서울대학교

SEOUL NATIONAL UNIVERSITY

Department of Chemistry

PChem 2

Physical Chemistry 2

Jiho Son

Physical Chemistry 2

Lecture 11. Diatomic molecules

July 26th, 2021

paradichlorobenzene1724@gmail.com
kadryjh1724@snu.ac.kr

"Please, do not distribute this lecture note without permission!"

Topics in Lecture 11

Atomic unit

Born-Oppenheimer approximation

Valence bond theory

H_2^+ **molecule**

MO of homonuclear diatomic molecules

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

9A Valence bond theory
9B MOT: the hydrogen molecule-ion
9C MOT: homonuclear diatomic molecules

서울대학교
SEOUL NATIONAL UNIVERSITY

Department of Chemistry

PChem 2

Physical Chemistry 2

Jiho Son

Atomic units

Very convenient unit system for quantum-mechanical systems!

TABLE 8.1
Atomic units and their SI equivalents.

Property	Atomic unit	SI Equivalent
mass	mass of an electron, m_e	9.1094×10^{-31} kg
charge	charge on a proton, e	1.6022×10^{-19} C
angular momentum	Planck constant divided by 2π, $\hbar$	1.0546×10^{-34} J·s
distance	Bohr radius, $a_0 = \dfrac{4\pi\varepsilon_0\hbar^2}{m_e e^2}$	5.2918×10^{-11} m
energy	$\dfrac{m_e e^4}{16\pi^2\varepsilon_0^2\hbar^2} = \dfrac{e^2}{4\pi\varepsilon_0 a_0} = E_h$	4.3597×10^{-18} J
permittivity	$4\pi\varepsilon_0$	1.1127×10^{-10} C^2·J^{-1}·m^{-1}

Atomic units

Consider the hamiltonian of helium atom.

$$\hat{H} = -\frac{\hbar^2}{2m_e}\nabla_1^2 - \frac{\hbar^2}{2m_e}\nabla_2^2 - \frac{2e^2}{4\pi\epsilon_0 r_1} - \frac{2e^2}{4\pi\epsilon_0 r_2} + \frac{e^2}{4\pi\epsilon_0 r_{12}}$$

It is quite complicated to write it down every time. In atomic units,

$$\hat{H} = -\frac{1}{2}\nabla_1^2 - \frac{1}{2}\nabla_2^2 - \frac{2}{r_1} - \frac{2}{r_2} + \frac{1}{r_{12}}$$

Much better!

PChem 2

Physical Chemistry 2

Jiho Son

서울대학교
SEOUL NATIONAL UNIVERSITY
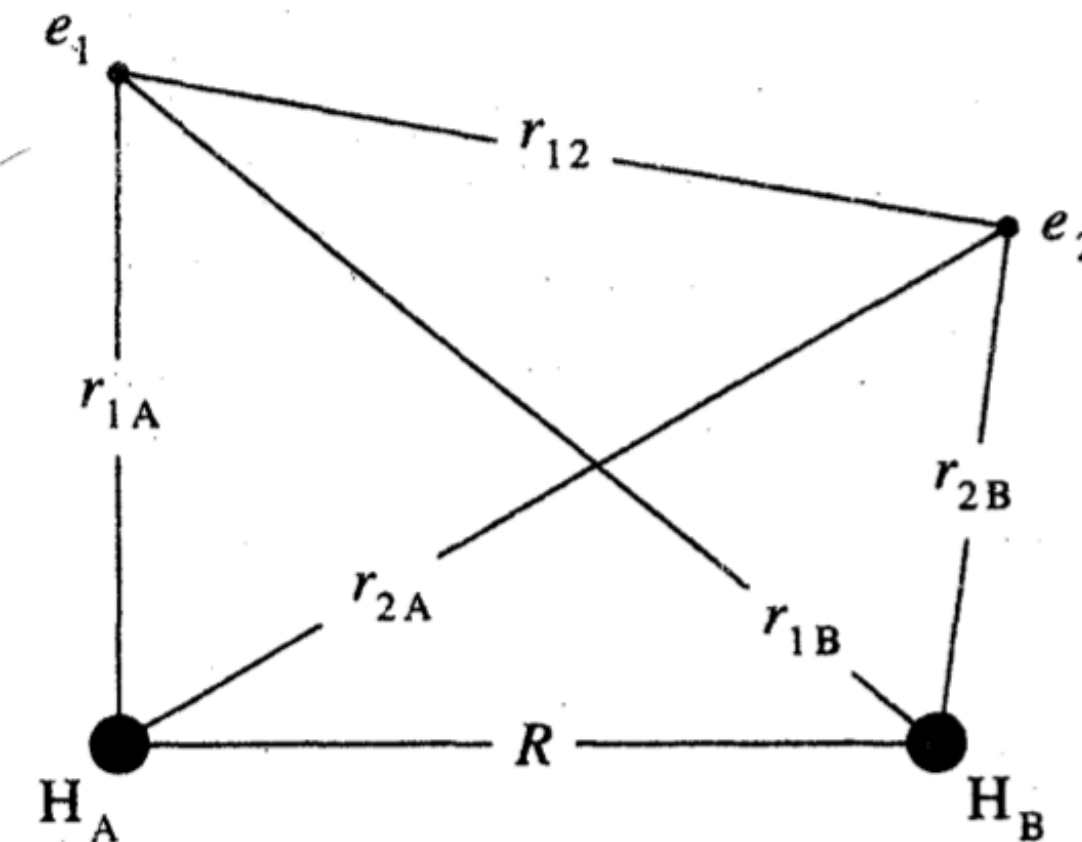
Department of Chemistry

Born-Oppenheimer approximation

Let's consider the simplest molecule, H_2. The hamiltonian is

$$\hat{H} = -\frac{\hbar^2}{2M}(\nabla_A^2 + \nabla_B^2) - \frac{\hbar^2}{2m_e}(\nabla_1^2 + \nabla_2^2) - \frac{e^2}{4\pi\epsilon_0 r_{1A}} - \frac{e^2}{4\pi\epsilon_0 r_{2A}} - \frac{e^2}{4\pi\epsilon_0 r_{1B}} - \frac{e^2}{4\pi\epsilon_0 r_{2B}} + \frac{e^2}{4\pi\epsilon_0 r_{12}} + \frac{e^2}{4\pi\epsilon_0 R}$$

This is very complicated. However, the mass of proton is much heavier than the mass of electron.
Born-Oppenheimer approximation: Neglect the nuclear motion.

$$\hat{H} = -\frac{\hbar^2}{2m_e}(\nabla_1^2 + \nabla_2^2) - \frac{e^2}{4\pi\epsilon_0 r_{1A}} - \frac{e^2}{4\pi\epsilon_0 r_{2A}} - \frac{e^2}{4\pi\epsilon_0 r_{1B}} - \frac{e^2}{4\pi\epsilon_0 r_{2B}} + \frac{e^2}{4\pi\epsilon_0 r_{12}}$$
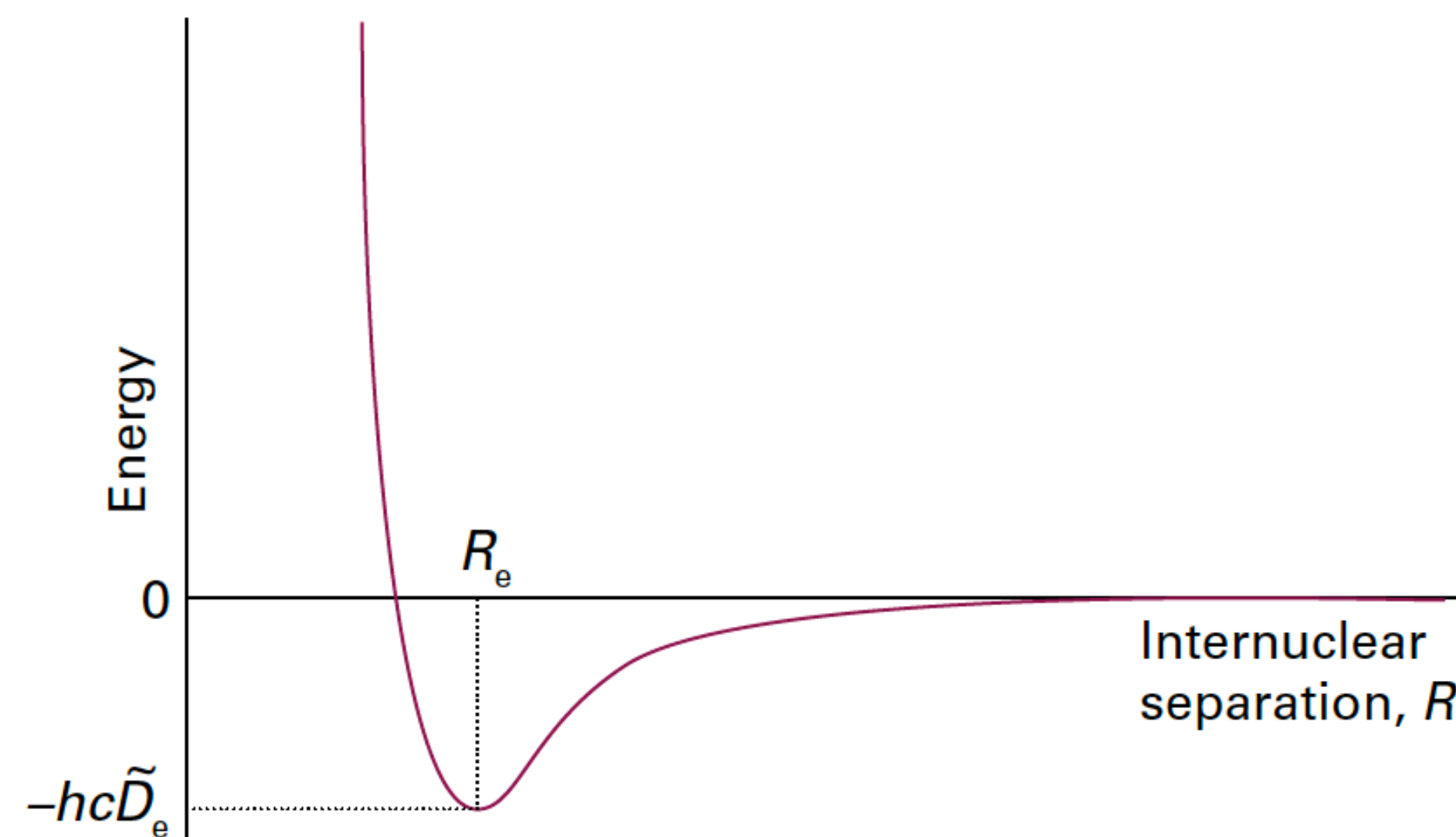
Born-Oppenheimer approximation

Internuclear separation, R, acts as a *parameter* of wavefunction and energy.

By changing the parameter R slightly, we can obtain the *molecular potential energy curve*.

A molecular potential energy curve. The equilibrium bond length corresponds to the energy minimum.

서울대학교
SEOUL NATIONAL UNIVERSITY

Department of Chemistry

PChem 2

Physical Chemistry 2

Jiho Son

Valence bond theory (VBT)

Consider the H_2 molecule. From the indistinguishability of electrons, the spatial wavefunction for an electron is

$$\Psi(1,2) = \psi_A(1)\psi_B(2) \pm \psi_A(2)\psi_B(1)$$

Indeed, linear combination with + sign has lower energy.

$\psi_A(1)\psi_B(2)$ $\psi_A(2)\psi_B(1)$

$\psi_A(1)\psi_B(2) + \psi_A(2)\psi_B(1)$ Enhanced electron density
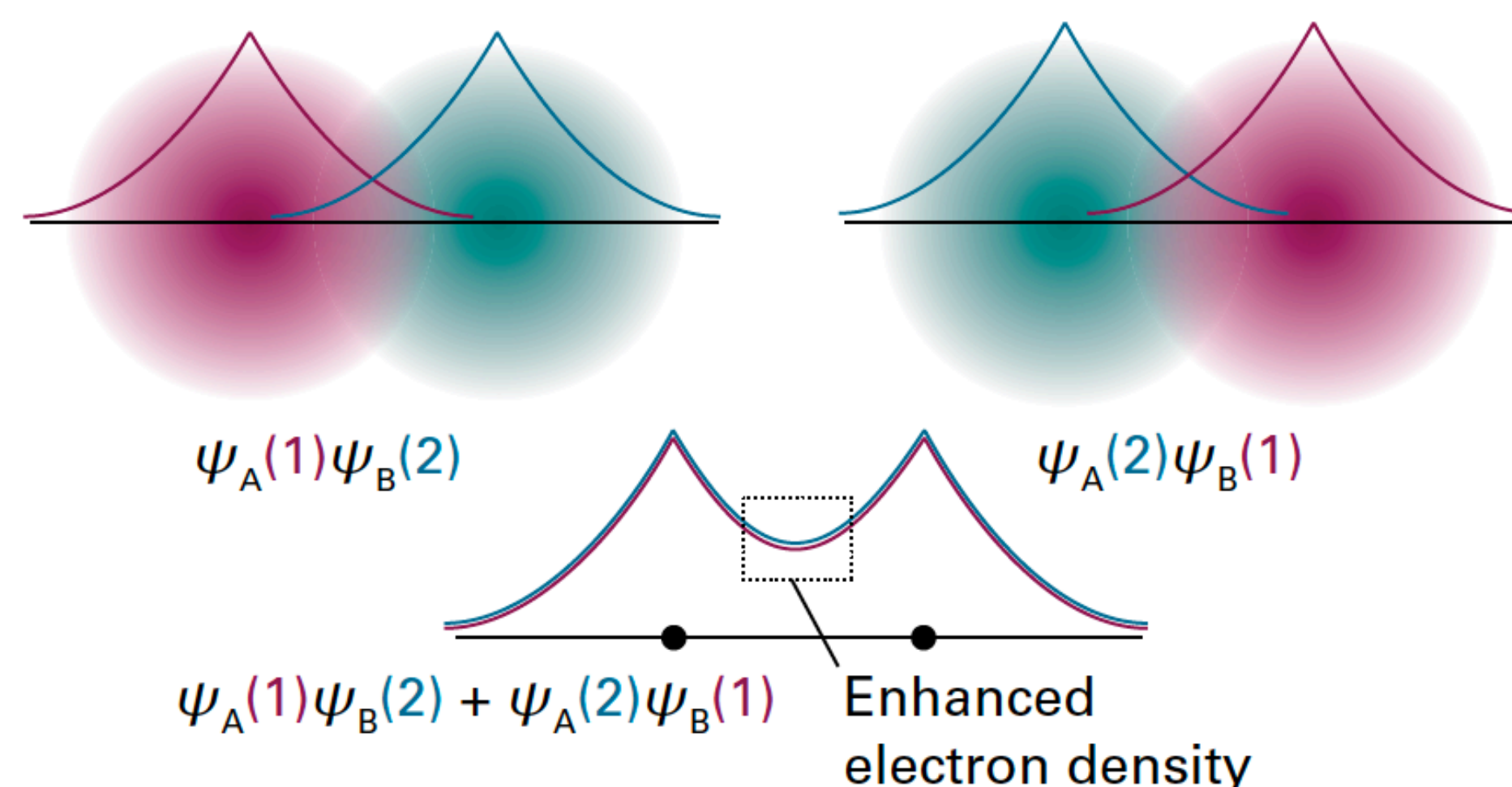
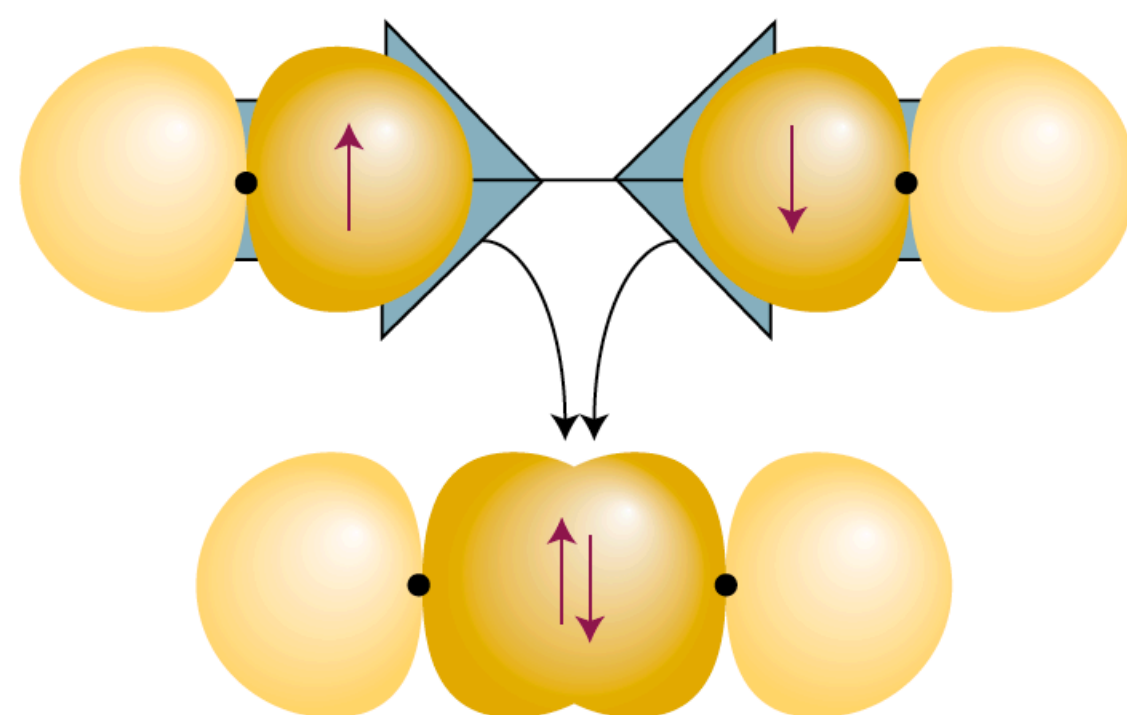The electron distribution described in wavefunction is called a σ bond.
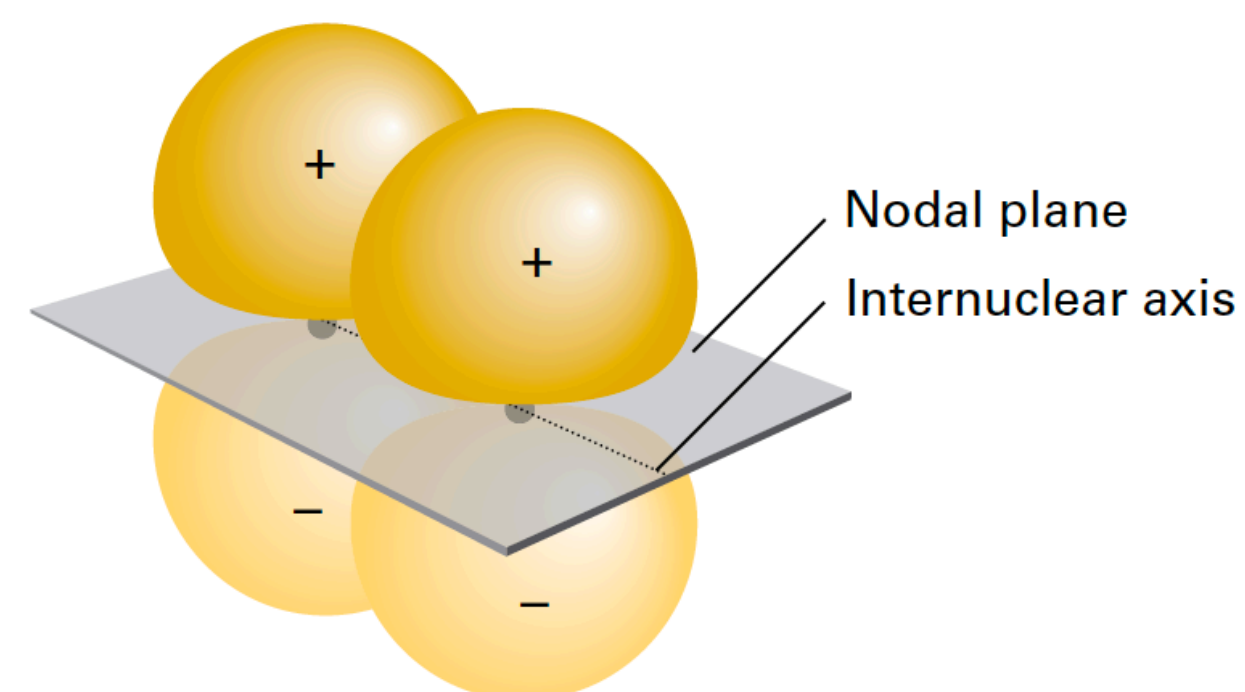
PChem 2

Physical Chemistry 2

Jiho Son

Valence bond theory (VBT)

For the other homonuclear diatomic molecules, p_z orbitals form head-on σ bonds.

Figure 9A.2 The orbital overlap and spin pairing between electrons in two collinear p orbitals that results in the formation of a σ bond.

Nodal plane

Internuclear axis

Figure 9A.3 A π bond results from orbital overlap and spin pairing between electrons in p orbitals with their axes perpendicular to the internuclear axis. The bond has two lobes of electron density separated by a nodal plane.

However, p_x and p_y orbitals cannot form head-on bonding. Instead of σ bonding, this bond results from orbital overlap of p orbitals with their axes perpendicular to the internuclear axis. The π bond has two lobes of electron density, separated by a nodal plane.

서울대학교
SEOUL NATIONAL UNIVERSITY
Department of Chemistry

PChem 2

Physical Chemistry 2

Jiho Son

Resonance

Resonance is the superposition of the wavefunctions representing different electron distributions, in the same nuclear framework. Consider the VB description of purely covalently bonded HCl molecule.

$$\Psi_{\text{HCl}} = \psi_A(1)\psi_B(2) + \psi_A(2)\psi_B(1)$$

This wavefunction represents the fair distribution of two electrons into H and Cl atom. However, this wavefunction cannot express the *ionic* nature of H-Cl single bond. Therefore, to describe this system better, writing the wavefunction as a superposition of the covalent and ionic descriptions is required.

$$\Psi_{\text{H}^+\text{Cl}^-} = \psi_B(1)\psi_B(2)$$

$$\Psi = \Psi_{\text{covalent}} + \lambda\Psi_{\text{ionic}}$$

It is called *ionic-covalent resonance*. This resonance hybrid state is not a flickering between the contributing states: it is a blending of their characteristics.

서울대학교

SEOUL NATIONAL UNIVERSITY

Department of Chemistry

MOT of H_2^+

The method we will use to describe the bonding properties of molecules is called *molecular orbital theory*. We will express molecular wavefunctions, in terms of determinants involving single-electron wavefunctions.

We will solve H_2^+ approximately. The Hamiltonian operator is

$$\hat{H} = -\frac{1}{2}\nabla^2 - \frac{1}{r_A} - \frac{1}{r_B} + \frac{1}{R}$$

We will use a *linear combination* of *atomic orbitals*, which are called a *LCAO-MO*.

$$\psi_\pm = c_1 1s_A \pm c_2 1s_B$$
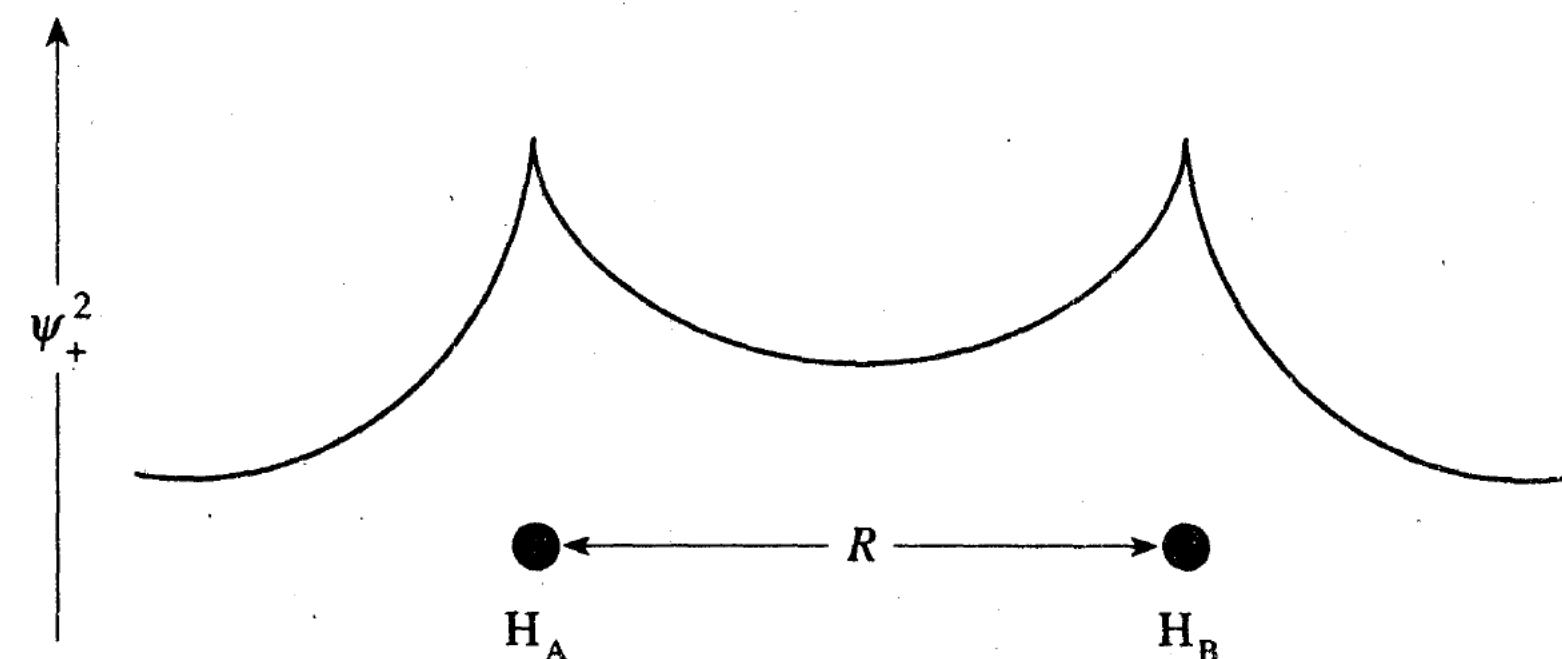
F I G U R E 9.3
A sketch of the H_2^+ molecular orbital formed by a sum of hydrogen atomic $1s$ orbitals situated on each nucleus. Note that the molecular orbital spreads over both nuclei, or over the entire molecule.

MOT of H_2^+

To find the coefficients, we will use *variational principle*. Consider the ground-state wavefunction ψ_0. Then

$$E_0 = \frac{\int \psi_0^* \hat{H} \psi_0 \, d\tau}{\int \psi_0^* \psi_0 \, d\tau}$$

If we substitute any other function ϕ for ψ_0, and calculate the corresponding energy,

$$E_\phi = \frac{\int \phi^* \hat{H} \phi \, d\tau}{\int \phi^* \phi \, d\tau} \geq E_0$$

Then E_ϕ will be grater than the ground-state energy. The coefficients, c_1 and c_2, can be optimized to yield lowest energy.

MOT of H_2^+

Since two hydrogen are equivalent, we will just set $c_1 = c_2 = 1$.

$$E_+ = \frac{\int \psi_+^* \hat{H} \psi_+ \, d\mathbf{r}}{\int \psi_+^* \psi_+ \, d\mathbf{r}}$$

Denominator is

$$\int \psi_+^* \psi_+ \, d\mathbf{r} = \int d\mathbf{r} \, 1s_A^* 1s_A + \int d\mathbf{r} \, 1s_A^* 1s_B + \int d\mathbf{r} \, 1s_B^* 1s_A + \int d\mathbf{r} \, 1s_B^* 1s_B = 1 + S + S + 1 = 2(1 + S)$$

Where S is called *overlap integral*. The overlap between two 1s orbital can be calculated:

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

Therefore, we can calculate normalization constants for $\psi_\pm$.

$$\psi_\pm = \frac{1}{\sqrt{2(1 \pm S)}}(1s_A \pm 1s_B)$$

PChem 2

Physical Chemistry 2

Jiho Son

서울대학교
SEOUL NATIONAL UNIVERSITY

Department of Chemistry

MOT of H_2^+

Numerator is

$$\int \psi_+^* \hat{H} \psi_+ \, d\mathbf{r} = \int d\mathbf{r} \, (1s_A^* + 1s_B^*) \left(-\frac{1}{2} \nabla^2 - \frac{1}{r_A} - \frac{1}{r_B} + \frac{1}{R} \right) (1s_A + 1s_B)$$

$$= \int d\mathbf{r} \, (1s_A^* + 1s_B^*) \left(-\frac{1}{2} \nabla^2 - \frac{1}{r_A} - \frac{1}{r_B} + \frac{1}{R} \right) 1s_A + \int d\mathbf{r} \, (1s_A^* + 1s_B^*) \left(-\frac{1}{2} \nabla^2 - \frac{1}{r_A} - \frac{1}{r_B} + \frac{1}{R} \right) 1s_B$$

$$= \int d\mathbf{r} \, (1s_A^* + 1s_B^*) \left(E_{1s} - \frac{1}{r_B} + \frac{1}{R} \right) 1s_A + \int d\mathbf{r} \, (1s_A^* + 1s_B^*) \left(E_{1s} - \frac{1}{r_A} + \frac{1}{R} \right) 1s_B$$

$$= 2E_{1s}(1 + S) + \int d\mathbf{r} \, 1s_A^* \left(-\frac{1}{r_B} + \frac{1}{R} \right) 1s_A + \int d\mathbf{r} \, 1s_B^* \left(-\frac{1}{r_B} + \frac{1}{R} \right) 1s_A$$

$$+ \int d\mathbf{r} \, 1s_A^* \left(-\frac{1}{r_A} + \frac{1}{R} \right) 1s_B + \int d\mathbf{r} \, 1s_B^* \left(-\frac{1}{r_A} + \frac{1}{R} \right) 1s_B$$

First and fourth term are denoted by J, and is called *Coulomb integral*.

Jiho Son

MOT of H_2^+

The origin of the name follows by noting that the charge in the volume $d\mathbf{r}\,1s_A^*1s_A$ interacts with a proton separate a distance r_B.

$$J = \int d\mathbf{r}\,1s_B^* \left(-\frac{1}{r_A} + \frac{1}{R} \right) 1s_B = \int d\mathbf{r}\,1s_A^* \left(-\frac{1}{r_B} + \frac{1}{R} \right) 1s_A = \int d\mathbf{r}\frac{1s_A^*1s_A}{r_B} + \frac{1}{R}$$

The second integral is denoted by K, and is called an *exchange integral*.

$$K = \int d\mathbf{r}\,1s_A^* \left(-\frac{1}{r_A} + \frac{1}{R} \right) 1s_B = \int d\mathbf{r}\,1s_B^* \left(-\frac{1}{r_B} + \frac{1}{R} \right) 1s_A = \int d\mathbf{r}\,\frac{1s_B^*1s_A}{r_B} + \frac{S}{R}$$

Therefore we have

$$\int d\mathbf{r}\,\psi_+^*\hat{H}\psi_+ = 2E_{1s}(1+S) + 2J + 2K \qquad \Delta E_+ = E_+ - E_{1s} = \frac{J+K}{1+S}$$

where

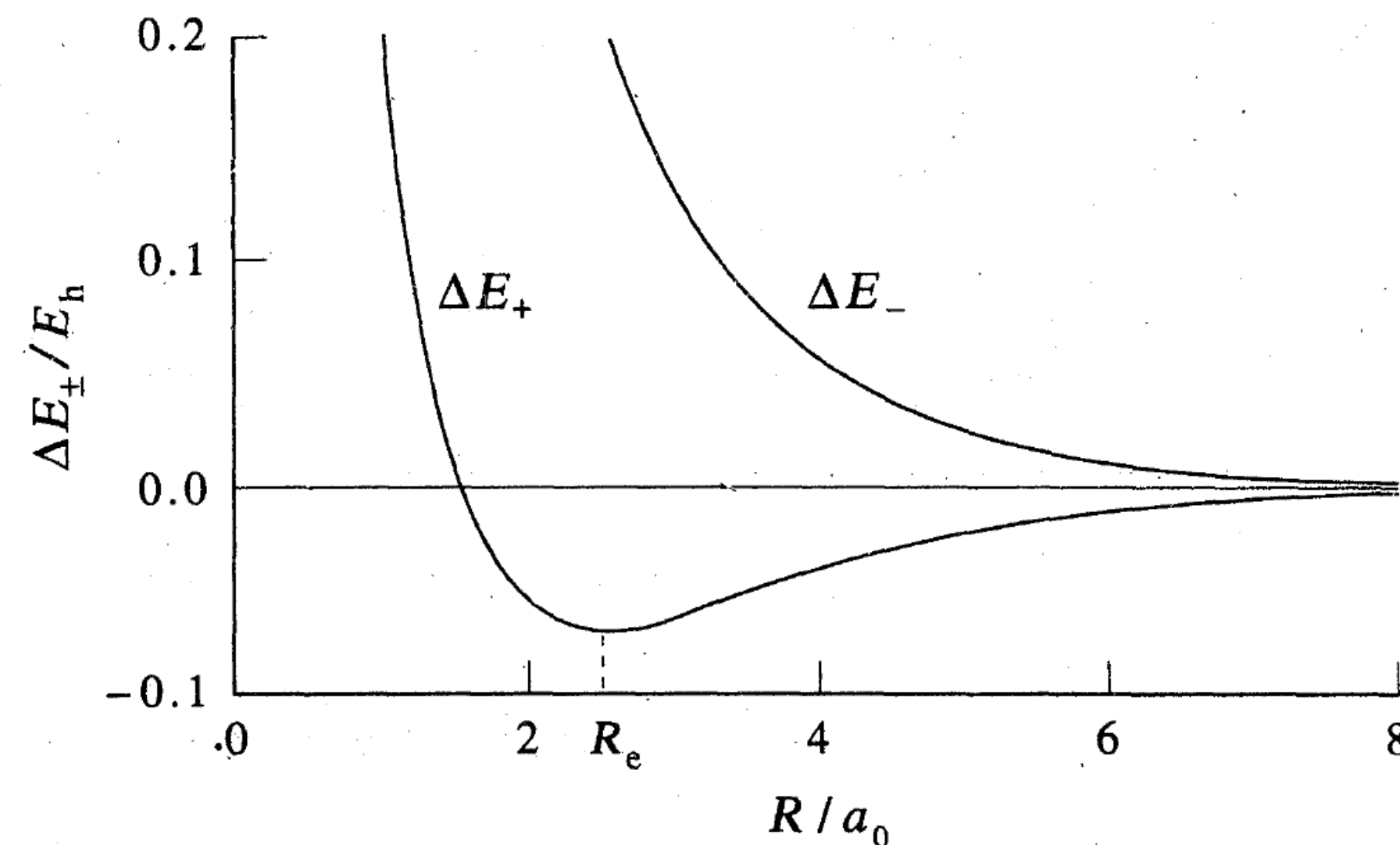$$J = e^{-2R}\left(1 + \frac{1}{R} \right), \quad K = \frac{S}{R} - e^{-R}(1+R)$$

MOT of H_2^+

Likewise, we can yield

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

332

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.

PChem 2

Physical Chemistry 2

Jiho Son

Department of Chemistry

MOT of H_2^+

서울대학교
SEOUL NATIONAL UNIVERSITY

Department of Chemistry

PChem 2

Physical Chemistry 2

Jiho Son

For the ΔE_+ term, note that J is always positive. Therefore, stabilizing effect of bonding purely comes from K term, which has no classical analogy; therefore, chemical bonding is purely quantum-mechanical phenomenon.
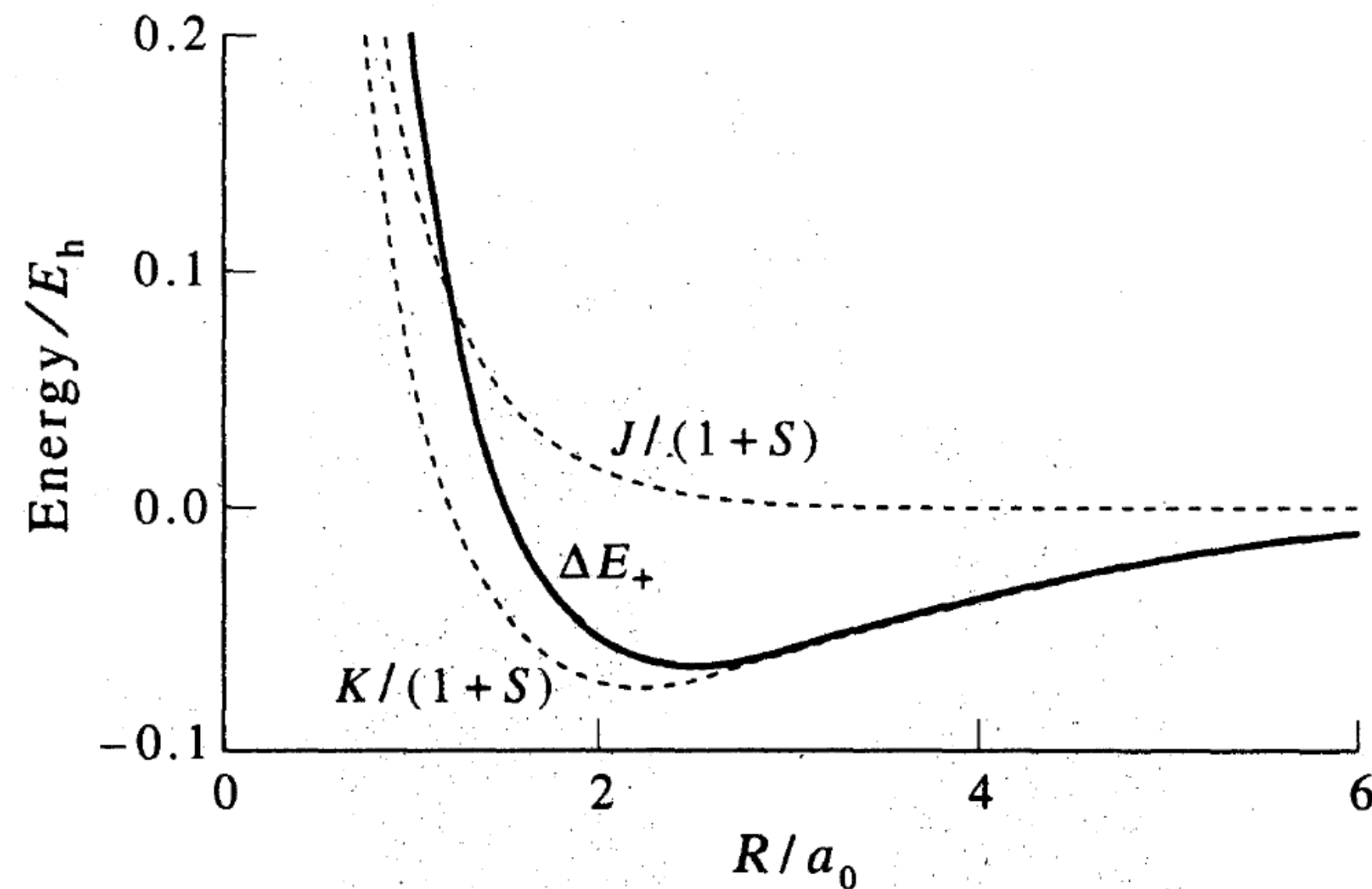
FIGURE 9.7
The separate contributions of the Coulomb integral, J, and the exchange integral, K, to the stability of H_2^+.

MOT of H_2^+

We yield *bonding* and *antibonding* orbitals.

$$\psi_b = \frac{1}{\sqrt{2(1+S)}}(1s_A + 1s_B), \quad \psi_a = \frac{1}{\sqrt{2(1-S)}}(1s_A - 1s_B)$$
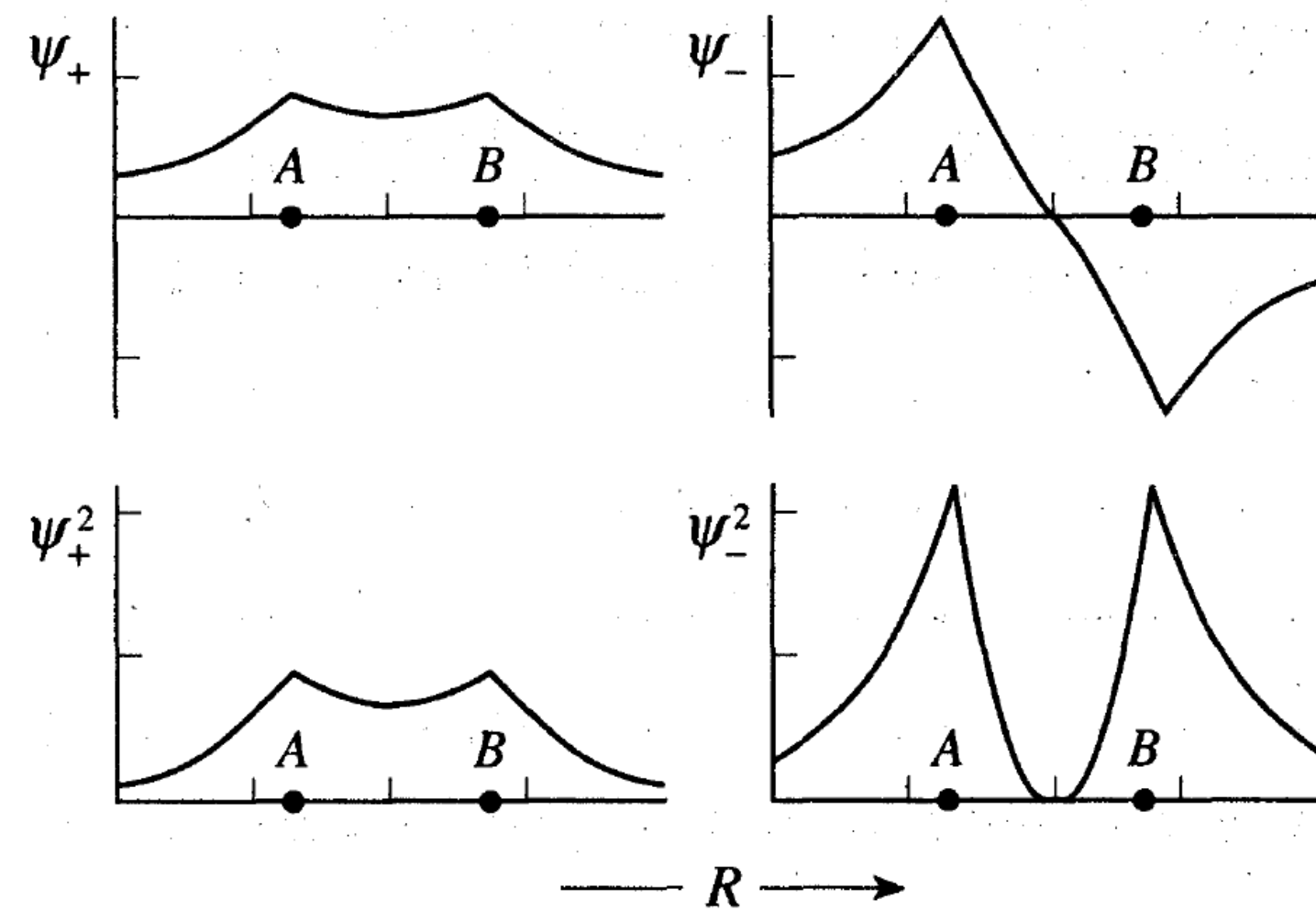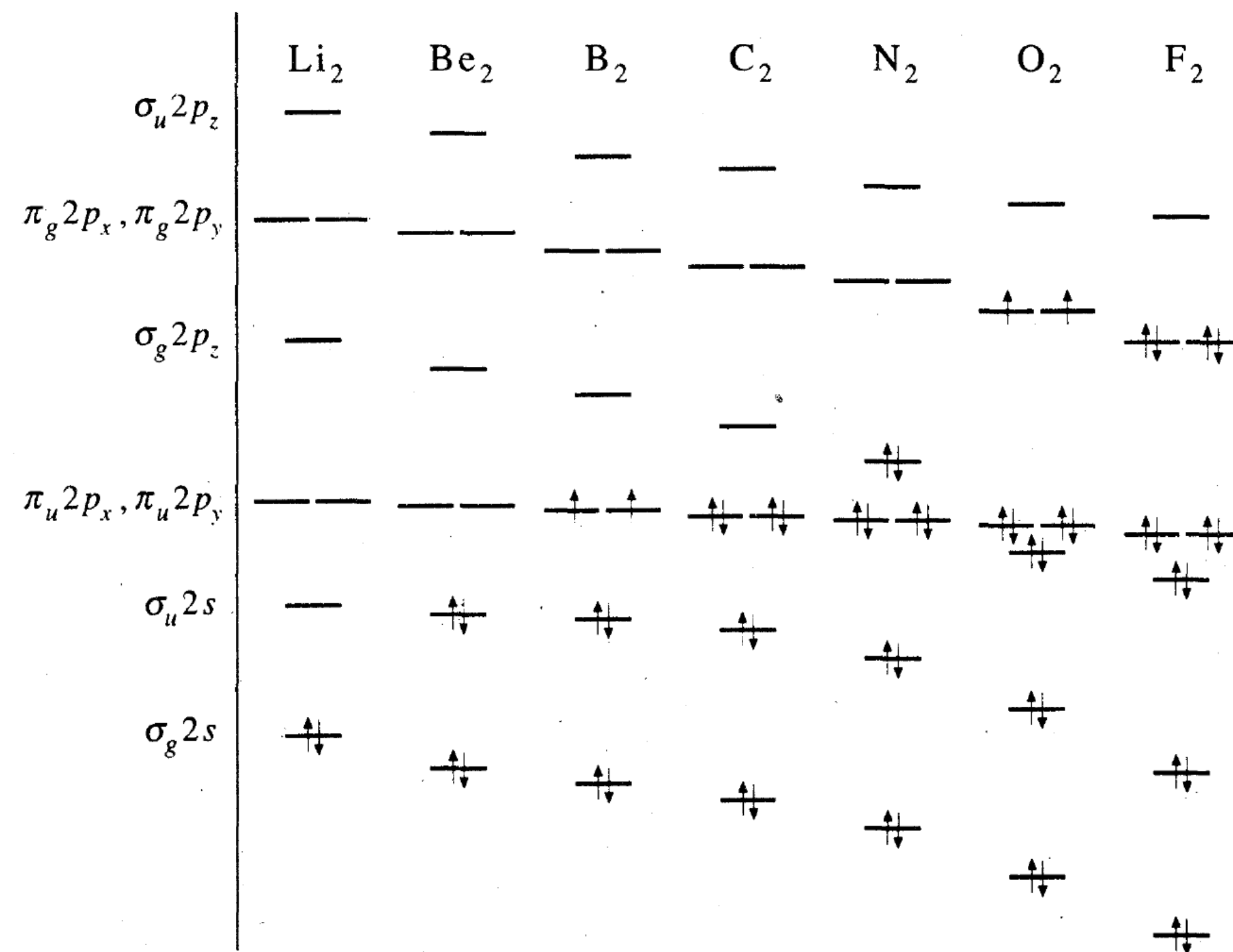

FIGURE 9.8
The molecular orbitals ψ_+ (bonding) and ψ_- (antibonding) and their squares are plotted along the internuclear axis.

MOT of homonuclear diatomics

FIGURE 9.13
The relative energies (not to scale) of the molecular orbitals for the homonuclear diatomic molecules Li_2 through F_2. The $\pi_u 2p_x$ and $\pi_u 2p_y$ orbitals are degenerate, as are the $\pi_g 2p_x$ and $\pi_g 2p_y$ orbitals.

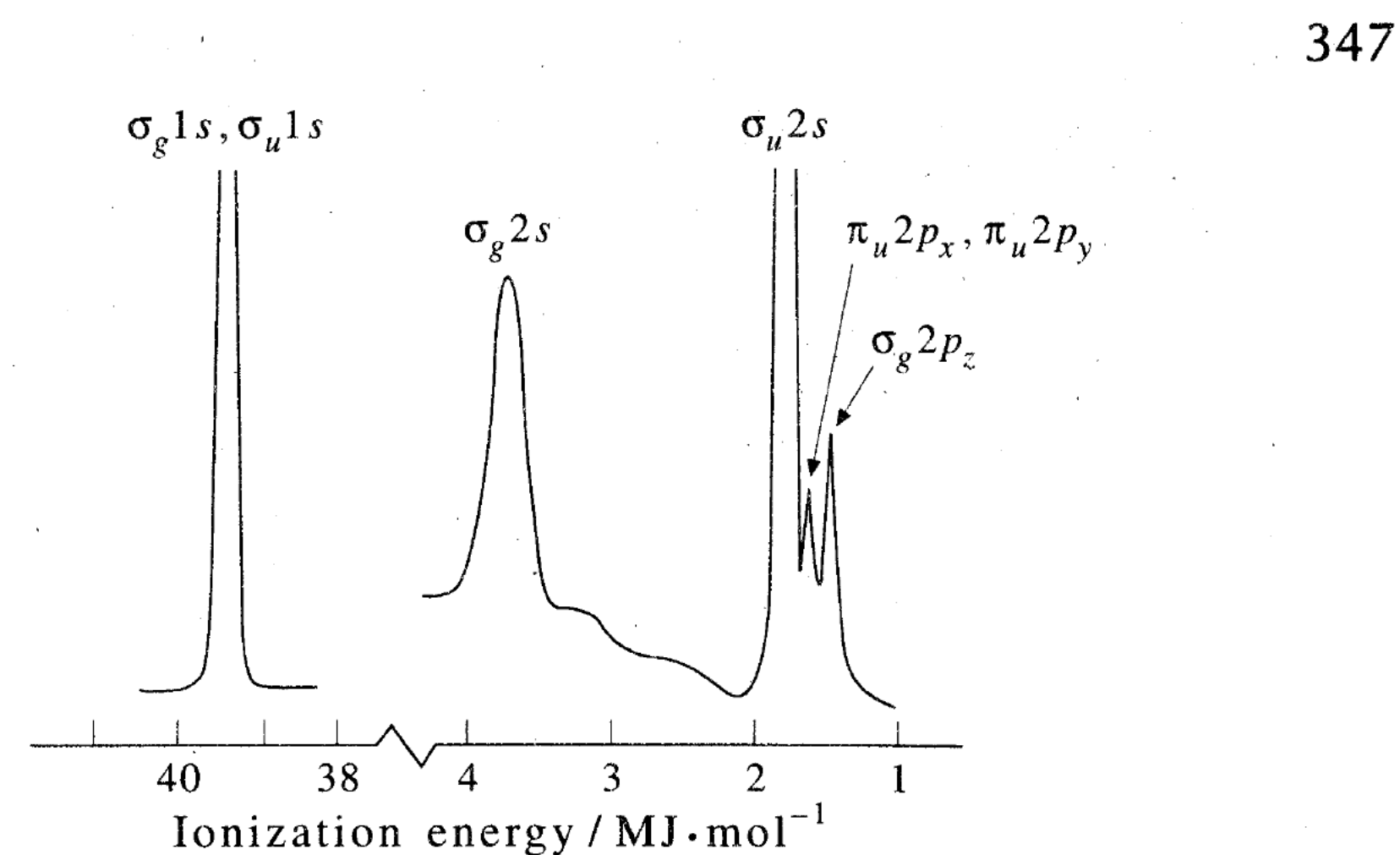# Photoelectron spectroscopy

347

FIGURE 9.16
The photoelectron spectrum of N$_2$. The peaks in this plot are caused by electrons being ejected from various molecular orbitals.
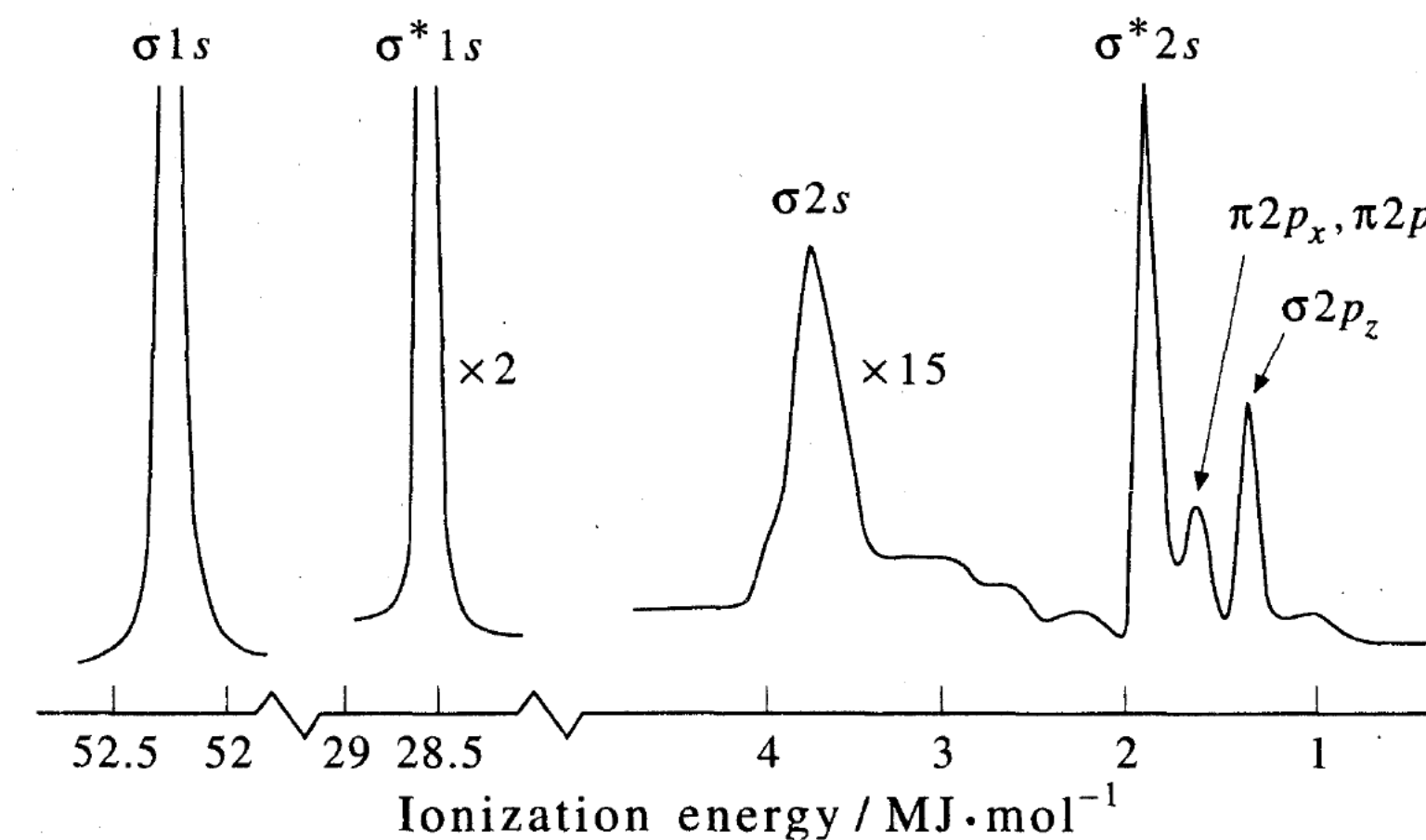

FIGURE 9.17
The photoelectron spectrum of CO. The energies associated with various molecular orbitals are identified. The $\sigma 1s$ and $\sigma^* 1s$ orbitals are essentially the $1s$ electrons of the oxygen and carbon atoms, respectively. The relatively large ionization energies of these electrons indicate that they are held tightly by the nuclei and play no role in bonding.

PChem 2

Physical Chemistry 2

Jiho Son