2.2 From Atomic Orbitals to Molecular Orbitals

The Hamilton Operator

- Hamiltonian operator $\hat{H}$ describes the total energy of the quantum system, which can be separated into kinetic energy operator $\hat{T}$ and a potential energy operator $\hat{V}$

$$\hat{H} = \hat{T} + \hat{V}$$

- for example, for the allowed states of a quantum system of an multiple atomic nuclei I and multiple electrons i, one has to consider all kinetic energy and potential energy contributions

$$\hat{H} = \underbrace{-\sum_{I=1}^{N} \frac{\hbar^2}{2m_{nu}} \nabla^2 - \sum_{i=1}^{n} \frac{\hbar^2}{2m_e} \nabla^2}_{\textbf{kinetic energies } \hat{T}_{nu} + \hat{T}_e} \underbrace{- \sum_{I=1}^{N} \sum_{i=1}^{n} \frac{Z_I e^2}{r_{iI}} + \sum_{i=1}^{n-1} \sum_{j=i+1}^{n} \frac{e^2}{r_{ij}} + \sum_{I=1}^{N-1} \sum_{J=I+1}^{N} \frac{Z_I Z_J e^2}{R_{IJ}}}_{\textbf{potential energies } \hat{V}_{nu,e} + \hat{V}_{e,e} + \hat{V}_{nu,nu}}$$

with the Laplace operator: $\Delta = \nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$ in 3D Cartesian coordinates

$\Delta = \nabla^2 = \frac{\partial^2}{\partial r^2} + \frac{1}{r}\frac{\partial}{\partial r} + \frac{1}{r^2}\frac{\partial^2}{\partial \theta^2}$ in polar coordinates

The Schrödinger Equation

- state vector of any quantum system has to fulfill the time-dependent Schödinger equation:

$$\hat{H}\,|\,\Psi(t)\rangle = i\hbar\frac{\partial}{\partial t}\,|\,\Psi(t)\rangle$$

- wavefunctions can form standing waves, called stationary states that can described by the time-independent Schrödinger equation:

$$\hat{H}_i\Psi = E_i\Psi$$

$$\frac{\hbar^2}{2m}\nabla^2\Psi_i + V\Psi_i = E_i\Psi$$

- the time-independent Schrödinger equation is an Eigenequation that describes the allowed wavefunctions Ψ_i (stationary states) of a particle of mass m , and the Eigenvalues are the associated energies E_i

Approximations to Solve the Schrödinger Equation

- except for the simplest cases, the time-independent Schrödinger equation cannot be solved analytically without approximations

  - Born Oppenheimer approximation: the nuclei do not move!

$$\hat{T}_{nu} = \sum_{I=1}^{N} \frac{\hbar^2}{2m_{nu}} \nabla^2 = \hat{0} \quad \text{and} \quad |\Psi(\mathbf{e}_1, \ldots, \mathbf{e}_n, \mathbf{nu}_1, \ldots, \mathbf{nu}_n)\rangle = |\Psi(\mathbf{e}_1, \ldots, \mathbf{e}_n,)\rangle$$

  - independent electron (orbital) approximation: electrons do not see each other!

$$\Rightarrow \hat{V}_{ee} = \sum_{i=1}^{n-1} \sum_{j=i+1}^{n} \frac{e^2}{r_{ij}} = \hat{0} \quad \text{and} \quad |\Psi(\mathbf{e}_1, \ldots, \mathbf{e}_n,)\rangle = \prod_{i=1}^{n} |\Psi(\mathbf{e}_i)\rangle$$

- **Born-Oppenheimer approximation reasonable due to drastically different masses**
- **the independent electron approximation results in significant error (that later need to by corrected for more accurate results)**

Quantum Numbers and Exclusion Principle

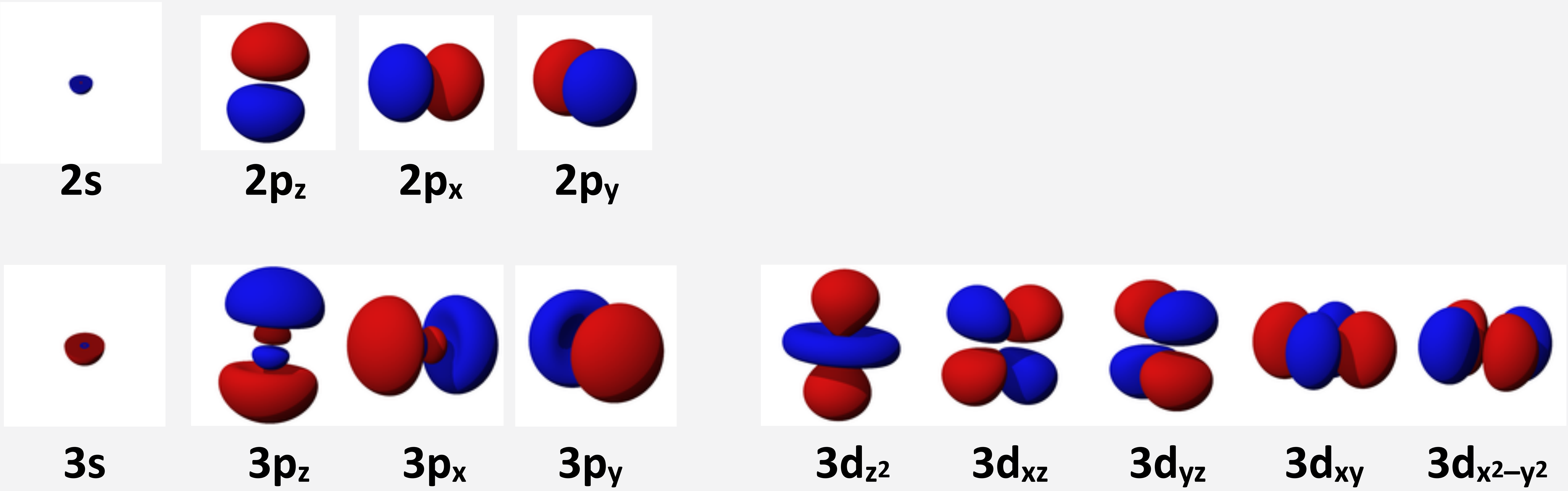
- allowed states can be decomposed into a product of a spatial function $|\Psi_i\rangle = \Psi_{nlm}$ and a spin function ξ that are described by unique combinations of quantum numbers and
- atomic orbitals are described by the spin-independent term Ψ_{nlm} of the wavefunctions

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* describe energy, angular momentum (“shape”), momentum vector component (“orientation”)**
- **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**

Atomic Orbitals

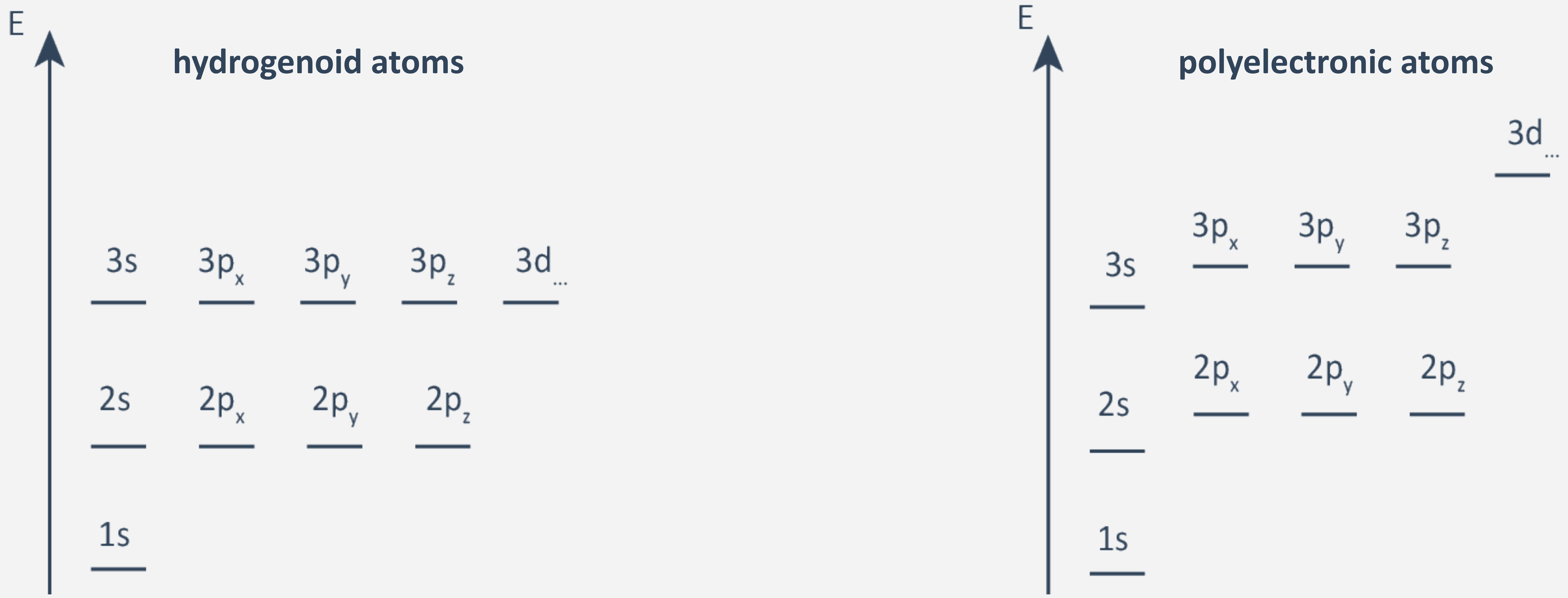
- atomic orbitals describe “space to find an electron” according to the spatial wave function Ψ_{nlm}
- graphically represented using the probability density $||\Psi_{nlm}\rangle|^2$
- more specifically, using contour surfaces , i. e., probability isosurfaces of $||\Psi_{nlm}\rangle|^2 = \text{const.}$



- **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** $||\Psi_{nlm}\rangle|^2 = 0$

Stationary States in Monoatomic Systems

- the energies E_n of the stationary states $|\Psi_n\rangle$ in hydrogenoid (monolectronic) atoms only depend on the main shell (principal QN n), subshells are degenerate
- for polyelectronic atoms the energies E_n depend on principal QN n and azimuthal QN l because the degeneracy is lifted due to different shielding of the nucleic charge

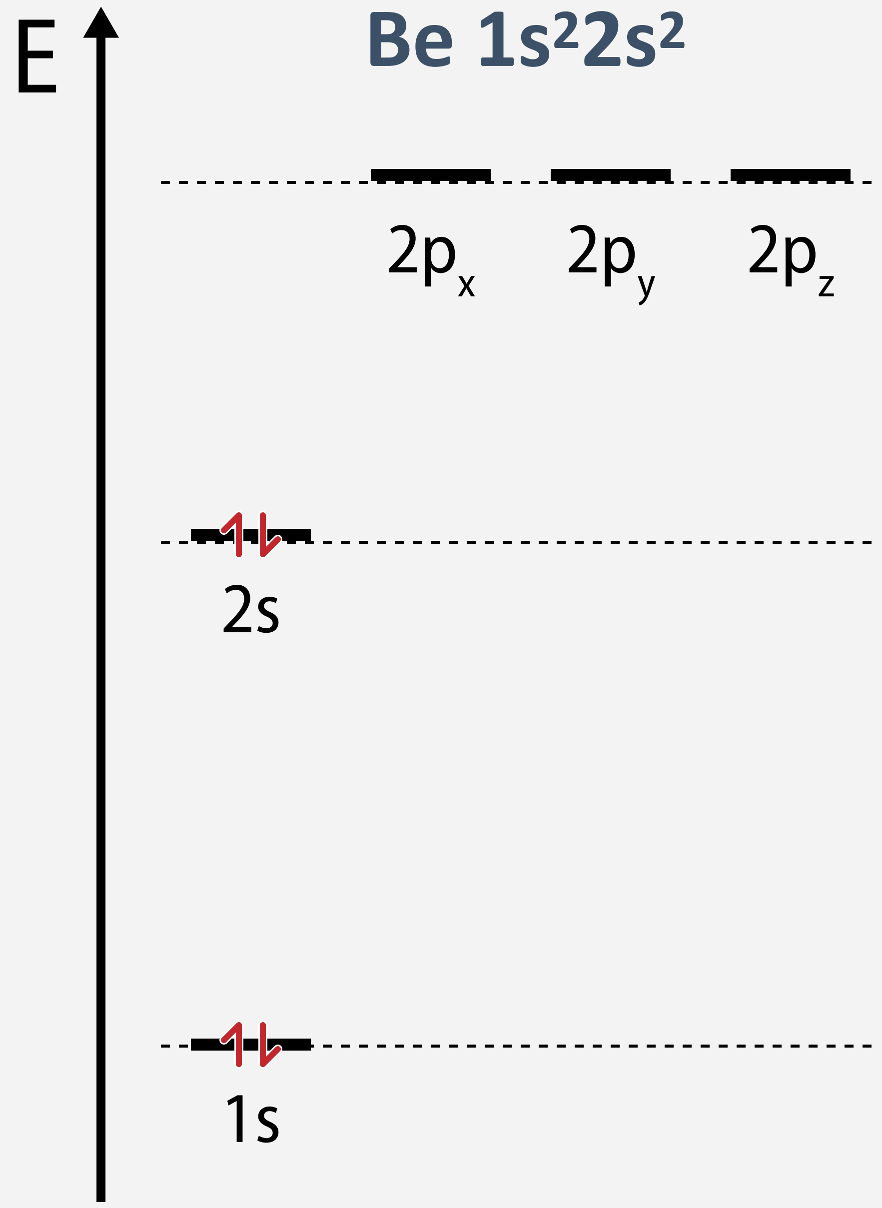


- **each energy level is degenerate in spin, that is, it is associated with both $\Psi_{nlm\uparrow}$ and $\Psi_{nlm\downarrow}$**

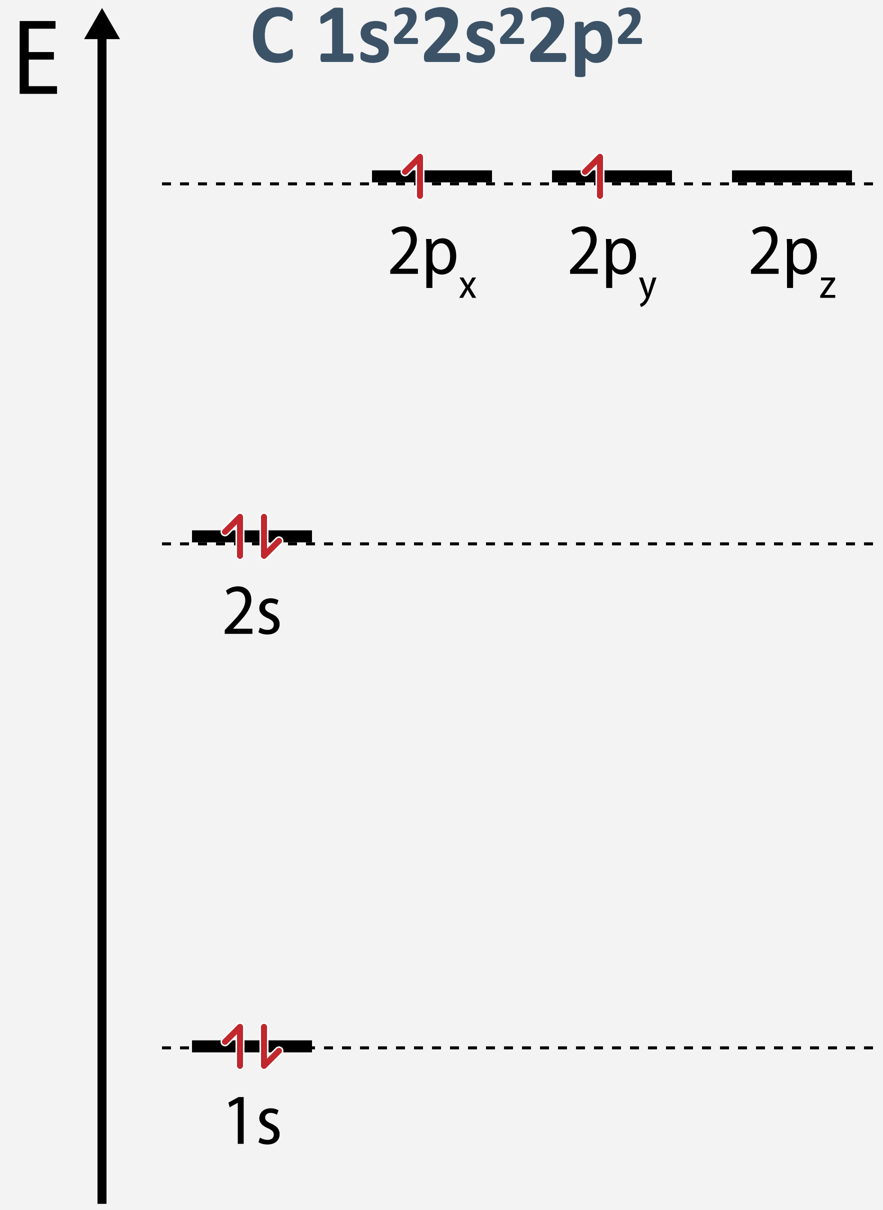
Electronic Configuration and Valence Electrons

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

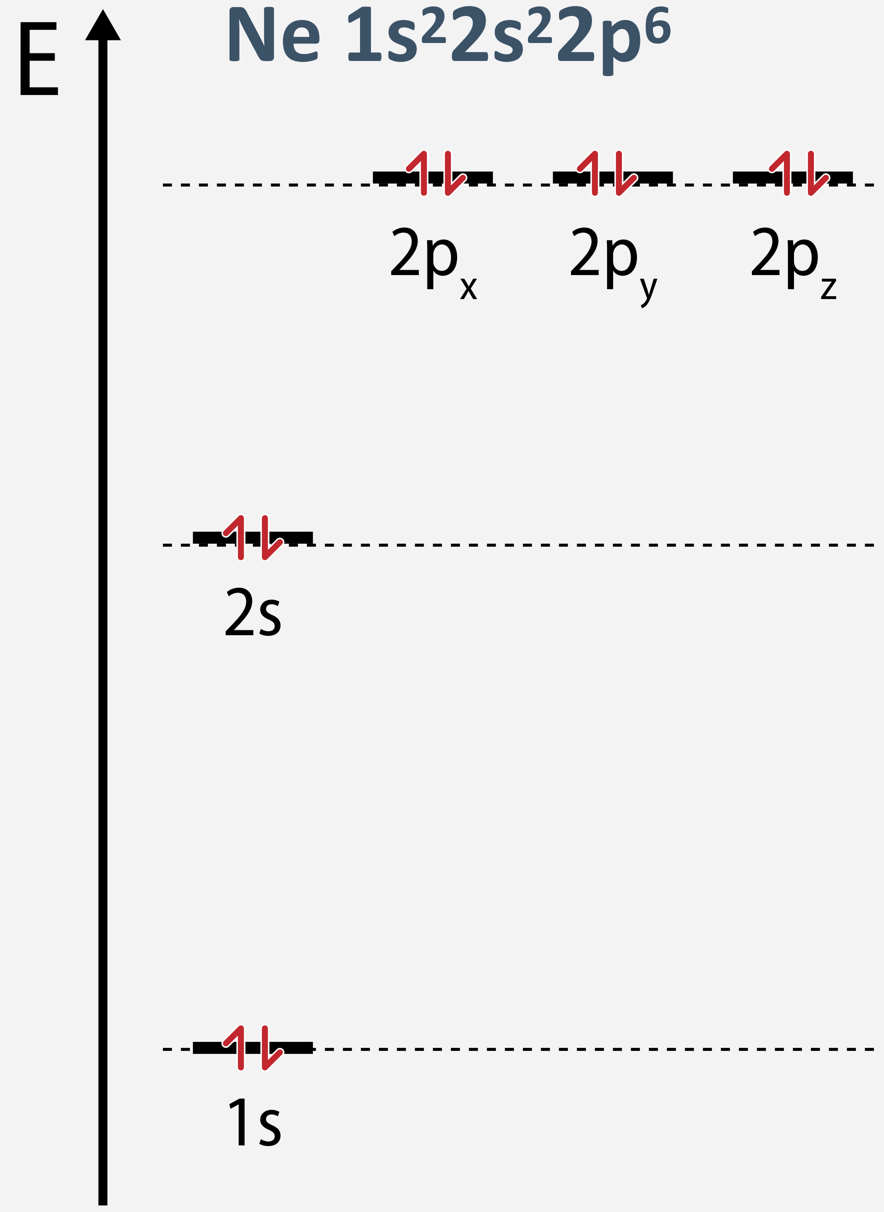
Be $1s^22s^2$



C $1s^22s^22p^2$



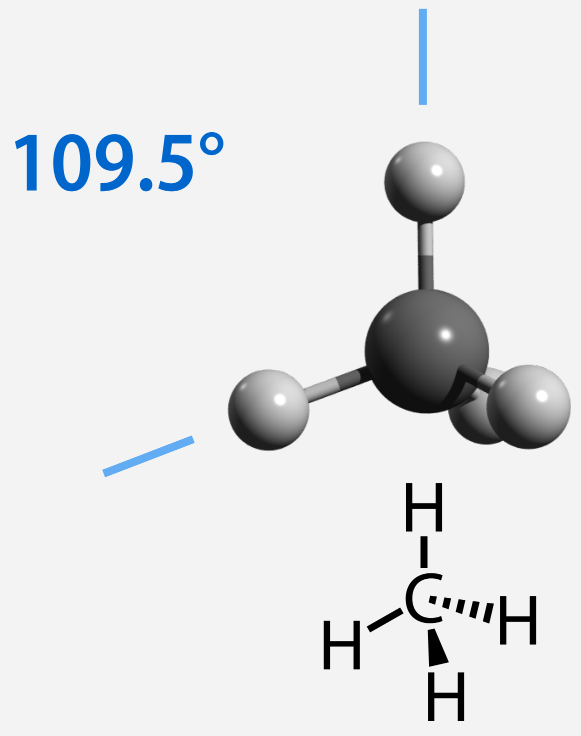
Ne $1s^22s^22p^6$



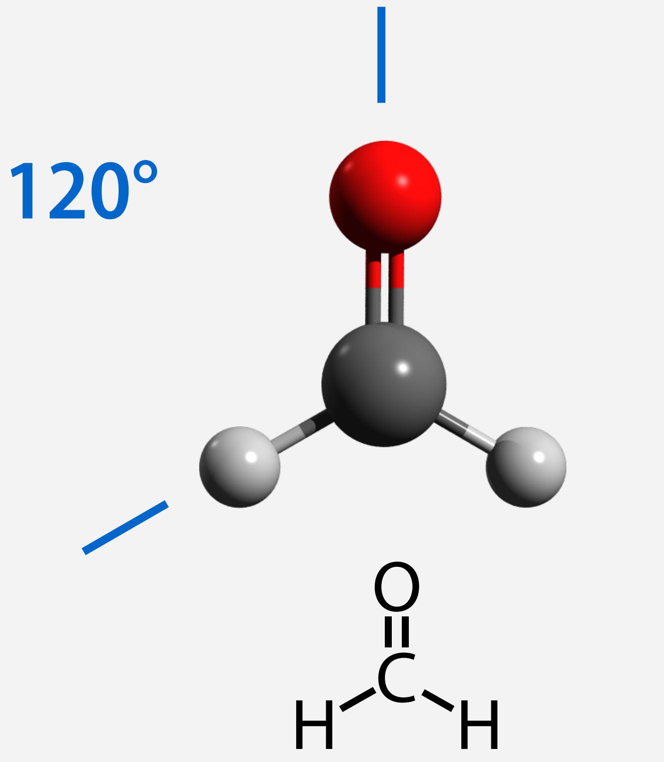
- **Pauli exclusion principle** requires all electrons to have a unique set of quantum numbers
- **Klechkovski rule (Aufbau principle)** demands to fill the orbitals from lower energies up
- **Hund's maximum multiplicity rule** postulates "spin pairing energy" of electrons in the same AO
- only **valence shell** (outer-most, highest-energy shell containing electrons, highest QN *n*) and **valence electrons** relevant for chemical bonding and reactions

Valence Shell Electron Pair Repulsion (VSEPR) Model

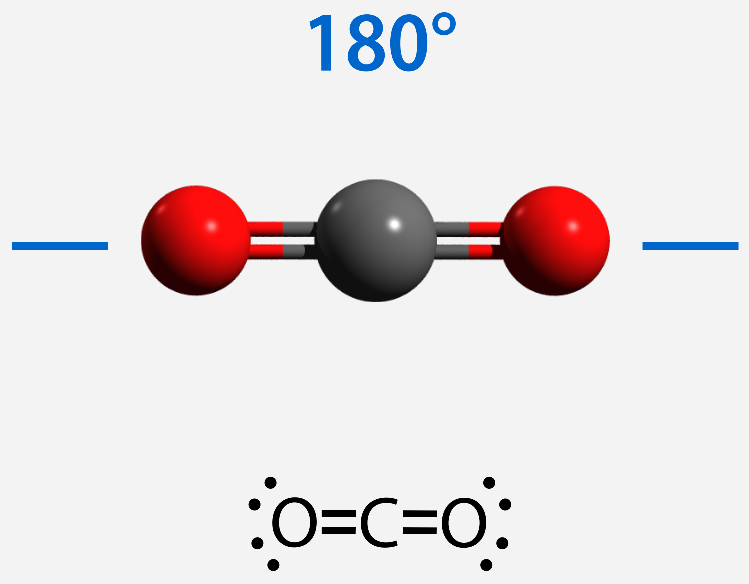
- atoms in real molecules have coordination geometries depending on the number of neighbors



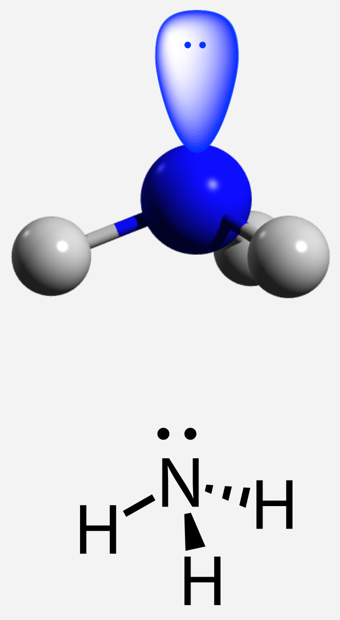
methane



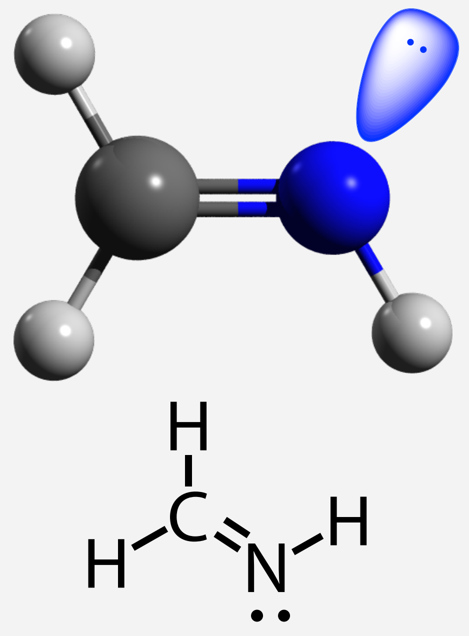
formaldehyde



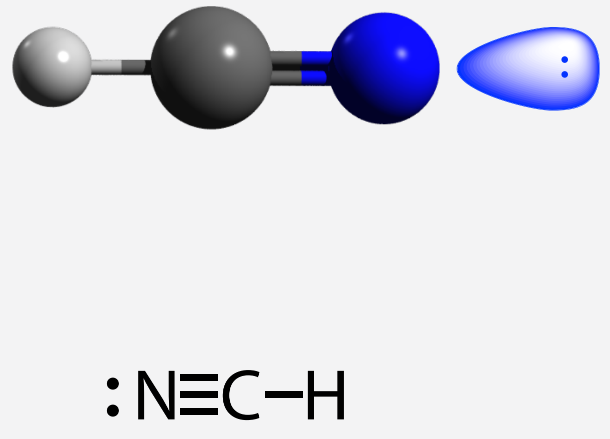
carbon dioxide



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)**

see reader *"Valence Bond Theory and Hybridization"* for details

Valence Bond Theory and Hybridization

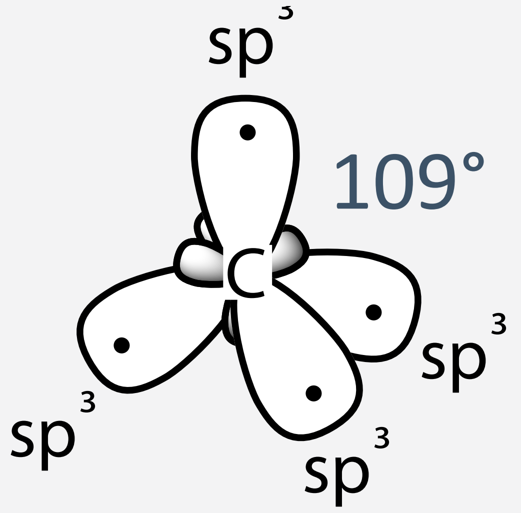
- Hermiticity: from a set of *n* solutions (an orthonormal basis), one can find a new set of n orthonormal solutions by linear combination

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

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

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

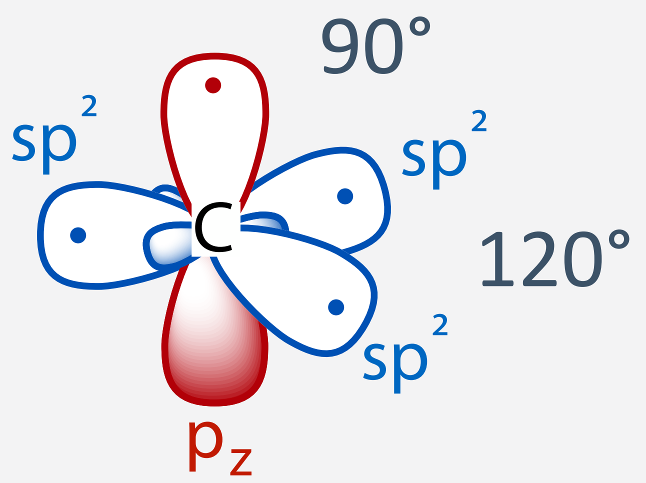
$$\Psi_4 = \frac{1}{2}(s - p_x - p_y + p_z)$$



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

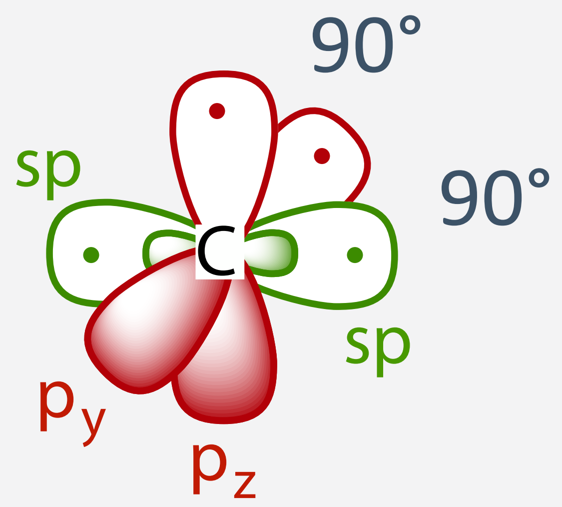
$$\Psi_2 = \frac{1}{\sqrt{3}}s - \frac{1}{\sqrt{6}}p_x + \frac{1}{\sqrt{2}}p_y$$

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



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

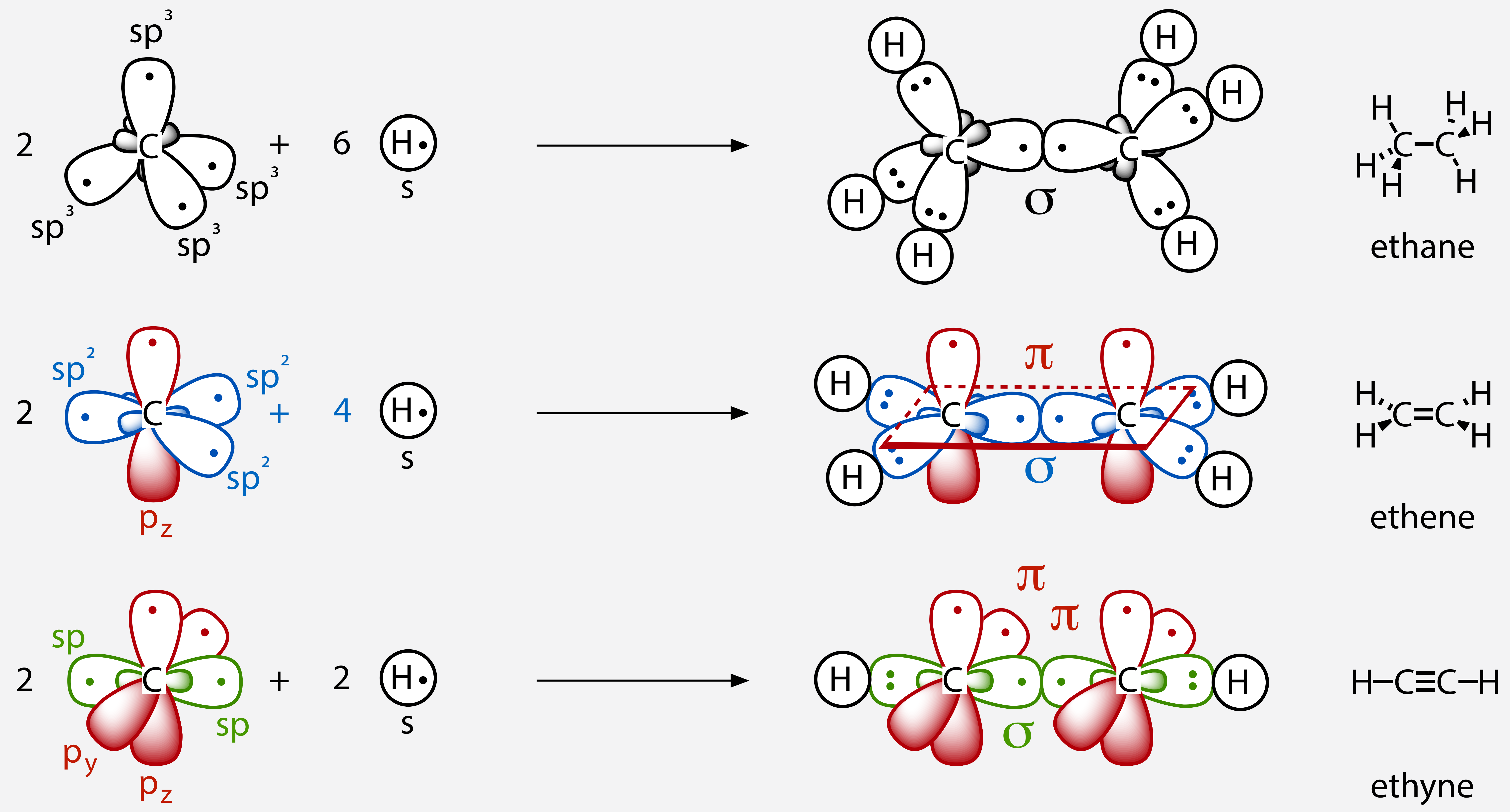
$$\Psi_2 = \frac{1}{\sqrt{2}}s - \frac{1}{\sqrt{2}}p_x$$



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

see reader *“Valence Bond Theory and Hybridization”* for details

Formation of Carbon-Carbon Single and Multiple Bonds



- **valence bond model: bonds are formed by electron pairing**
- **double or triple bonds are one σ-bond plus one or two π-bonds, respectively**
- **π-bonds formed between p orbitals, node plane along bond, no rotational but lateral symmetry**

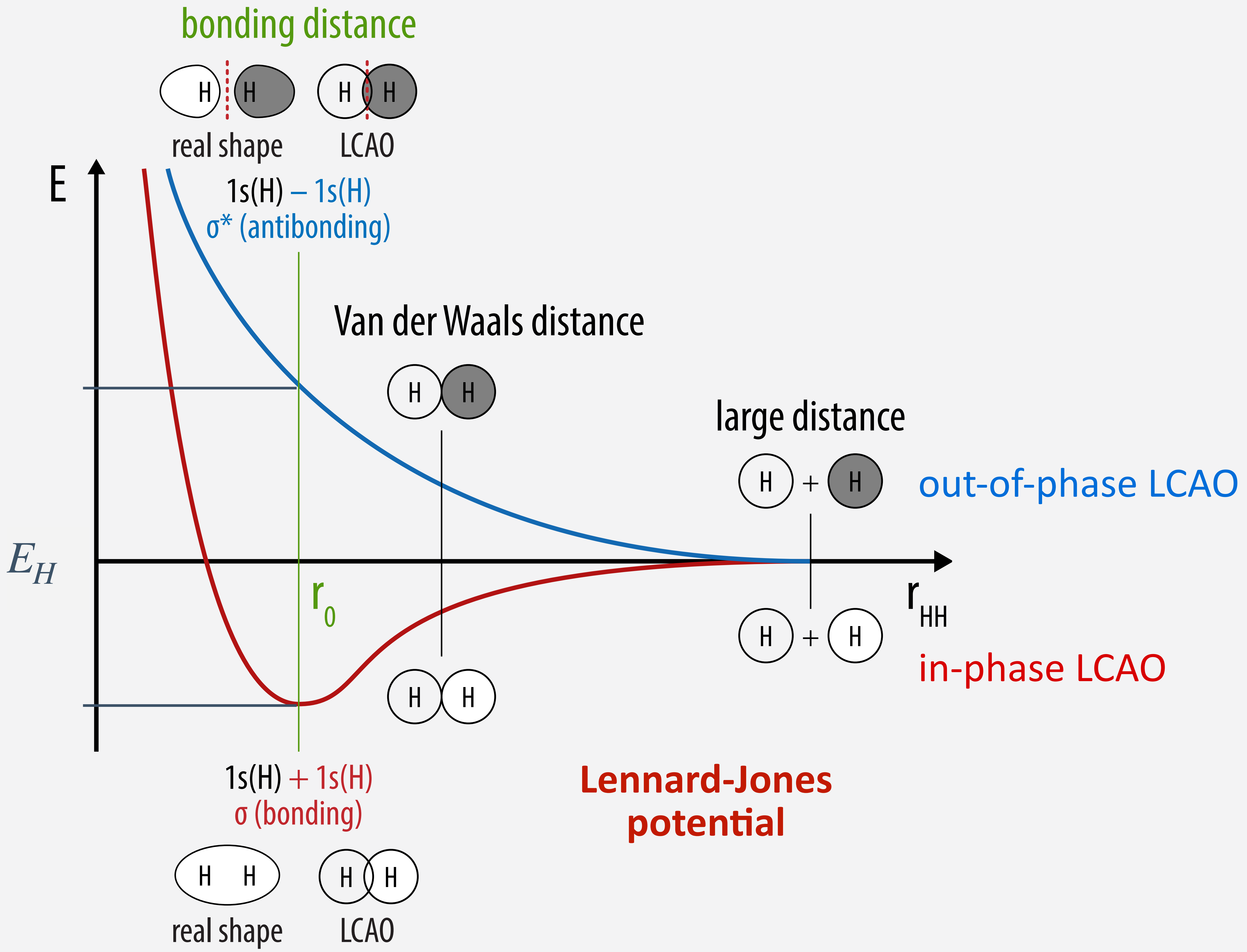
Molecular Orbital Theory Description of the Covalent Bond

- **Molecular Orbital (MO) theory does not assign electrons to particular bonds between pairs of atoms but assumes they are delocalized throughout molecules**

- **Schrödinger equation for polyatomic, polyelectronic quantum system can only be solved with further approximations**
    - Born-Oppenheimer approximation: polyelectronic wavefunctions
    - independent electrons approximation: product of monoelectronic wavefunctions
    - LCAO approximation: due to Hermiticity, monoelectronic molecular orbitals Ψ_i can be derived from linear combinations of atomic orbitals (LCAO) $\psi_m(\mathbf{e}_i)$

$$\Psi_i(\mathbf{e}_i) = \sum_{m=1}^{n} c_{m,i}\psi_m(\mathbf{e}_i), \quad i \in \{1 \ldots n\}$$

Towards an Exact Solution

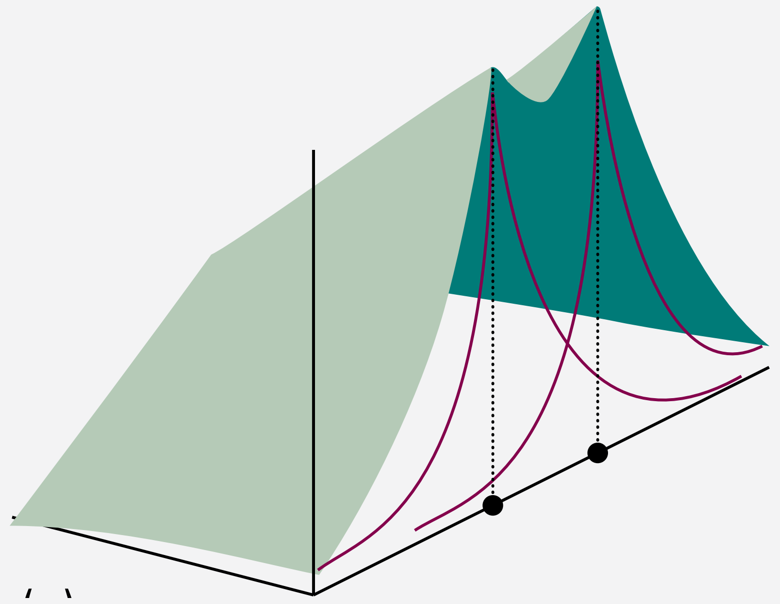


- **with decreasing distance between atoms, atomic orbitals interact and split energetically**
- **number of orbitals conserved, LCAO with one “in phase” and one “out of phase”**

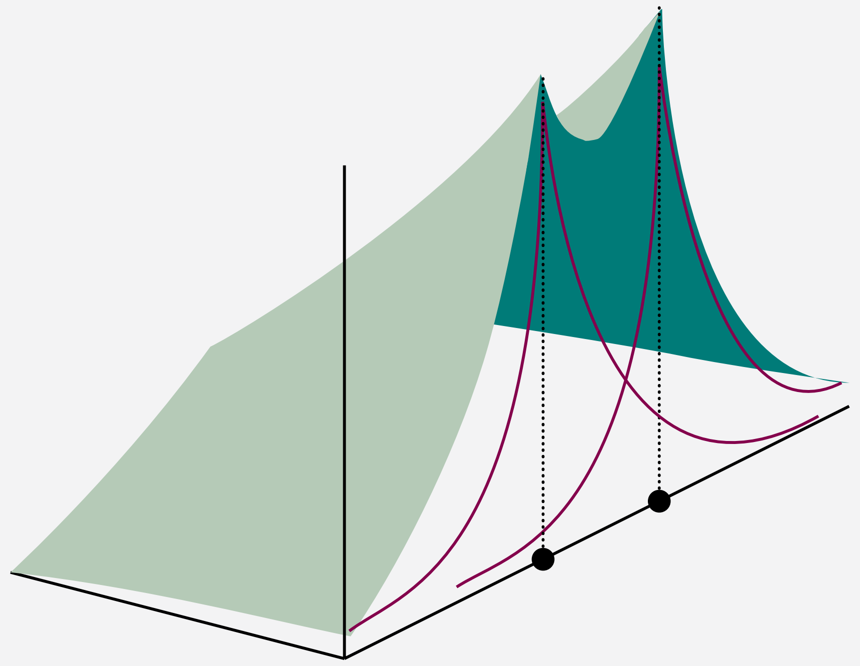
Bonding and Antibonding Orbitals

- bonding orbitals

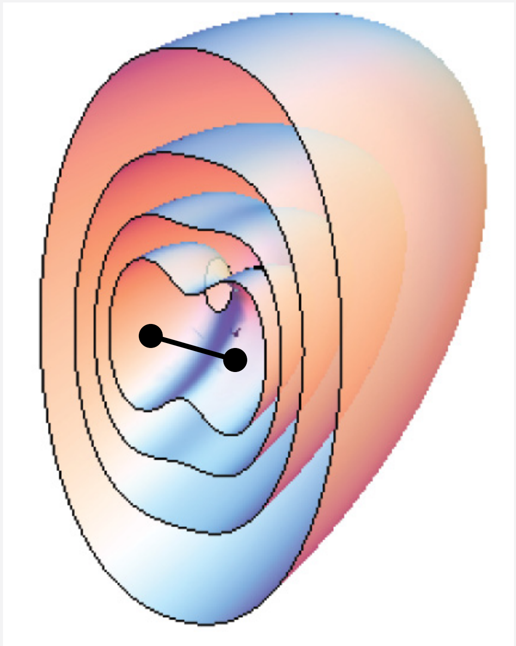
amplitude (ψ)



electron denisity ($|\psi|^2$)

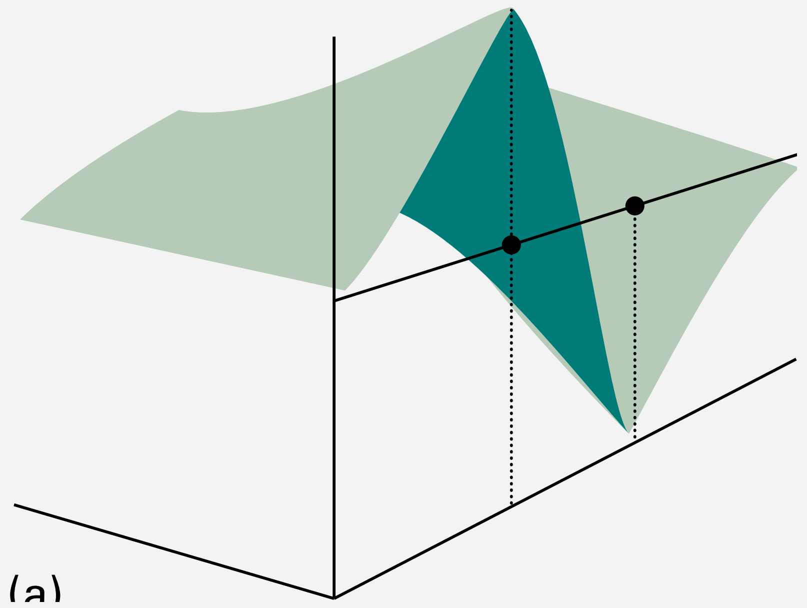


contour surfaces

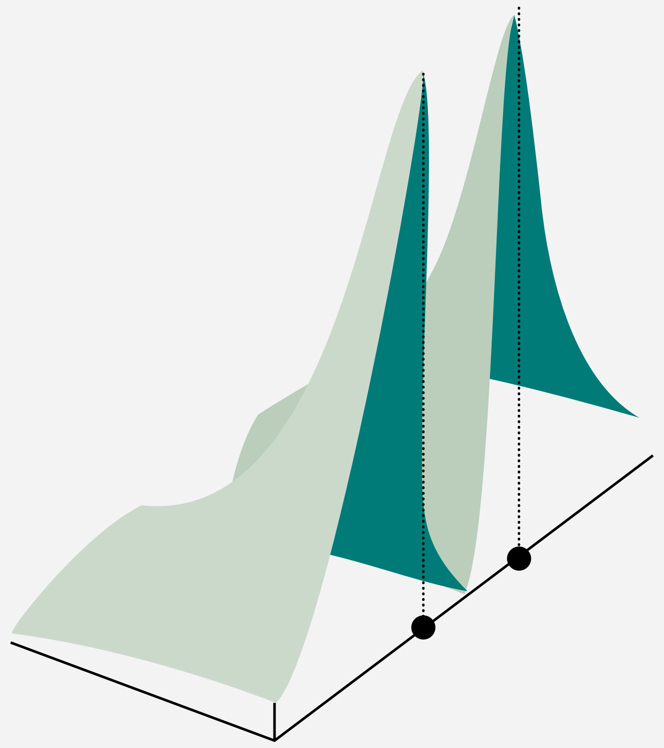


- antibonding orbitals

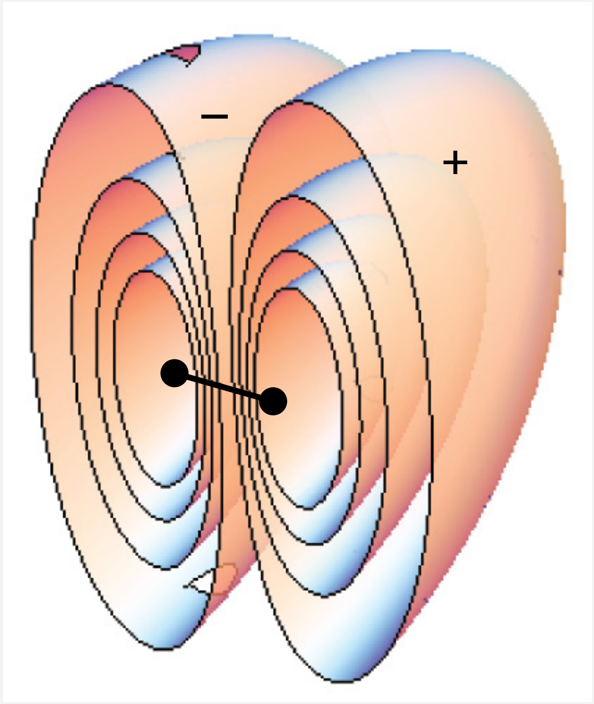
amplitude (ψ)



electron denisity ($|\psi|^2$)



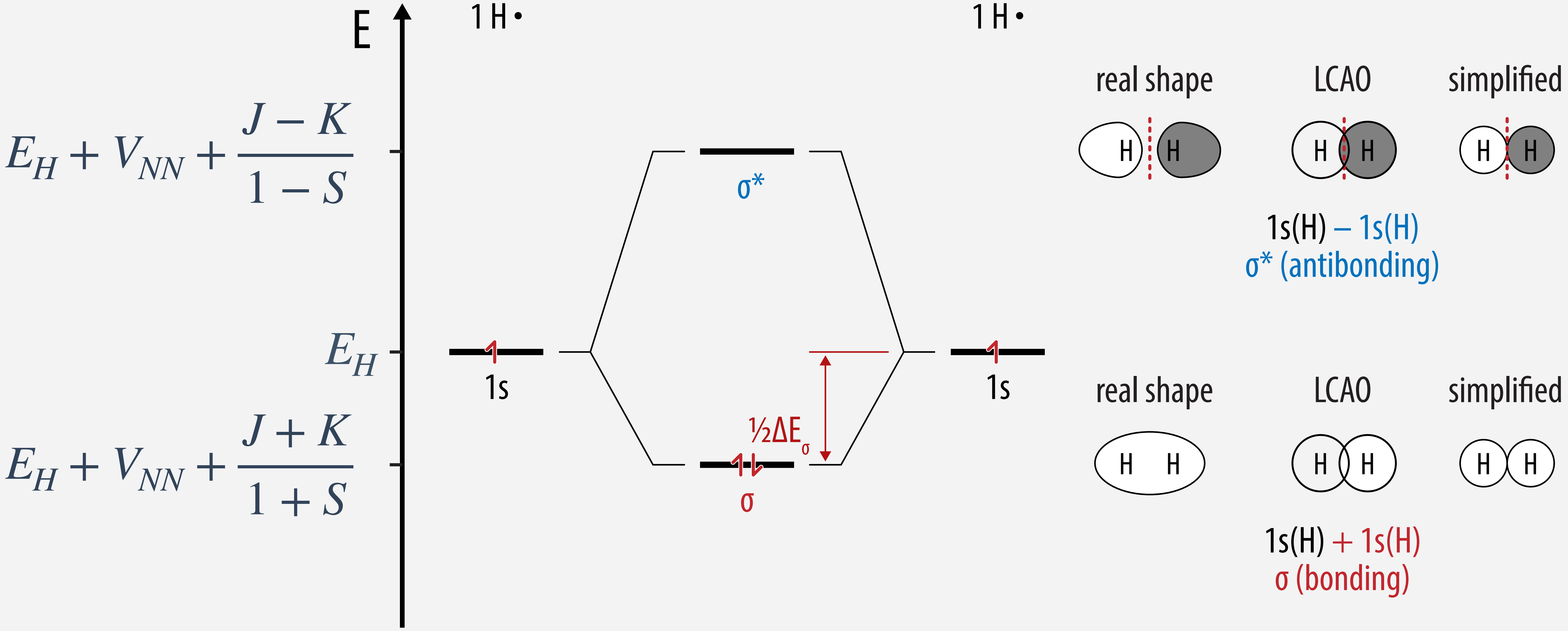
contour surfaces



P. W. Atkins, *Physical Chemistry*, 11th ed., **2018**, p. 352–355

Description of MO Using the LCAO Approximation

- schematic MO energy diagram from LCAO for a symmetric diatomic molecule, such as H_2

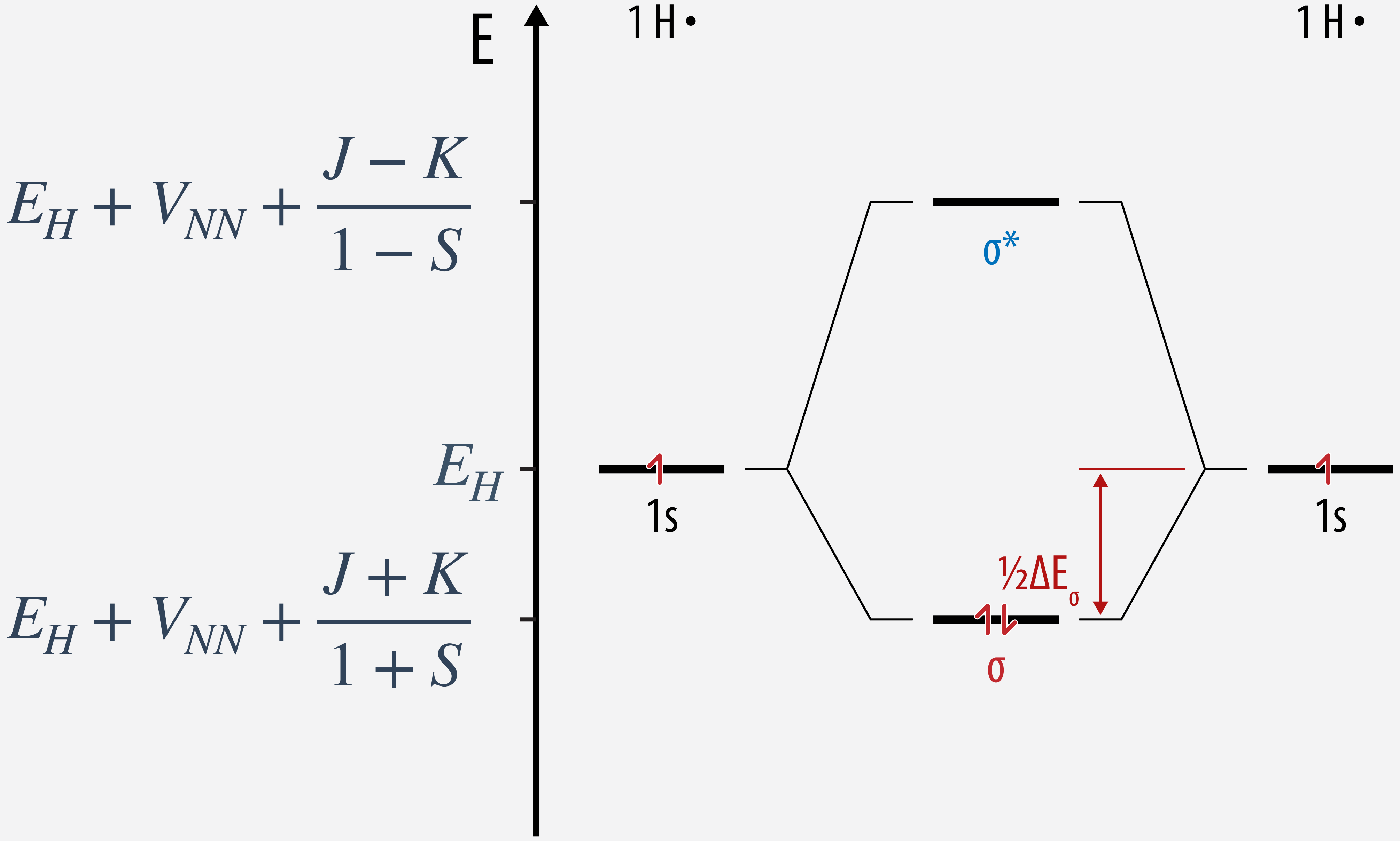


- **energy splitting between bonding σ MO and anti-bonding σ* MO**
- **electron density and hence sum of orbital energies increase**

see reader “ *Molecular Orbital Theory Description of H_2^+*” for details

Using the LCAO Approximation

- hydrogen atom energy E_H serves as a reference point
- internuclear repulsion V_{NN} is always positive (but not large at bonding distance)



- Coulomb integral interaction of the electron in AO i with nucleus j

$$J = -\left\langle \psi_{1s_i} \middle| \frac{e^2}{4\pi\varepsilon_0 r_j} \middle| \psi_{1s_i} \right\rangle$$

- resonance integral for exchange of electron from AO i to AO j

$$K = -\left\langle \psi_{1s_i} \middle| \frac{e^2}{4\pi\varepsilon_0 r_i} \middle| \psi_{1s_j} \right\rangle$$

- overlap integral

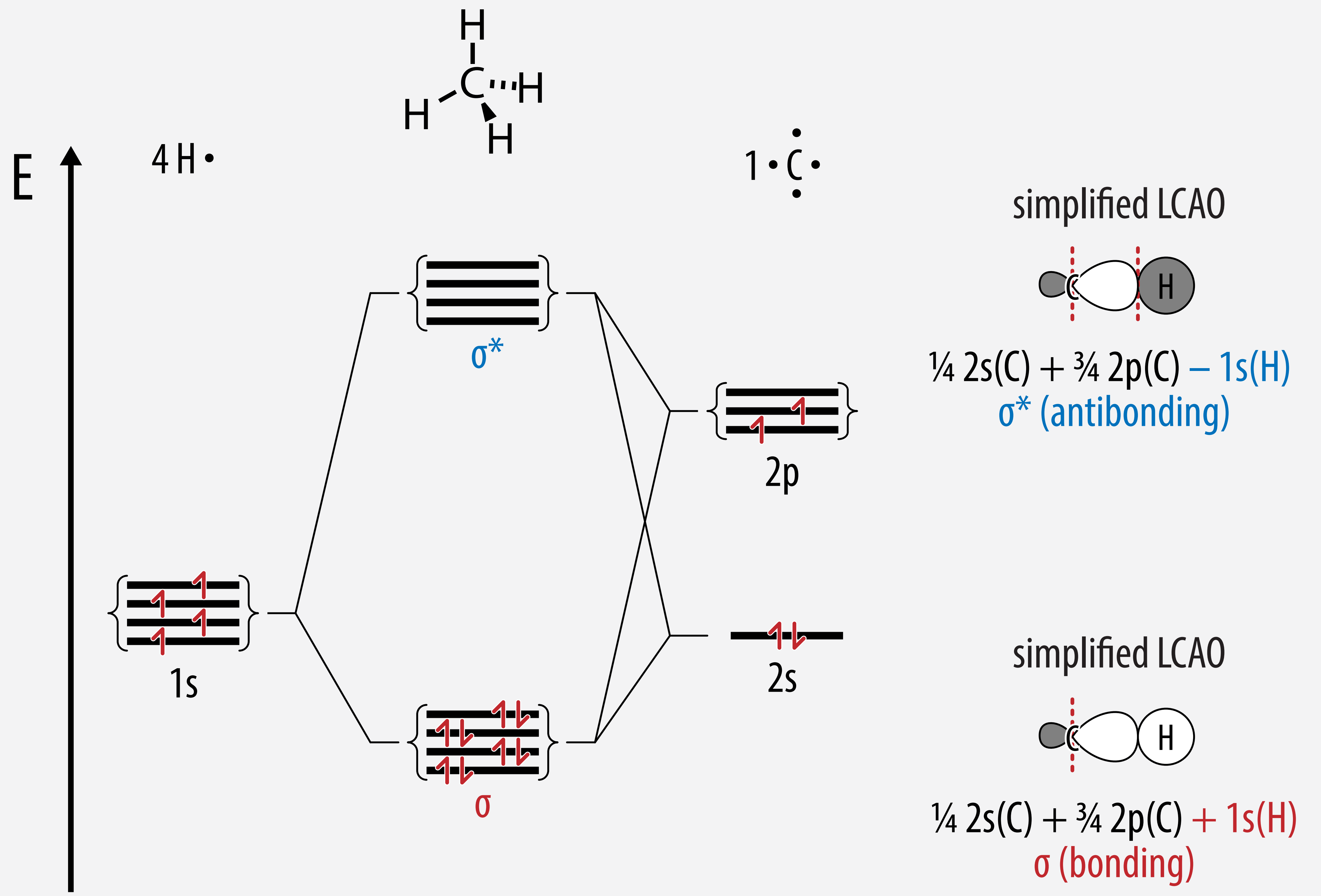
$$S = \left\langle \psi_{1s_i} \middle| \psi_{1s_j} \right\rangle$$

- **energy splitting between σ and σ* MO is not symmetric relative to E_{H} due to (small) increase in internuclear repulsion V_{NN} but in particular overlap integral *S* (inrease in electron density)**

see reader *“ Molecular Orbital Theory Description of H_2^+”* for details

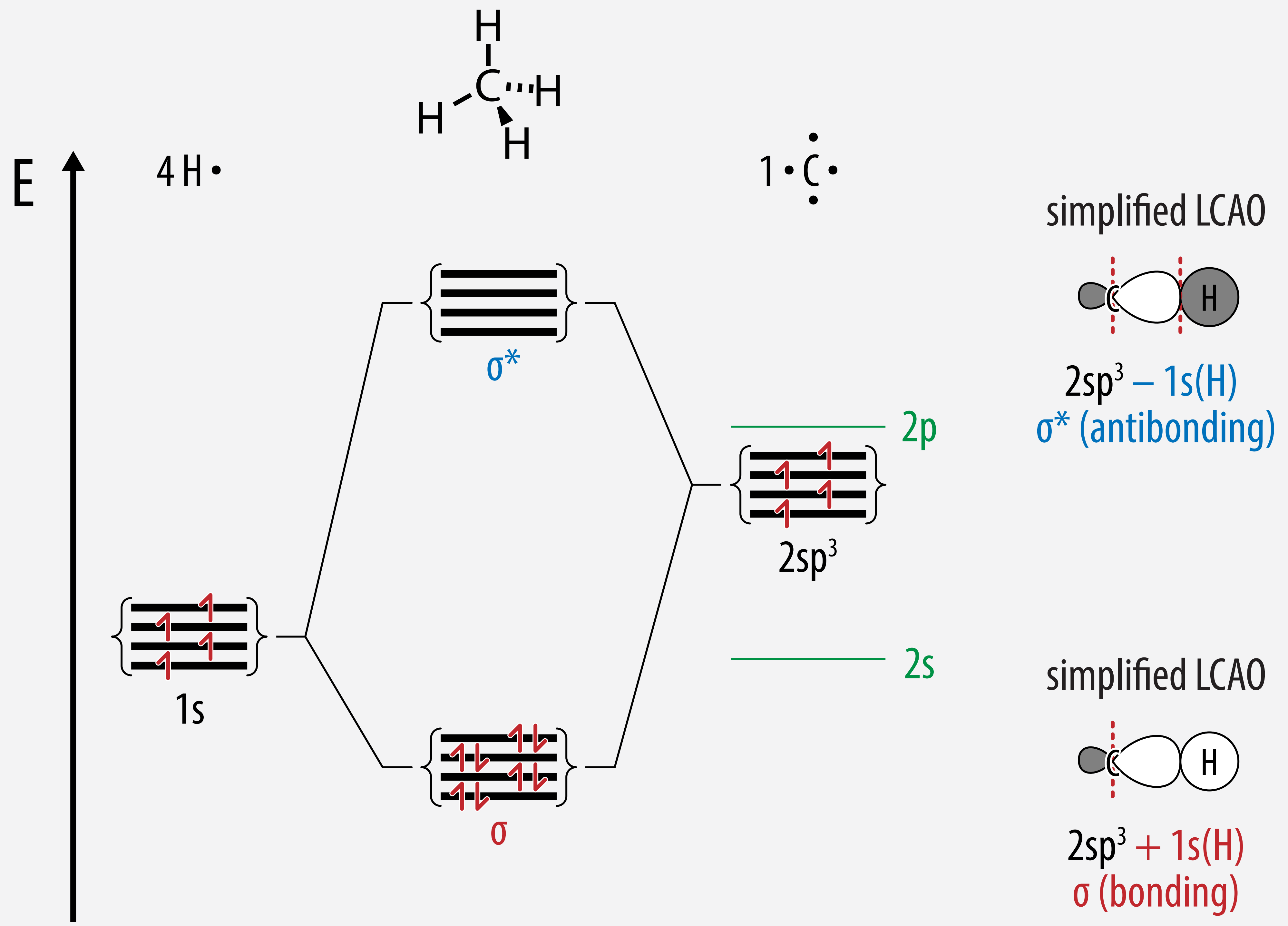
Molecular Orbital View of the Covalent Bond in Multiatom Molecules

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



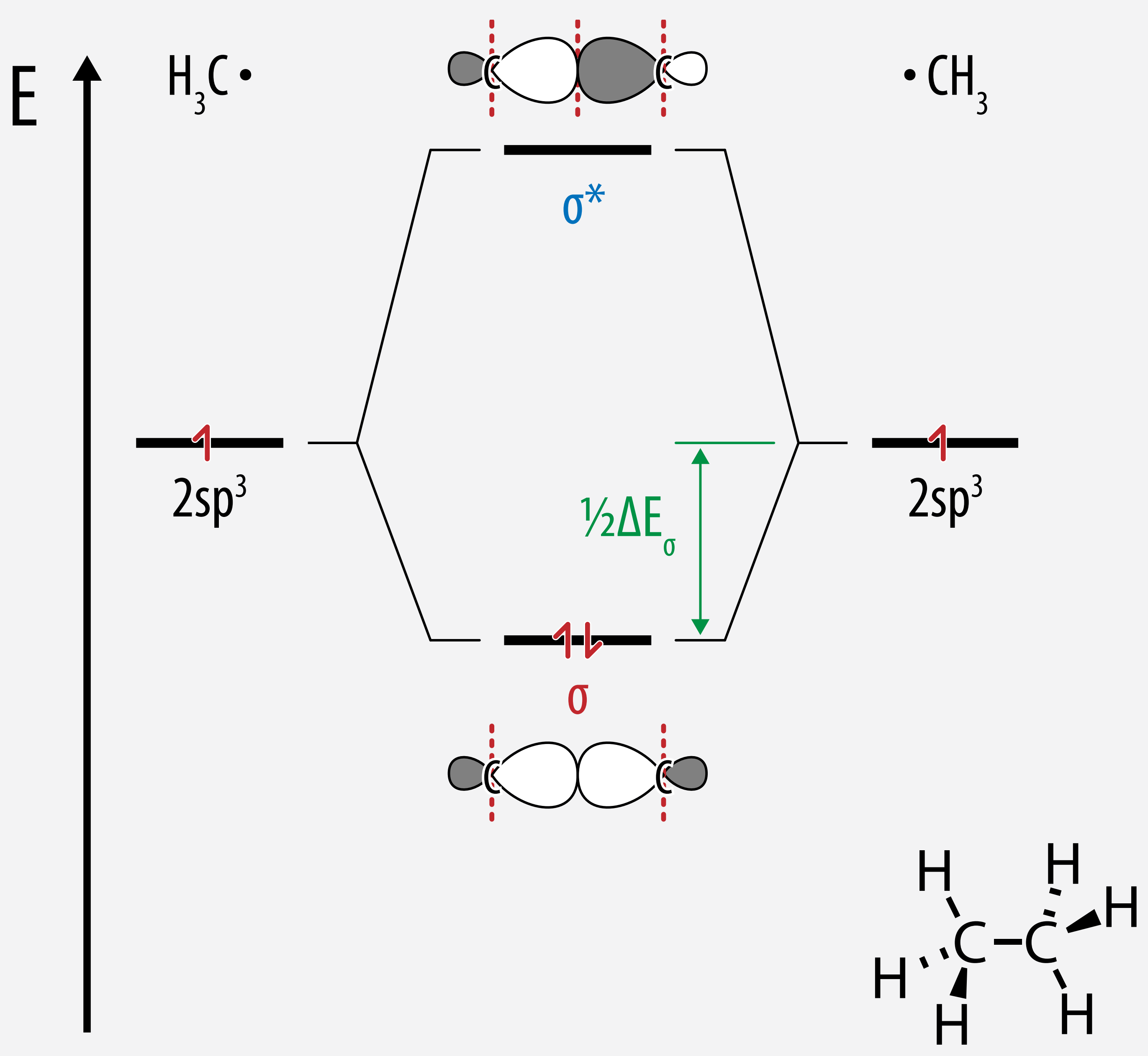
- **a more correct approach would start from atomic orbitals instead of hybrid orbitals**
- **result will be (almost) the same due to “mixing” of orbitals**
- **VSEPR model and hybridization are useful and valid simplifications**

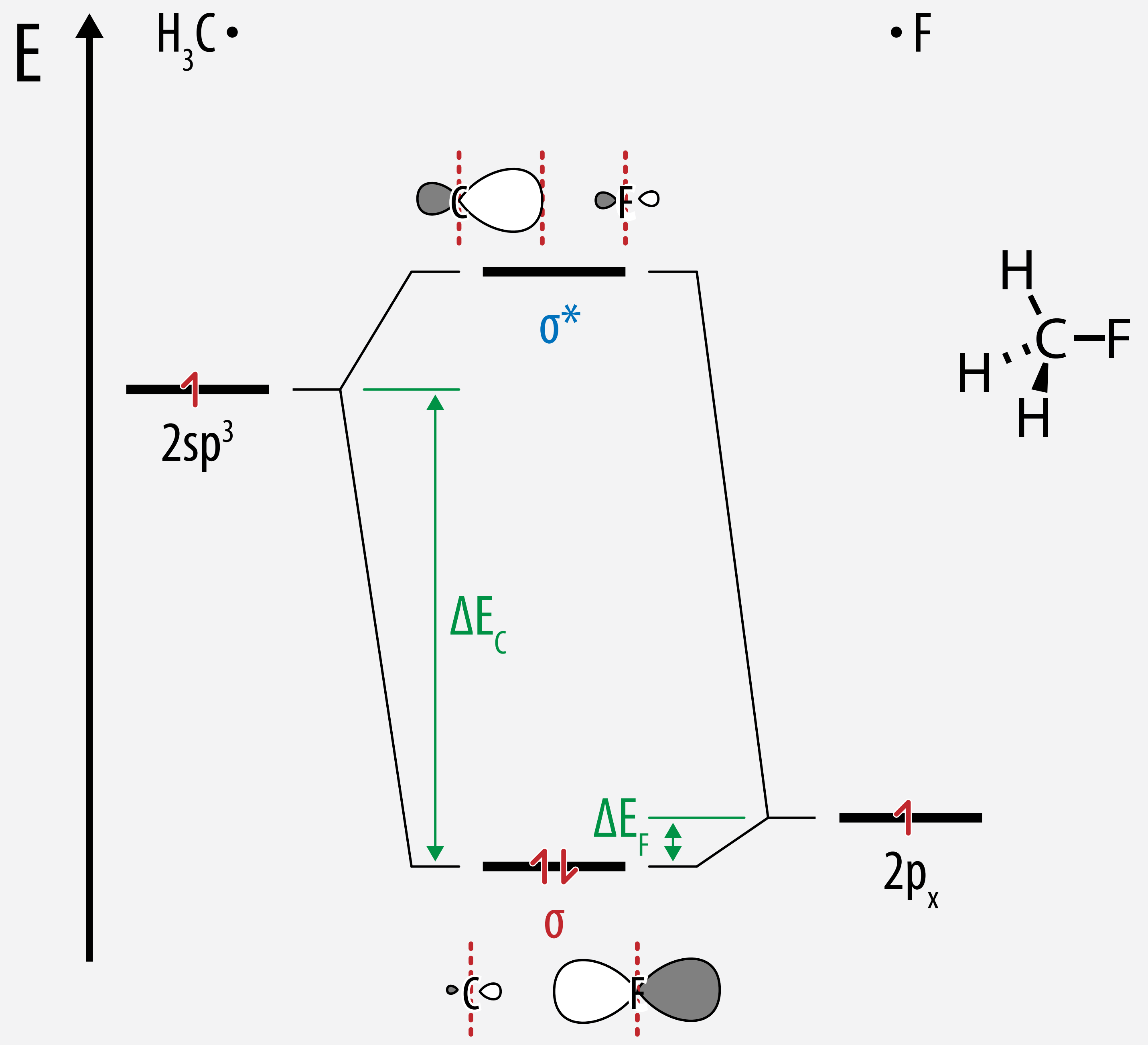
Complementarity of VB and MO theories



- **molecular orbital can be constructed from LCAO of hybrid orbitals**
- **interactions between orbitals of matching symmetry, i. e., not orthogonal** $\langle \Psi_1 | \Psi_2 \rangle \neq 0$

Molecular Orbital Energy Diagrams of Polarized Bond

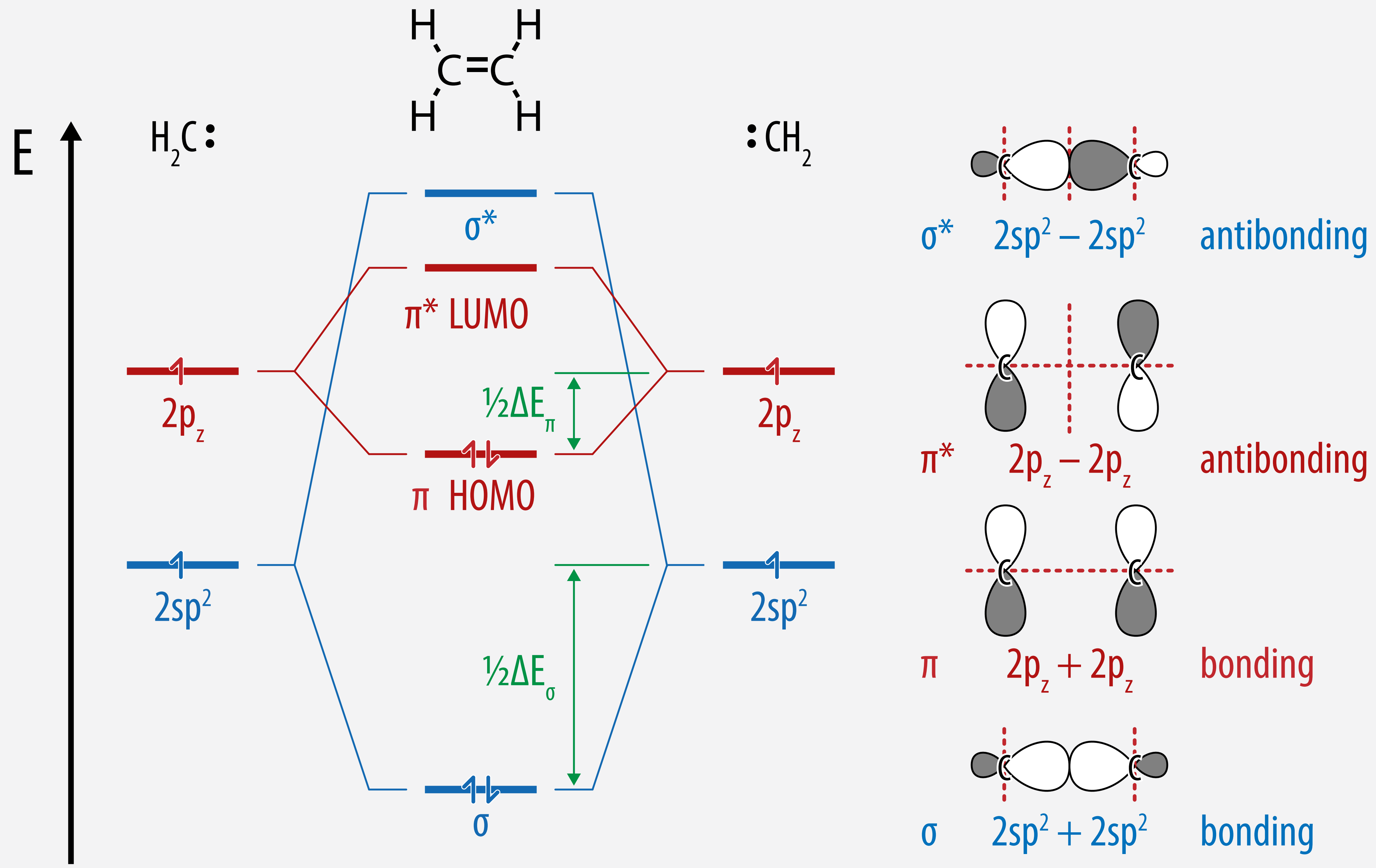




- **atomic orbitals of more electronegative atoms lower in energy (higher electron affinity)**
- **increasing energy difference between bonding partners implies less resonance interaction *K***

Molecular Orbital View of the Carbon-Carbon Double Bond

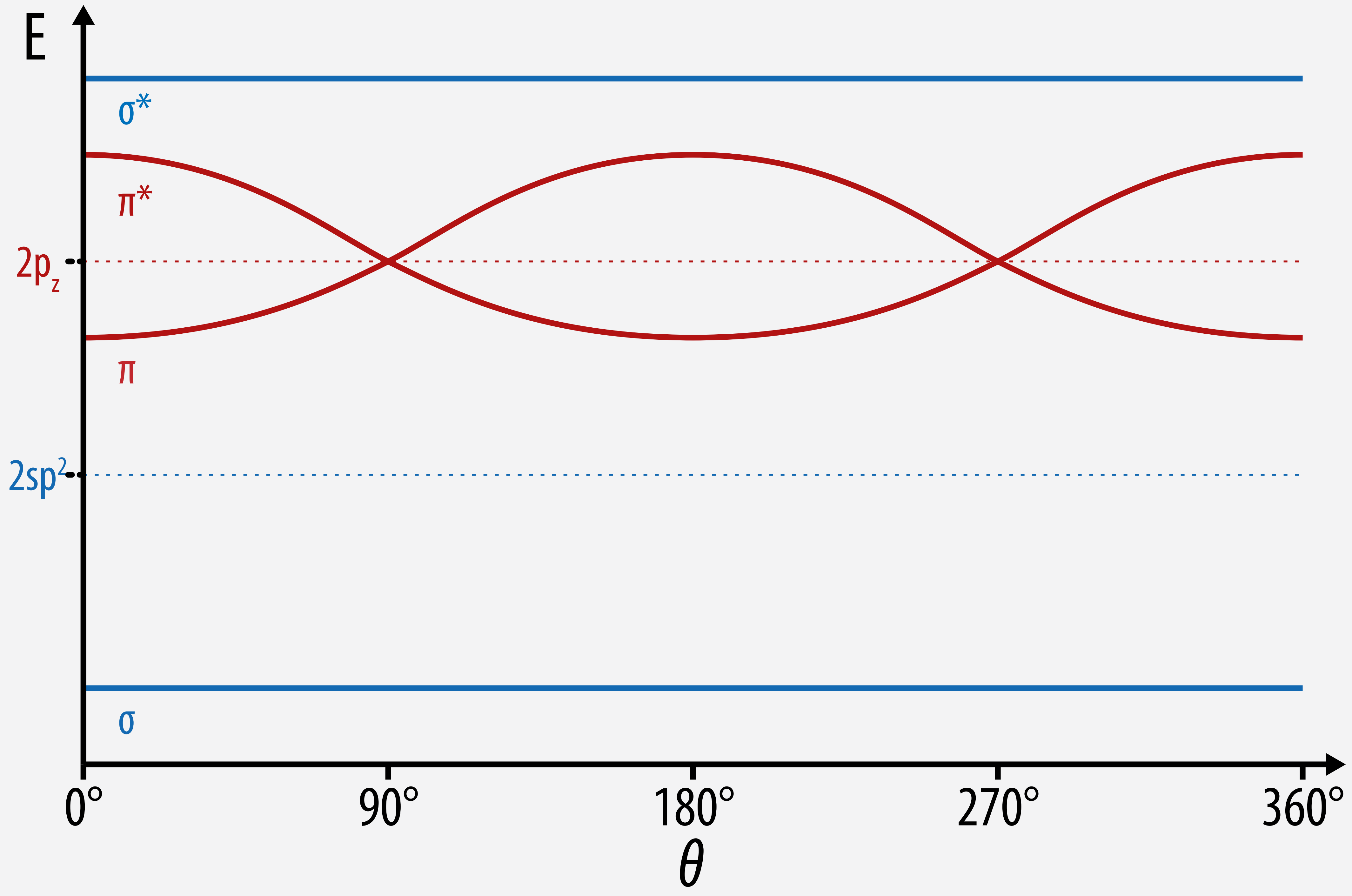
- simplified and schematic molecular orbital energy diagram of the ethene molecule

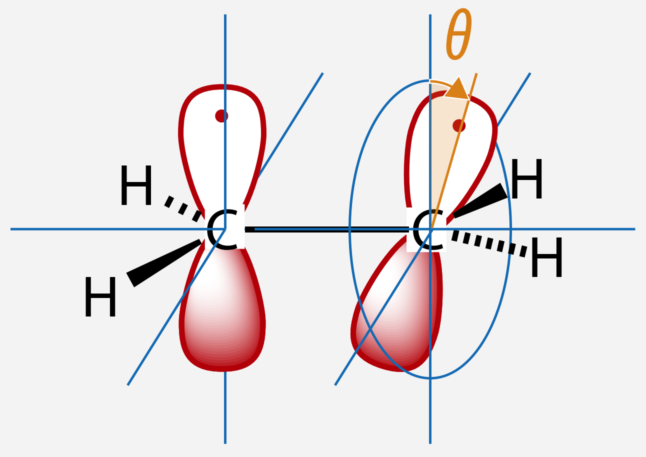


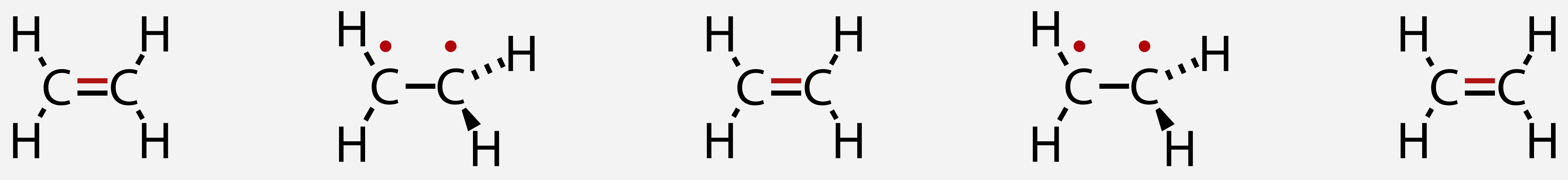
- **σ-π separability: only non-orthogonal orbitals (matching symmetry & orientation) interact**
- **σ-bond (from two sp^2) and π-bond (from two p$_z$) with different bond energies, symmetries**
- **chemistry defined by highest occupied MO (HOMO) and lowest unoccupied MO (LUMO)**

Rotation Around a Double Bond

- σ bond has rotational symmetry with respect to carbon-carbon bond axis
- π bond has lateral symmetry with respect to carbon-carbon bond axis



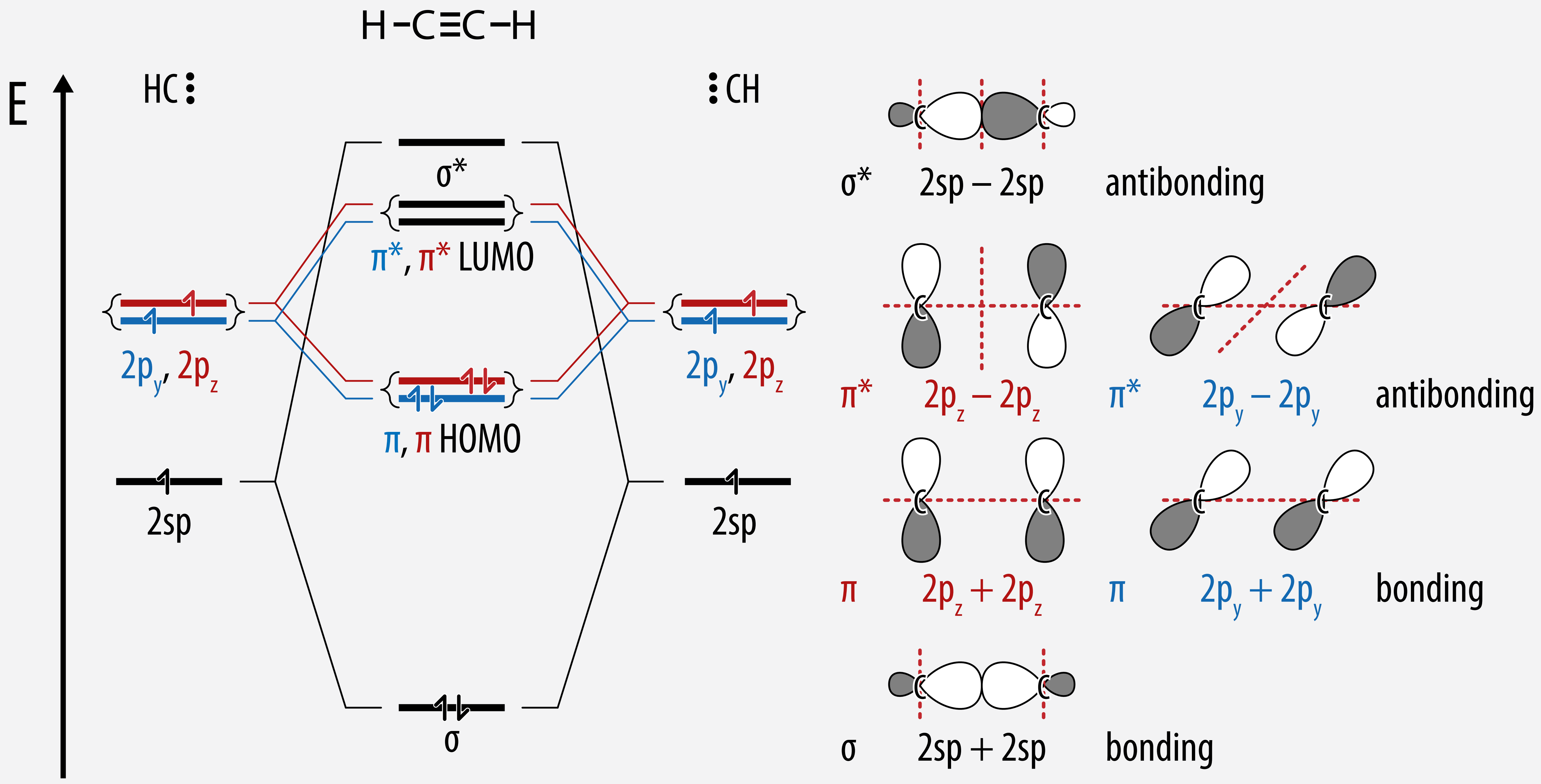




- **rotating p orbitals by 90° breaks the π bond (≈260 kJ/mol), energetically unfavorable**

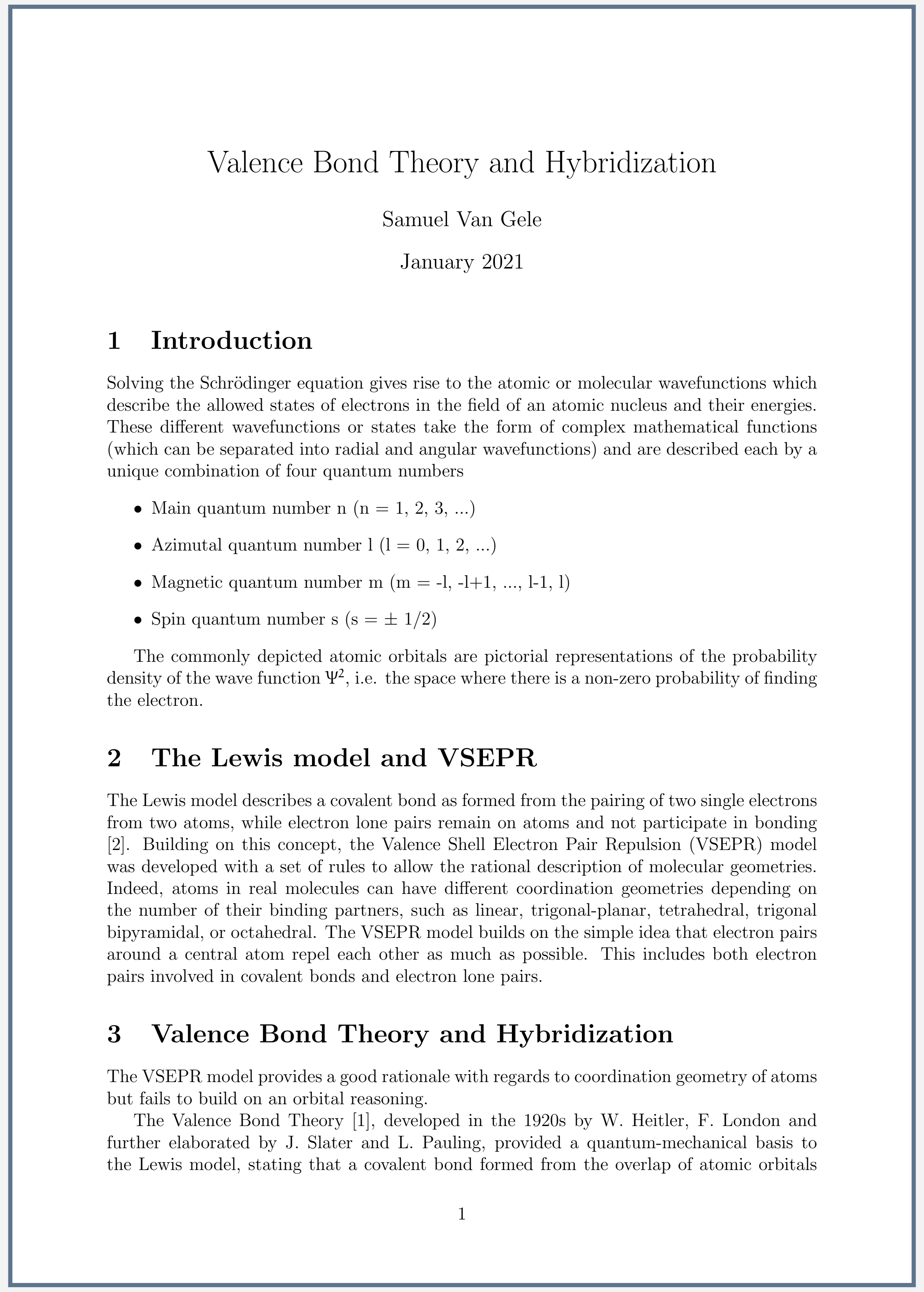
Molecular Orbital View of the Carbon-Carbon Triple Bond

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



- **σ-π separability: only non-orthogonal orbitals (matching symmetry & orientation) interact**
- **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 defined by π HOMO and π* LUMO, hence reactivity of ethyne similar to ethene**

Homework and Reading Assignments



Valence Bond Theory and Hybridization

Samuel Van Gele

January 2021

1 Introduction

Solving the Schrödinger equation gives rise to the atomic or molecular wavefunctions which describe the allowed states of electrons in the field of an atomic nucleus and their energies. These different wavefunctions or states take the form of complex mathematical functions (which can be separated into radial and angular wavefunctions) and are described each by a unique combination of four quantum numbers

- Main quantum number n (n = 1, 2, 3, ...)
- Azimutal quantum number l (l = 0, 1, 2, ...)
- Magnetic quantum number m (m = -l, -l+1, ..., l-1, l)
- Spin quantum number s (s = ± 1/2)

The commonly depicted atomic orbitals are pictorial representations of the probability density of the wave function Ψ^2, i.e. the space where there is a non-zero probability of finding the electron.

2 The Lewis model and VSEPR

The Lewis model describes a covalent bond as formed from the pairing of two single electrons from two atoms, while electron lone pairs remain on atoms and not participate in bonding [2]. Building on this concept, the Valence Shell Electron Pair Repulsion (VSEPR) model was developed with a set of rules to allow the rational description of molecular geometries. Indeed, atoms in real molecules can have different coordination geometries depending on the number of their binding partners, such as linear, trigonal-planar, tetrahedral, trigonal bipyramidal, or octahedral. The VSEPR model builds on the simple idea that electron pairs around a central atom repel each other as much as possible. This includes both electron pairs involved in covalent bonds and electron lone pairs.

3 Valence Bond Theory and Hybridization

The VSEPR model provides a good rationale with regards to coordination geometry of atoms but fails to build on an orbital reasoning.

The Valence Bond Theory [1], developed in the 1920s by W. Heitler, F. London and further elaborated by J. Slater and L. Pauling, provided a quantum-mechanical basis to the Lewis model, stating that a covalent bond formed from the overlap of atomic orbitals

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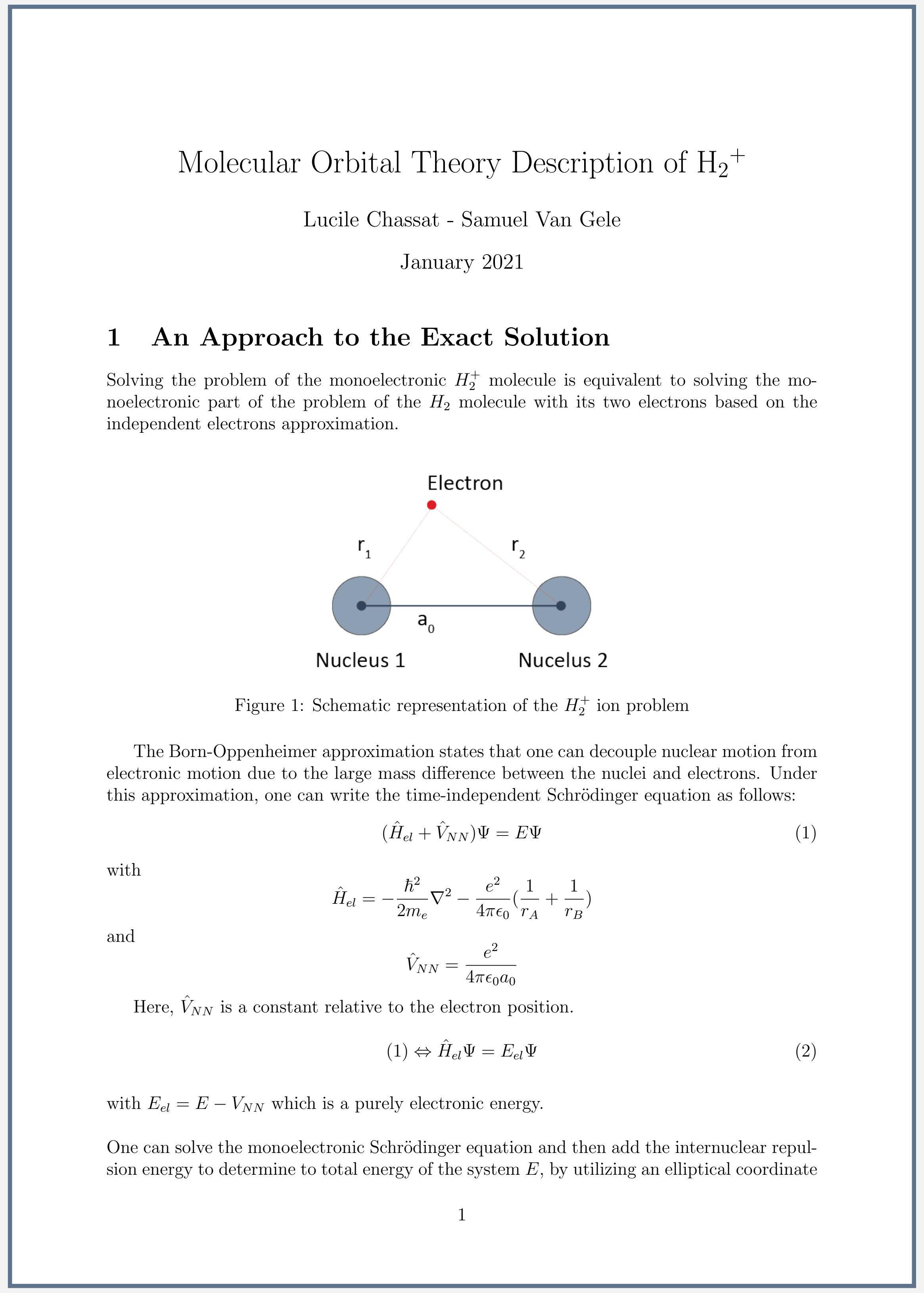

Molecular Orbital Theory Description of H_2^+

Lucile Chassat - Samuel Van Gele

January 2021

1 An Approach to the Exact Solution

Solving the problem of the monoelectronic H_2^+ molecule is equivalent to solving the monoelectronic part of the problem of the H_2 molecule with its two electrons based on the independent electrons approximation.

Figure 1: Schematic representation of the H_2^+ ion problem

The Born-Oppenheimer approximation states that one can decouple nuclear motion from electronic motion due to the large mass difference between the nuclei and electrons. Under this approximation, one can write the time-independent Schrödinger equation as follows:

$$(\hat{H}_{el} + \hat{V}_{NN})\Psi = E\Psi \tag{1}$$

with

$$\hat{H}_{el} = -\frac{\hbar^2}{2m_e}\nabla^2 - \frac{e^2}{4\pi\epsilon_0}(\frac{1}{r_A} + \frac{1}{r_B})$$

and

$$\hat{V}_{NN} = \frac{e^2}{4\pi\epsilon_0 a_0}$$

Here, $\hat{V}_{NN}$ is a constant relative to the electron position.

$$(1) \Leftrightarrow \hat{H}_{el}\Psi = E_{el}\Psi \tag{2}$$

with $E_{el} = E - V_{NN}$ which is a purely electronic energy.

One can solve the monoelectronic Schrödinger equation and then add the internuclear repulsion energy to determine to total energy of the system E, by utilizing an elliptical coordinate

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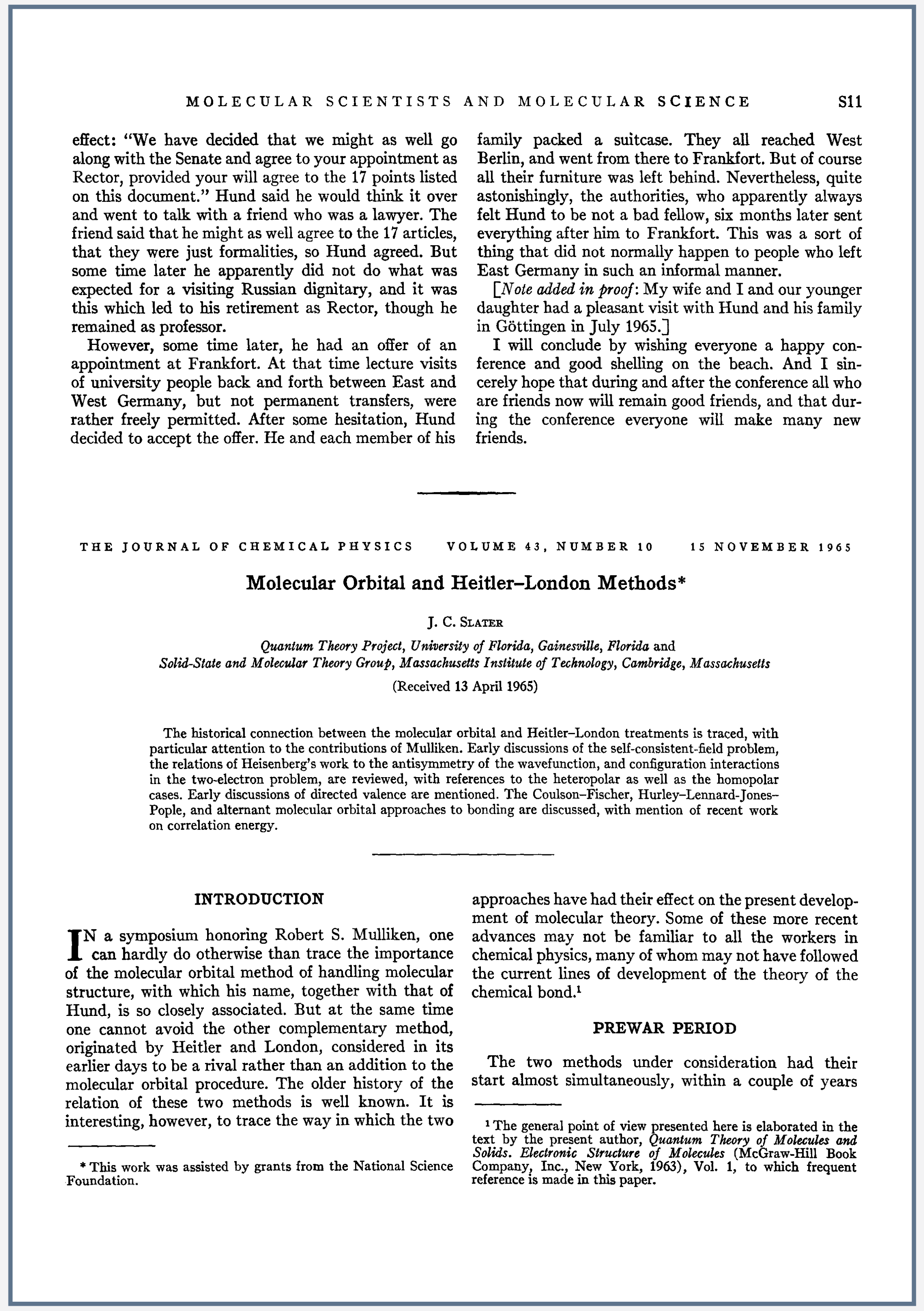

effect: "We have decided that we might as well go along with the Senate and agree to your appointment as Rector, provided your will agree to the 17 points listed on this document." Hund said he would think it over and went to talk with a friend who was a lawyer. The friend said that he might as well agree to the 17 articles, that they were just formalities, so Hund agreed. But some time later he apparently did not do what was expected for a visiting Russian dignitary, and it was this which led to his retirement as Rector, though he remained as professor.

However, some time later, he had an offer of an appointment at Frankfort. At that time lecture visits of university people back and forth between East and West Germany, but not permanent transfers, were rather freely permitted. After some hesitation, Hund decided to accept the offer. He and each member of his family packed a suitcase. They all reached West Berlin, and went from there to Frankfort. But of course all their furniture was left behind. Nevertheless, quite astonishingly, the authorities, who apparently always felt Hund to be not a bad fellow, six months later sent everything after him to Frankfort. This was a sort of thing that did not normally happen to people who left East Germany in such an informal manner.

[*Note added in proof*: My wife and I and our younger daughter had a pleasant visit with Hund and his family in Göttingen in July 1965.]

I will conclude by wishing everyone a happy conference and good shelling on the beach. And I sincerely hope that during and after the conference all who are friends now will remain good friends, and that during the conference everyone will make many new friends.

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Molecular Orbital and Heitler–London Methods*

J. C. Slater

Quantum Theory Project, University of Florida, Gainesville, Florida and
Solid-State and Molecular Theory Group, Massachusetts Institute of Technology, Cambridge, Massachusetts

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The historical connection between the molecular orbital and Heitler–London treatments is traced, with particular attention to the contributions of Mulliken. Early discussions of the self-consistent-field problem, the relations of Heisenberg's work to the antisymmetry of the wavefunction, and configuration interactions in the two-electron problem, are reviewed, with references to the heteropolar as well as the homopolar cases. Early discussions of directed valence are mentioned. The Coulson–Fischer, Hurley–Lennard-Jones–Pople, and alternant molecular orbital approaches to bonding are discussed, with mention of recent work on correlation energy.

INTRODUCTION

IN a symposium honoring Robert S. Mulliken, one can hardly do otherwise than trace the importance of the molecular orbital method of handling molecular structure, with which his name, together with that of Hund, is so closely associated. But at the same time one cannot avoid the other complementary method, originated by Heitler and London, considered in its earlier days to be a rival rather than an addition to the molecular orbital procedure. The older history of the relation of these two methods is well known. It is interesting, however, to trace the way in which the two approaches have had their effect on the present development of molecular theory. Some of these more recent advances may not be familiar to all the workers in chemical physics, many of whom may not have followed the current lines of development of the theory of the chemical bond.[1]

PREWAR PERIOD

The two methods under consideration had their start almost simultaneously, within a couple of years

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[1] The general point of view presented here is elaborated in the text by the present author, *Quantum Theory of Molecules and Solids. Electronic Structure of Molecules* (McGraw-Hill Book Company, Inc., New York, 1963), Vol. 1, to which frequent reference is made in this paper.

P. W. Atkins, *Physical Chemistry*, Chaptes 7–9, 11th edition, Oxford University Press, **2017**.

Learning Outcome

- **covalent bond described by molecular orbitals, delocalized over two atoms**
- **molecular orbitals by linear combination of atomic or hybrid orbitals**
- **interactions only between non-orthogonal orbitals**
- **number of orbitals preserved but sum of all orbital energies increases**
- **multiple bonds can be described as distinct σ bond plus one or two π bonds**
    - σ bond has rotational symmetry with respect to carbon-carbon bond axis
    - π bond has lateral symmetry; rotation requires breaking it
- **chemistry & physics dominated by frontier orbitals: π HOMO and π* LUMO**