서울대학교
SEOUL NATIONAL UNIVERSITY

Department of Chemistry

Physical Chemistry 2

PChem 2

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The Last Lecture. Polyatomic molecules

July 28th, 2021

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Topics in Lecture 11

MO of heteronuclear diatomic molecules

Hybrid orbitals

π-electron approximation

Brief introduction to the group theory

In Atkins' *Physical Chemistry* (11th ed.),

9D MOT: heteronuclear diatomic molecules
9E MOT: polyatomic molecules
10A Shape and symmetry

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MO of heteronuclear diatomics

For heteronuclear diatomic molecules, difference in *electronegativity* occurs. Therefore, we cannot just set $c_A = c_B$ simply. Therefore, we need to find the optimizing value of coefficients.

Consider a heteronuclear diatomic molecule with atom A and B. Then, wavefunction is:

$$\psi = c_A \psi_a + c_B \psi_B$$

Then, energy calculated from this wavefunction is

$$E = \frac{\int \psi \hat{H} \psi \, d\tau}{\int \psi^2 \, d\tau} = E(c_A, c_B)$$

Denominator:

$$\int \psi^2 \, d\tau = \int (c_A \psi_A + c_B \psi_B)(c_A \psi_A + c_B \psi_B) \, d\tau = c_A^2 + c_B^2 + 2c_A c_B S$$

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Numerator:

$$\int \psi \hat{H} \psi \, d\tau = \int (c_A \psi_A + c_B \psi_B) \hat{H} (c_A \psi_A + c_B \psi_B) \, d\tau$$

$$= c_A^2 \int \psi_A \hat{H} \psi_A \, d\tau + c_B^2 \int \psi_B \hat{H} \psi_B \, d\tau + c_A c_B \int \psi_A \hat{H} \psi_B \, d\tau + c_B c_A \int \psi_B \hat{H} \psi_A \, d\tau$$

$$\equiv c_A^2 H_{AA} + c_B^2 H_{BB} + 2 c_A c_B H_{AB}$$

Therefore, we have

$$E \cdot (c_A^2 + c_B^2 + 2 c_A c_B S) = c_A^2 H_{AA} + c_B^2 H_{BB} + 2 c_A c_B H_{AB}$$

Differentiate both side with respect to c_A and c_B.

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Therefore

$$E \cdot (c_A^2 + c_B^2 + 2c_A c_B S) = c_A^2 H_{AA} + c_B^2 H_{BB} + 2c_A c_B H_{AB}$$

$$\frac{\partial E}{\partial c_A}(c_A^2 + c_B^2 + 2c_A c_B S) + E(2c_A + 2c_B S) = 2c_A H_{AA} + 2c_B H_{AB} \implies \frac{\partial E}{\partial c_A} = 0, \; c_A(H_{AA} - E) + c_B(H_{AB} - ES) = 0$$

$$\frac{\partial E}{\partial c_B}(c_A^2 + c_B^2 + 2c_A c_B S) + E(2c_B + 2c_A S) = 2c_B H_{BB} + 2c_A H_{AB} \implies \frac{\partial E}{\partial c_B} = 0, \; c_A(H_{AB} - ES) + c_B(H_{BB} - E) = 0$$

We yield *secular equations*.

$$c_A(H_{AA} - E) + c_B(H_{AB} - ES) = 0$$
$$c_A(H_{AB} - ES) + c_B(H_{BB} - E) = 0$$

Note that $c_A = c_B = 0$ is a trivial solution of secular equation. To require that secular equations have nontrivial solutions, we need

$$\begin{vmatrix} H_{AA} - E & H_{AB} - ES \\ H_{AB} - ES & H_{BB} - E \end{vmatrix} = 0$$

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From the secular equation, we yield the energy eigenvalues.

For the simplification, let $S = 0$ (complete neglection of overlap). Then eigenvalues are
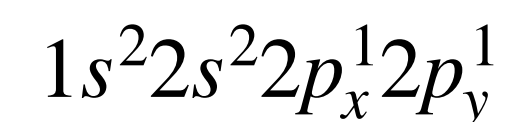
$$E_{\pm} = \frac{H_{AA} + H_{BB}}{2} \pm \frac{H_{AA} - H_{BB}}{2} \sqrt{1 + \left(\frac{2H_{AB}}{H_{AA} - H_{BB}} \right)^2}$$

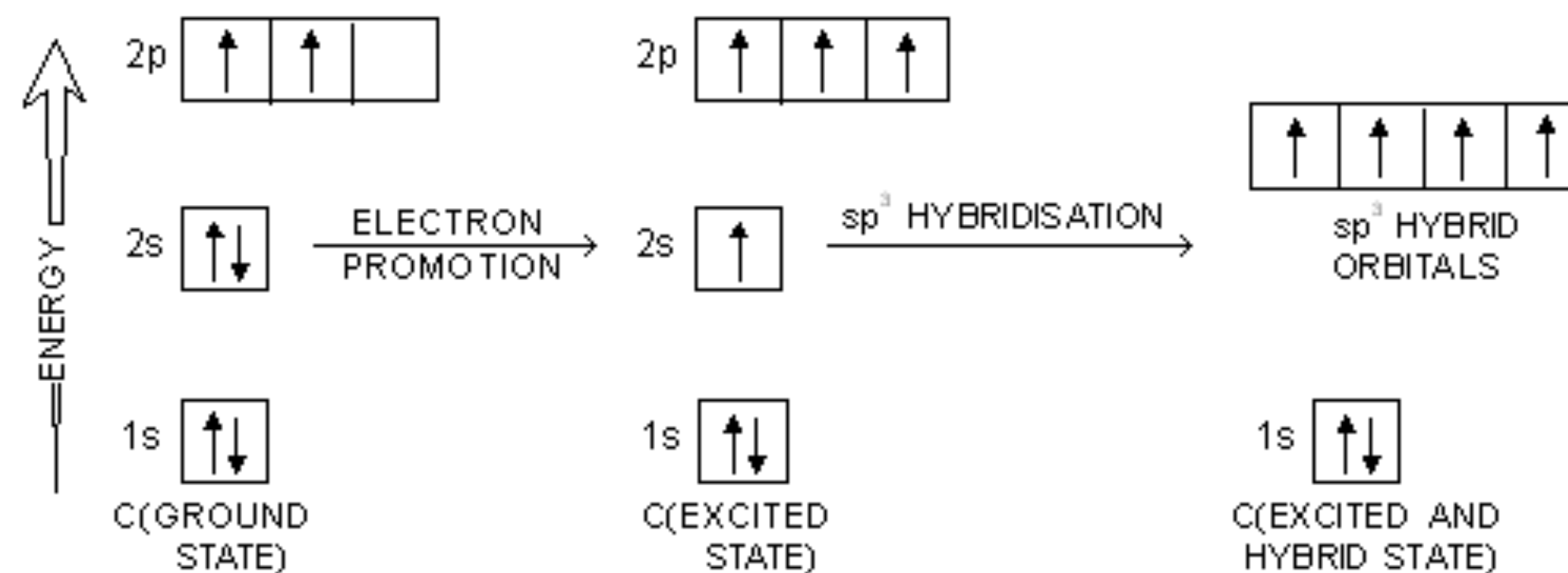Coefficients corresponding to each eigenvalues can be calculated. Do it yourself!

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Hybrid orbitals

The ground state electron configuration of a carbon atom,

$$1s^2 2s^2 2p_x^1 2p_y^1$$

does not seem to lead to the tetrahedral bonding in methane and other saturated hydrocarbons. This problem is overcome with *promotion*.

After the promotion, *hybridization* follows.

sp orbitals

Consider first the linear molecule, BeH_2. We know that this molecule has two equivalent Be-H bonds, with bond angle of 180˚. However, BeH_2 has electronic configuration of $1s^2 2s^2$.

To counter this problem, we *mix* p_z orbital, to form *sp* hybrid orbital.

The two *sp* orbitals are equivalent, and are directed 180˚ from each other.
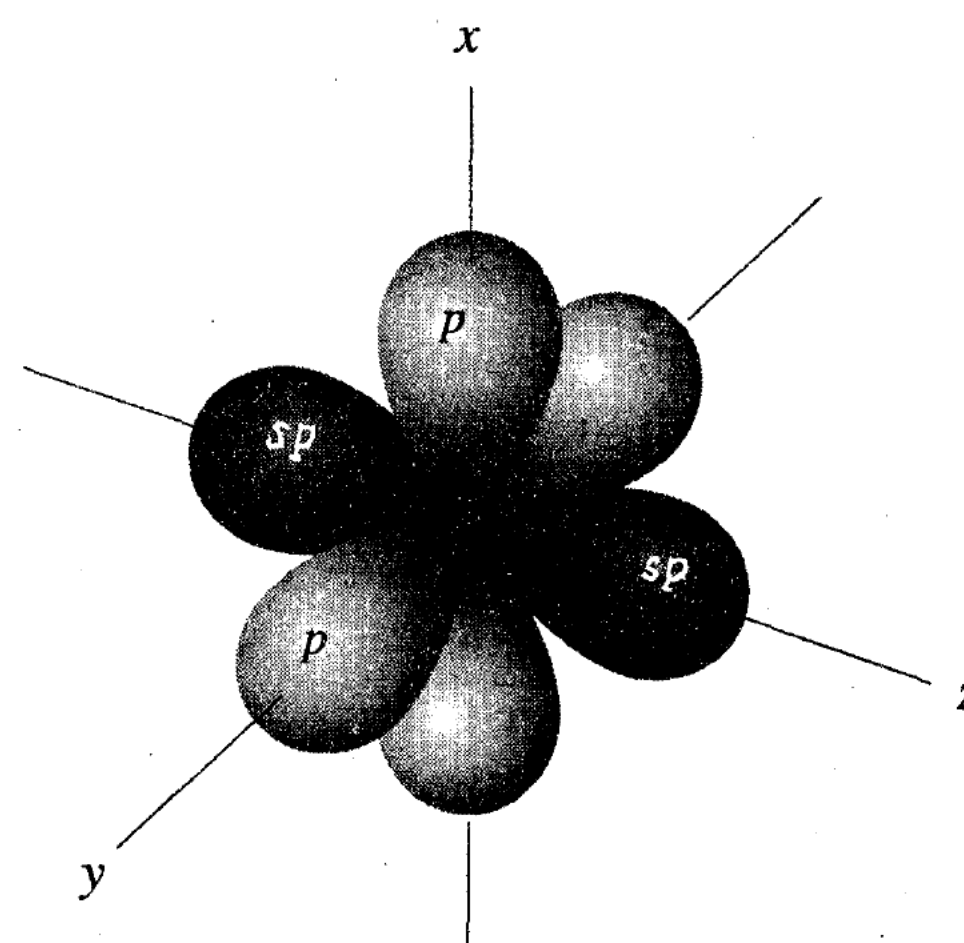
$$\psi_{sp} = \frac{1}{\sqrt{2}}(2s \pm 2p_z)$$

FIGURE 10.1
An illustration of the *sp* hybrid orbitals. The two *sp* hybrid orbitals are equivalent and are directed 180° from each other. The two remaining $2p$ orbitals are perpendicular to each other and to the line formed by the *sp* orbitals.

sp^2 **orbitals**

Same approach can be applied to BH_3. To make three equivalent bonds directed 120° from each other, we need to mix p_x and p_y orbitals with s orbital.

$$\psi_1 = \frac{1}{\sqrt{3}}2s + \sqrt{\frac{2}{3}}2p_y$$

$$\psi_2 = \frac{1}{\sqrt{3}}2s + \frac{1}{\sqrt{2}}2p_x - \frac{1}{\sqrt{6}}2p_y$$

$$\psi_3 = \frac{1}{\sqrt{3}}2s - \frac{1}{\sqrt{2}}2p_x - \frac{1}{\sqrt{6}}2p_y$$
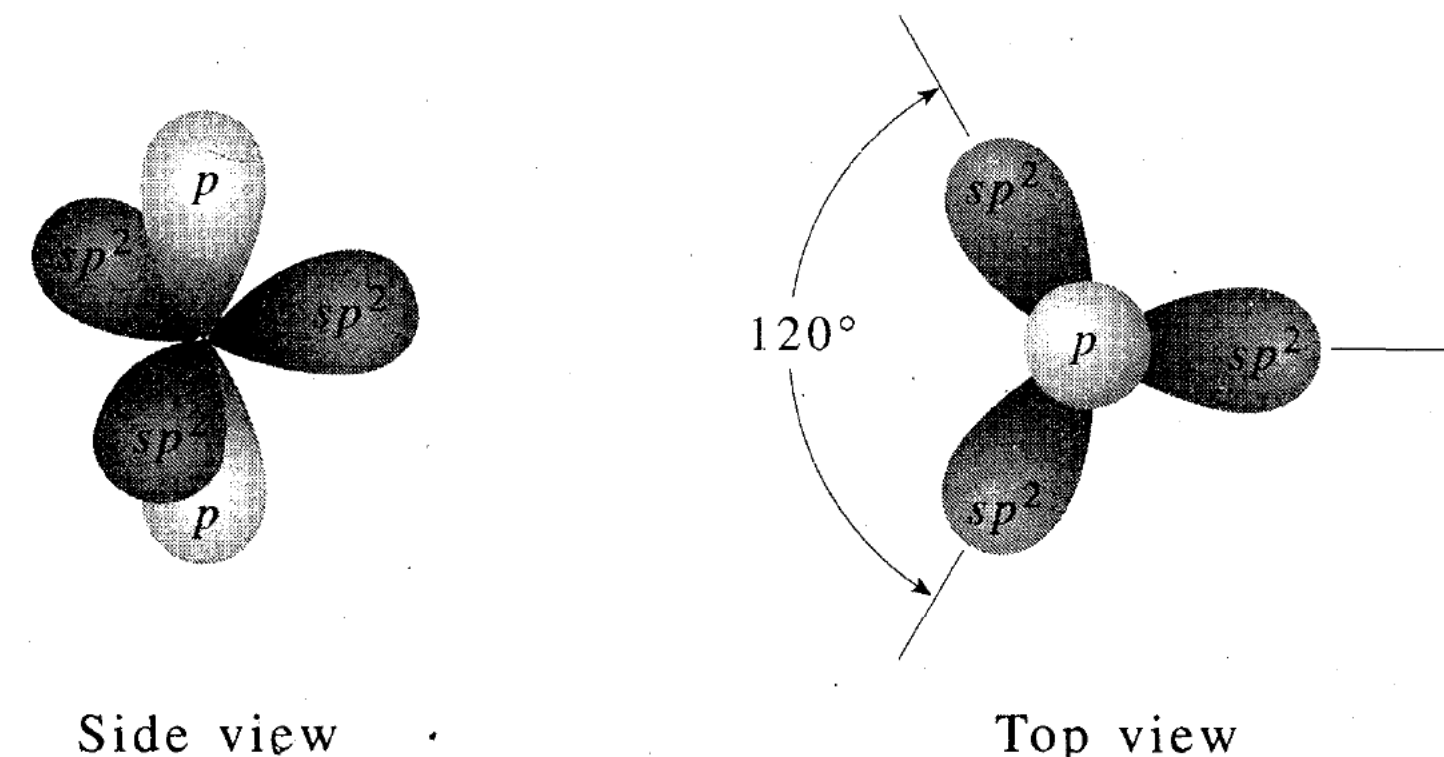

Side view · Top view

FIGURE 10.4
The geometry associated with sp^2 orbitals. The three sp^2 orbitals lie in a plane and point to the vertices of an equilateral triangle. The remaining $2p$ orbital is perpendicular to the plane formed by the three sp^2 orbitals.

These orbitals are not solutions of Schrödinger equation: hybrid orbitals are VBT concept, and they are custom-made to describe molecules we cannot deal in VBT.
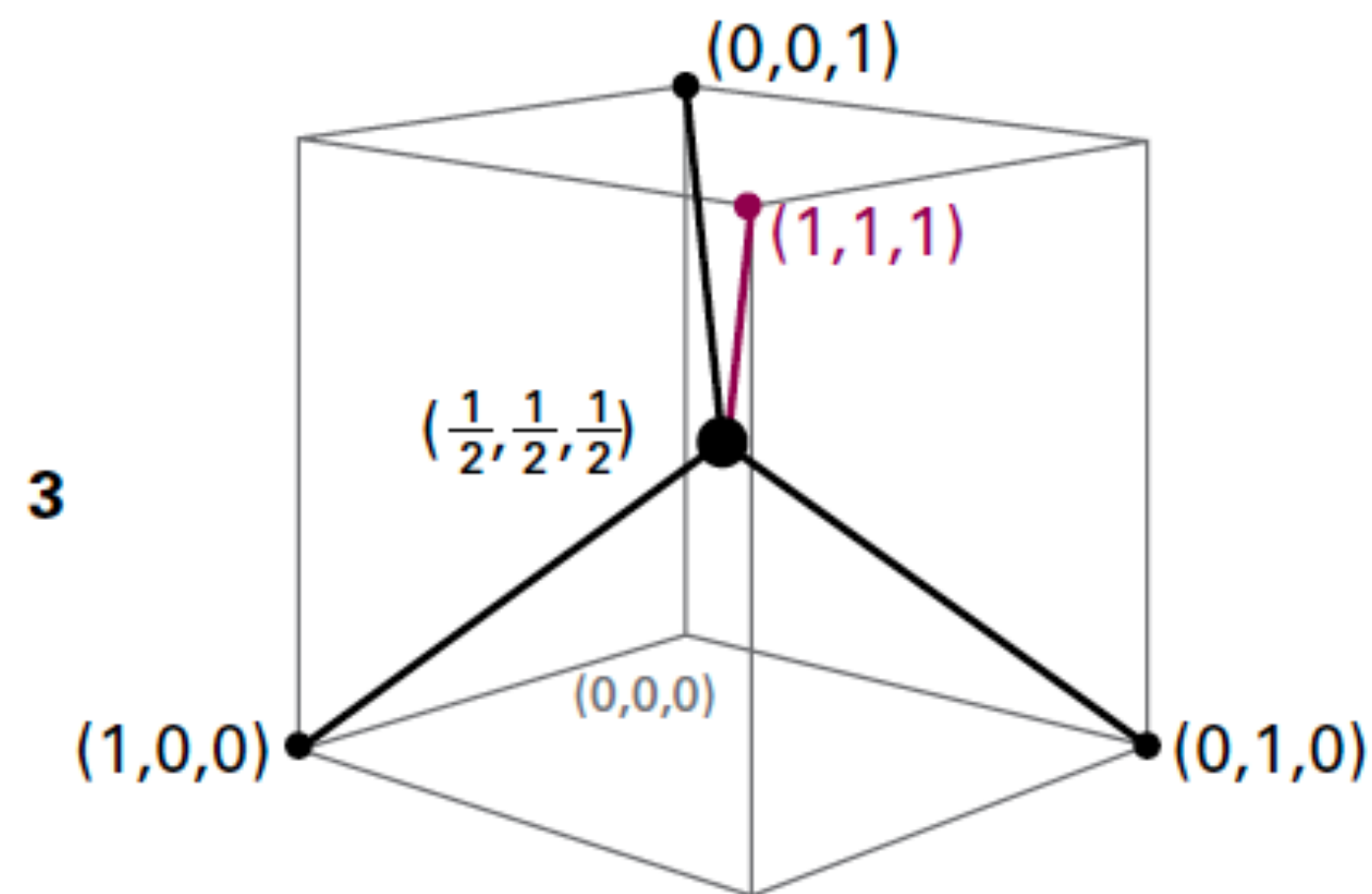
sp^3 orbitals

For CH_4, we need four orbitals pointing tetrahedral points.

$$\psi_1 = \frac{1}{2}(2s + 2p_x + 2p_y + 2p_z)$$

$$\psi_2 = \frac{1}{2}(2s - 2p_x - 2p_y + 2p_z)$$

$$\psi_3 = \frac{1}{2}(2s + 2p_x - 2p_y - 2p_z)$$

$$\psi_4 = \frac{1}{2}(2s - 2p_x + 2p_y - 2p_z)$$

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We have learned that PES (PhotoElectron Spectroscopy) can blow a cover of electronic structure of certain molecule. However, PES result does not coincide with hybrid orbital results.

Therefore, we need MOT to describe polyatomic molecules qualitatively.

sp^3 **orbitals**

C
orbitals

CH$_4$
orbitals

H
orbitals

$2t_2$

$3a_1$

$2p's$

$1s_a$ $1s_b$ $1s_c$ $1s_d$

Energy

$2s$

$1t_2$

$2a_1$
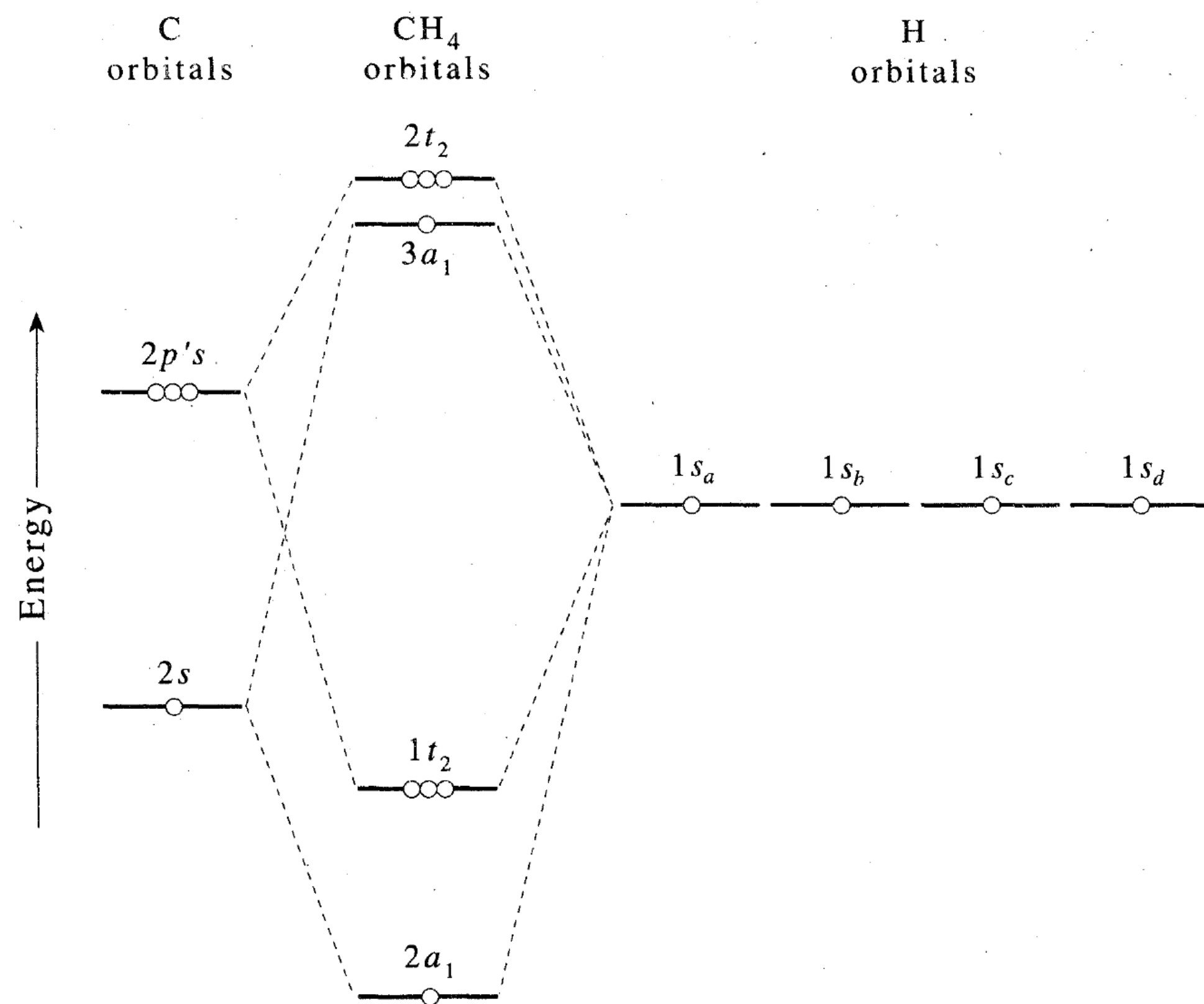
FIGURE 10.15
A molecular-orbital energy-level diagram for the valence electrons in CH$_4$.

$1t_2$

$2a_1$

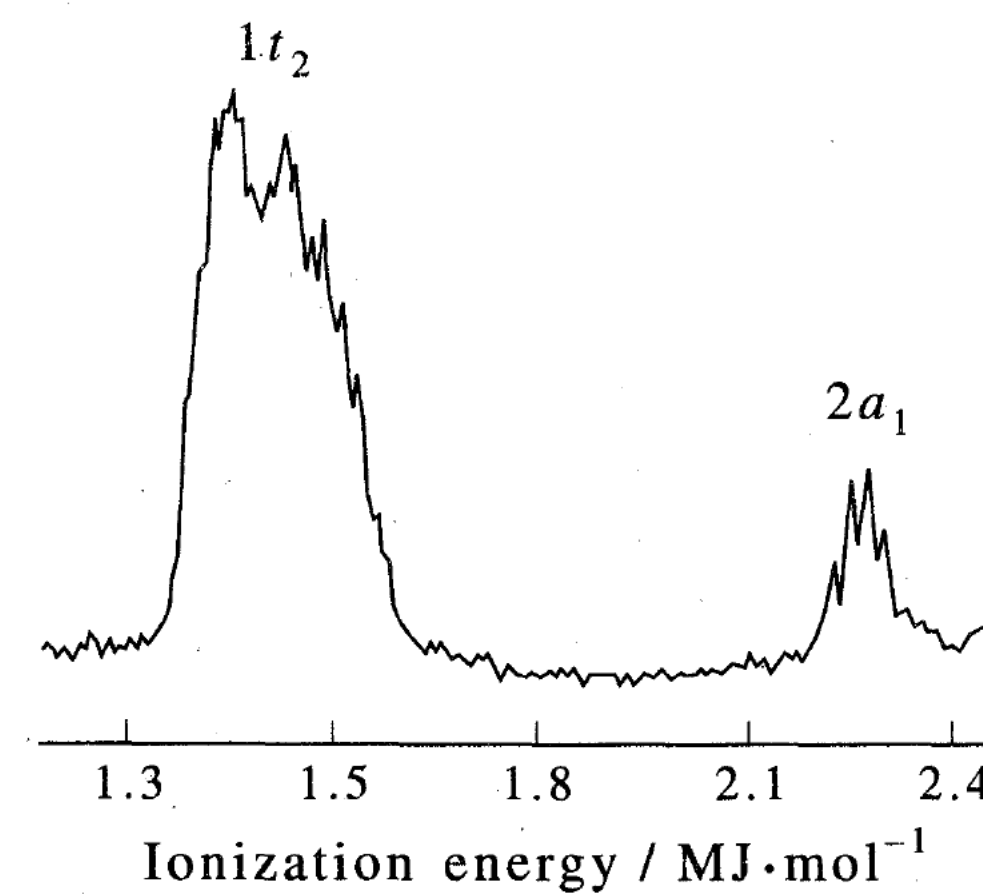1.3   1.5   1.8   2.1   2.4

Ionization energy / MJ·mol^{-1}

FIGURE 10.16
The photoelectron spectrum of methane. The two lines observed in the photoelectron spectrum reflect the ionization of electrons from the $1t_2$ and $2a_1$ molecular orbitals. The energy difference between these two lines corresponds to the energy difference between the $1t_2$ and $2a_1$ molecular orbitals (see Figure 10.15). The lines are broad because ionization occurs from many different vibrational levels of the molecules.

π-electron approximation

Unsaturated hydrocarbons can be treated simply, by separating σ bonds and π bonds.
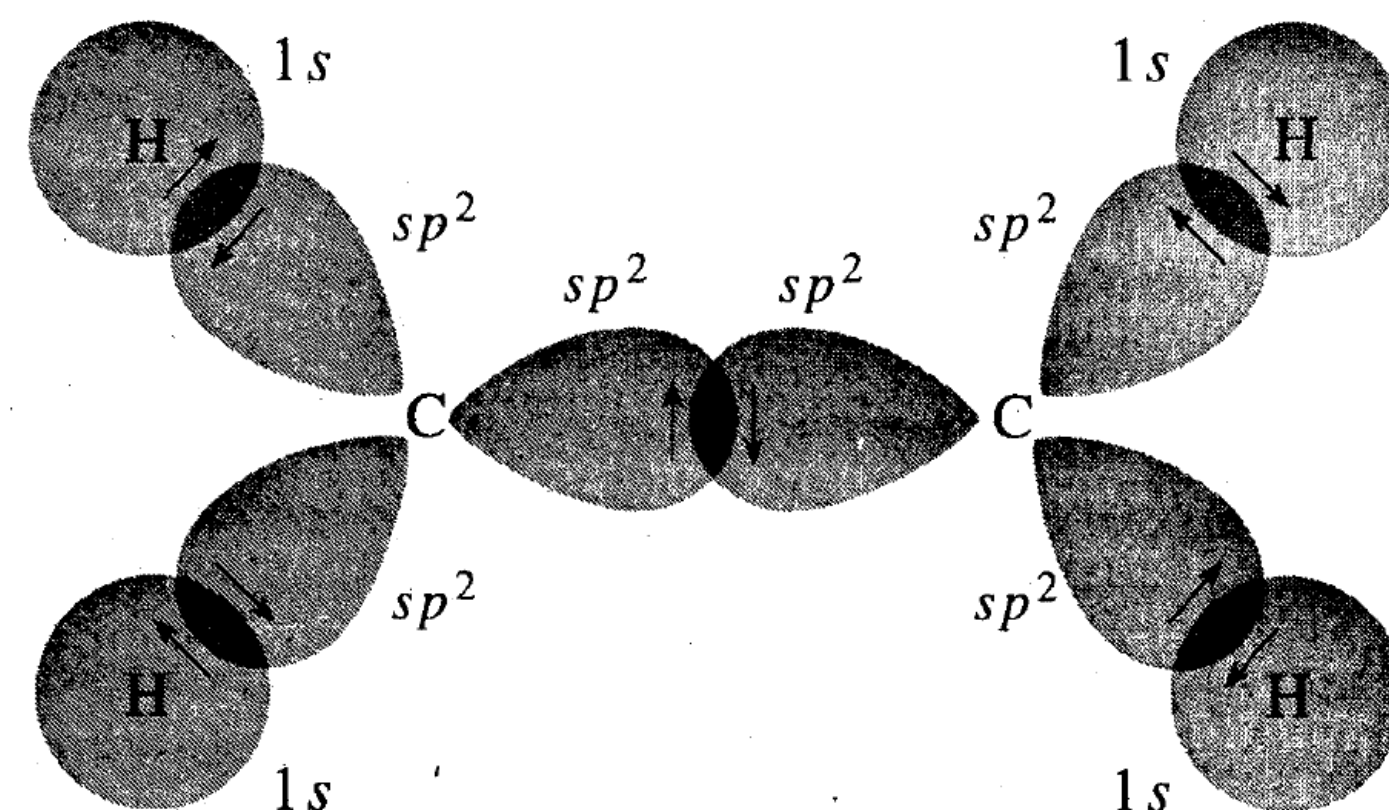
σ bonds are relatively more localized between nucleui, than π bonds. Therefore, we ignore *σ-bond framework*, and only consider π electrons. This is π-electron approximation.

For example, consider the simplest conjugated π system, ethylene. Only remaining π contribution is from two $2p_z$ orbitals.

$$\psi_\pi = c_1 2p_{zA} + c_2 2p_{zB}$$

π-electron approximation

We can calculate secular determinant associated with that wavefunction.

$$\psi_\pi = c_1 2p_{zA} + c_2 2p_{zB}$$

$$\begin{vmatrix} H_{11} - ES_{11} & H_{12} - ES_{12} \\ H_{12} - ES_{12} & H_{22} - ES_{12} \end{vmatrix} = 0$$

where H_{11} and H_{22} defined same as previous problem. They are called *Coulomb integral*.
The off-diagonal element of Hamiltonian, H_{12}, is called *exchange integral*.

Here, we examine an approximation proposed by Erich Hückel in 1930.

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Hückel approximation

There are three simple assertions of Hückel molecular orbital theory.

[1] Overlap integrals, $S_{ij} = \delta_{ij}$. i.e., ignore all overlaps between different atoms.

[2] All Coulomb integrals are assumed to be the same for all carbon atoms, $H_{11} = H_{22} = \alpha$.

[3] The exchange integrals involving nearest-neighbor carbon atoms are assumed to be the same, and are denoted by $H_{12} = \beta$. If two carbon are not adjacent, $H_{ij} = 0$.

$$\begin{vmatrix} \alpha - E & \beta \\ \beta & \alpha - E \end{vmatrix} = 0 \implies E = \alpha \pm \beta$$

Since α approximates the energy of an electron in an isolated $2p$ orbital, we use it as a reference of energy. Note that $\beta < 0$ in general. Therefore, ground state is $E = \alpha + \beta$.

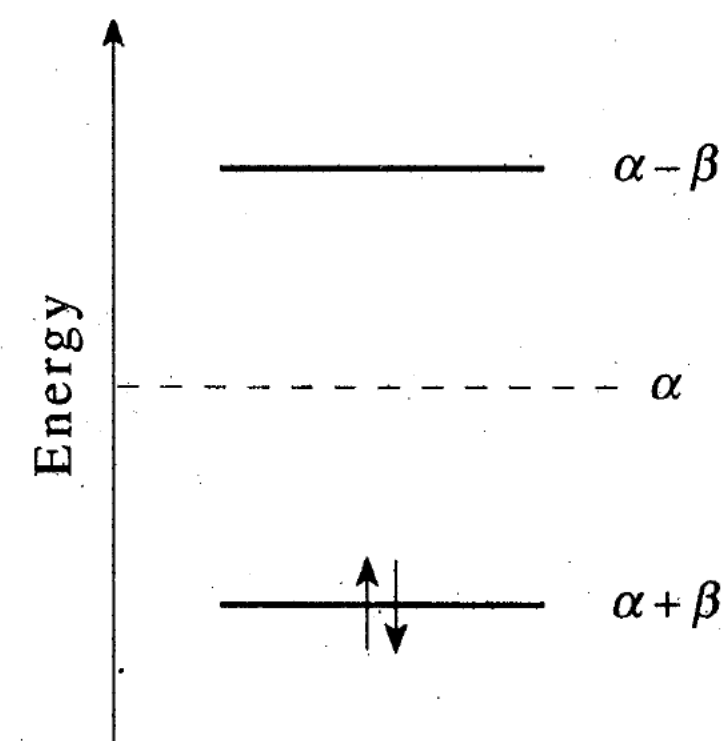# Hückel approximation

For ethylene,

FIGURE 10.20
The ground-state electron configuration of the π electrons in ethene.
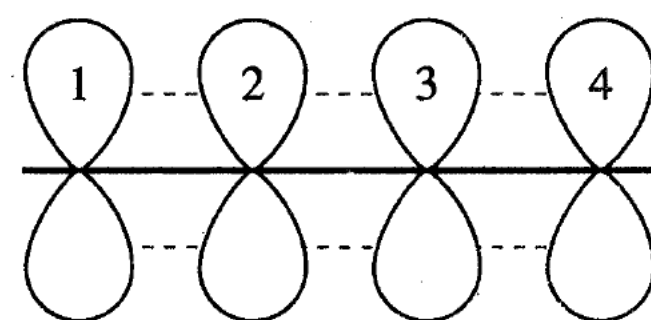
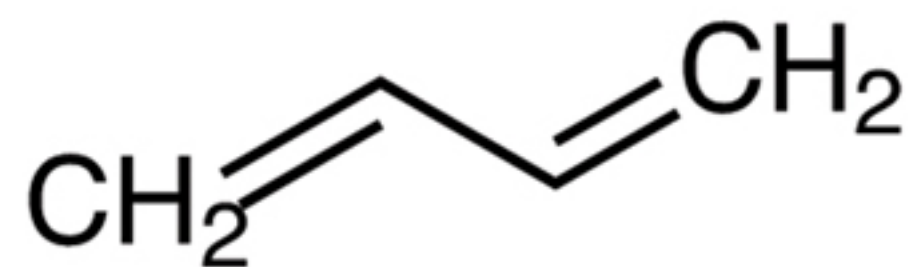We can do similar thing with butadiene molecule.

FIGURE 10.21
A schematic representation of the $2p_z$ orbitals of each of the carbon atoms in a butadiene molecule.

Hückel approximation

Write down the secular determinant.

$$\begin{vmatrix} \alpha - E & \beta & 0 & 0 \\ \beta & \alpha - E & \beta & 0 \\ 0 & \beta & \alpha - E & \beta \\ 0 & 0 & \beta & \alpha - E \end{vmatrix} = 0$$

By letting $x = (\alpha - E)/\beta$, we yield

$$\beta^4 \begin{vmatrix} x & 1 & 0 & 0 \\ 1 & x & 1 & 0 \\ 0 & 1 & x & 1 \\ 0 & 0 & 1 & x \end{vmatrix} = 0 \implies x = \pm 1.618, \pm 0.618$$
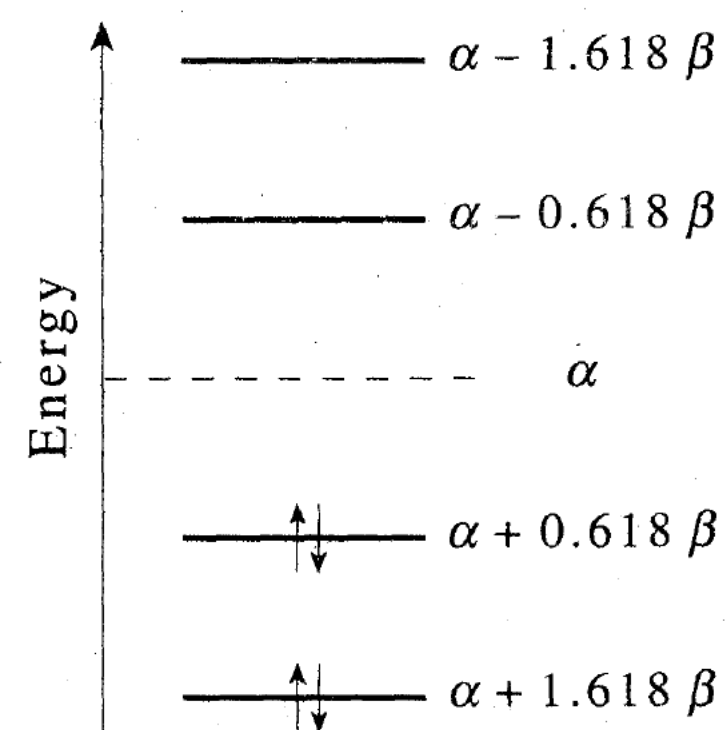

Energy

$\alpha - 1.618\,\beta$

$\alpha - 0.618\,\beta$

α

$\alpha + 0.618\,\beta$

$\alpha + 1.618\,\beta$

FIGURE 10.22
The ground-state electron configuration of the π electrons in butadiene.

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Delocalization energy

Since butadiene has four π electrons, total energy of π electrons is

$$E_\pi = 2(\alpha + 1.618\beta) + 2(\alpha + 0.618\beta) = 4\alpha + 4.472\beta$$

Compared to energy of two ethylene molecules ($2E = 4\alpha + 4\beta$), energy of butadiene is lower.

$$E_{\text{deloc}} = E_\pi(\text{butadiene}) - 2E_\pi(\text{ethylene}) = 0.472\beta < 0$$

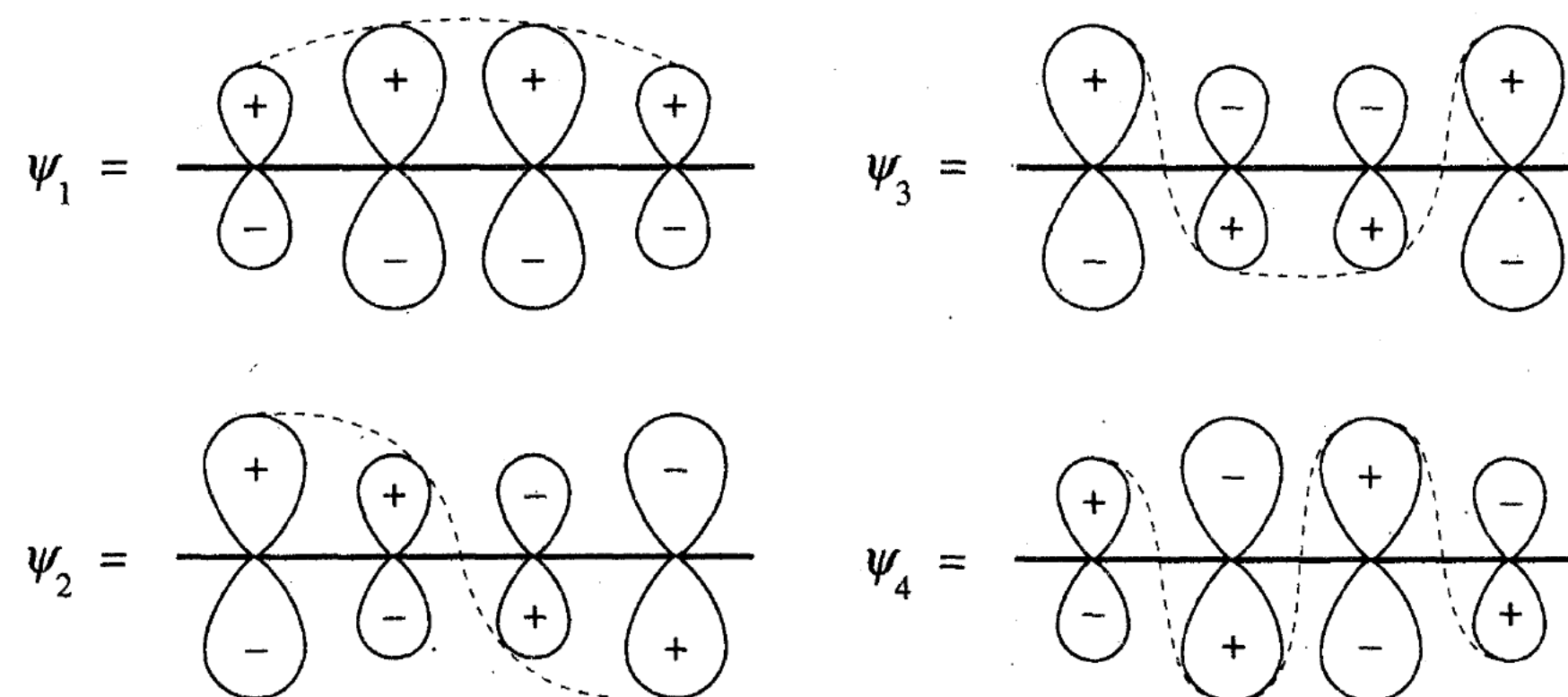This extra stabilization is called *delocalization energy*.

FIGURE 10.23
A schematic representation of the π molecular orbitals of butadiene. Note that the corresponding energy increases with the number of nodes.

Hückel approximation

You can do the same thing with benzene molecule.

$$\psi_1 = \frac{1}{\sqrt{6}}(2p_{z1} + 2p_{z2} + 2p_{z3} + 2p_{z4} + 2p_{z5} + 2p_{z6}) \qquad E_1 = \alpha + 2\beta$$

$$\psi_2 = \frac{1}{\sqrt{4}}(2p_{z2} + 2p_{z3} - 2p_{z5} - 2p_{z6}) \qquad E_2 = \alpha + \beta$$

$$\psi_3 = \frac{1}{\sqrt{3}}(2p_{z1} + \tfrac{1}{2}2p_{z2} - \tfrac{1}{2}2p_{z3} - 2p_{z4} - \tfrac{1}{2}2p_{z5} + \tfrac{1}{2}2p_{z6}) \qquad E_3 = \alpha + \beta$$

$$\psi_4 = \frac{1}{\sqrt{4}}(2p_{z2} - 2p_{z3} + 2p_{z5} - 2p_{z6}) \qquad E_4 = \alpha - \beta$$

$$\psi_5 = \frac{1}{\sqrt{3}}(2p_{z1} - \tfrac{1}{2}2p_{z2} - \tfrac{1}{2}2p_{z3} + 2p_{z4} - \tfrac{1}{2}2p_{z5} - \tfrac{1}{2}2p_{z6}) \qquad E_5 = \alpha - \beta$$

$$\psi_6 = \frac{1}{\sqrt{6}}(2p_{z1} - 2p_{z2} + 2p_{z3} - 2p_{z4} + 2p_{z5} - 2p_{z6}) \qquad E_6 = \alpha - 2\beta$$
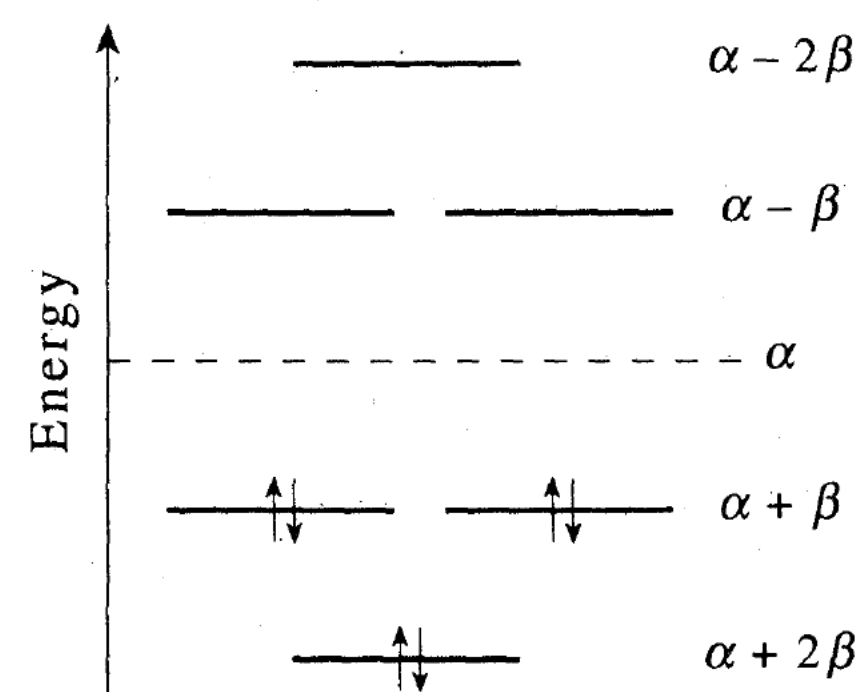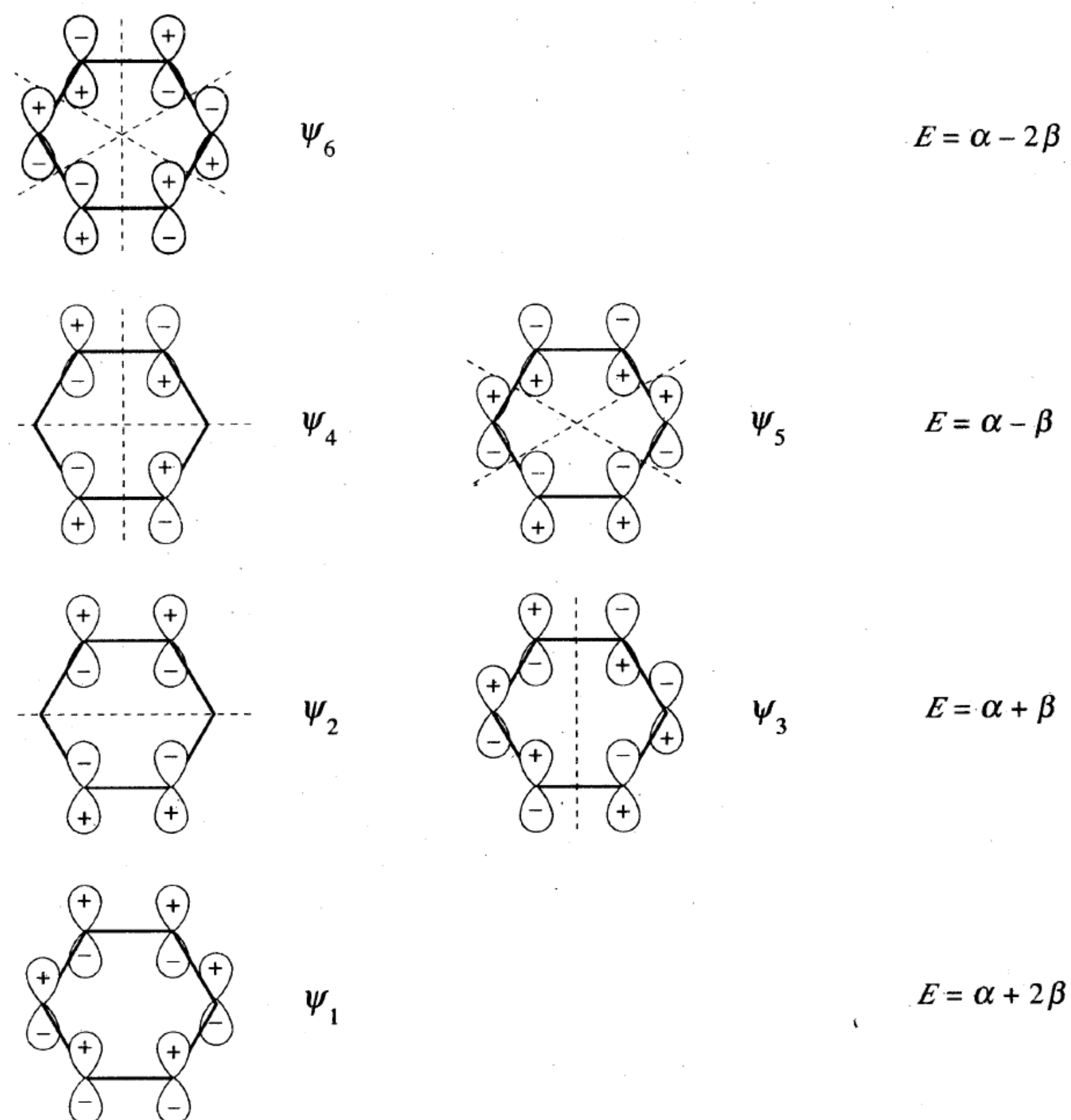
(10.31)

FIGURE 10.24
The ground-state electron configuration of the π electrons in benzene.

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Group theory

For the small molecules, considering symmetry can help you solving electronic problems.

If you are interested in symmetry and its interesting consequences, attend *Inorganic Chemistry 1 & 2* courses.

This is the end of **SNU CNS summer major school 2021, Physical Chemistry 2 course**.

Stay safe at home, wash your hands, and avoid social contacts.

I hope this course can help you in your fall semester.

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