MOLECULES

$$H\Psi = E\Psi$$

$$H = -\frac{\hbar^2}{2m}\sum_{i=1}^{N}\Delta_i + V_{ne} + V_{ee}$$

$$V_{ne} = -\sum_{\alpha=1}^{M}\sum_{i=1}^{N}\frac{Z_\alpha e^2}{r_{\alpha i}} \quad ; \quad V_{ee} = \sum_{i<j}^{N}\frac{e^2}{r_{ij}}$$

$$H = \sum_{i=1}^{N} h(i) + \sum_{i<j}^{N}\frac{e^2}{r_{ij}}$$

SINGLE PARTICLE APPROXIMATION : MO

N-ELECTRON FUNCTION OF PROPER SYMMETRY:

$$\Phi = \frac{1}{\sqrt{N!}}\begin{vmatrix} \varphi_1(1) & \varphi_1(2) & \dots & \varphi_1(N) \\ \varphi_2(1) & \varphi_2(2) & \dots & \varphi_2(N) \\ \vdots & \vdots & & \\ \varphi_N(1) & \varphi_N(2) & \dots & \varphi_N(N) \end{vmatrix}$$

BUILT OF MO's

VARIATIONAL PRINCIPLE

H-F EQUATIONS => H-F-R EQUATIONS (ALGEBRAIC)

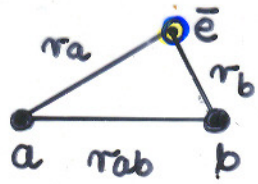
MO LCAO EACH MO DESCRIBES MOTION OF AN ELECTRON IN AN AVERAGE FIELD PRODUCED BY ALL NUCLEI AND REMAINING ELECTRONS

H ATOM	MODEL SYSTEM	FOR	ALL MANY ELECTRON ATOMS
H_2^+ MOLECULE	MODEL SYSTEM	FOR	ALL MANY ELECTRON MOLECULES

EXACT SOLUTIONS!

APPROXIMATE SOLUTIONS WITH „ARBITRARY" ACCURACY!

H_2^+



$$H = -\frac{\hbar^2}{2m}\Delta - \frac{e^2}{r_a} - \frac{e^2}{r_b}$$

$$H\Psi = E\Psi$$

1º

$$H_a = -\frac{\hbar^2}{2m}\Delta - \frac{e^2}{r_a} \qquad H_a\chi_a = E_H\chi_a$$

$$\chi_a = Ne^{-r/a_0}$$

2º

$$H_b = -\frac{\hbar^2}{2m}\Delta - \frac{e^2}{r_b} \qquad H_b\chi_b = E_H\chi_b$$

$$\chi_b = Ne^{-r/a_0}$$

IN REALITY Ψ HAS TO REPRESENT BOTH SITUATIONS

$\Psi = C_a\chi_a(1) + C_b\chi_b(1)$ MO (ONE COORDINATE)

$|C_a|^2$ PROBABILITY OF SITUATION 1º

$|C_b|^2$ PROBABILITY OF SITUATION 2º

$$\Psi(1) = C_a\left(\chi_a + \frac{C_b}{C_a}\chi_b\right) = N\left(\chi_a + \lambda\chi_b\right)$$

$$\lambda = \frac{C_b}{C_a}$$ VARIATIONAL PARAMETER

$\langle\Psi|\Psi\rangle = 1$

LINEAR COMBINATION OF ATOMIC ORBITALS

$\lambda > 1 \Rightarrow C_b > C_a$: SITUATION 2º MORE PROBABLE

$\lambda < 1 \Rightarrow C_a > C_b$: SITUATION 1º MORE PROBABLE

BUT BOTH NUCLEI ARE IDENTICAL!

$\lambda^2 = 1 \Rightarrow \lambda = \pm 1 \Rightarrow C_a = \pm C_b$

TWO MOLECULAR ORBITALS:

$$\Psi_+(1) = N_+\left[\chi_a(1) + \chi_b(1)\right]$$

$$\Psi_-(1) = N_-\left[\chi_a(1) - \chi_b(1)\right]$$

(*) HOMEWORK:

EVALUATE $N_\pm = (2 \pm 2S)^{-1/2}$

WHERE $S = \langle\chi_a|\chi_b\rangle$

$$\psi_+ = (2+2S)^{-1/2}\,[\chi_a(1)+\chi_b(1)]$$

$$\psi_- = (2-2S)^{-1/2}\,[\chi_a(1)-\chi_b(1)]$$

χ_a AND χ_b ARE NOT ORTHOGONAL! THEY ARE CENTERED ON DIFFERENT NUCLEI.
THE OVERLAP INTEGRAL S IS A FUNCTION OF THE INTER-NUCLEAR DISTANCE r_{ab}:

AO $\longrightarrow 0$ FOR $r \longrightarrow \infty$

$\begin{cases} r_{ab} \longrightarrow \infty & S \to 0 \\ r_{ab} \to 0 & S \to 1 \text{ AND } \chi_a \equiv \chi_b \end{cases}$ THERE IS NO OVERLAP BETWEEN χ_a AND χ_b

CONCLUSION:

$$0 \leqslant S \leqslant 1$$

WHAT IS THE ENERGY OF ψ_+ AND ψ_- ?

$$E_\pm = \langle \psi_\pm | H | \psi_\pm \rangle$$

$$E_\pm = \frac{H_{aa} \pm H_{ab}}{1 \pm S}$$

$H_{aa} = \langle \chi_a | H | \chi_a \rangle$
$H_{bb} = \langle \chi_b | H | \chi_b \rangle$
$H_{ab} = H_{ba} = \langle \chi_a | H | \chi_b \rangle$
$S = \langle \chi_a | \chi_b \rangle$

$$H_{aa} = \langle \chi_a | H | \chi_a \rangle =$$

$$= \langle \chi_a | -\frac{\hbar^2}{2m}\Delta - \frac{e^2}{r_a} | \chi_a \rangle - \langle \chi_a | \frac{e^2}{r_b} | \chi_a \rangle$$

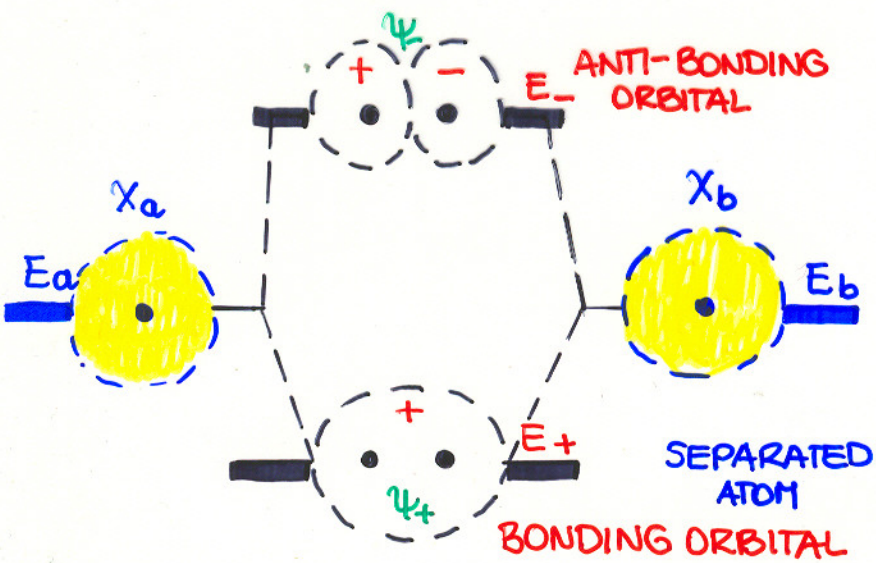
$\underbrace{\qquad\qquad}$ $E_H \langle \chi_a | \chi_a \rangle$

INTERACTION BETWEE $\bar{e}$ CLOSE TO NUCLEUS a (χ_a) AND NUCLEUS b

APPROXIMATION: $H_{aa} \approx E_H$, $S \ll 1$

$$E_\pm = E_H \pm H_{ab}$$

FOR $r_{ab} \to \infty$ $H_{ab} \to 0$ (HYDROGEN ATOMS)



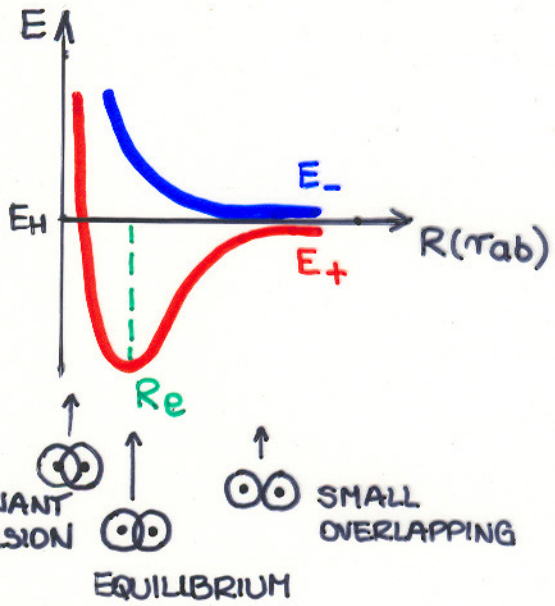
$H_{ab} \leqslant 0$

$E_+ \leqslant E_H \quad E_- \geqslant E_H$

ψ_+ – STABLE STATE OF H_2^+

HYDROGEN ATOM: $\bar{e}$ IS ON THE ORBITAL ψ_+ AND IT ATTRACTS POSITIVE NUCLEUS, ENERGY IS LOWERED AND THE MOLECULE H_2^+ IS FORMED

TOTAL ENERGY OF H_2^+:

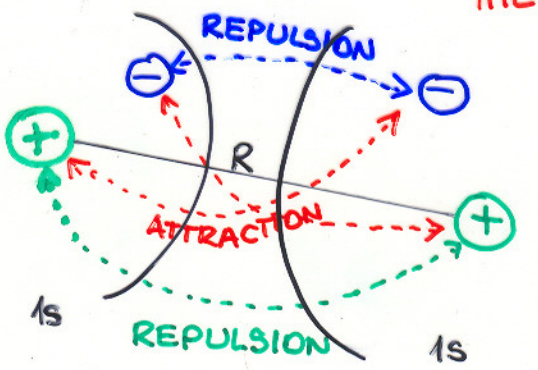


$$\mathcal{E}_{\pm} = E_{\pm} + \frac{e^2}{r_{ab}}$$

$E_{\pm}$: ENERGY OF ELECTRONS

$\frac{e^2}{r_{ab}}$: REPULSION BETWEEN THE NUCLEI

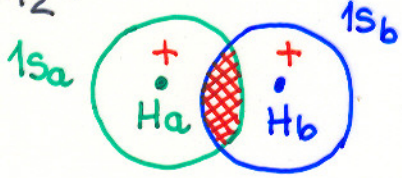
THE BOUND STATE IMPLIES A NET ATTRACTIVE FORCE BETWEEN THE ATOMS



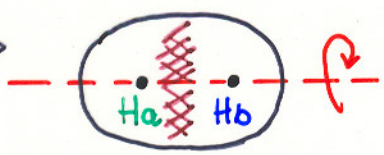
MOLCAO IS EFFECTIVE IF

1. THE ENERGIES OF AO'S ARE COMPARABLE
2. THERE IS AN OVERLAP BETWEEN AO'S

H_2^+:



$1s_a + 1s_b \Rightarrow$

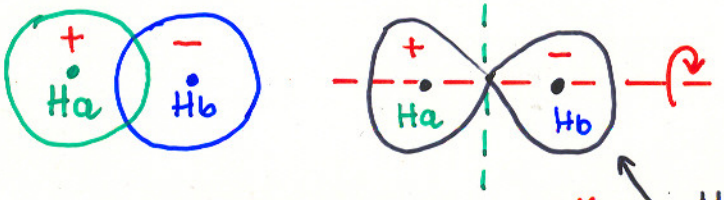


BONDING MO: $\sigma^b (\equiv \sigma)$

CYLINDRICAL SYMMETRY:

MOLECULAR ORBITAL SYMMETRIC WITH RESPECT TO ROTATION AROUND AXIS || TO THE BOND (CONNECTS TWO NUCLEI) = INTERNUCLEAR AXIS

$1s_a - 1s_b \Rightarrow$



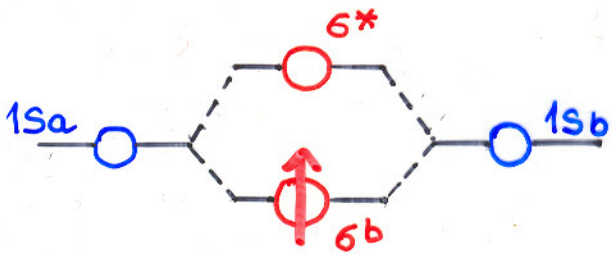
ANTI BONDING MO: σ^*

NODE BETWEEN THE NUCLEI = DENSITY (PROBABILITY) = 0

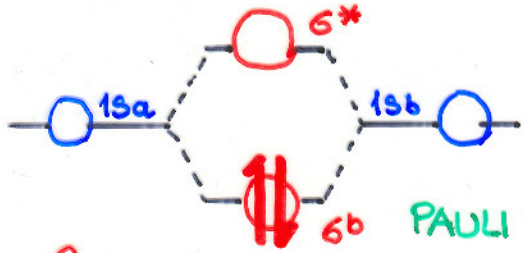
LESS STABLE THAN ISOLATED AO 1S OF H ATOM

HIGHEST PROBABILITY OUTSIDE THE OVERLAP REGION

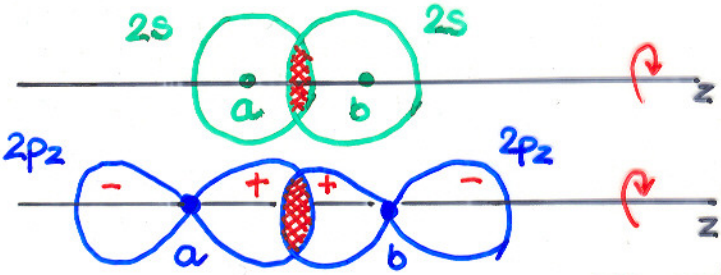
H_2^+ : σ^b GROUND CONFIGURATION



H_2 : $\overset{+}{\sigma}{}^b\,\overset{-}{\sigma}{}^b \equiv (\sigma^b)^2$

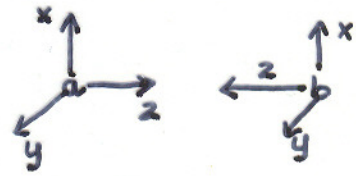


PAULI PRINCIPLE !



MO: σ^b

INTERNUCLEAR AXIS ≡ z



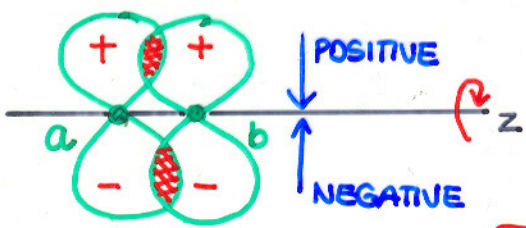
HOMO

$$\psi(\sigma_s^b) = \frac{1}{\sqrt{2}}(2s_a + 2s_b) \qquad \psi(\sigma_s^*) = \frac{1}{\sqrt{2}}(2s_a - 2s_b)$$

$$\psi(\sigma_z^b) = \frac{1}{\sqrt{2}}(2p_{za} + 2p_{zb}) \qquad \psi(\sigma_z^*) = \frac{1}{\sqrt{2}}(2p_{za} - 2p_{zb})$$

$$\psi(\sigma^b) = \frac{1}{\sqrt{2}}(2s_a + 2p_{zb}) \qquad \psi(\sigma^*) = \frac{1}{\sqrt{2}}(2s_a - 2p_{zb})$$

HETERONUCLEAR DIATOMIC MOLECULE



ROTATION BY 180° ⇒ CHANGE OF SIGN

PLUS LOBE ↔ MINUS LOBE

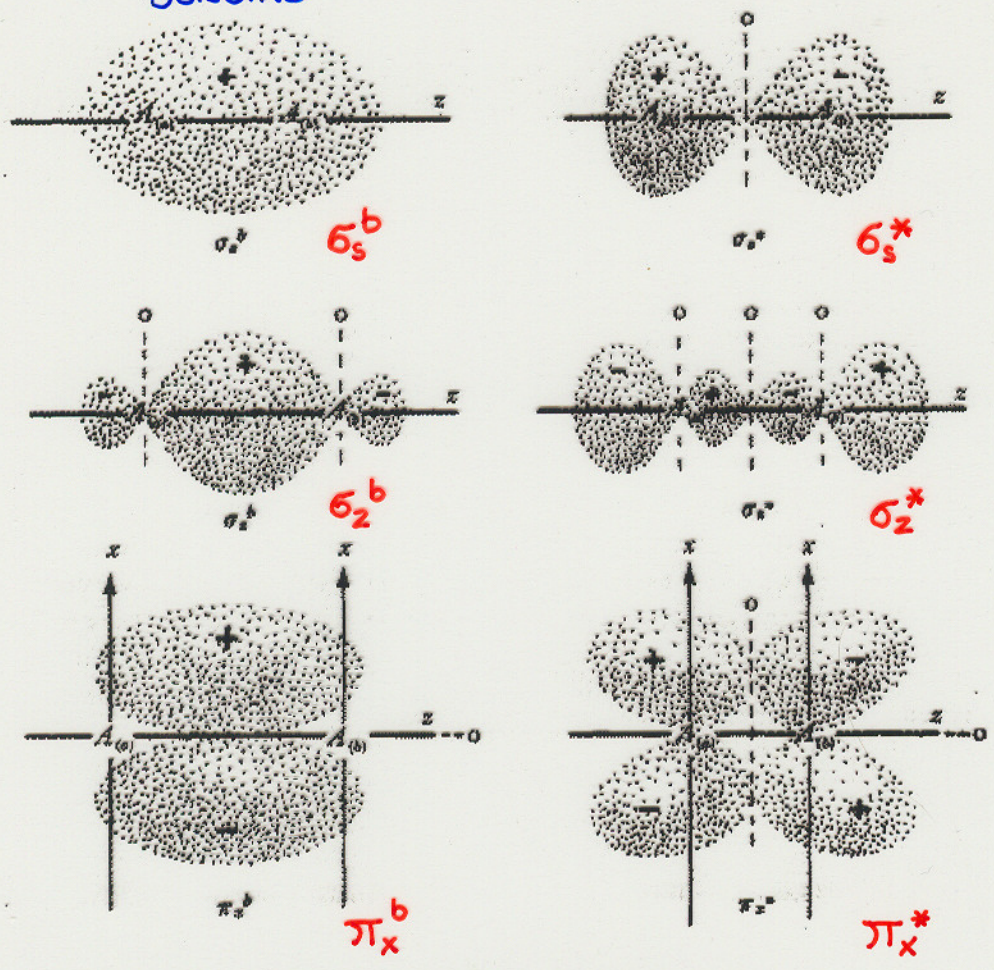
NODE IN THE yz PLANE

π MOLECULAR ORBITAL

$$\psi(\pi_x^b) = \frac{1}{\sqrt{2}}(2p_{xa} + 2p_{xb}) \qquad \psi(\pi_x^*) = \frac{1}{\sqrt{2}}(2p_{xa} - 2p_{xb})$$

$$\psi(\pi_y^b) = \frac{1}{\sqrt{2}}(2p_{ya} + 2p_{yb}) \qquad \psi(\pi_y^*) = \frac{1}{\sqrt{2}}(2p_{ya} - 2p_{yb})$$

BONDING ANTIBONDING



σ_s^b σ_s^* σ_z^b σ_z^* π_x^b π_x^*

Figure 2-14 Boundary surfaces of the σ and π molecular orbitals formed from s and p valence orbitals for a homonuclear diatomic molecule.

osed of the two 2s atomic orbitals only if the 2s–2p energy differ-
ice is large. For small 2s–2p energy differences, we must consider
ie two 2s and the two $2p_z$ orbitals together in an LCAO-MO
heme. The most stable MO would be the combination

$$\psi(\sigma_s^b) = \frac{1}{\sqrt{2(1+\tau^2)}}(2s_a + \tau 2p_{z_a} + 2s_b + \tau 2p_{z_b})$$

! SP HYBRIDIZATION

here the coefficient τ is less than unity and represents the amount of
) included in the σ_s^b MO.

H. B. GRAY, "ELECTRONS AND CHEMICAL BONDING"
W. A. BENJAMIN, INC., 1965

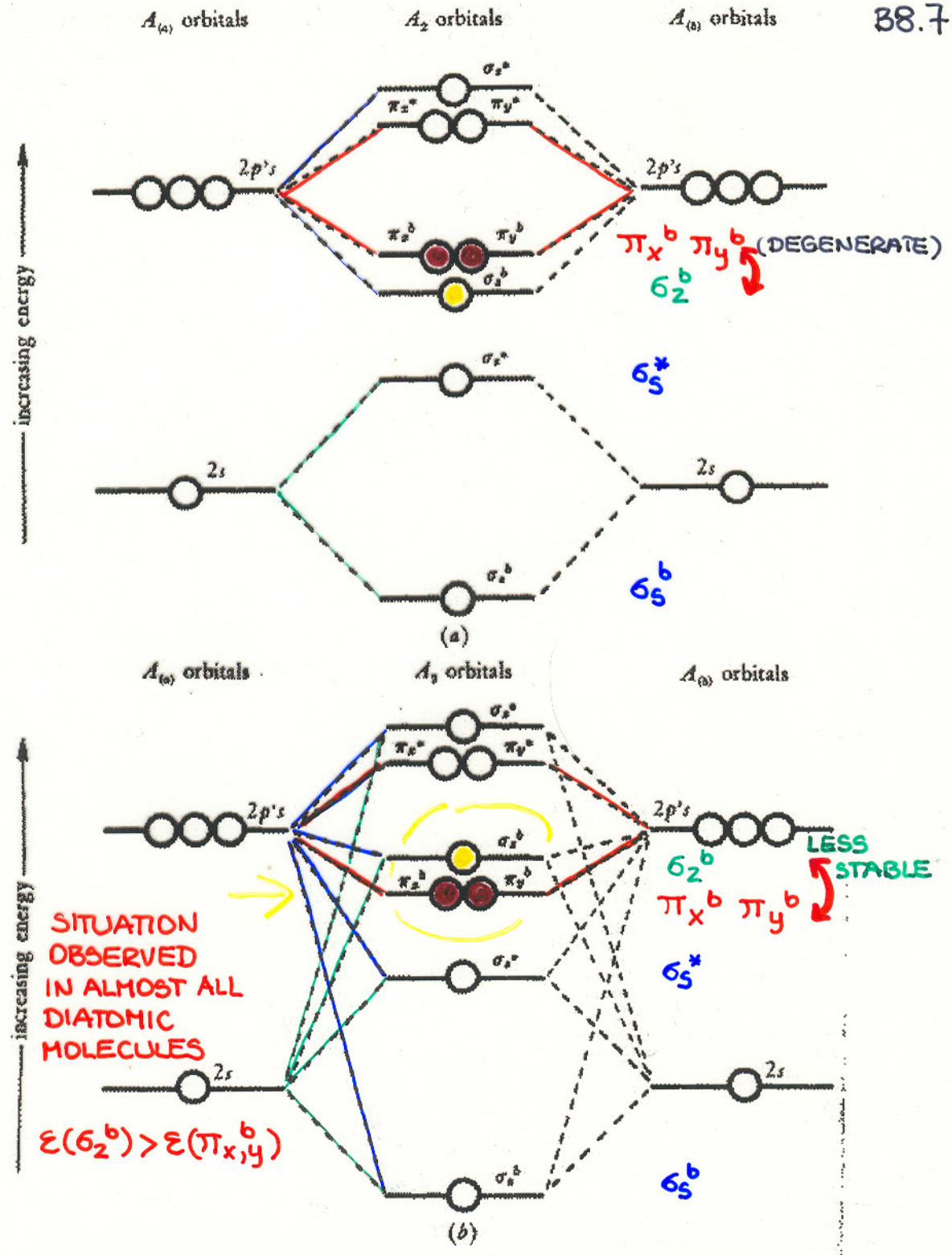


Figure 2-15 Molecular-orbital energy-level diagrams for a homonuclear diatomic molecule (*a*) with no σ_s–σ_s interaction; (*b*) with appreciable σ_s–σ_s interaction.

H.B. GRAY

THEORETICAL QUANTITY:

MINUS!

$$\text{NUMBER OF BONDS} = \frac{1}{2}\{(\text{NUMBER OF ELECTRONS IN BONDING MO's}) - (\text{NUMBER OF ELECTRONS IN ANTIBOND. MO's})\}$$

ONE ELECTRON IN AN ANTIBONDING MO CANCELS OUT THE BONDING STABILITY OF ONE ELECTRON IN A BONDING MO

$H_2^+ : (\sigma^b)^1 \Rightarrow$ HALF A σ BOND

$H_2 : (\sigma^b)^2 \Rightarrow$ ONE σ BOND

STRONGER
IS IT SHORTER?

BOND LENGTH R = EQUILIBRIUM INTERNUCLEAR DISTANCE

EXPERIMENTAL QUANTITY

$R_{H_2^+} = 1.06\text{Å}$

$R_{H_2} = 0.74\text{Å}$

REFLECTS THE STRUCTURE OF A MOLECULE

exp.

BOND-DISSOCIATION ENERGY FOR A BOND BETWEEN TWO ATOMS = ENERGY REQUIRED TO BREAK THE BOND, GIVING ISOLATED GROUND-STATE ATOMS

$$H_2 + \text{BOND DISS. ENERGY} \longrightarrow H + H$$

$DE_{H_2^+} = 61.06$ kcal/mol

$DE_{H_2} = 103.24$ kcal/mol