B. 4. Molekula H_2^+ a související systémy

$1s_A$ $1s_B$
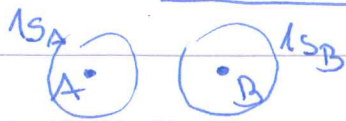
metoda MO-LCAO

$$\tilde{\Psi}(c_A, c_B) = c_A 1s_A + c_B 1s_B$$

c_A, c_B ?

(1) Uvážíme souměrnost molekuly

$$c_A^2 = c_B^2 \implies c_A = \pm c_B$$

VF musí být normovaná, tím jsou koeficienty jednoznačně určeny.

(2) Obecný způsob (např. mol. HHe^+)

Energie pro nějak zvolené hodnoty c_A, c_B

$$\overline{E}(c_A, c_B) = \frac{\int (c_A 1s_A + c_B 1s_B)^* \hat{H} (c_A 1s_A + c_B 1s_B) \, d\tau}{\int (c_A 1s_A + c_B 1s_B)^* (c_A 1s_A + c_B 1s_B) \, d\tau} \geq E_0$$

Přesná energie základního stavu

VARIAČNÍ TEORÉM

$$\implies \frac{\partial \overline{E}}{\partial c_A} = \frac{\partial \overline{E}}{\partial c_B} = 0$$

$$E\left(c_A, c_B\right) = \frac{\text{čitatel}}{\text{jmenovatel}} \quad , \quad \text{uvažujeme pouze REÁLNÉ funkce a koeficienty}$$

minule: čitatel $= c_A c_A H_{AA} + c_A c_B H_{AB} + c_B c_A H_{BA} + c_B c_B H_{BB}$

jmenovatel $= c_A c_A S_{AA} + c_A c_B S_{AB} + c_B c_A S_{BA} + c_B c_B S_{BB}$

co znamená např. $S_{AB} = \int 1s_A^{*} 1s_B \, d\tilde{c} \, ?$

$\downarrow$

Tzv. PŘEKRYVOVÝ $\int$ VÝZNAM?

$$H_{AB} = \int 1s_A \hat{H} 1s_B \, d\tilde{c} \, ?$$
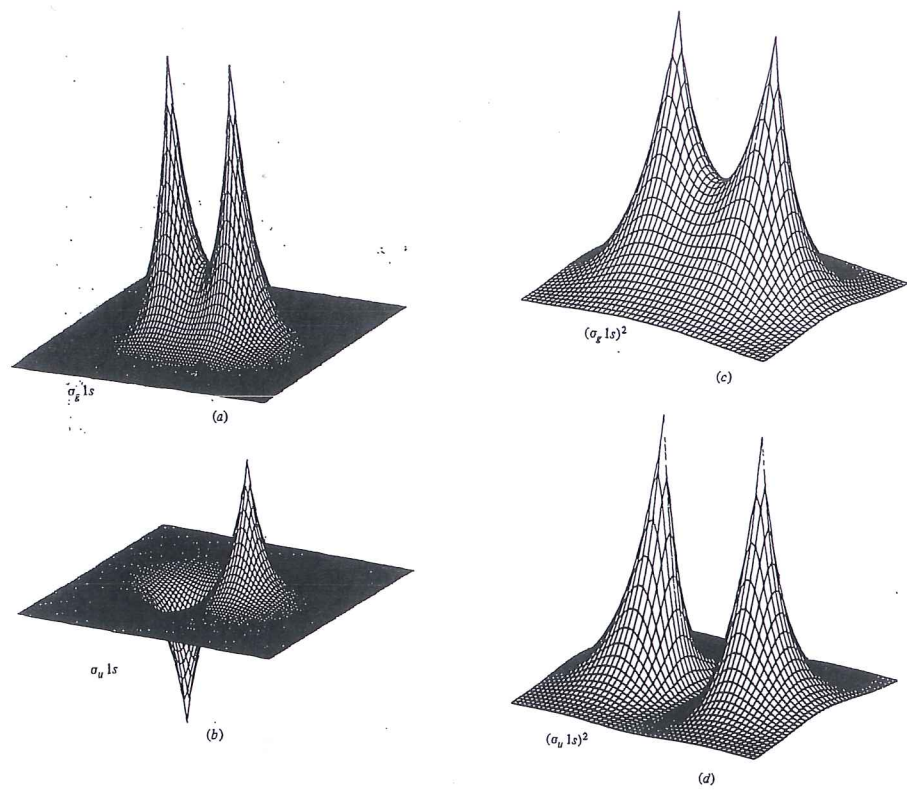
$\downarrow$

Tzv. INTERAKČNÍ $\int$ VÝZNAM?

FIGURE 12-7
Surface plots of (a) the $\sigma_g 1s$ and (b) the $\sigma_u 1s$ wavefunctions of the H_2^+, together with (c) and (d), the corresponding probability densities $(\sigma_g 1s)^2$ and $(\sigma_u 1s)^2$. The $\sigma_g 1s$ and $(\sigma_g 1s)^2$ plots look very similar in that both indicate a buildup of the function between the two nuclei. In the case of $(\sigma_g 1s)^2$, this buildup may be interpreted as bonding of the two nuclei. The $\sigma_u 1s$ and $(\sigma_u 1s)^2$ plots show no buildup between the nuclei; in fact, there is a node between the two parts of the functions and a buildup *outside* the internuclear region. Thus $\sigma_u 1s$ describes an *antibonding* state.
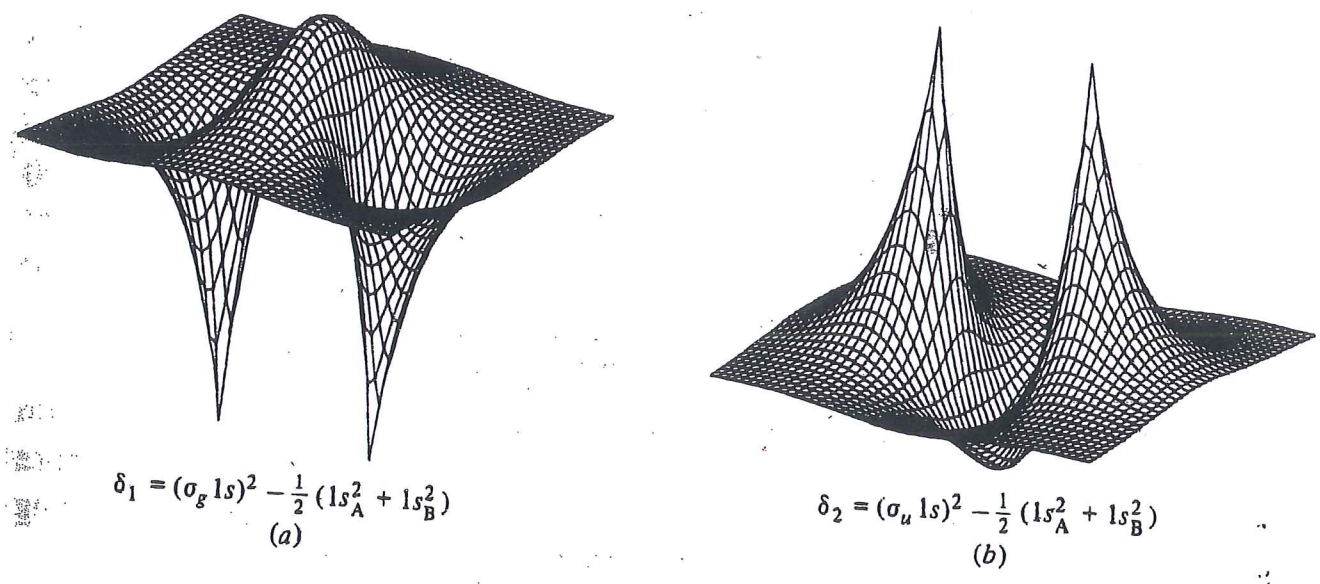
$$\delta_1 = (\sigma_g 1s)^2 - \tfrac{1}{2}(1s_A^2 + 1s_B^2)$$
(a)

$$\delta_2 = (\sigma_u 1s)^2 - \tfrac{1}{2}(1s_A^2 + 1s_B^2)$$
(b)

FIGURE 12-8
Differences in probability densities between (a) the bonding $\sigma_g 1s$ function and (b) the antibonding $\sigma_u 1s$ function of H_2^+ according to Eq. (12-34). The two upward-pointing peaks of (b) represent a buildup of probability density *outside* the internuclear region; the sag between these peaks represents a decrease in probability density between the nuclei. Note that this decrease and increase are relative to the density due to two noninteracting $1s^2$ atomic probability densities. The two downward-pointing peaks of (a) represent a decrease of probability density outside the internuclear region, and the mound between these indicates an increase of probability density between the nuclei.

TABLE 13.2   Properties of Homonuclear Diatomic Molecules in Their Ground Electronic States

Molecule	Ground Term	Bond Order	D_e/eV	$R_e/\text{Å}$	$\tilde{\nu}_e/\text{cm}^{-1}$
H_2^+	$^2\Sigma_g^+$	$\frac{1}{2}$	2.79	1.06	2322
H_2	$^1\Sigma_g^+$	1	4.75	0.741	4403
He_2^+	$^2\Sigma_u^+$	$\frac{1}{2}$	2.5	1.08	1698
He_2	$^1\Sigma_g^+$	0	0.0009	3.0	
Li_2	$^1\Sigma_g^+$	1	1.07	2.67	351.4
Be_2	$^1\Sigma_g^+$	0	0.10	2.45	
B_2	$^3\Sigma_g^-$	1	3.1	1.59	1051
C_2	$^1\Sigma_g^+$	2	6.3	1.24	1855
N_2^+	$^2\Sigma_g^+$	$2\frac{1}{2}$	8.85	1.12	2207
N_2	$^1\Sigma_g^+$	3	9.91	1.10	2358
O_2^+	$^2\Pi_g$	$2\frac{1}{2}$	6.78	1.12	1905
O_2	$^3\Sigma_g^-$	2	5.21	1.21	1580
F_2	$^1\Sigma_g^+$	1	1.66	1.41	892
Ne_2	$^1\Sigma_g^+$	0	0.0036	3.1	14

Data from K. P. Huber and G. Herzberg, *Constants of Diatomic Molecules* (vol. IV of *Molecular Spectra and Molecular Structure*), Van Nostrand Reinhold, 1979; and (for Be$_2$) V. E. Bondybey, *Chem. Phys. Lett.*, **109**, 463 (1984).

3.6. Conclusions

It is useful to collect together the main results associated with the interaction of two atomic orbitals located on two centers.

(i) Orbitals can only interact if their overlap integral is non-zero.

(ii) The interaction of two AOs leads to the formation of two MOs, one bonding and one antibonding.

(iii) The bonding MO is more stable than the lower energy orbital of the starting AOs.

(iv) The antibonding MO is less stable than the higher energy orbital of the starting AOs.

(v) The bonding orbital is stabilized less than the antibonding orbital is destabilized.

(vi) If the AOs are degenerate, their interaction is proportional to their overlap integral, S.

(vii) If the AOs are non-degenerate, their interaction is proportional to $S^2/\Delta\varepsilon$, where $\Delta\varepsilon$ is the energy separation between the AOs. In this case the bonding MO is preferentially localized on the atom with the deeper lying AO, usually the more electronegative atom. The antibonding MO is preferentially localized on the atom which holds the higher energy AO.

TABLE 13.2   Properties of Homonuclear Diatomic Molecules in Their Ground Electronic States

Molecule	Ground Term	Bond Order	D_e/eV	R_e/Å	$\tilde{\nu}_e$/cm^{-1}
H_2^+	$^2\Sigma_g^+$	$\frac{1}{2}$	2.79	1.06	2322
H_2	$^1\Sigma_g^+$	1	4.75	0.741	4403
He_2^+	$^2\Sigma_u^+$	$\frac{1}{2}$	2.5	1.08	1698
He_2	$^1\Sigma_g^+$	0	0.0009	3.0	
Li_2	$^1\Sigma_g^+$	1	1.07	2.67	351.4
Be_2	$^1\Sigma_g^+$	0	0.10	2.45	
B_2	$^3\Sigma_g^-$	1	3.1	1.59	1051
C_2	$^1\Sigma_g^+$	2	6.3	1.24	1855
N_2^+	$^2\Sigma_g^+$	$2\frac{1}{2}$	8.85	1.12	2207
N_2	$^1\Sigma_g^+$	3	9.91	1.10	2358
O_2^+	$^2\Pi_g$	$2\frac{1}{2}$	6.78	1.12	1905
O_2	$^3\Sigma_g^-$	2	5.21	1.21	1580
F_2	$^1\Sigma_g^+$	1	1.66	1.41	892
Ne_2	$^1\Sigma_g^+$	0	0.0036	3.1	14

3.2.1. Interaction of two identical AOs

The two MOs for the homonuclear diatomic molecule thus become

$$\phi_+ = \frac{1}{[2(1+S)]^{1/2}}(\chi_1 + \chi_2) \qquad \phi_- = \frac{1}{[2(1-S)]^{1/2}}(\chi_1 - \chi_2) \qquad (12)$$

So, starting off from two AOs, χ_1 and χ_2, we have obtained two MOs ϕ_+ and ϕ_-. This relationship between the number of AOs and the number of MOs they generate is a general one, even in more complex systems; n AOs give rise to n MOs. If we calculate the overlap between the MOs we get

$$\langle \phi_+ \mid \phi_- \rangle = \frac{1}{2(1-S^2)^{1/2}}(\langle \chi_1 \mid \chi_1 \rangle + \langle \chi_1 \mid \chi_2 \rangle - \langle \chi_1 \mid \chi_2 \rangle - \langle \chi_2 \mid \chi_2 \rangle)$$

$$= \frac{1}{2(1-S^2)^{1/2}}(1 + S - S - 1)$$
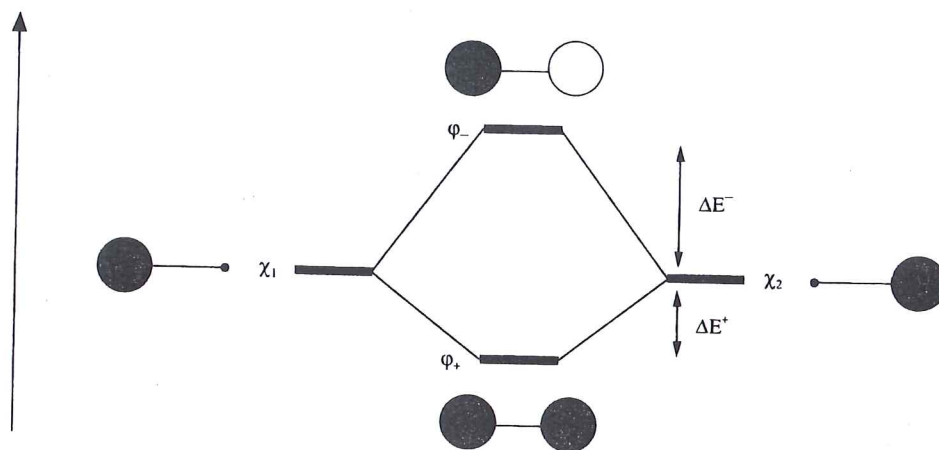
$$= 0 \qquad (13)$$

Figure 3.1. Molecular orbital diagram showing the interaction between two identical atomic orbitals in a homonuclear molecule.
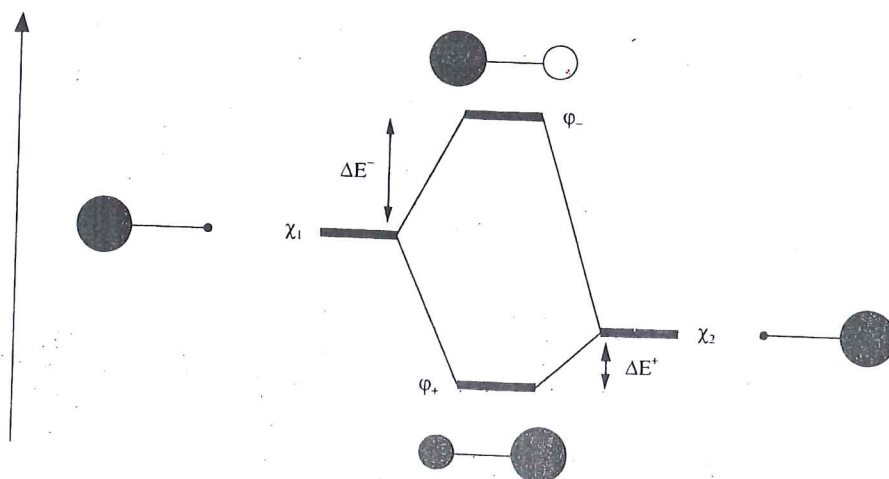
3.2.2. Interaction of two different AOs

Figure 3.2. Molecular orbital diagram showing the interaction between two different atomic orbitals in a heteronuclear molecule.
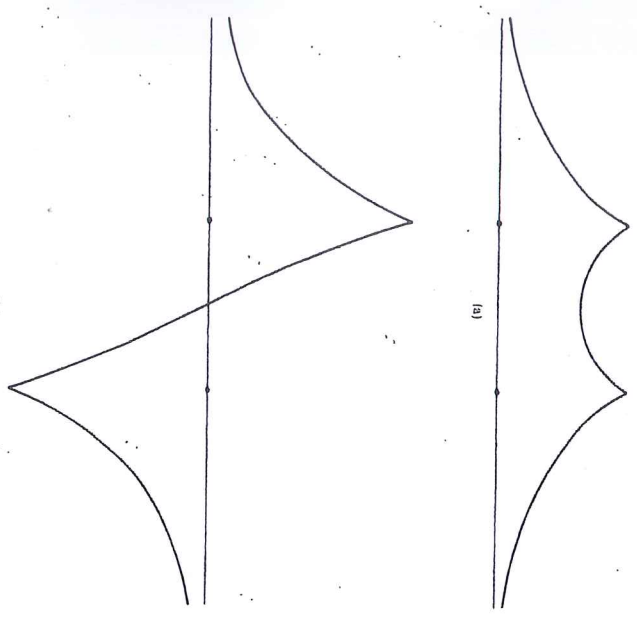
(a)

(b)

FIG. 7-9 (a) Plot of ψ_+ along the z axis. [Eq. (7-100)]. (b) Plot of ψ_- along the z axis [Eq. (7-101)]. (This figure continues on subsequent pages.)
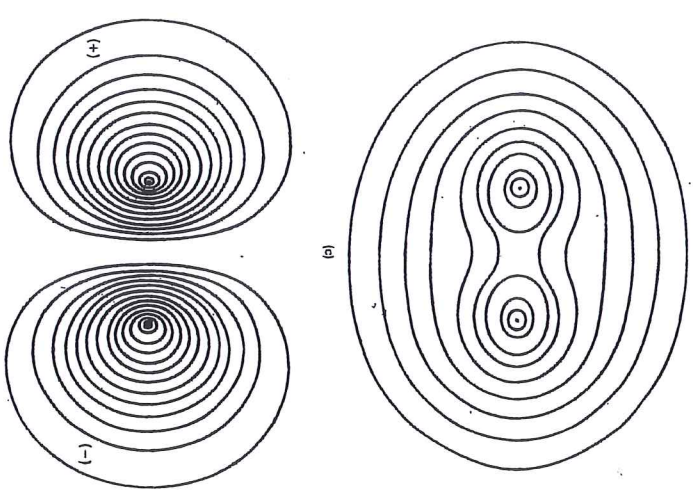
(c)

(+)

(−)

(d)

FIG. 7-9 (c) Contour diagram of ψ_+. (d) Contour diagram of ψ_-.

(e)

(f)
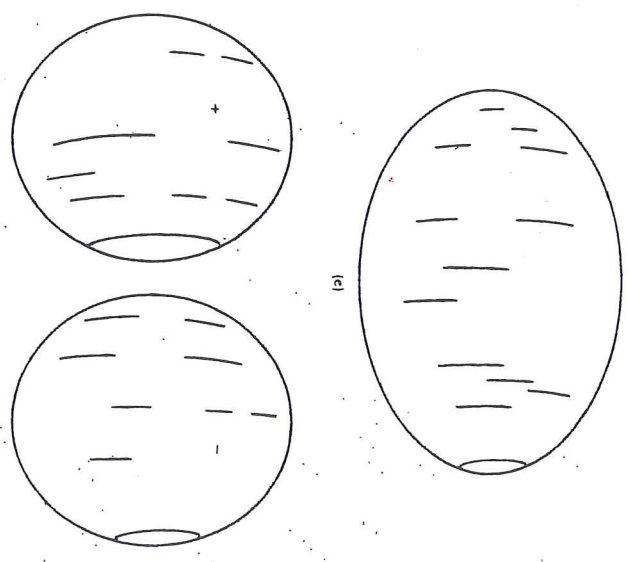
FIG. 7-9 (e) Three-dimensional sketch of contour envelope for ψ_+ and (f) for ψ_-.

$-\frac{1}{2}$ a.u.

$E_- + \frac{1}{R}$

$E_+ + \frac{1}{R}$

$-\frac{1}{2}$ a.u.

FIG. 7-7 Separated atom energies and energies at an intermediate R for H_2^+.

$E_- + \frac{1}{R}$

$E_+ + \frac{1}{R}$

E (a.u.)

0.3
0.2
0.1
0.0
−0.1
−0.2
−0.3
−0.4
−0.5
−0.6
−0.7
−0.8

R (a.u.)

FIG. 7-8 $E_\pm + 1/R$ versus R for H_2^+. (——) Calculation described in text. (-----) Exact calculation.

$E_- + \frac{1}{R}$

$E_+ + \frac{1}{R}$

$H_{AA} - H_{AB}$

$\dfrac{H_{AA} - H_{AB}}{1 - S_{AB}} = E_-$

$\dfrac{H_{AA} + H_{AB}}{1 + S_{AB}} = E_+$

H_{AA}

$H_{AA} + H_{AB}$

H atom energy

Energy (a.u.)

−0.2
−0.3
−0.4
−0.5
−0.6
−0.7
−0.8
−0.9
−1.0
−1.1
−1.2
−1.3
−1.4
−1.5
−1.6
−1.7
−1.8

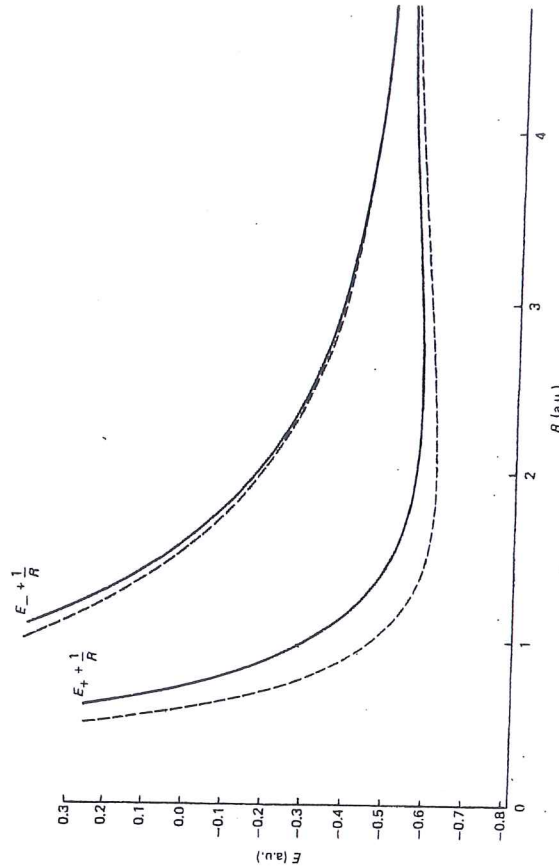FIG. 7-6 Contributions to energy of H_2^+ at $R = 2$ in minimal basis LCAO–MO calculation.