A Gentle Intro to Tight-Binding Modeling

1 author:

Kamil Walczak
Pace University
103 PUBLICATIONS   **254** CITATIONS

Some of the authors of this publication are also working on these related projects:

"Transport Phenomena in Memristive Neuronal Networks" View project

"Coulomb Interactions and Charging Effects in Nanoscale Transport" View project

"A Gentle Intro to Tight-Binding Modeling"

OBJECTIVES

➢ To justify tight-binding modeling by building it on variational method in quantum mechanics.

➢ To show how superposition of states and quantum interference effects create bonding, non-bonding, and anti-bonding orbitals.

➢ To explain the concepts of singlet and triplet states, orbital hybridization, and Hückel theory.
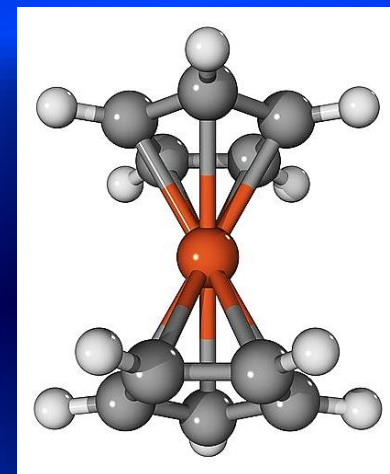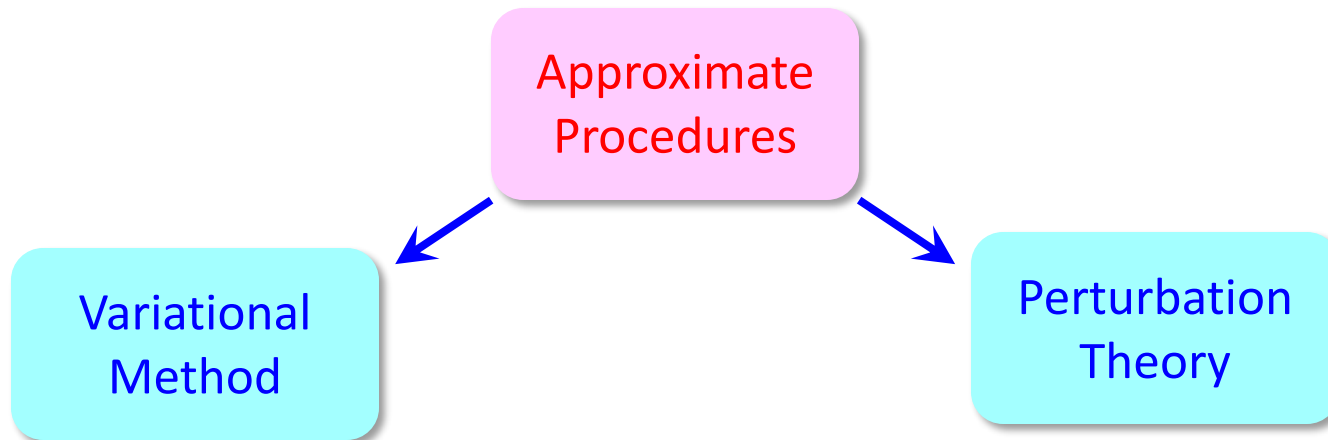
"Organometallic Chemistry"

Dr. Kamil Walczak

Department of Chemistry and Physical Sciences, Pace University
1 Pace Plaza, New York City, NY 10038

For any trial wavefunction, the expectation value of energy is always larger or equal to the true ground-state energy of the system under consideration:

$$\text{(Rayleigh Ratio)} = \frac{\int \Psi_t^+ \hat{H} \Psi_t dV}{\int \Psi_t^+ \Psi_t dV} \equiv \frac{\langle \Psi_t | \hat{H} | \Psi_t \rangle}{\langle \Psi_t | \Psi_t \rangle} \geq E_{gs}$$

(integral representation)   (Dirac notation)

The variational method is an effective tool for ground-state energy evaluation via minimization of energy condition by using reasonable trial wavefunctions!

In further analysis, we assume that trial wavefunctions are normalized:

$$\int \Psi_t^+ \Psi_t dV \equiv \langle \Psi_t | \Psi_t \rangle = 1$$

According to Born theorem, the trial wavefunctions can be expressed as a linear combination of orthonormal eigenfunctions of analyzed Hamiltonian:

$$\Psi_t = \sum_{m=1}^{\infty} a_m \phi_m \qquad \text{where} \qquad \hat{H}\phi_m = E_m \phi_m$$

Consider the following expression:

$$\int \Psi_t^+ \left(\hat{H} - E_{gs}\right) \Psi_t dV = \sum_{m,n=1}^{\infty} c_m^+ c_n \int \phi_m^+ \left(\hat{H} - E_{gs}\right) \phi_n dV$$

$$= \sum_{m,n=1}^{\infty} c_m^+ c_n \left(E_n - E_{gs}\right)\underbrace{\int \phi_m^+ \phi_n dV}_{\delta_{mn}} = \sum_{n=1}^{\infty} \underbrace{|c_n|^2}_{\geq 0} \underbrace{\left(E_n - E_{gs}\right)}_{\geq 0} \geq 0$$

$$\Rightarrow \int \Psi_t^+ \left(\hat{H} - E_{gs}\right) \Psi_t dV \geq 0 \Rightarrow \int \Psi_t^+ \hat{H} \Psi_t dV \geq E_{gs}$$

Variational principle is defined via the so-called Rayleigh ratio:

$$\varepsilon = \frac{\langle \Psi_t | \hat{H} | \Psi_t \rangle}{\langle \Psi_t | \Psi_t \rangle} \geq E_{gs}$$

<u>Ritz trick</u>: trial wavefunction is a linear combination of N known basis functions φ (like Gaussian, Slater, Lorentzian, etc.):
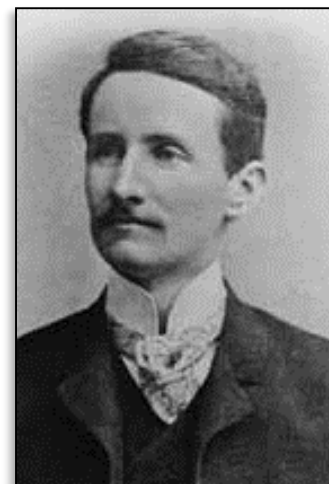
$$\left| \Psi_t \right\rangle = \sum_{i=1}^{N} c_i \left| \phi_i \right\rangle$$

Collecting all terms on one side, we obtain N secular equations:

$$\sum_{j=1}^{N} c_j \left(H_{kj} - \varepsilon\, S_{kj} \right) = 0$$

for $\quad k = 1,2,3,...,N$

with $\quad \varepsilon,\ \{c_j\}\quad$ unknown

Walther Ritz

Swiss Physicist

(1878-1909)

$$S_{ij} = \left\langle \phi_i \middle| \phi_j \right\rangle \quad \longleftarrow \quad$$ Overlap integrals

$$H_{ij} = \left\langle \phi_i \middle| \hat{H} \middle| \phi_j \right\rangle \quad \longleftarrow \quad$$ Hamiltonian elements

Let us differentiate both sides of previous equation with respect to conjugated expansion coefficients:

$$\varepsilon \sum_{i=1}^{N} \sum_{j=1}^{N} \underbrace{\frac{\partial c_i^+}{\partial c_k^+}}_{\delta_{ik}} c_j S_{ij} = \sum_{i=1}^{N} \sum_{j=1}^{N} \underbrace{\frac{\partial c_i^+}{\partial c_k^+}}_{\delta_{ik}} c_j H_{ij}$$

Collecting all terms on one side, we obtain N secular equations:

$$\sum_{j=1}^{N} c_j \left(H_{kj} - \varepsilon\, S_{kj} \right) = 0 \qquad \begin{cases} \text{for} \quad k = 1,2,3,...,N \\ \text{with} \quad \varepsilon,\ \{c_j\} \quad \text{unknown} \end{cases}$$

This is a homogeneous set of linear equations with respect to column vector c. Non-trivial solution is expected when the appropriate determinant vanishes:

$$\det\left[H - \varepsilon\, S \right] = 0$$

Hydrogen Molecule: Tight-Binding

Secular equations for hydrogen molecule:

$$\begin{bmatrix} E_H - \varepsilon & -U - \varepsilon S \\ -U - \varepsilon S & E_H - \varepsilon \end{bmatrix} \begin{pmatrix} c_A \\ c_B \end{pmatrix} = 0$$

Trial wavefunction (LCAO method):

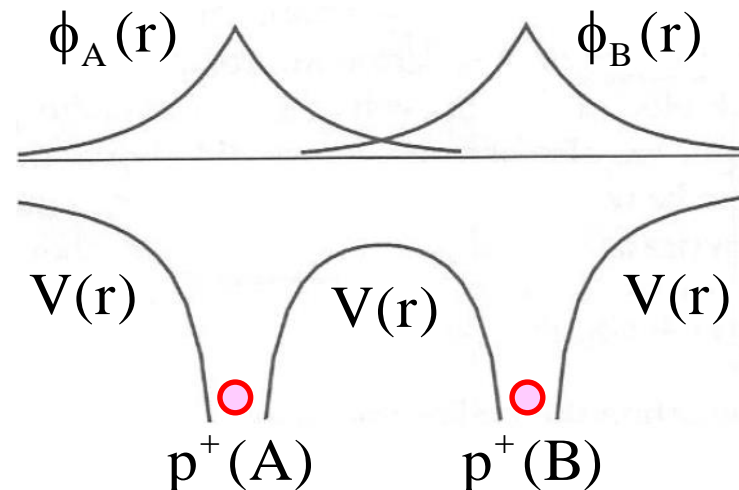$$\Psi_S(r_1, r_2) = c_A \phi_A(r_1) + c_B \phi_B(r_2)$$

Nomenclature (parameterization):

$$E_H = \langle \phi_A | \hat{H} | \phi_A \rangle = \langle \phi_B | \hat{H} | \phi_B \rangle$$ ← (on-site electronic energy)

$$\langle \phi_A | \phi_A \rangle = \langle \phi_B | \phi_B \rangle = 1$$ ← (normalization condition)

$$U = -\langle \phi_A | \hat{H} | \phi_B \rangle = -\langle \phi_B | \hat{H} | \phi_A \rangle > 0$$ ← (intersite el-el interaction)

$$S = \langle \phi_A | \phi_B \rangle = \langle \phi_B | \phi_A \rangle \in \langle 0, 1 \rangle$$ ← (overlap integral)
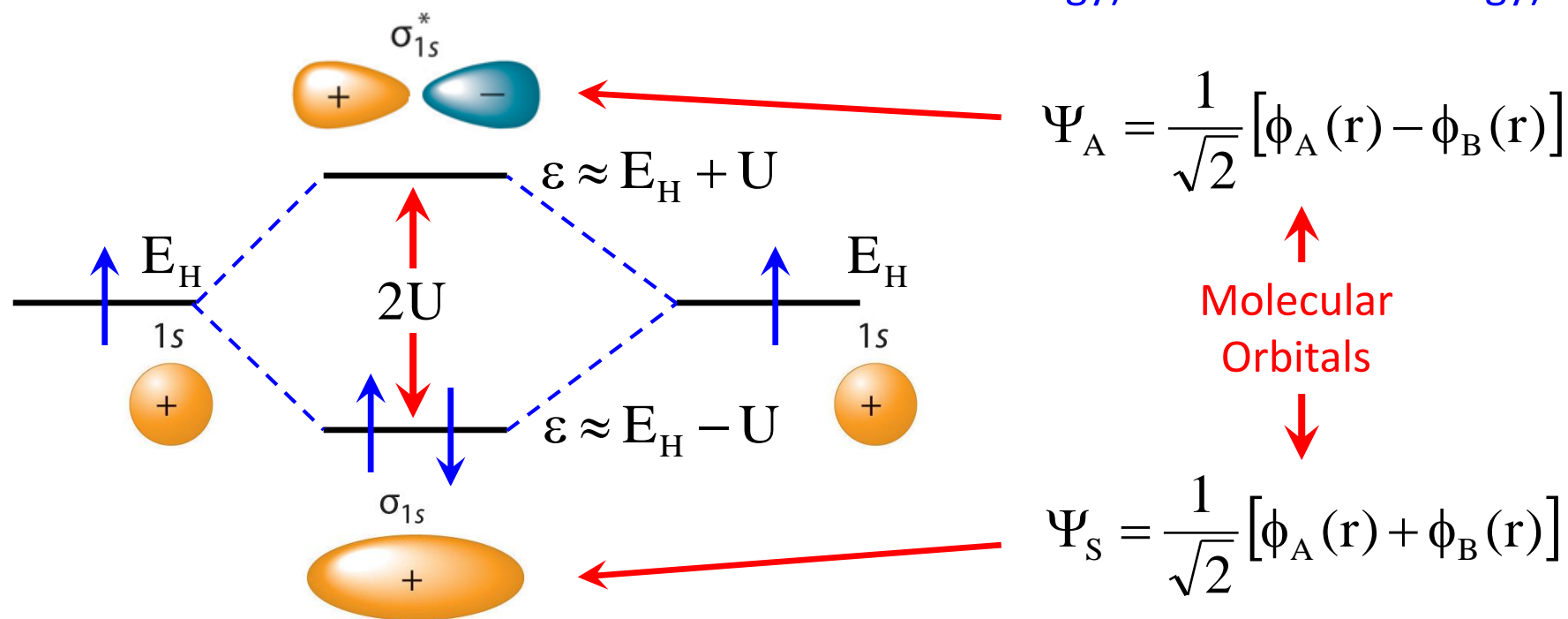

$\phi_A(r)$ $\phi_B(r)$

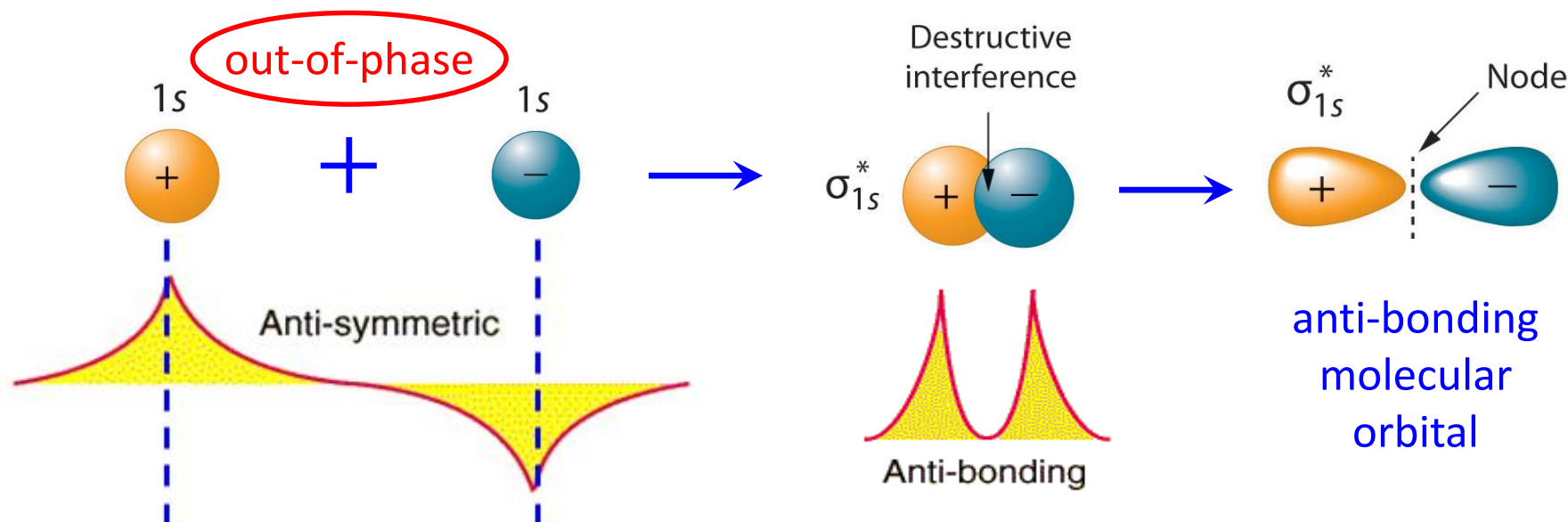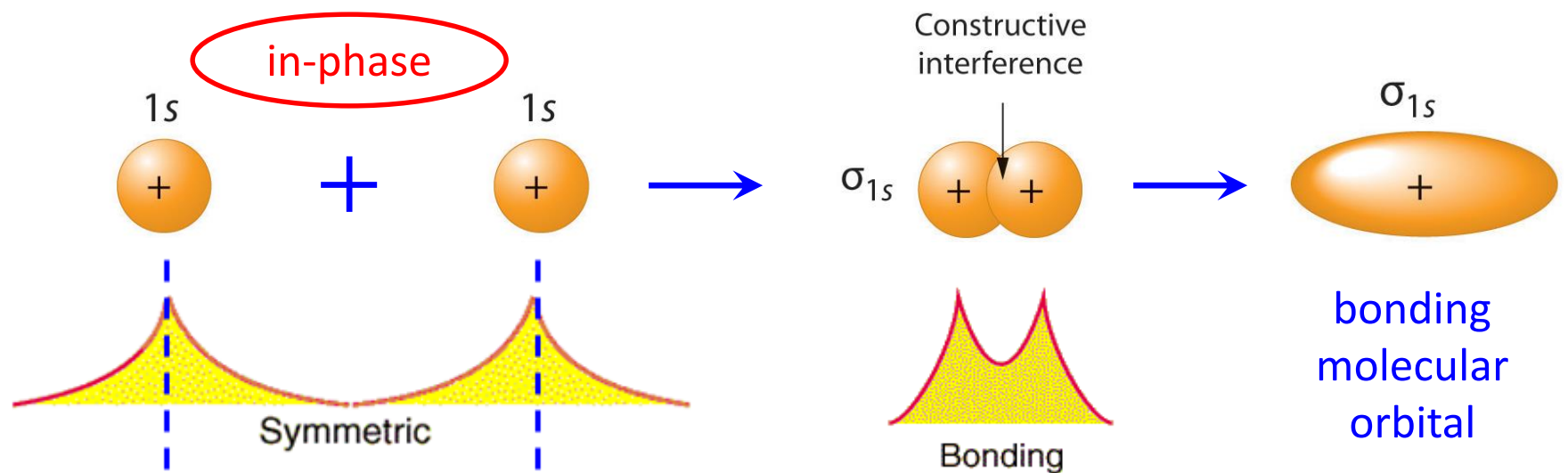$V(r)$ $V(r)$ $V(r)$

$p^+(A)$ $p^+(B)$

Solving quadratic equation by making secular determinant equal to zero:

$$\det \begin{bmatrix} E_H - \varepsilon & -U - \varepsilon\, S \\ -U - \varepsilon\, S & E_H - \varepsilon \end{bmatrix} = 0 \longrightarrow \varepsilon = \frac{E_H - U}{1 + S} \qquad \varepsilon = \frac{E_H + U}{1 - S}$$
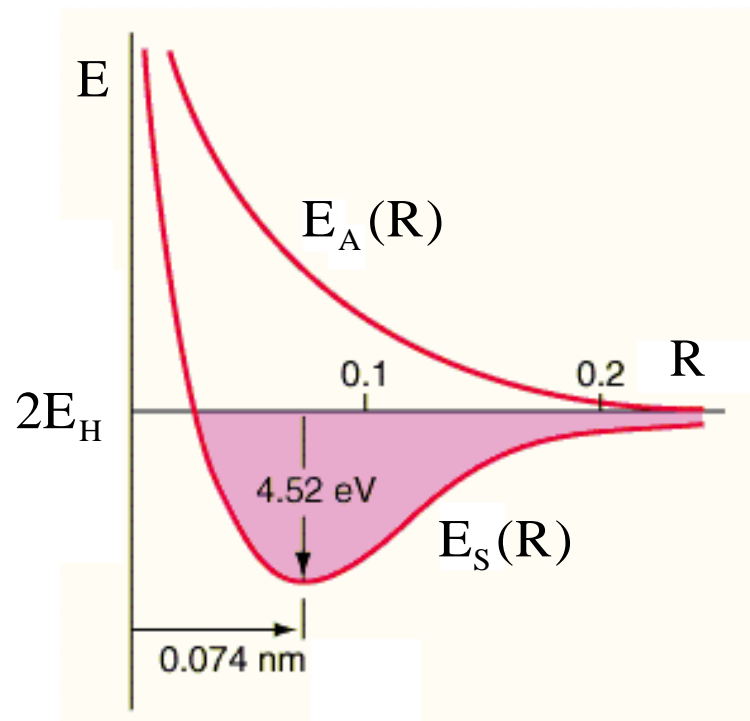
(bonding state energy)   (anti-bonding state energy)

σ_{1s}^*

$\varepsilon \approx E_H + U$

E_H E_H

$1s$ $1s$

$2U$

$\varepsilon \approx E_H - U$

σ_{1s}

$$\Psi_A = \frac{1}{\sqrt{2}} \big[\phi_A(r) - \phi_B(r) \big]$$

Molecular Orbitals

$$\Psi_S = \frac{1}{\sqrt{2}} \big[\phi_A(r) + \phi_B(r) \big]$$

Molecular Orbitals

Dissociation energy:

$$D = 4.52 \; [eV]$$

Interatomic separation:

$$R_{eq} = 0.074 \; [nm]$$

TB parameters for hydrogen molecule:

$$S \approx 0$$

$$E_H = -13.6 \; [eV]$$

$$U = 18.12 \; [eV]$$

Ground-state energy for hydrogen molecule:

$$E_{gs} = -31.72 \; [eV]$$

Two spin-1/2 particles – four basis states:

$$\uparrow\uparrow \qquad \uparrow\downarrow \qquad \downarrow\uparrow \qquad \downarrow\downarrow$$

$$\left|1\ 1\right\rangle = \uparrow\uparrow$$

$$\left|1\ 0\right\rangle = \left(\uparrow\downarrow + \downarrow\uparrow\right)/\sqrt{2}$$

$$\left|1\ -1\right\rangle = \downarrow\downarrow$$

$s = 1$ (triplet combination)

$$\left|0\ 0\right\rangle = \left(\uparrow\downarrow - \downarrow\uparrow\right)/\sqrt{2}$$

$s = 0$ (singlet combination)

Almost all molecules encountered in daily life exist in a singlet state!
(oxygen diatomic molecule is one exception)

Spatial wavefunctions for indistinguishable quantum particles:

$$\Psi_S(r_1, r_2) = N[\Psi_A(r_1)\Psi_B(r_2) + \Psi_B(r_1)\Psi_A(r_2)] = \Psi_S(r_2, r_1)$$

(symmetric wavefunction for bosons = integer spin)

$$\Psi_A(r_1, r_2) = N[\Psi_A(r_1)\Psi_B(r_2) - \Psi_B(r_1)\Psi_A(r_2)] = -\Psi_A(r_2, r_1)$$

(anti-symmetric wavefunction for fermions = half-integer spin)

To obtain the overall anti-symmetric wavefunction for two electrons:

$$\Psi_S(r_1, r_2) \times \text{(singlet)}$$

$$\Psi_A(r_1, r_2) \times \text{(triplet)}$$

Solving quadratic equation for determinant being equal to zero:

$$\det\begin{bmatrix} E_H - \varepsilon & -U \\ -U & E_{Li} - \varepsilon \end{bmatrix} = 0$$

$$\varepsilon = \frac{E_H + E_{Li}}{2} - \sqrt{\frac{(E_H - E_{Li})^2}{4} + U^2}$$

(bonding state energy)

$$\varepsilon = \frac{E_H + E_{Li}}{2} + \sqrt{\frac{(E_H - E_{Li})^2}{4} + U^2}$$
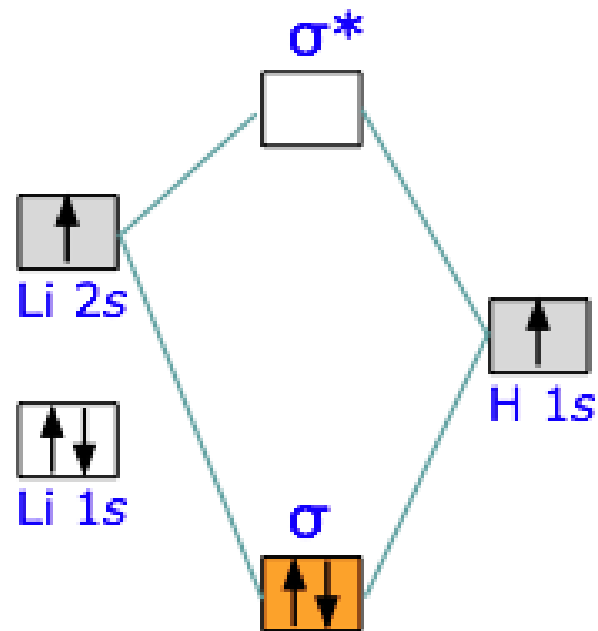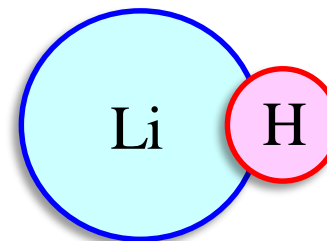
(anti-bonding state energy)

HOMO-LUMO gap:

$$E_g = \sqrt{(E_H - E_{Li})^2 + 4U^2}$$

Ionic contribution (electronegativity)

Covalent bonding contribution (overlapping)

HOMO – Highest Occupied Molecular Orbital

LUMO – Lowest Unoccupied Molecular Orbital

Electronegativity is a general tendency of an atom or a functional group to attract electrons (shift electron density) towards themselves!

(covalency)

$$\alpha_C = \frac{2U}{\sqrt{(E_H - E_{Li})^2 + 4U^2}}$$

(polarity)

$$\alpha_P = \frac{|E_H - E_{Li}|}{\sqrt{(E_H - E_{Li})^2 + 4U^2}}$$

Molecular orbitals related to bond polarity parameter:

$$\Psi_S = \sqrt{\frac{1+\alpha_P}{2}} \; \phi_H(r) + \sqrt{\frac{1-\alpha_P}{2}} \; \phi_{Li}(r)$$

$$\Psi_A = \sqrt{\frac{1-\alpha_P}{2}} \; \phi_H(r) - \sqrt{\frac{1+\alpha_P}{2}} \; \phi_{Li}(r)$$

For all bonds:

$$\alpha_C^2 + \alpha_P^2 = 1$$

Sigma bond ("σ") – the strongest type of covalent bonds, formed by head-on overlapping between atomic orbitals, electrons strongly localized within bond!

Pi bond ("π") – weak covalent bonds, formed by overlapping between two lobes of two atomic orbitals involved, electrons are highly delocalized (spread all over)!

"The fundamental laws necessary for the mathematical treatment of a large part of physics and the whole of chemistry are thus completely known, and the difficulty lies only in the fact that application of these laws leads to equations that are too complex to be solved!"
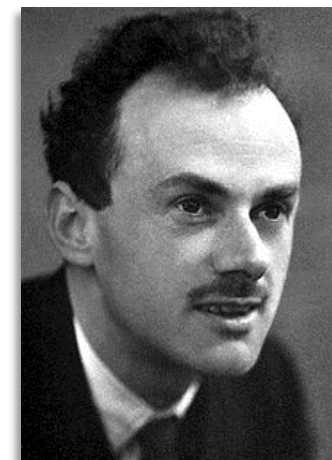
Paul Dirac

(1902-1984)

Molecular Hamiltonian (+ Born-Oppenheimer Approximation):

$$\hat{H} = -\frac{\hbar^2}{2m}\sum_{i=1}^{N}\Delta_i - k_e q^2 \sum_{i=1}^{N}\sum_{\mu=1}^{M}\frac{Z_\mu}{r_{i\mu}} + \frac{k_e q^2}{2}\sum_{i \neq j}^{N}\frac{1}{|\vec{r_i}-\vec{r_j}|} + \frac{k_e q^2}{2}\sum_{\mu \neq \nu}^{M}\frac{Z_\mu Z_\nu}{R_{\mu\nu}}$$

| kinetic energy of electrons | potential energy of electron-nuclei attraction | potential energy of electron-electron repulsion | potential energy of interaction between nuclei |

Orbital hybridization – the concept of mixing atomic orbitals to form new hybrid orbitals suitable for qualitative description of atomic bonding and explanation of the shape of molecular orbitals for molecules!
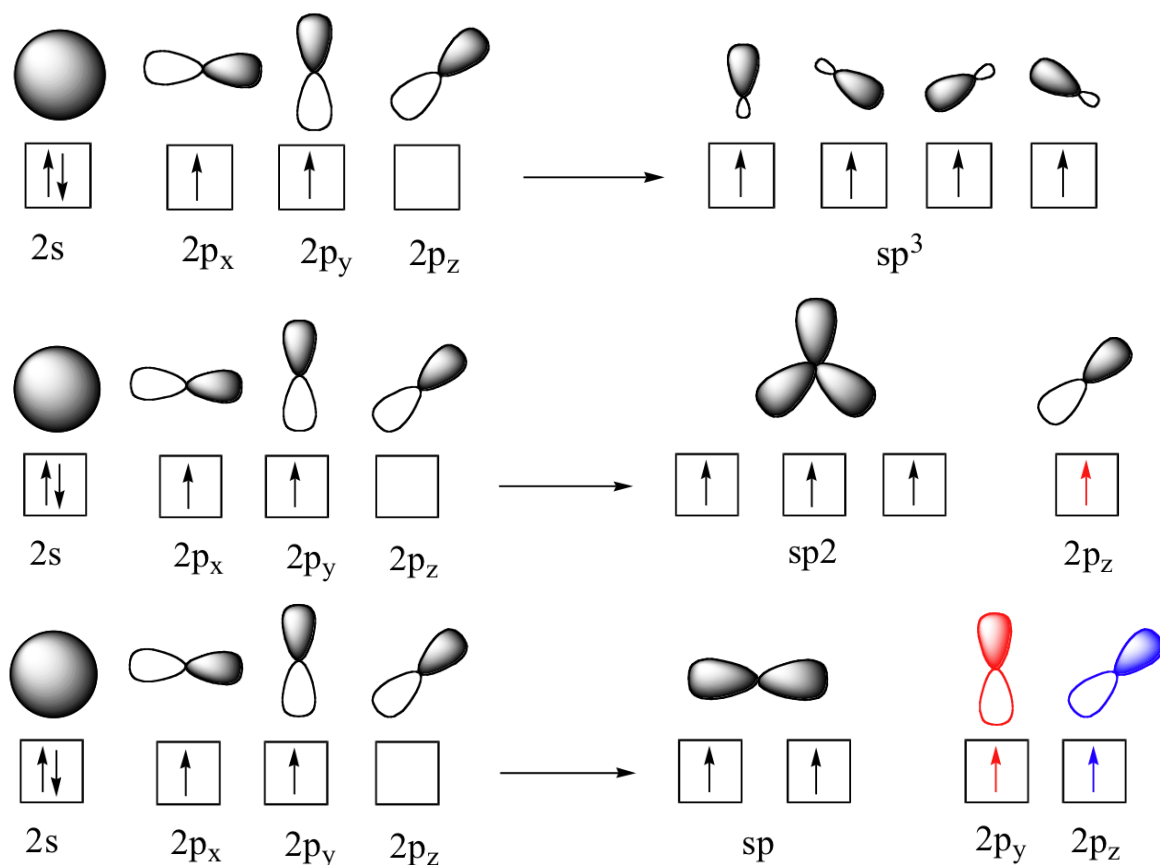
Linus Pauling

American Chemist

(1901-1994)

<u>Hückel Molecular Orbital (HMO) theory</u> – semi-empirical method used to determine stability, energy levels, and approximated molecular orbitals of delocalized "π" electrons in aromatic and conjugated organic molecules!

Sigma-pi separability – since "sigma" and "pi" orbitals in planar molecules are orthogonal, both subsystems are separable!

Negligence of sigma electrons – since only "pi"-type electrons determine most properties of organic molecules, skeleton electrons of "sigma"-bonds may be neglected!

Linear Combination of Atomic Orbitals (LCAO) – where one electron described by "2pz" per carbon atom is included:

$$\Psi_t = \sum_{i=1}^{N} c_i \phi_i \qquad \text{where} \qquad \phi_i = 2p_z(r_i)$$

Erich Hückel
German Physicist
(1896-1980)

E. Hückel, Z. Phys. **70**, 204 (1931); **72**, 310 (1931)

Secular equations in the Rayleigh-Ritz variational method:

$$\sum_{k=1}^{N} \left(H_{jk} - \varepsilon\, S_{jk} \right) c_k = 0$$

Hückel parameters:

$$H_{jk} = \left\langle \phi_j \left| \hat{H} \right| \phi_k \right\rangle = \begin{cases} \alpha = -6.6 \ [\text{eV}] & \text{for } j = k \text{ (Coulomb integral)} \\ -\beta = -2.7 \ [\text{eV}] & \text{for bonded } j \text{ and } k \text{ (resonance integral)} \\ 0 & \text{otherwise} \end{cases}$$

$$S_{jk} = \left\langle \phi_j \middle| \phi_k \right\rangle = \begin{cases} 1 & \text{for } j = k \text{ (overlap integral)} \\ 0 & \text{otherwise} \end{cases}$$

Procedure: first we need to evaluate the values of the parameter ε by making secular determinant equal to zero to determine the eigenvalues of energies. Then we need to solve a homogeneous set of linear equations for coefficients "c" with given energies to determine the corresponding molecular orbitals!
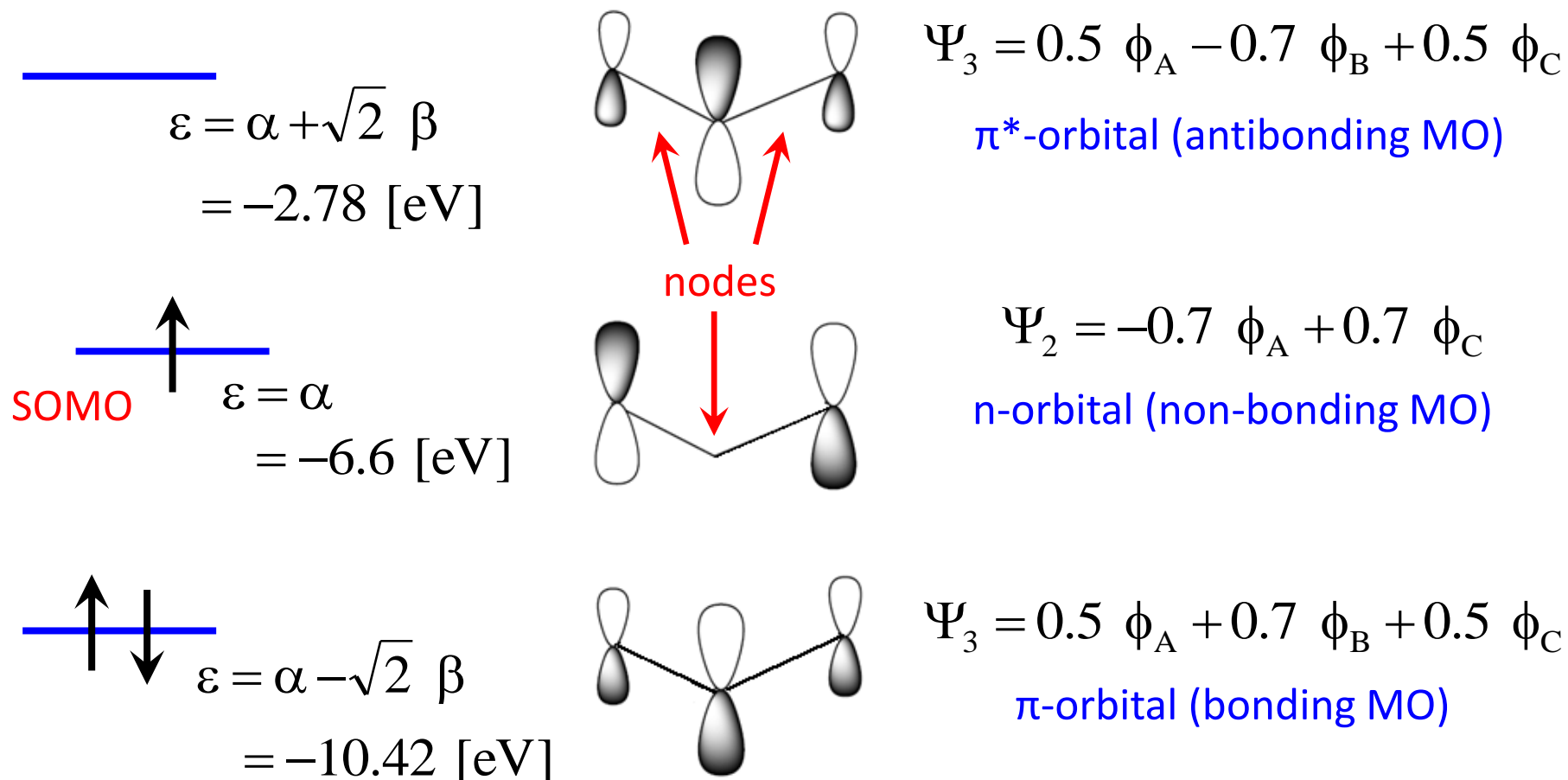
$$H_2C = CH_2$$
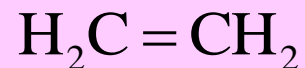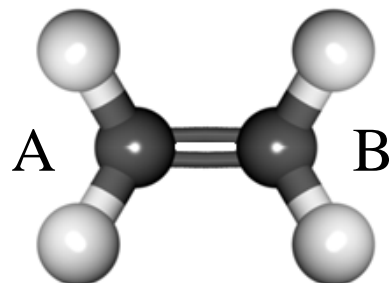
Trial wavefunction (LCAO method):

$$\Psi_t = c_A \phi_A + c_B \phi_B$$

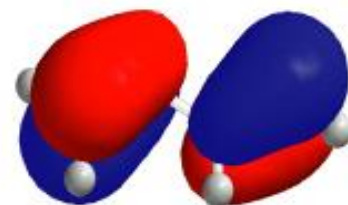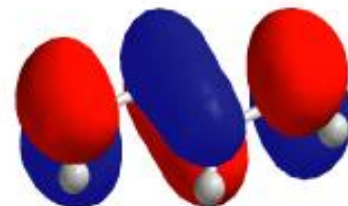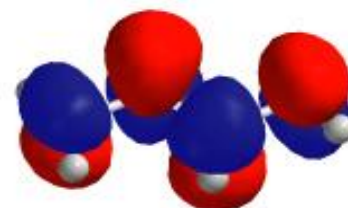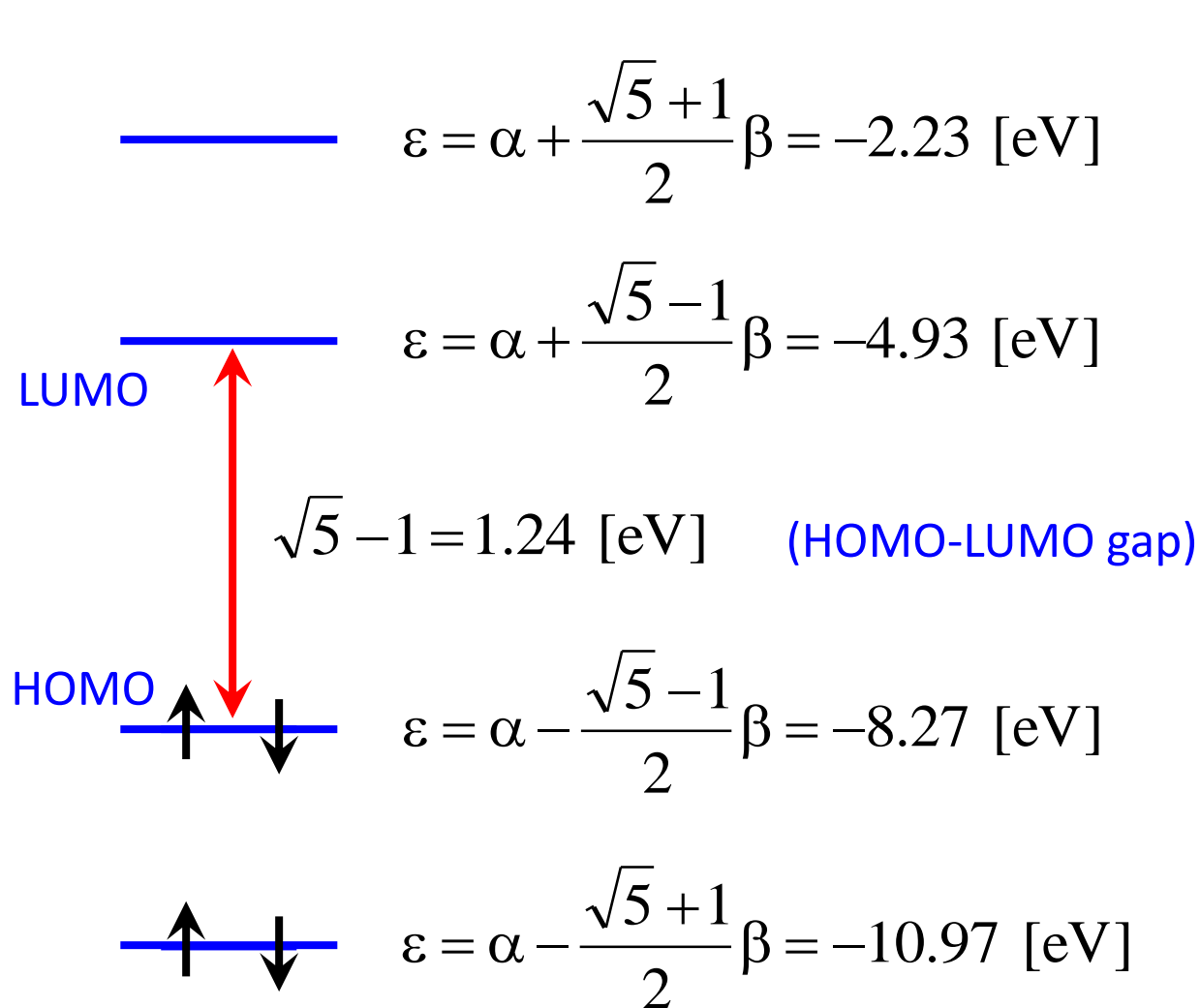Secular equations for ethylene molecule:

$$\begin{bmatrix} \alpha - \varepsilon & -\beta \\ -\beta & \alpha - \varepsilon \end{bmatrix} \begin{pmatrix} c_A \\ c_B \end{pmatrix} = 0$$

Solving quadratic equation by making secular determinant equal to zero:

$$\det \begin{bmatrix} \alpha - \varepsilon & -\beta \\ -\beta & \alpha - \varepsilon \end{bmatrix} = 0 \longrightarrow \varepsilon = \alpha - \beta \ , \quad \varepsilon = \alpha + \beta$$

π*-orbital
(antibonding MO)

$$\Psi_A = \frac{1}{\sqrt{2}}\left[\phi_A(r) - \phi_B(r)\right]$$

$$\varepsilon = \alpha + \beta$$

$2p_z$

2β

$2p_z$

Molecular
Orbitals

$$\varepsilon = \alpha - \beta$$
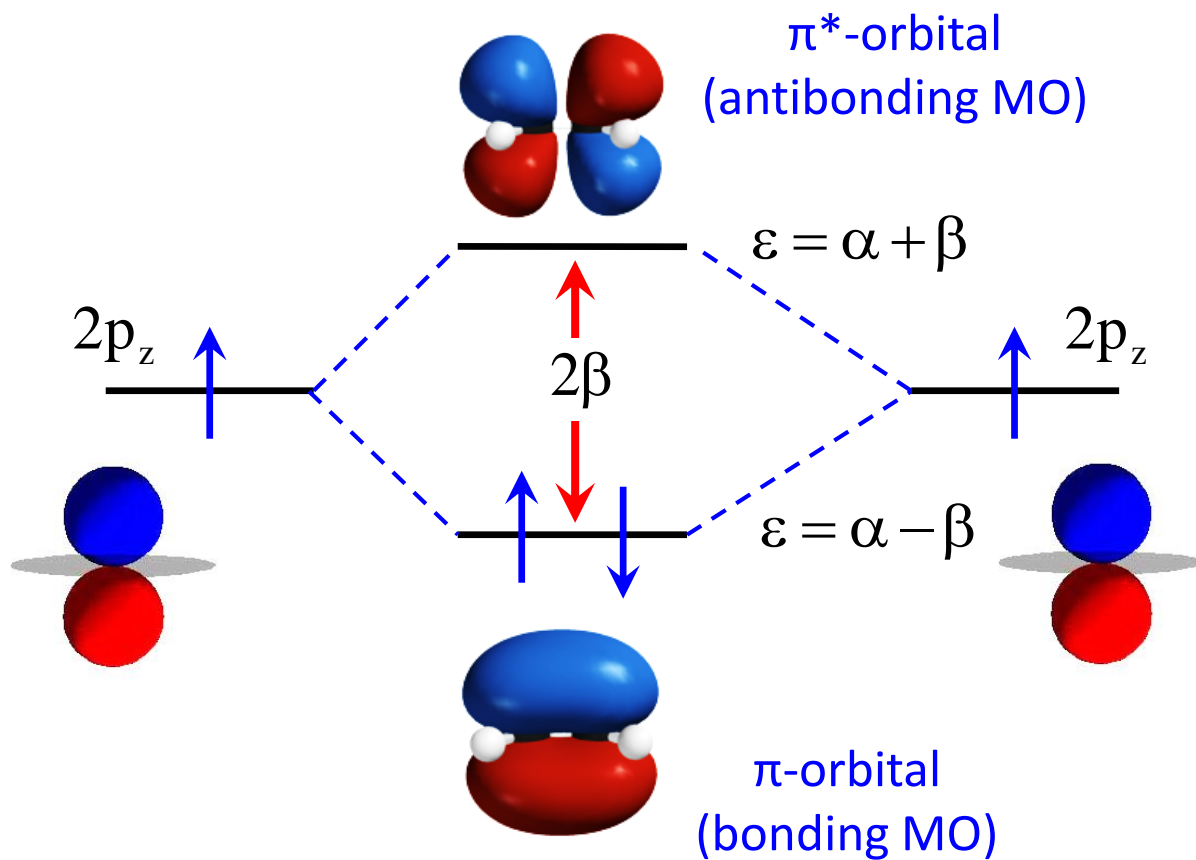
π-orbital
(bonding MO)

$$\Psi_S = \frac{1}{\sqrt{2}}\left[\phi_A(r) + \phi_B(r)\right]$$
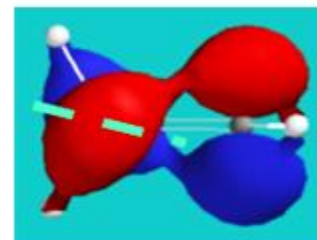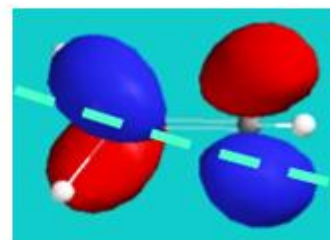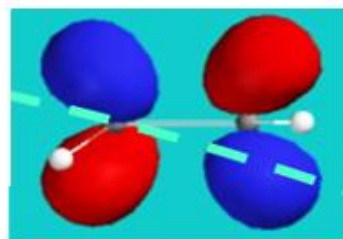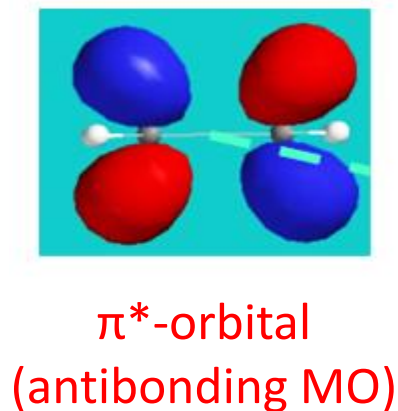
"Loss of antibonding overlap"
(stabilization of π* orbital)

π*-orbital
(antibonding MO)

π-orbital
(bonding MO)
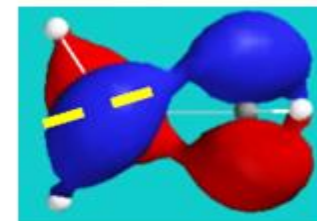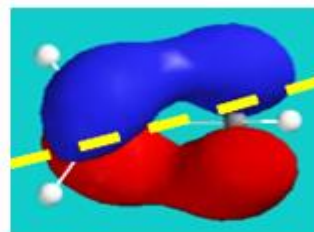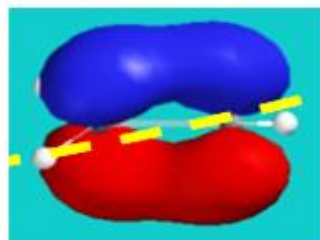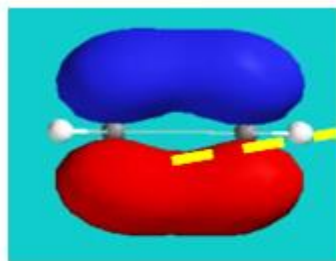
"Loss of bonding overlap"
(destabilization of π orbital)
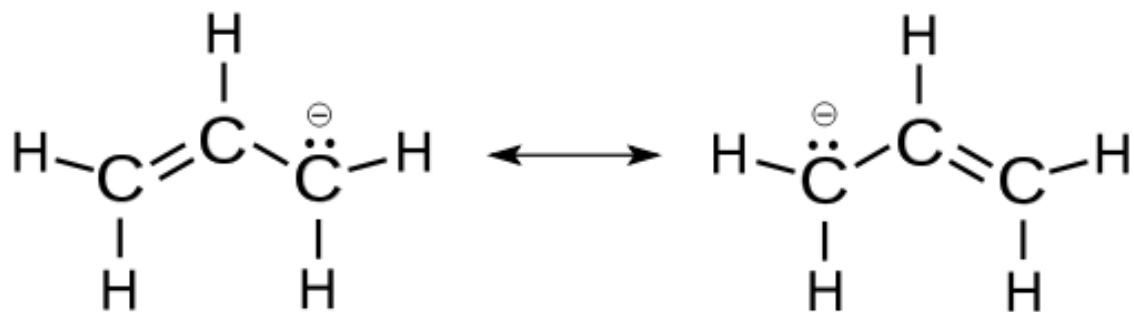
Resonance structures (canonical forms; mesomerism)

Trial wavefunction (LCAO method):

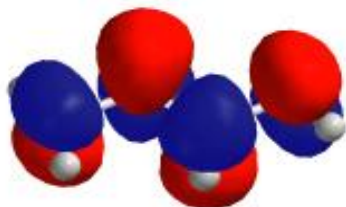$$\Psi_t = c_A \phi_A + c_B \phi_B + c_C \phi_C$$

Secular equations for allyl anion:

$$\begin{bmatrix} \alpha - \varepsilon & -\beta & 0 \\ -\beta & \alpha - \varepsilon & -\beta \\ 0 & -\beta & \alpha - \varepsilon \end{bmatrix} \begin{pmatrix} c_A \\ c_B \\ c_C \end{pmatrix} = 0$$

$$\varepsilon = \alpha + \sqrt{2}\ \beta$$
$$= -2.78\ [\text{eV}]$$

$$\Psi_3 = 0.5\ \phi_A - 0.7\ \phi_B + 0.5\ \phi_C$$

π*-orbital (antibonding MO)

nodes

SOMO

$$\varepsilon = \alpha$$
$$= -6.6\ [\text{eV}]$$

$$\Psi_2 = -0.7\ \phi_A + 0.7\ \phi_C$$

n-orbital (non-bonding MO)

$$\varepsilon = \alpha - \sqrt{2}\ \beta$$
$$= -10.42\ [\text{eV}]$$

$$\Psi_3 = 0.5\ \phi_A + 0.7\ \phi_B + 0.5\ \phi_C$$

π-orbital (bonding MO)

SOMO – Singly Occupied Molecular Orbital

$$H_2C = CH - CH = CH_2$$
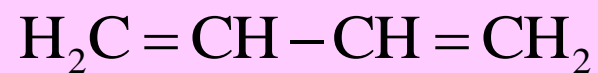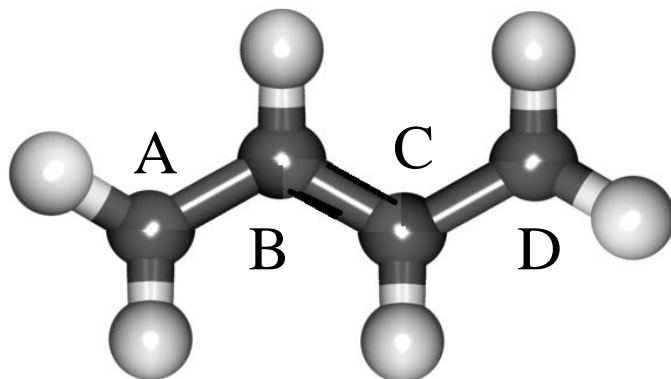
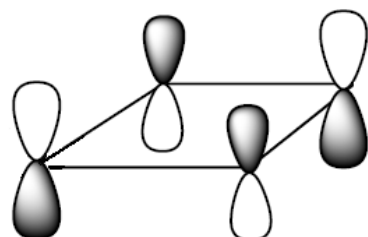Trial wavefunction (LCAO method):
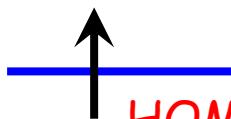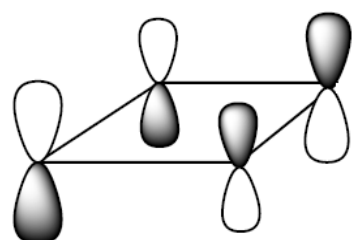
$$\Psi_t = c_A\phi_A + c_B\phi_B + c_C\phi_C + c_D\phi_D$$

Secular equations for butadiene molecule:

$$\begin{bmatrix} \alpha-\varepsilon & -\beta & 0 & 0 \\ -\beta & \alpha-\varepsilon & -\beta & 0 \\ 0 & -\beta & \alpha-\varepsilon & -\beta \\ 0 & 0 & -\beta & \alpha-\varepsilon \end{bmatrix} \begin{pmatrix} c_A \\ c_B \\ c_C \\ c_D \end{pmatrix} = 0$$
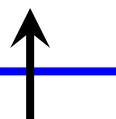
$$\varepsilon = \alpha + \frac{\sqrt{5}+1}{2}\beta = -2.23 \ [\text{eV}]$$

$$\varepsilon = \alpha + \frac{\sqrt{5}-1}{2}\beta = -4.93 \ [\text{eV}]$$

LUMO

$$\sqrt{5}-1 = 1.24 \ [\text{eV}] \qquad \text{(HOMO-LUMO gap)}$$

HOMO

$$\varepsilon = \alpha - \frac{\sqrt{5}-1}{2}\beta = -8.27 \ [\text{eV}]$$

$$\varepsilon = \alpha - \frac{\sqrt{5}+1}{2}\beta = -10.97 \ [\text{eV}]$$
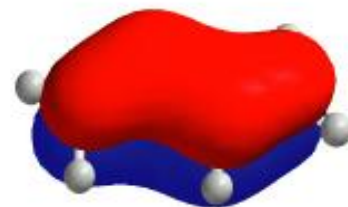
Antibonding molecular orbitals:

$$\Psi_4 = -0.37\ \phi_A + 0.60\ \phi_B - 0.60\ \phi_C + 0.37\ \phi_D$$
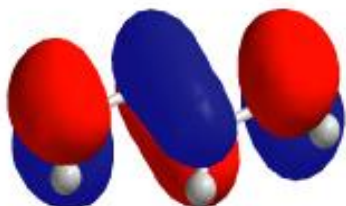
$$\Psi_3 = 0.60\ \phi_A - 0.37\ \phi_B - 0.37\ \phi_C + 0.60\ \phi_D$$

$$\phi_x = 2p_z(r_x) \quad \text{where} \quad x = A, B, C, D.$$

Bonding molecular orbitals:
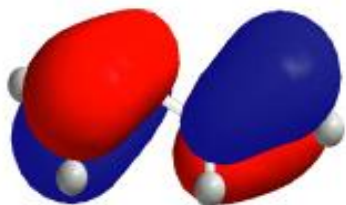
$$\Psi_2 = -0.60\ \phi_A - 0.37\ \phi_B + 0.37\ \phi_C + 0.60\ \phi_D$$
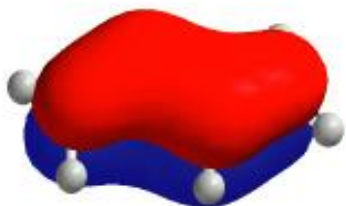
$$\Psi_1 = 0.37\ \phi_A + 0.60\ \phi_B + 0.60\ \phi_C + 0.37\ \phi_D$$

$$CH = CH \atop | \quad\quad |$$
$$CH = CH$$
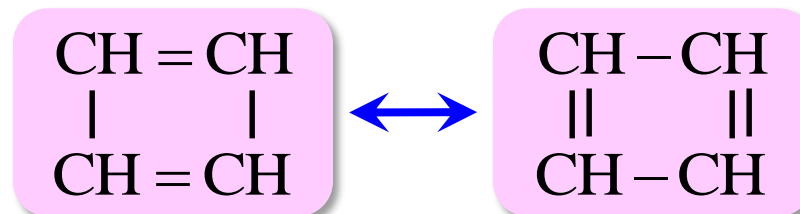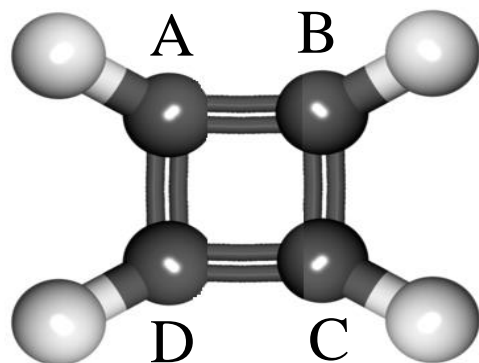
$\longleftrightarrow$

$$CH - CH \atop || \quad\quad ||$$
$$CH - CH$$

Resonance structures
(canonical forms; mesomerism)

Trial wavefunction (LCAO method):

$$\Psi_t = c_A \phi_A + c_B \phi_B + c_C \phi_C + c_D \phi_D$$

Secular equations for cyclobutadiene molecule:

$$\begin{bmatrix} \alpha - \varepsilon & -\beta & 0 & -\beta \\ -\beta & \alpha - \varepsilon & -\beta & 0 \\ 0 & -\beta & \alpha - \varepsilon & -\beta \\ -\beta & 0 & -\beta & \alpha - \varepsilon \end{bmatrix} \begin{pmatrix} c_A \\ c_B \\ c_C \\ c_D \end{pmatrix} = 0$$

$$\varepsilon = \alpha + 2\beta = -1.2 \ [eV]$$

HOMO = LUMO

$$\varepsilon = \alpha = -6.6 \ [eV]$$

$$\varepsilon = \alpha - 2\beta = -12.0 \ [eV]$$
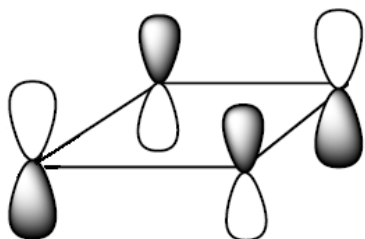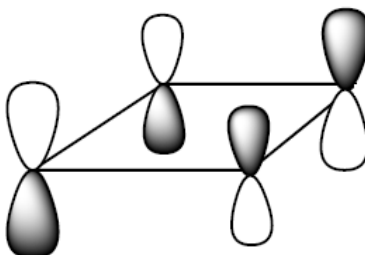
Antibonding molecular orbitals:

$$\Psi_4 = 0.5 \ \phi_A - 0.5 \ \phi_B + 0.5 \ \phi_C - 0.5 \ \phi_D$$
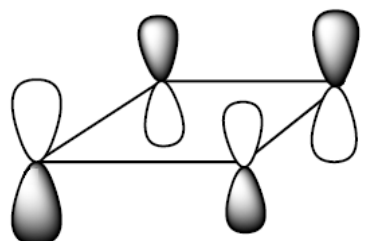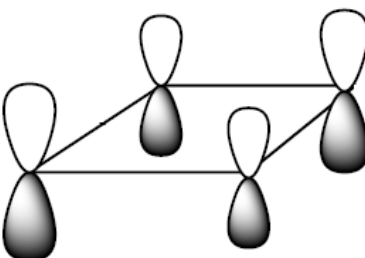
Non-bonding molecular orbitals:

$$\Psi_3 = 0.5 \ \phi_A - 0.5 \ \phi_B - 0.5 \ \phi_C + 0.5 \ \phi_D$$

$$\phi_x = 2p_z(r_x) \quad \text{where} \quad x = A, B, C, D.$$

Non-bonding molecular orbitals:

$$\Psi_2 = 0.5 \ \phi_A + 0.5 \ \phi_B - 0.5 \ \phi_C - 0.5 \ \phi_D$$

Bonding molecular orbitals:

$$\Psi_1 = 0.5 \ \phi_A + 0.5 \ \phi_B + 0.5 \ \phi_C + 0.5 \ \phi_D$$

Total energy of "π" electrons in butadiene:

$$E_\pi = 2\alpha - \left(\sqrt{5} + 1\right)\beta + 2\alpha - \left(\sqrt{5} - 1\right)\beta = 4\alpha - 2\sqrt{5}\ \beta = -38.5\ [eV]$$
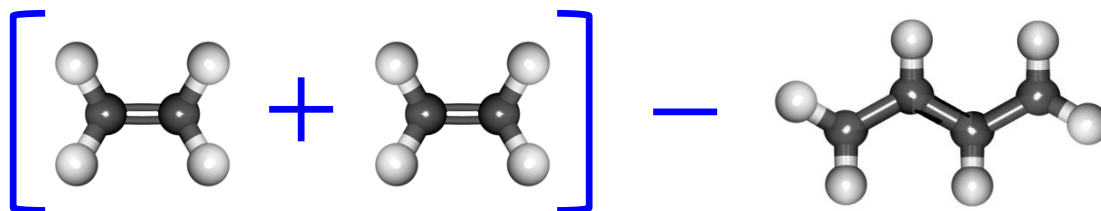
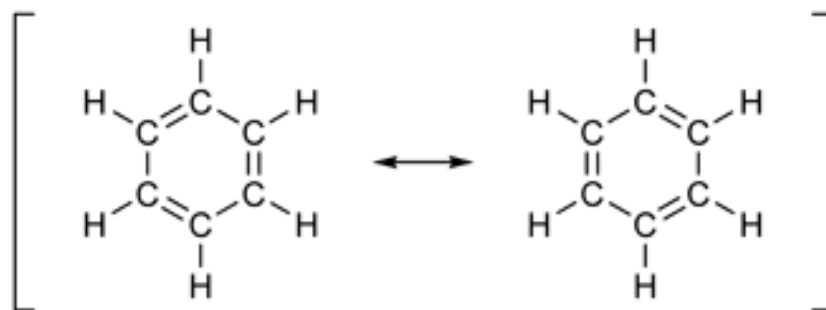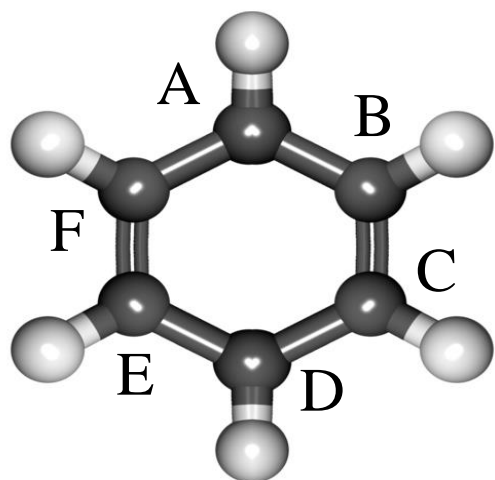$$E_{del} = 2(2\alpha - 2\beta) - \left(4\alpha - 2\sqrt{5}\ \beta\right) = \left(2\sqrt{5} - 4\right)\beta = 1.27\ [eV]$$

Total energy of "π" electrons in cyclobutadiene:

$$E_\pi = 2\alpha - 4\beta + 2\alpha = 4\alpha - 4\beta = -37.2\ [eV]$$
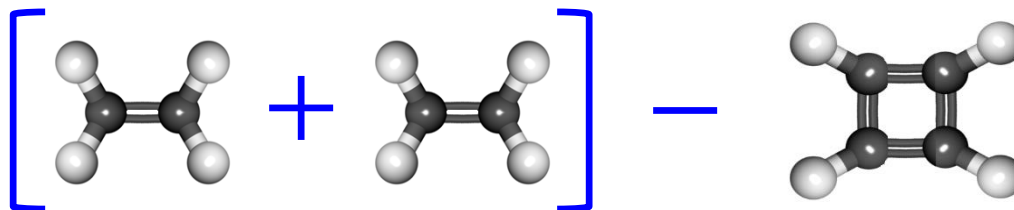
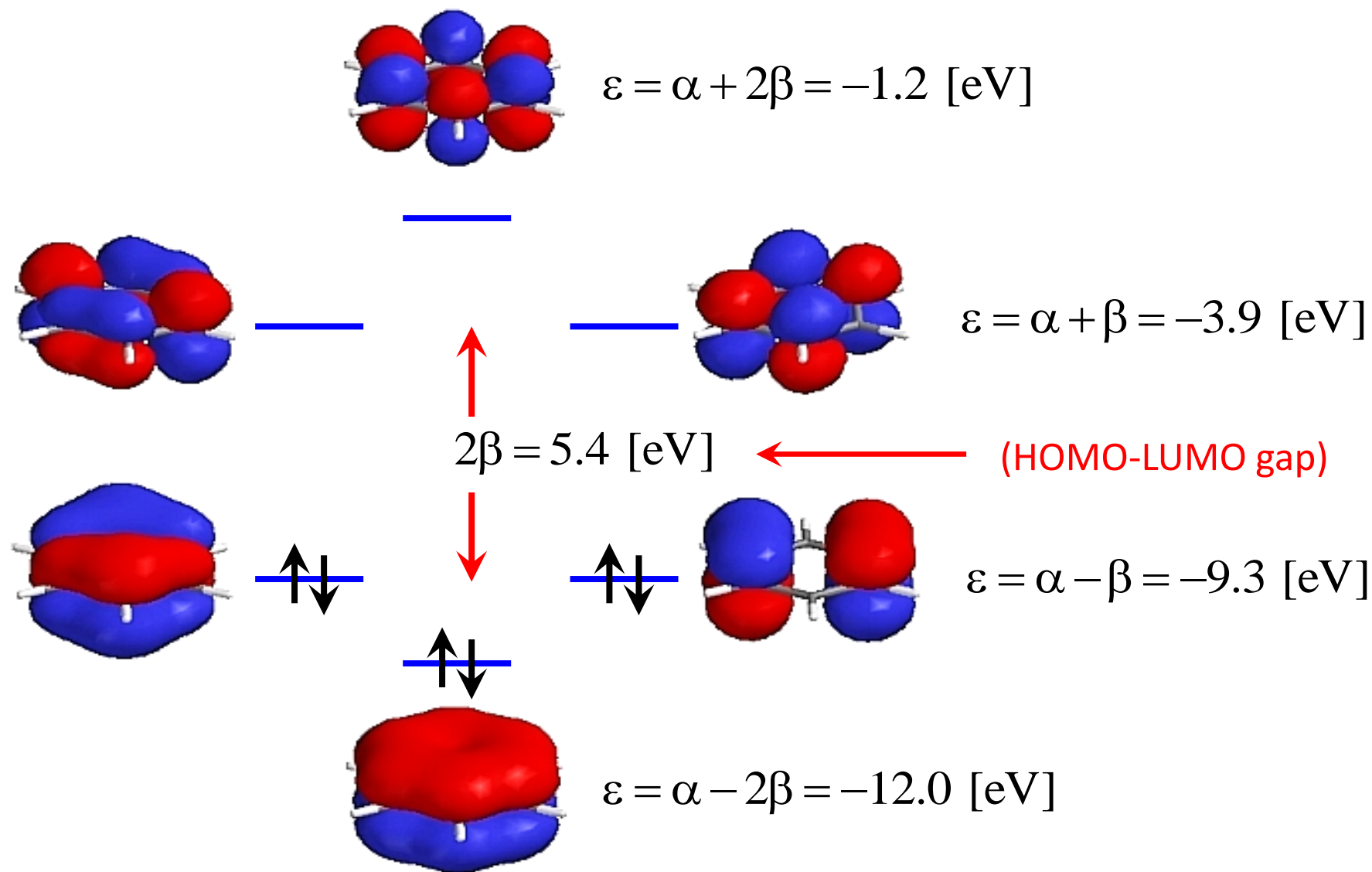$$E_{del} = 2(2\alpha - 2\beta) - (4\alpha - 4\beta) = 0$$

C−C: 154 [pm]

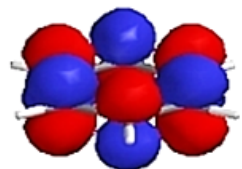C=C: 133 [pm]

Resonance structures
(canonical forms; mesomerism)

Secular equations for benzene molecule:

$$
\begin{bmatrix}
\alpha-\varepsilon & -\beta & 0 & 0 & 0 & -\beta \\
-\beta & \alpha-\varepsilon & -\beta & 0 & 0 & 0 \\
0 & -\beta & \alpha-\varepsilon & -\beta & 0 & 0 \\
0 & 0 & -\beta & \alpha-\varepsilon & -\beta & 0 \\
0 & 0 & 0 & -\beta & \alpha-\varepsilon & -\beta \\
-\beta & 0 & 0 & 0 & -\beta & \alpha-\varepsilon
\end{bmatrix}
\begin{pmatrix}
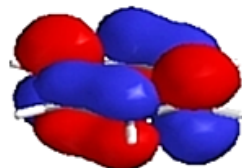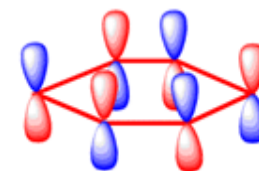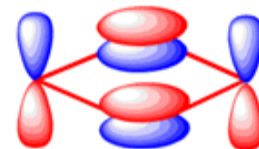c_A \\ c_B \\ c_C \\ c_D \\ c_E \\ c_F
\end{pmatrix} = 0
$$

$$\varepsilon = \alpha + 2\beta = -1.2 \ [eV]$$

$$\varepsilon = \alpha + \beta = -3.9 \ [eV]$$

$$2\beta = 5.4 \ [eV] \qquad \text{(HOMO-LUMO gap)}$$

$$\varepsilon = \alpha - \beta = -9.3 \ [eV]$$
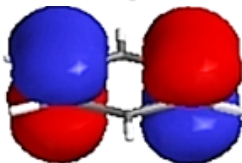
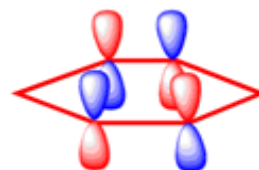$$\varepsilon = \alpha - 2\beta = -12.0 \ [eV]$$

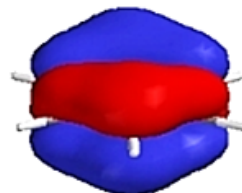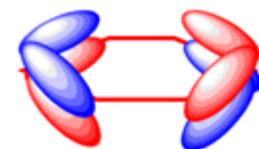$$\Psi_6 = \frac{1}{\sqrt{6}}\left(-\phi_A + \phi_B - \phi_C + \phi_D - \phi_E + \phi_F\right)$$

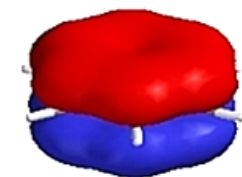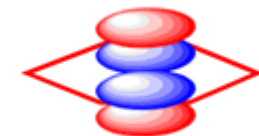$$\Psi_5 = \frac{1}{2}\left(-\phi_A + \phi_C - \phi_D + \phi_F\right)$$

$$\Psi_4 = \frac{1}{2}\left(-\phi_A + \phi_B - \phi_D + \phi_E\right)$$
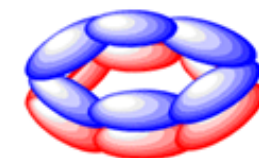
$$\Psi_3 = \frac{1}{2}\left(\phi_A - \phi_C - \phi_D + \phi_F\right)$$

$$\Psi_2 = \frac{1}{2}\left(-\phi_A - \phi_B + \phi_D + \phi_E\right)$$
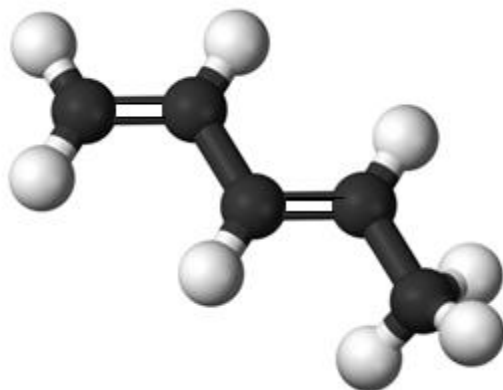
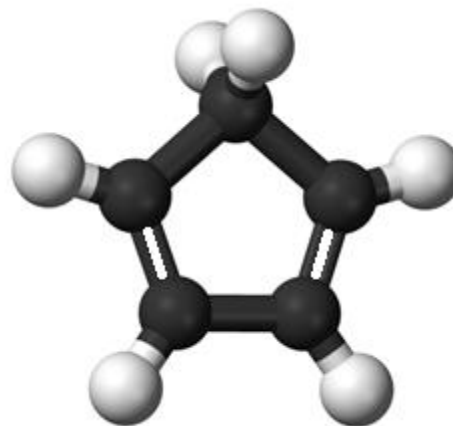$$\Psi_1 = \frac{1}{\sqrt{6}}\left(\phi_A + \phi_B + \phi_C + \phi_D + \phi_E + \phi_F\right)$$

Use Hückel method to calculate and analyze: (a) the accessible energy levels, (b) molecular orbitals, and (c) delocalization energy for pentadiene and cyclopentadiene!

PENTADIENE

CYCLOPENTADIENE (Stable)

$$H_2C = CH - CH = CH - CH_3$$

$$C_5H_6$$

Since cyclopentadiene belongs to stable organic compounds, it may be used to build organometallic compounds which contain chemical bonds between carbon atoms and metal atoms (alkaline, alkaline earth, transition metal, etc.)! Those organometallic compounds may be connected to gold electrodes via sulfur atoms (thiol groups) through which transport may occur!

Au Contact   S   S   **Au Contact**

Cyclopentadiene

$$\begin{bmatrix} Fe, & Co, & Mg \\ Ti, & Mo, & Cr \end{bmatrix}$$