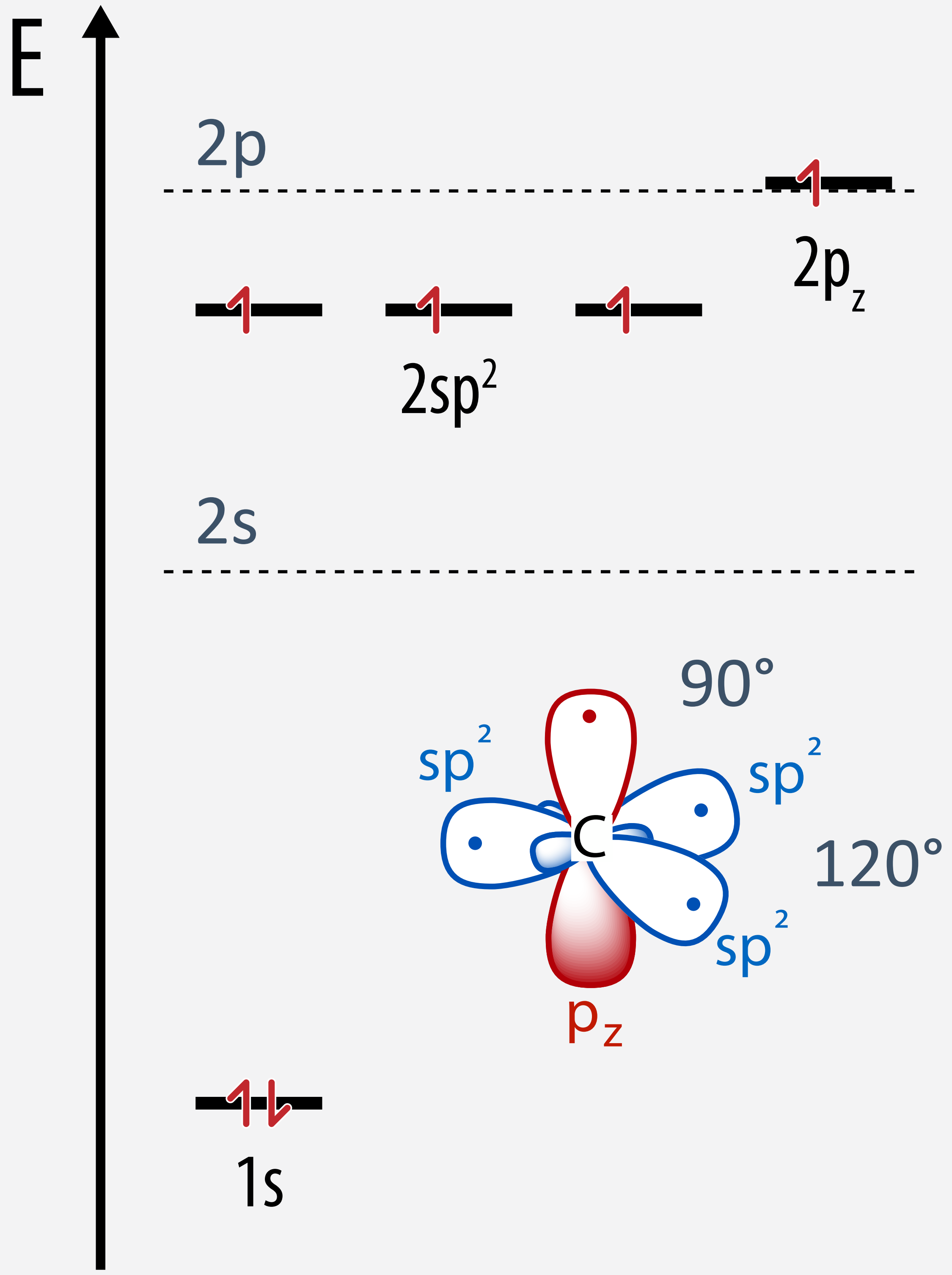


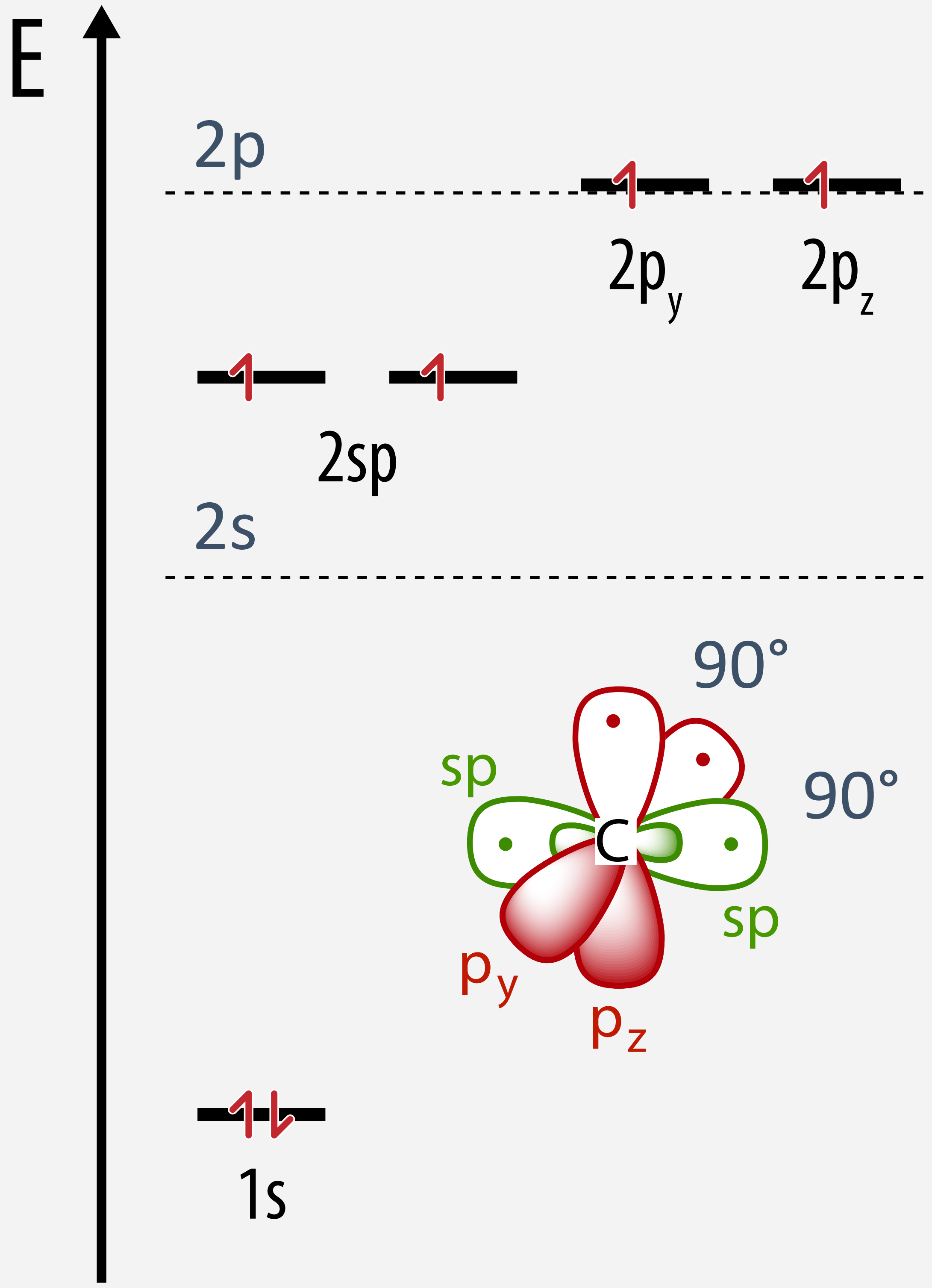
- hybrid orbitals (mixed states) by linear combination of atomic orbitals (pure states)
- hybridization reconciles molecular geometries with available valence shell orbitals

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