

Lecture 4. Molecular Orbital Theory

Physical Chemistry 1, Winter 2022

Department of Chemistry

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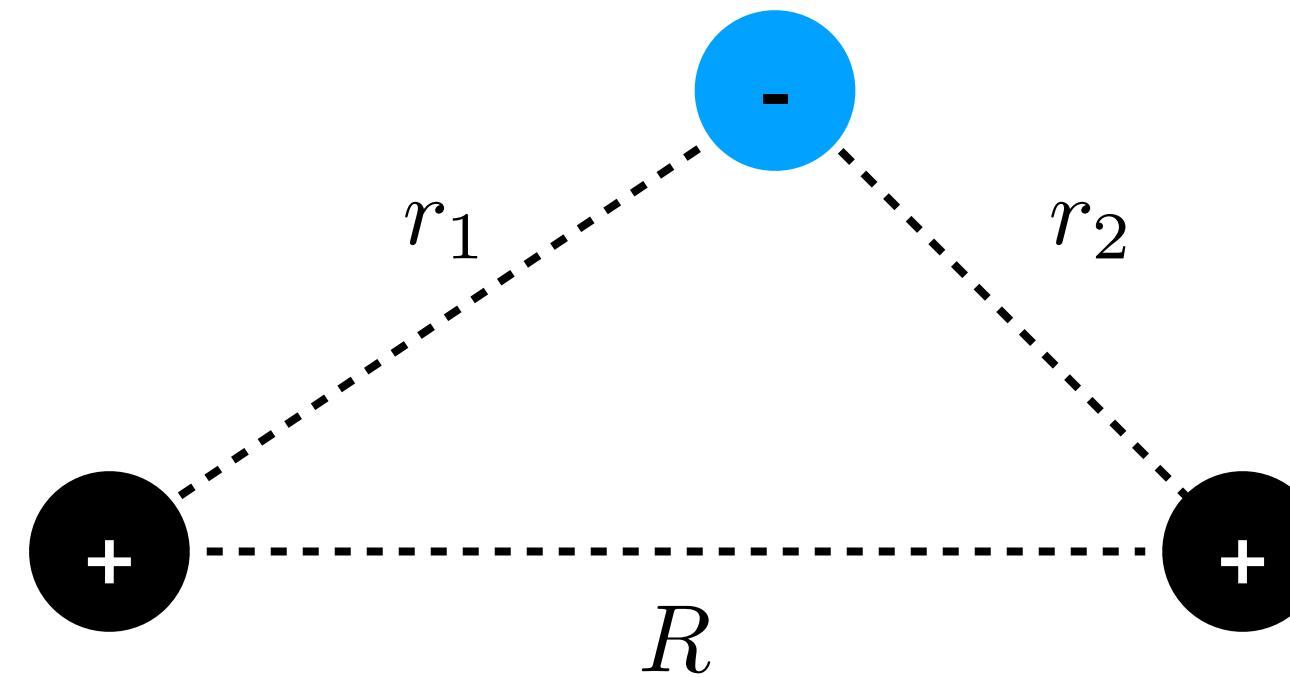
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Simplest molecule

... is a H_2^+ ion. This ion have two protons (nuclei) and one electron. Therefore, Hamiltonian of this molecular ion in atomic unit is

$$\hat{H} = -\frac{1}{2}\nabla^2 - \frac{1}{r_1} - \frac{1}{r_2} + \frac{1}{R}$$

Q. What is the appropriate wavefunction for this system? What would be the appropriate approximation?



LCAO-MO

The answer is **LCAO-MO**, which is an abbreviation of

Linear Combination Atomic Orbital-Molecular Orbital

Let's denote two hydrogen nuclei as hydrogen A and B. Then linear combination of AOs, 1s orbital here, is

$$\psi = c_1 1s_A + c_2 1s_B$$

Note that (1) this wavefunction is not normalized yet, and (2) since two hydrogen nuclei are indistinguishable, magnitude of c_1 and c_2 should be identical. In other words,

$$\psi_{\pm} = 1s_A \pm 1s_B$$

LCAO-MO

Energy: $\hat{H}\psi_+ = E_+\psi_+$, so (note that the normalization factor is in the denominator)

$$E_+ = \frac{\int \psi_+^* \hat{H} \psi_+ d\tau}{\int \psi_+^* \psi_+ d\tau}$$

$$\begin{aligned} \int \psi_+^* \psi_+ d\tau &= \int d\tau (1s_A^* + 1s_B^*)(1s_A + 1s_B) \\ &= \int d\tau (1s_A^* 1s_A + 1s_A^* 1s_B + 1s_B^* 1s_A + 1s_B^* 1s_B) \\ &= 1 + S + S + 1 = 2 + 2S \text{ where } S = \int d\tau 1s_A^* 1s_B = \int d\tau 1s_B^* 1s_A \end{aligned}$$

S is called an **overlap integral**, which measures the degree of overlap between two orbitals.

LCAO-MO

$$\begin{aligned}\int \psi_+^* \hat{H} \psi_+ d\tau &= \int d\tau (1s_A^* + 1s_B^*) \left(-\frac{1}{2} \nabla^2 - \frac{1}{r_A} - \frac{1}{r_B} + \frac{1}{R} \right) (1s_A + 1s_B) \\ &= \int d\tau (1s_A^* + 1s_B^*) \left(-\frac{1}{2} \nabla^2 - \frac{1}{r_A} - \frac{1}{r_B} + \frac{1}{R} \right) 1s_A + \int d\tau (1s_A^* + 1s_B^*) \left(-\frac{1}{2} \nabla^2 - \frac{1}{r_A} - \frac{1}{r_B} + \frac{1}{R} \right) 1s_B\end{aligned}$$

Note that each atomic orbitals should satisfy

$$\left(-\frac{1}{2} \nabla^2 - \frac{1}{r_A} \right) 1s_A = E_{1s} 1s_A, \quad \left(-\frac{1}{2} \nabla^2 - \frac{1}{r_B} \right) 1s_B = E_{1s} 1s_B$$

Therefore

$$\int \psi_+^* \hat{H} \psi_+ d\tau = \int d\tau (1s_A^* + 1s_B^*) \left(E_{1s} - \frac{1}{r_B} + \frac{1}{R} \right) 1s_A + \int d\tau (1s_A^* + 1s_B^*) \left(E_{1s} - \frac{1}{r_A} + \frac{1}{R} \right) 1s_B$$

LCAO-MO

Separate terms involving E_{1s} :

$$\begin{aligned} \int \psi_+^* \hat{H} \psi_+ d\tau &= 2E_{1s}(1 + S) + \int d\tau 1s_A^* \left(-\frac{1}{r_B} + \frac{1}{R} \right) 1s_A + \int d\tau 1s_B^* \left(-\frac{1}{r_B} + \frac{1}{R} \right) 1s_A \\ &\quad + \int d\tau 1s_A^* \left(-\frac{1}{r_A} + \frac{1}{R} \right) 1s_B + \int d\tau 1s_B^* \left(-\frac{1}{r_A} + \frac{1}{R} \right) 1s_B \end{aligned}$$

Define two terms called **Coulomb integral** and **Exchange integral**.

$$\begin{aligned} J &= \int d\tau 1s_A^* \left(-\frac{1}{r_B} + \frac{1}{R} \right) 1s_A = - \int d\tau \frac{1s_A^* 1s_A}{r_B} + \frac{1}{R} \\ K &= \int d\tau 1s_B^* \left(-\frac{1}{r_B} + \frac{1}{R} \right) 1s_A = - \int d\tau \frac{1s_B^* 1s_A}{r_B} + \frac{S}{R} \end{aligned}$$

LCAO-MO

Then

$$\int d\tau \psi_+^* \hat{H} \psi_+ = 2E_{1s}(1 + S) + 2J + 2K$$

$$\int d\tau \psi_+^* \psi_+ = 2(1 + S)$$

Note. The Coulomb integral, J , has classical analogue. This represents the electron-electron repulsion energy and its value is always positive (energetically not favorable).

However, K has no classical analogue: we just ran into it while collecting terms. This term takes critical role in *chemical bond formation*, and it is purely quantum-mechanical. In other words, to describe the nature of chemical bond, quantum mechanics is unavoidable.

LCAO-MO

ΔE represents the energy of H_2^+ ion relative to the completely dissociated species.

$$\Delta E_+ = E_+ - E_{1s} = \frac{J + K}{1 + S}$$

where S, J, K has following form (it can be computed in *elliptical coordinates*)

$$S(R) = e^{-R} \left(1 + R + \frac{R^2}{3} \right), \quad J(R) = e^{-2R} \left(1 + \frac{1}{R} \right), \quad K(R) = \frac{S}{R} - e^{-R}(1 + R)$$

One can repeat this whole process for $\psi_- = 1s_A - 1s_B$. Then

$$\Delta E_- = E_- - E_{1s} = \frac{J - K}{1 - S}$$

Bonding and antibonding orbitals

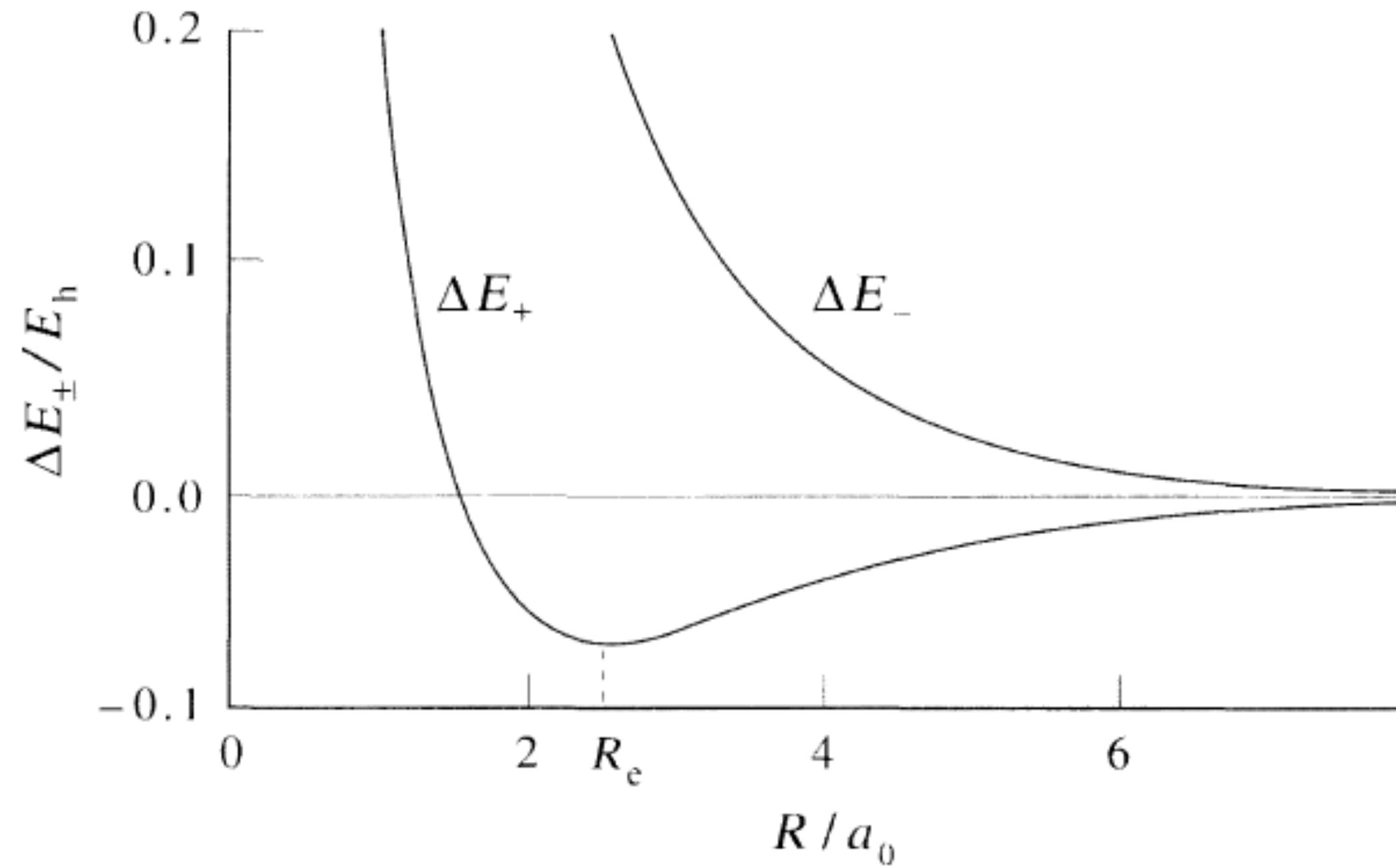


FIGURE 9.6

The energies $\Delta E_+ = E_+ - E_{1s}$ and $\Delta E_- = E_- - E_{1s}$ corresponding to the ψ_+ and ψ_- molecular orbital wave functions given in Equation 9.6 (with $c_1 = c_2$) plotted as a function of intermolecular separation R for H_2^+ . The plot shows that ψ_+ leads to a bonding molecular orbital whereas ψ_- leads to an antibonding molecular orbital.

Chemical bonding is purely QM phenomenon

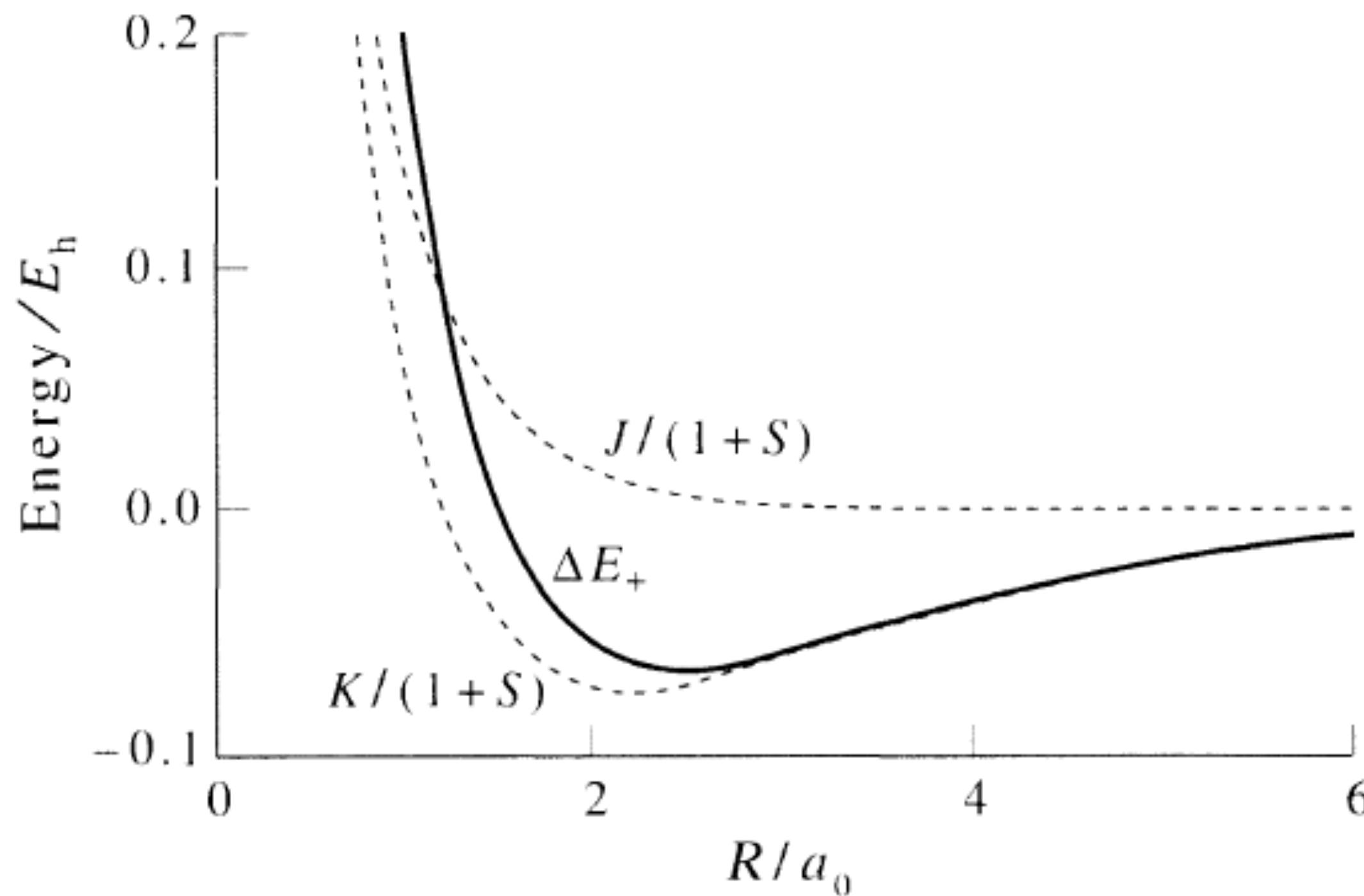


FIGURE 9.7

The separate contributions of the Coulomb integral, J , and the exchange integral, K , to the stability of H_2^+ .

LCAO-MO

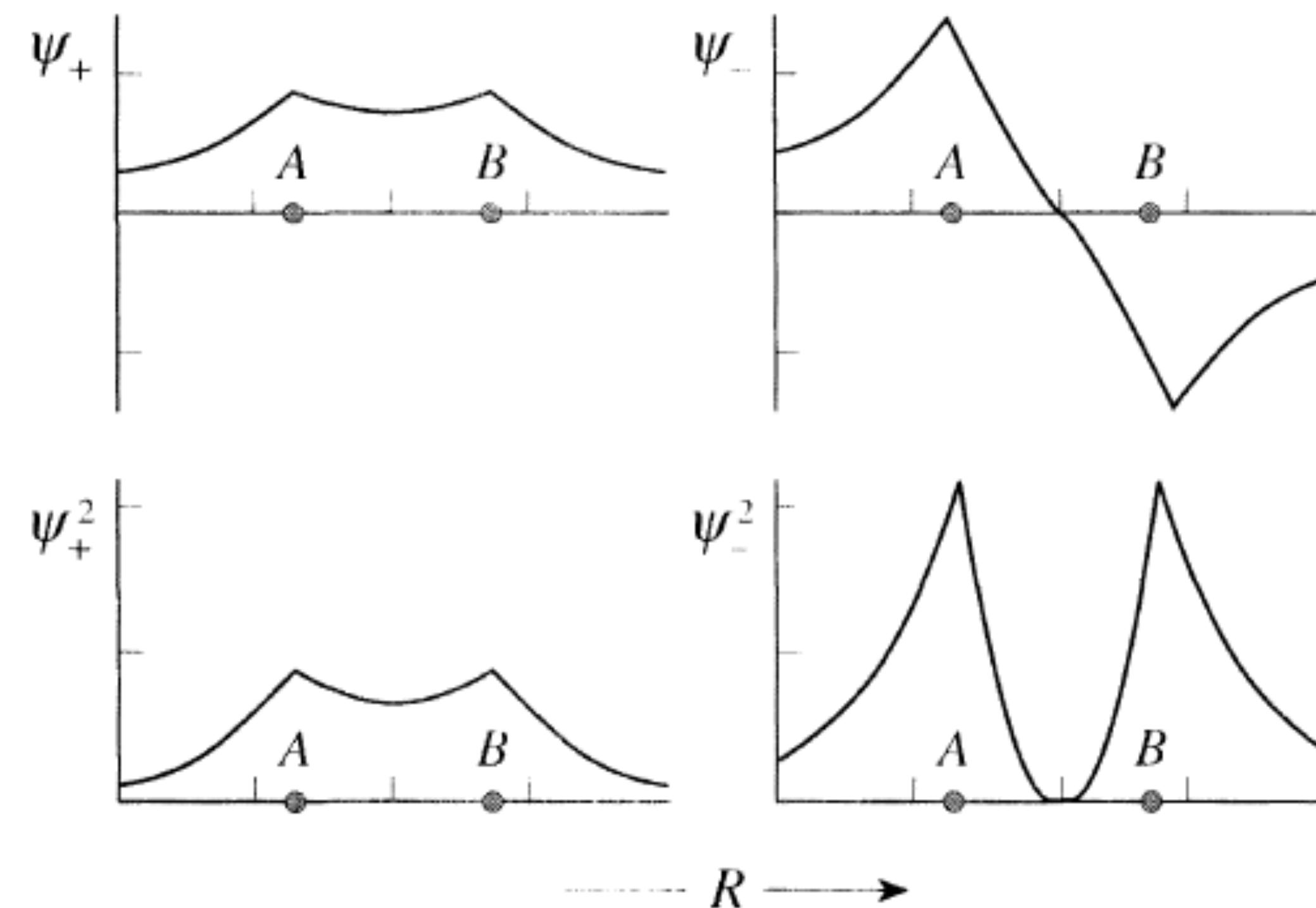


FIGURE 9.8

The molecular orbitals ψ_+ (bonding) and ψ_- (antibonding) and their squares are plotted along the internuclear axis.

LCAO-MO

For H_2^+ ion, using two 1s orbitals are sufficient. In case of more complicate molecules with more electrons, one can use more flexible *trial function*, such as

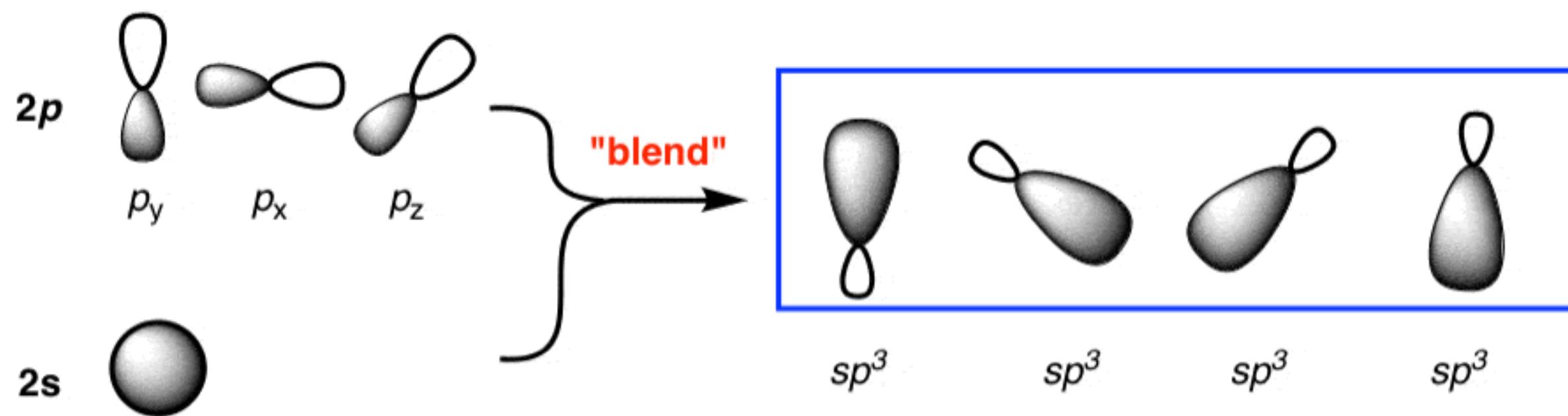
$$\psi = c_1 1s_A + c_2 1s_B + c_3 2s_A + c_4 2s_B + c_5 2p_{zA} + c_6 2p_{zB} + \dots$$

Frequently misunderstood concepts

Do you remember *hybrid orbitals*?

One answer to the question: **sp^3 "Hybrid" Orbitals**

Three 2p orbitals and a single 2s orbital "hybridize" (blend) to make four identical sp^3 "hybrid" orbitals



4 unhybridized orbitals (2s, 2p_x, 2p_y, 2p_z)

Three higher-energy 2p orbitals and one lower-energy 2s orbital

Linus Pauling "The Nature of The Chemical Bond" (1931)

4 hybridized sp^3 orbitals

Four sp^3 hybrid orbitals of identical energy which each have 25% s character and 75% p character

Oriented at 109.5° relative to each other

Frequently misunderstood concepts

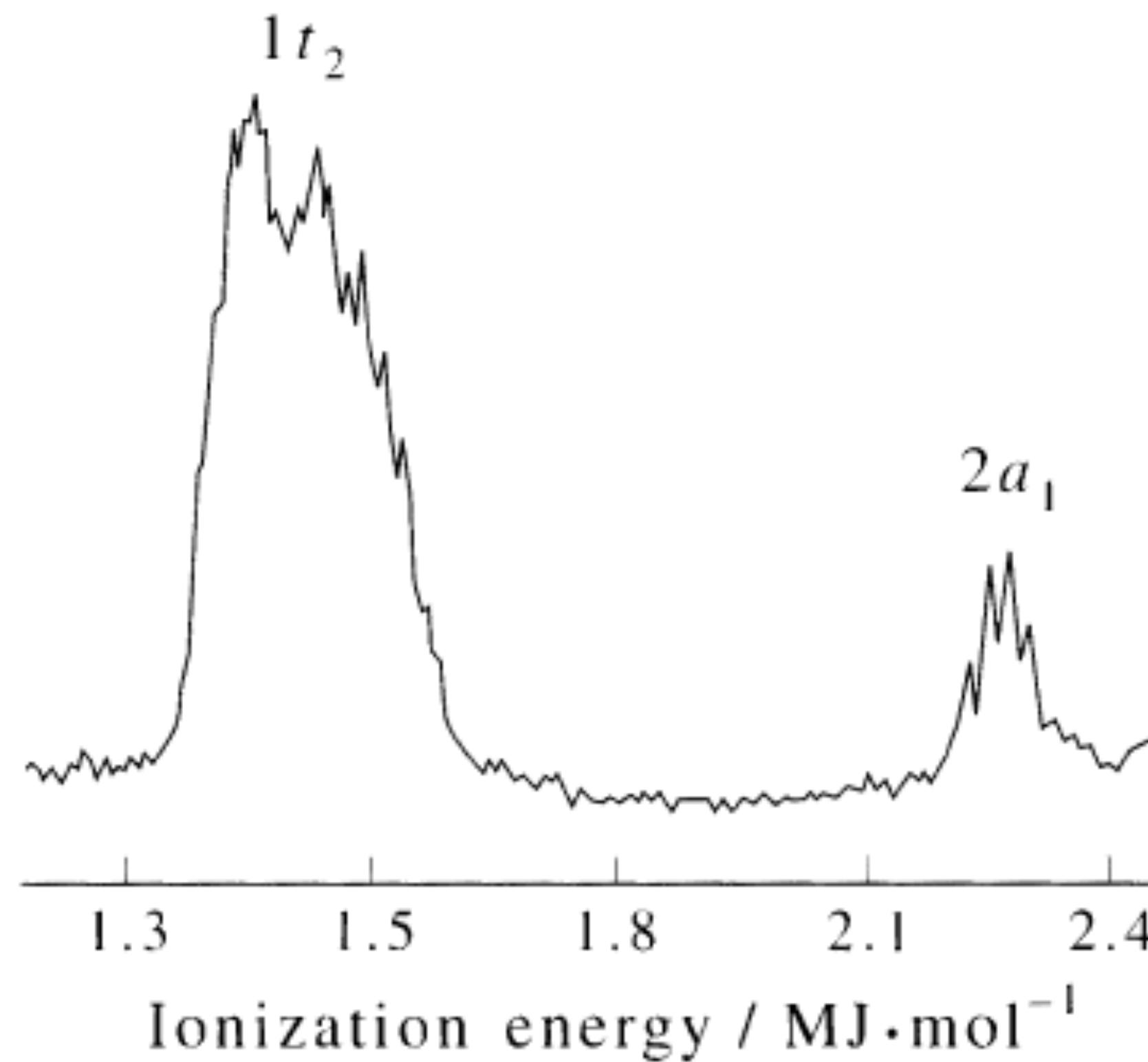


FIGURE 10.16

The photoelectron spectrum of methane. The two bands 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 bands corresponds to the energy difference between the $1t_2$ and $2a_1$ molecular orbitals (see Figure 10.15). The bands are broad because ionization occurs to many different vibrational levels of the molecules.

Frequently misunderstood concepts

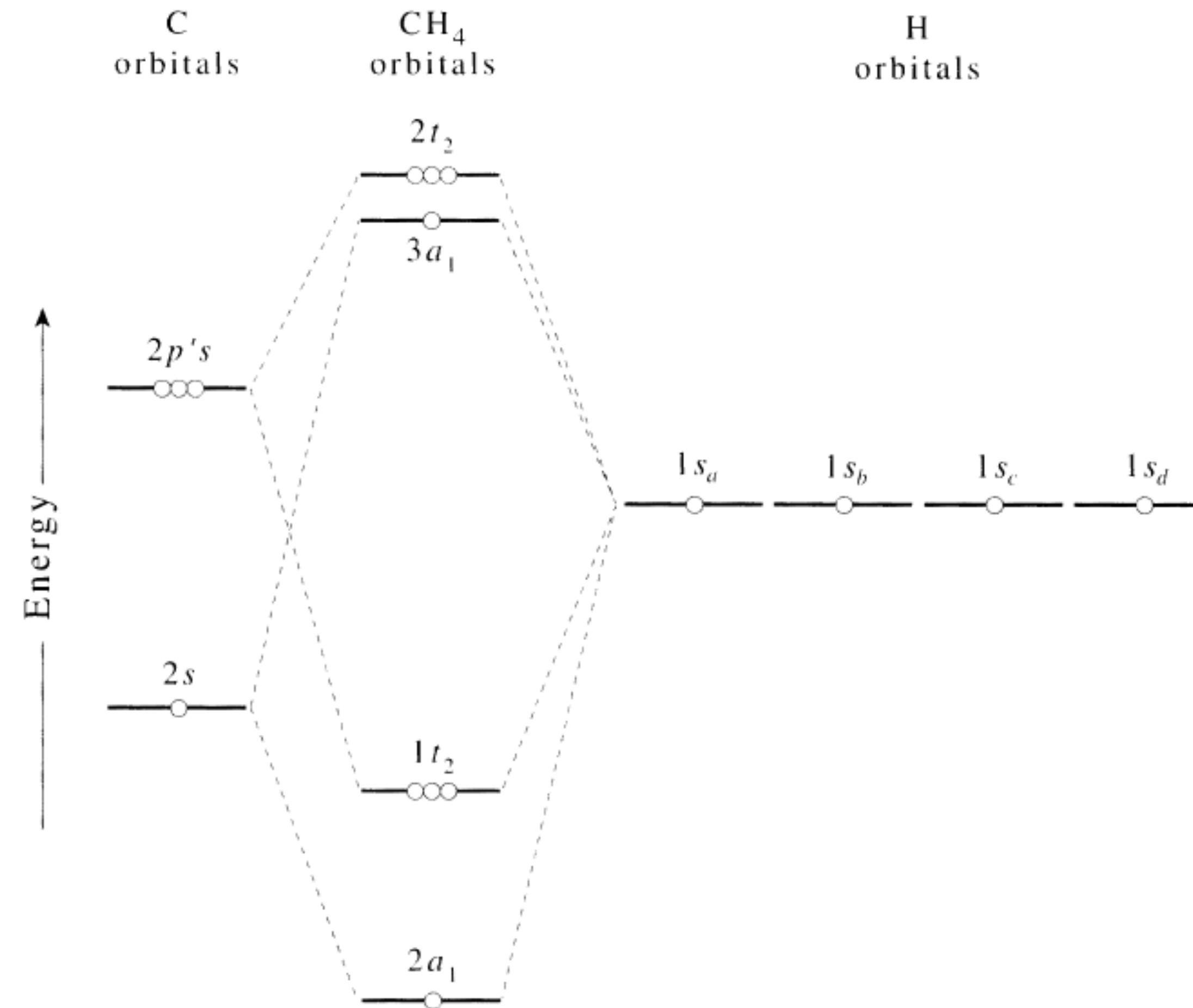
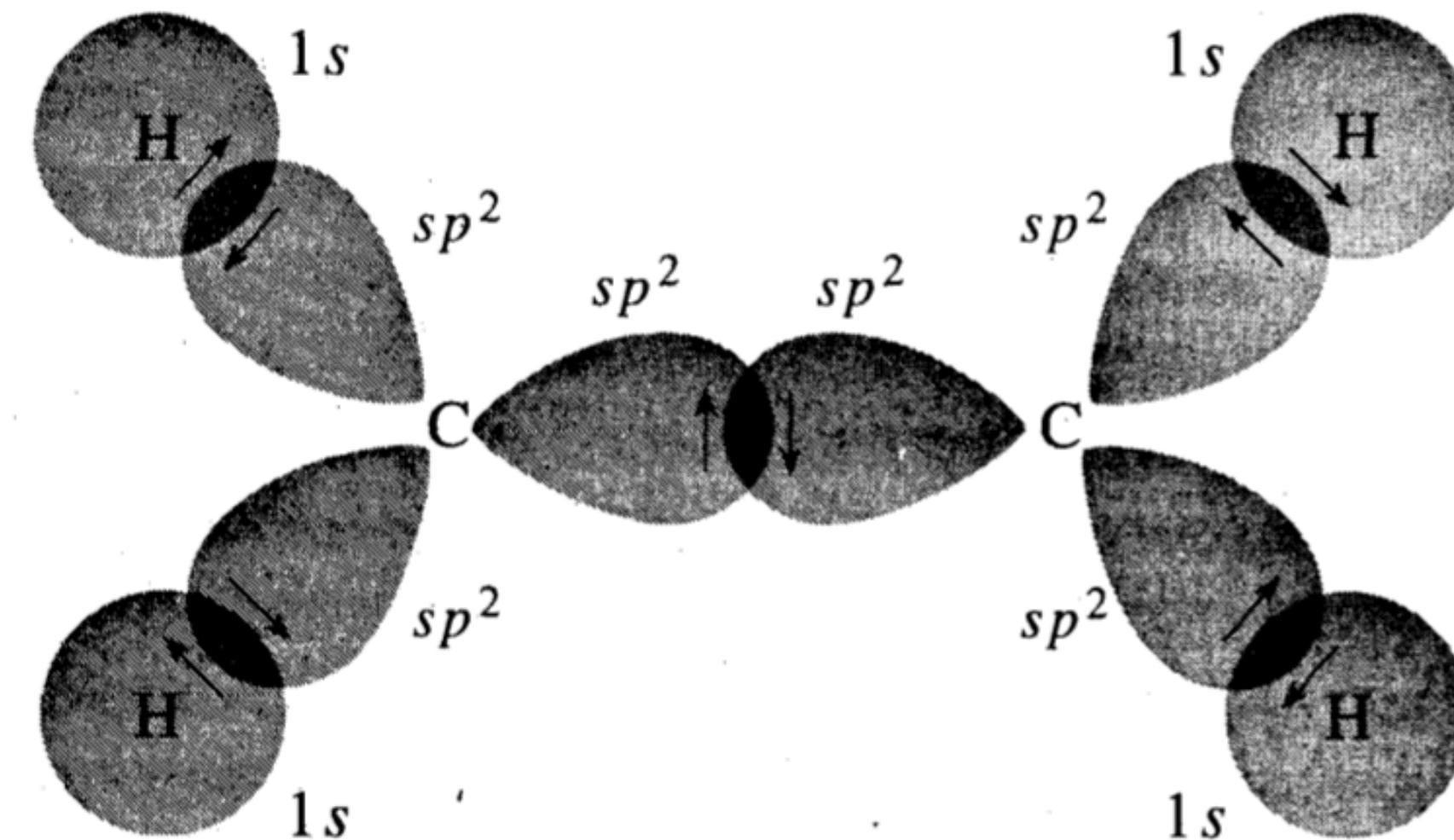


FIGURE 10.15
A molecular-orbital energy-level diagram for the valence electrons in CH_4 .

π -electron approximation

Molecules like *ethene* bears σ -bond framework and π electrons. The σ -bond framework is a (relatively) rigid, electrostatic charge distribution in fixed location. We may consider π electrons moving in the field generated by σ -bond framework. This is called the **π -electron approximation**.

This approximation is useful for conjugated π system.



Math: Variational theorem

Suppose that there is a Schrödinger equation whose solution is unknown, and let ϕ be our approximation to the solution. In other words, ϕ is the guess, and not a true solution of this Schrödinger equation.

$$\hat{H}\psi_n = E_n\psi_n$$

Even though this is not a solution, but we can pretend to calculate energy eigenvalue corresponding to this trial wavefunction.

$$E_\phi = \frac{\int \phi^* \hat{H} \phi d\tau}{\int \phi^* \phi d\tau}$$

The variational theorem states that (approximate) energy calculated in this way is always larger than the true ground state energy.

$$E_\phi \geq E_0$$

Math: Variational theorem

In other words, if our wavefunction were described by some parameters, minimizing the energy would result closer to the true wavefunction.

Consider the simplest trial function with two coefficients.

$$\phi = c_1 f_1 + c_2 f_2$$

Assume that coefficients and functions are all real. Then

$$\begin{aligned}\int \phi^* \hat{H} \phi \, d\tau &= \int (c_1 f_1 + c_2 f_2) \hat{H} (c_1 f_1 + c_2 f_2) \, d\tau \\ &= c_1^2 \int f_1 \hat{H} f_1 \, d\tau + c_2^2 \int f_2 \hat{H} f_2 \, d\tau + 2c_1 c_2 \int f_1 \hat{H} f_2 \, d\tau \\ &\equiv c_1^2 H_{11} + c_2^2 H_{22} + 2c_1 c_2 H_{12}\end{aligned}$$

Math: Variational theorem

Similarly

$$\begin{aligned}\int \phi^* \phi d\tau &= \int (c_1 f_1 + c_2 f_2)(c_1 f_1 + c_2 f_2) d\tau \\ &= c_1^2 \int f_1 f_1 d\tau + c_2^2 \int f_2 f_2 d\tau + 2c_1 c_2 \int f_1 f_2 d\tau \\ &\equiv c_1^2 S_{11} + c_2^2 S_{22} + 2c_1 c_2 S_{12}\end{aligned}$$

Therefore, energy parametrized by two parameters is

$$E(c_1, c_2) = \frac{c_1^2 H_{11} + c_2^2 H_{22} + 2c_1 c_2 H_{12}}{c_1^2 S_{11} + c_2^2 S_{22} + 2c_1 c_2 S_{12}} \text{ or } (c_1^2 S_{11} + c_2^2 S_{22} + 2c_1 c_2 S_{12}) E(c_1, c_2) = c_1^2 H_{11} + c_2^2 H_{22} + 2c_1 c_2 H_{12}$$

Math: Variational theorem

At minimum, energy should satisfy

$$\frac{\partial E}{\partial c_1} = 0, \quad \frac{\partial E}{\partial c_2} = 0$$

Differentiate both side with respect to c_1 . Then

$$(2c_1 S_{11} + 2c_2 S_{12})E + \cancel{\frac{\partial E}{\partial c_1}}(c_1^2 S_{11} + 2c_1 c_2 S_{12} + c_2^2 S_{22}) = 2c_1 H_{11} + 2c_2 H_{12}$$

$$c_1(H_{11} - ES_{11}) + c_2(H_{12} - ES_{12}) = 0$$

Similar for c_2 .

$$c_1(H_{12} - ES_{12}) + c_2(H_{22} - ES_{22}) = 0$$

Math: Variational theorem

We need *non-trivial* solution for this algebraic equation. Therefore, coefficients should satisfy

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

This is called a **secular determinant**. From here, energy eigenvalues (which are approximate) can be obtained.

If you use more functions, then you will get n by n determinant.

Hückel approximation

For ethene, π electrons are “stored” in two $2p_z$ orbitals of carbon atoms. Therefore, our *trial function* is

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

Calculate the secular determinant: and you get energy eigenvalues.

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

Question is, how can we evaluate H and S values?

Hückel approximation

Hückel approximation makes things simpler.

1. All H_{ii} has same value, $H_{ii} = \alpha$ (Coulomb integral).
2. H_{ij} is nonzero only when atom i and j are adjacent. In that case, $H_{ij} = \beta$ (resonance or exchange integral)
3. Overlap integral $S_{ij} = \delta_{ij}$.

In case of ethene,

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

Note that $\beta < 0$.

Hückel approximation

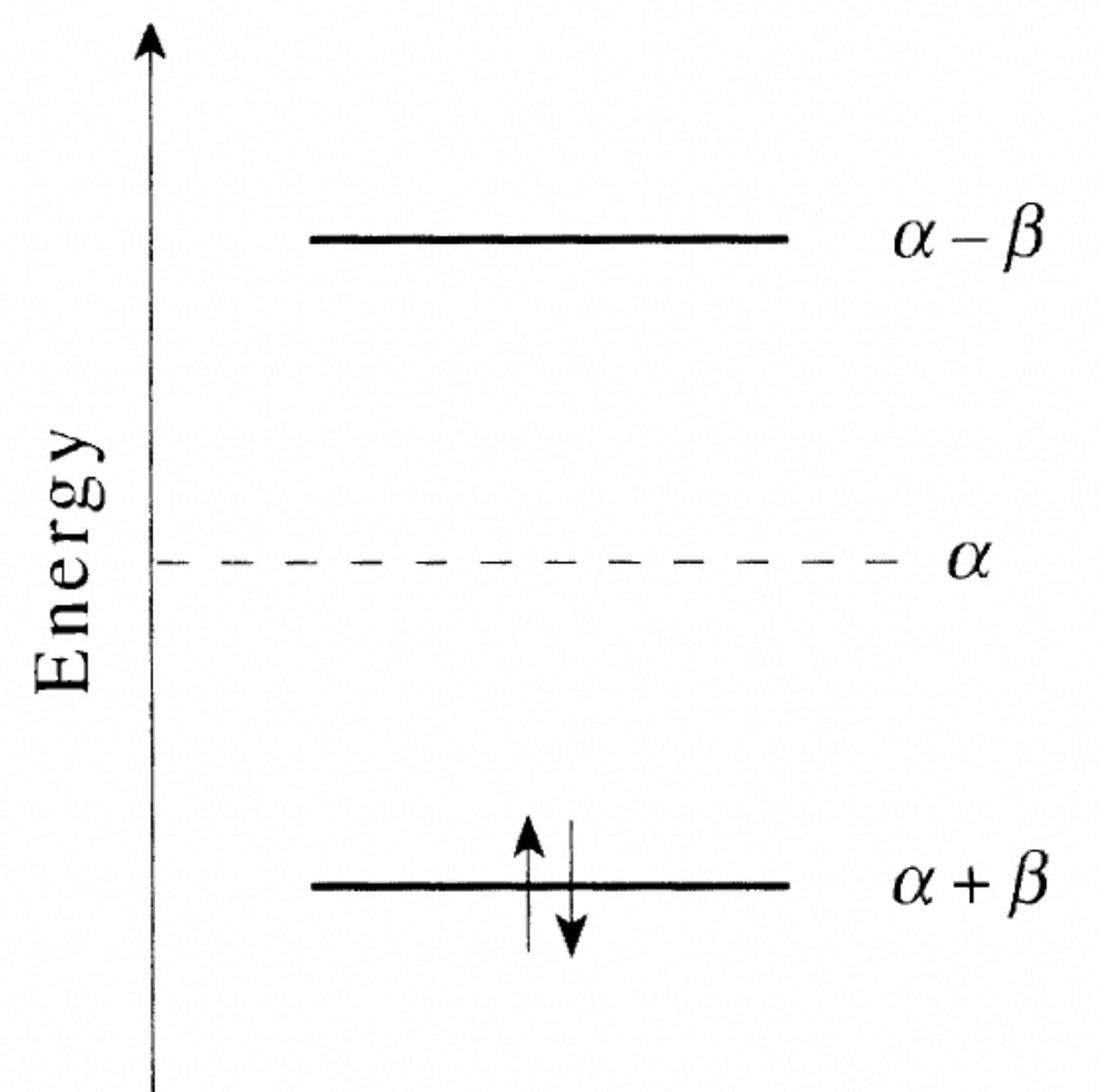


FIGURE 10.20

The ground-state electron configuration of the π electrons in ethene.

Hückel approximation

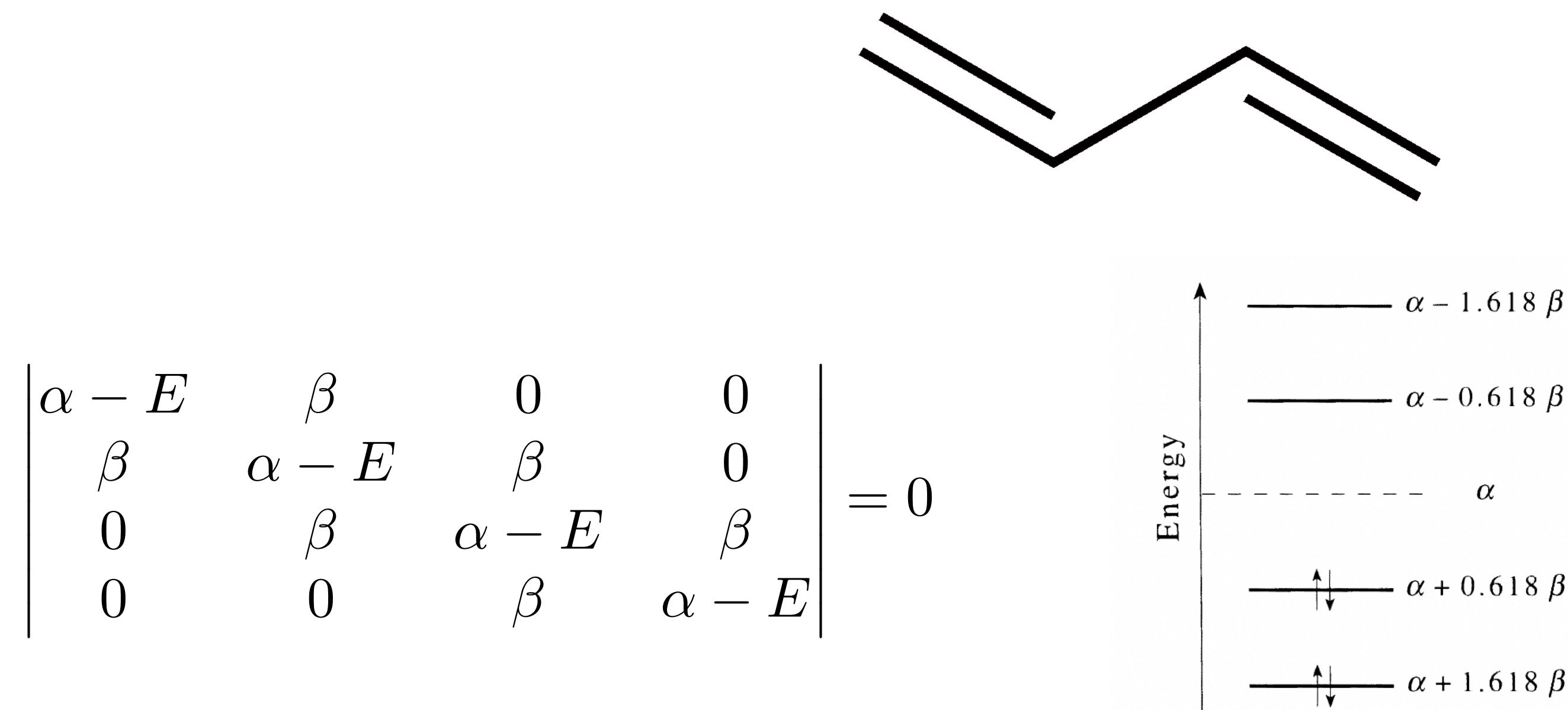


FIGURE 10.22

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

Delocalization energy: stabilization energy from the pi conjugation

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

Hückel approximation

Coefficients can be calculated from the obtained energy values.

$$\psi_1 = 0.3717 \cdot 2p_{z1} + 0.6015 \cdot 2p_{z2} + 0.6015 \cdot 2p_{z3} + 0.3717 \cdot 2p_{z4}$$

$$E_1 = \alpha + 1.618\beta$$

$$\psi_2 = 0.6015 \cdot 2p_{z1} + 0.3717 \cdot 2p_{z2} - 0.3717 \cdot 2p_{z3} - 0.6015 \cdot 2p_{z4}$$

$$E_2 = \alpha + 0.618\beta$$

(10.26)

$$\psi_3 = 0.6015 \cdot 2p_{z1} - 0.3717 \cdot 2p_{z2} - 0.3717 \cdot 2p_{z3} + 0.6015 \cdot 2p_{z4}$$

$$E_3 = \alpha - 0.618\beta$$

$$\psi_4 = 0.3717 \cdot 2p_{z1} - 0.6015 \cdot 2p_{z2} + 0.6015 \cdot 2p_{z3} - 0.3717 \cdot 2p_{z4}$$

$$E_4 = \alpha - 1.618\beta$$

Hückel approximation

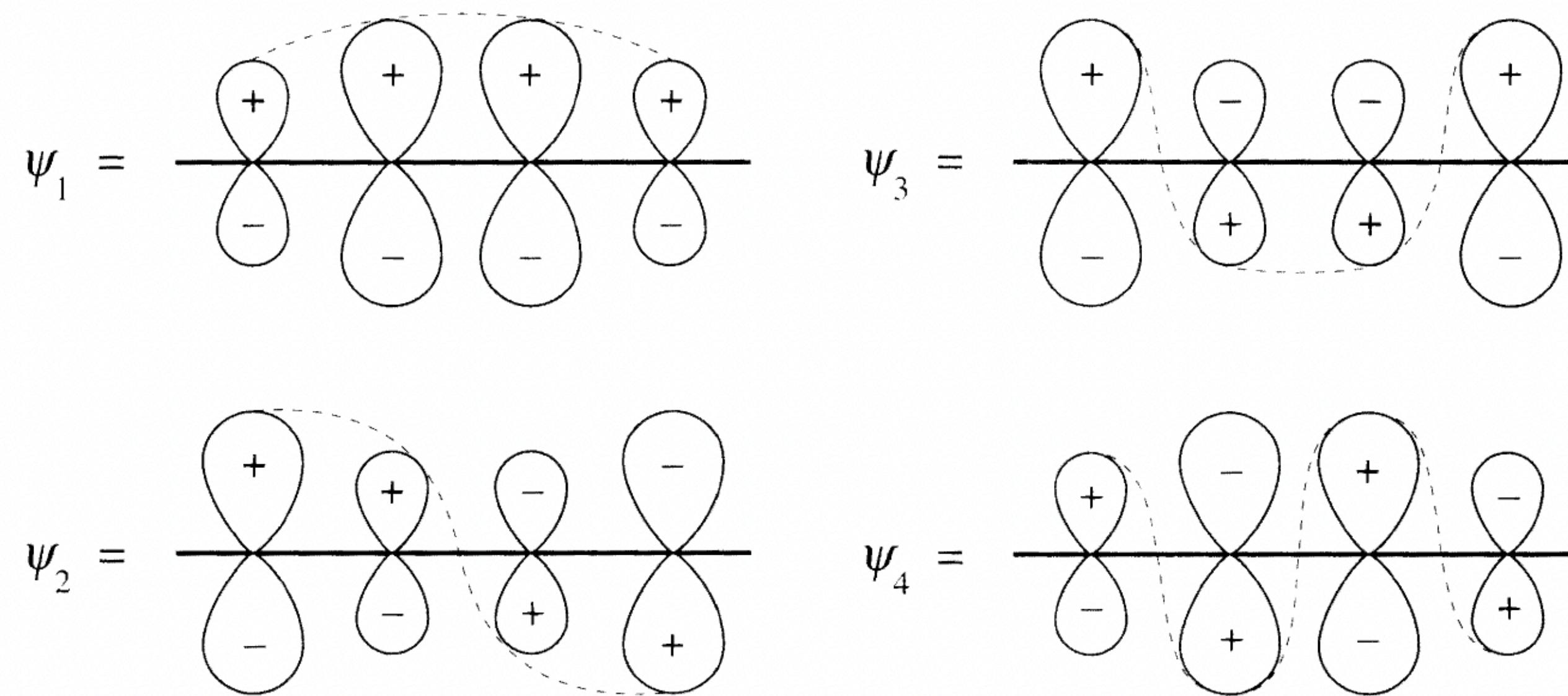


FIGURE 10.23

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

Hückel approximation

Benzene?

$$\begin{vmatrix} \alpha - E & \beta & 0 & 0 & 0 & \beta \\ \beta & \alpha - E & \beta & 0 & 0 & 0 \\ 0 & \beta & \alpha - E & \beta & 0 & 0 \\ 0 & 0 & \beta & \alpha - E & \beta & 0 \\ 0 & 0 & 0 & \beta & \alpha - E & \beta \\ \beta & 0 & 0 & 0 & \beta & \alpha - E \end{vmatrix} = 0 \quad (10.27)$$

$$\begin{aligned} \psi_1 &= \frac{1}{\sqrt{6}}(2p_{z1} + 2p_{z2} + 2p_{z3} + 2p_{z4} + 2p_{z5} + 2p_{z6}) & E_1 &= \alpha + 2\beta \\ \psi_2 &= \frac{1}{\sqrt{4}}(2p_{z2} + 2p_{z3} - 2p_{z5} - 2p_{z6}) & E_2 &= \alpha + \beta \\ \psi_3 &= \frac{1}{\sqrt{3}}(2p_{z1} + \frac{1}{2}2p_{z2} - \frac{1}{2}2p_{z3} - 2p_{z4} - \frac{1}{2}2p_{z5} + \frac{1}{2}2p_{z6}) & E_3 &= \alpha + \beta \\ \psi_4 &= \frac{1}{\sqrt{4}}(2p_{z2} - 2p_{z3} + 2p_{z5} - 2p_{z6}) & E_4 &= \alpha - \beta \\ \psi_5 &= \frac{1}{\sqrt{3}}(2p_{z1} - \frac{1}{2}2p_{z2} - \frac{1}{2}2p_{z3} + 2p_{z4} - \frac{1}{2}2p_{z5} - \frac{1}{2}2p_{z6}) & E_5 &= \alpha - \beta \\ \psi_6 &= \frac{1}{\sqrt{6}}(2p_{z1} - 2p_{z2} + 2p_{z3} - 2p_{z4} + 2p_{z5} - 2p_{z6}) & E_6 &= \alpha - 2\beta \end{aligned} \quad (10.31)$$

Hückel approximation

Benzene?

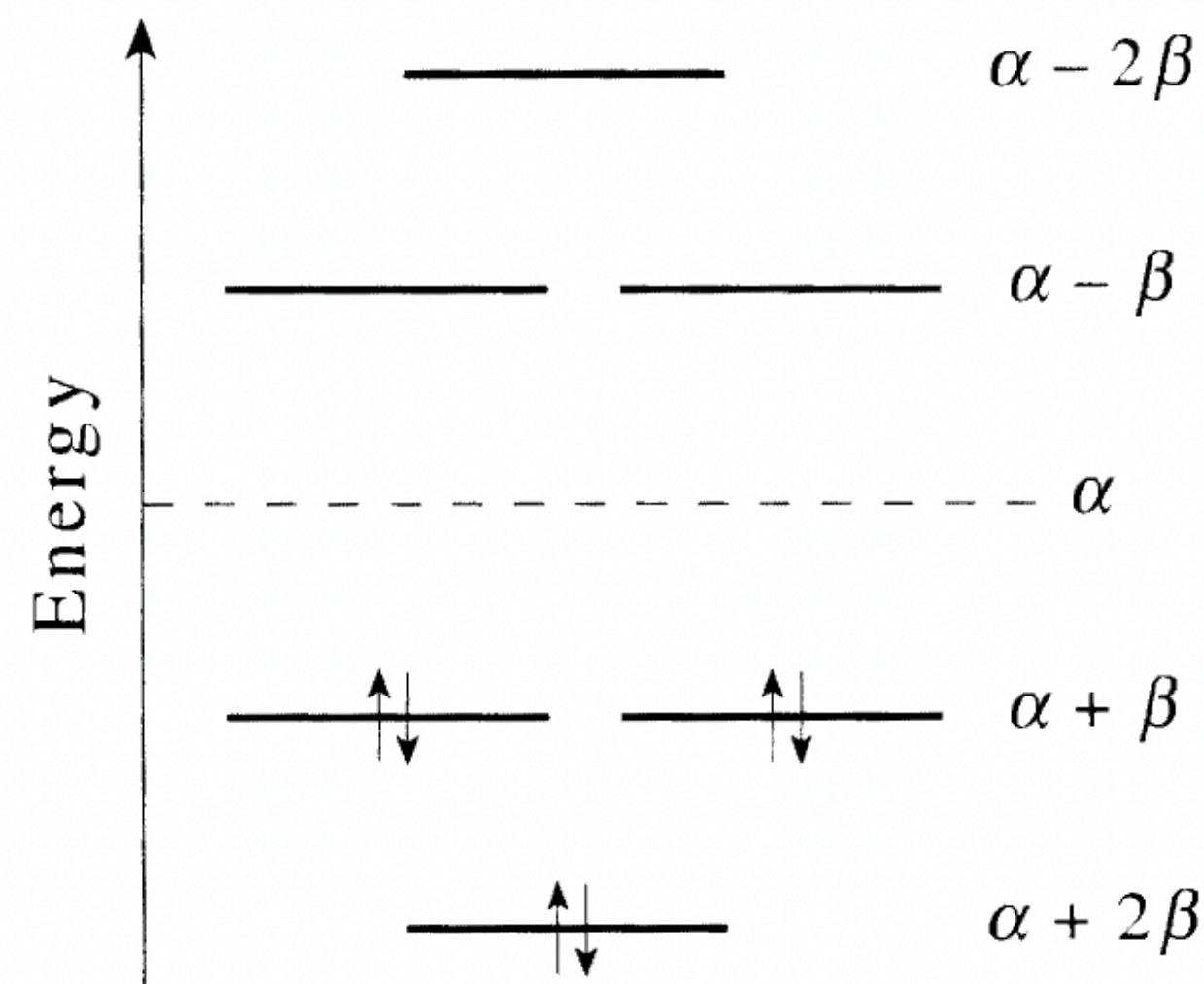
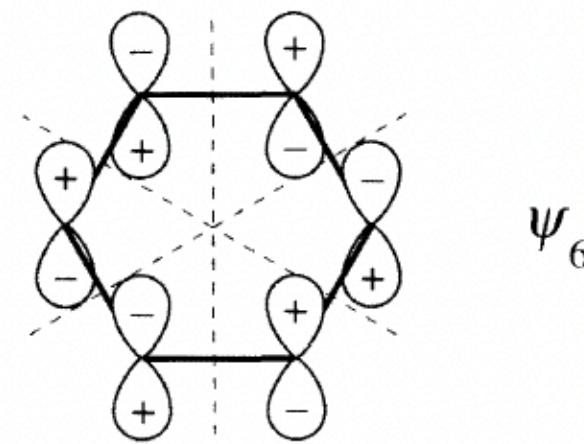


FIGURE 10.24

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

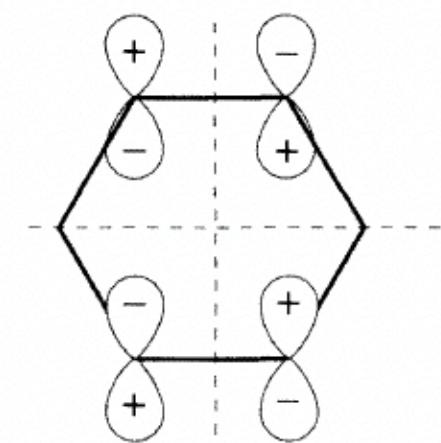
Hückel approximation

Benzene?

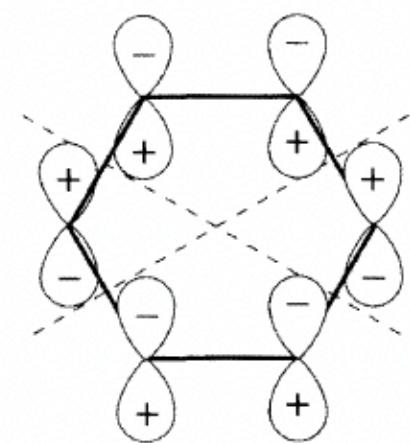


ψ_6

$$E = \alpha - 2\beta$$

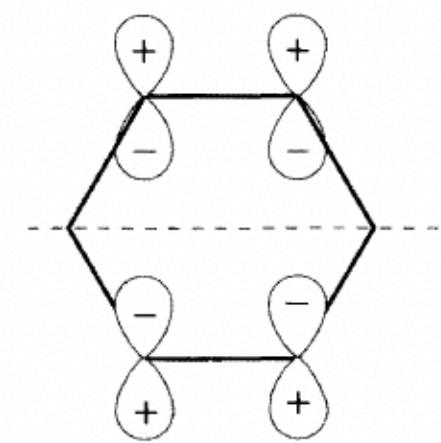


ψ_4

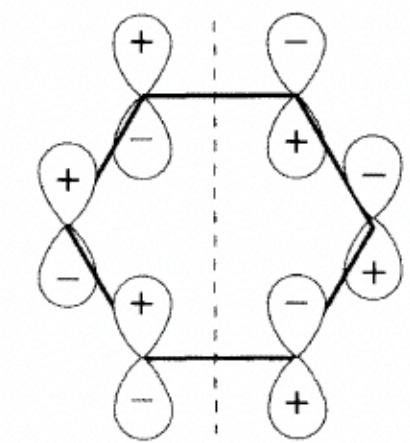


ψ_5

$$E = \alpha - \beta$$

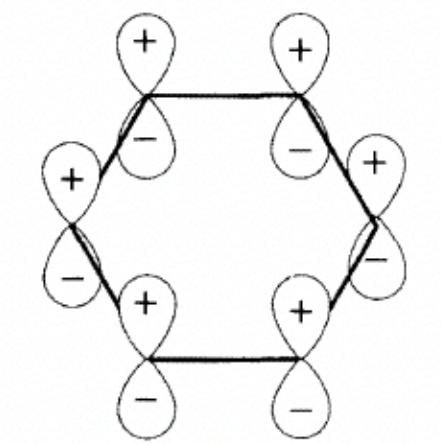


ψ_2



ψ_3

$$E = \alpha + \beta$$



ψ_1

$$E = \alpha + 2\beta$$