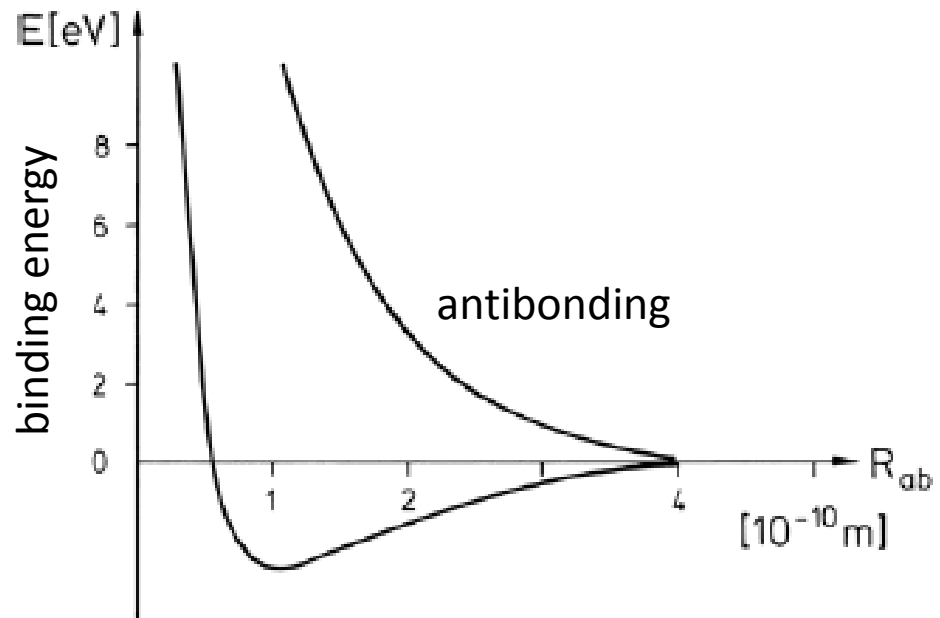
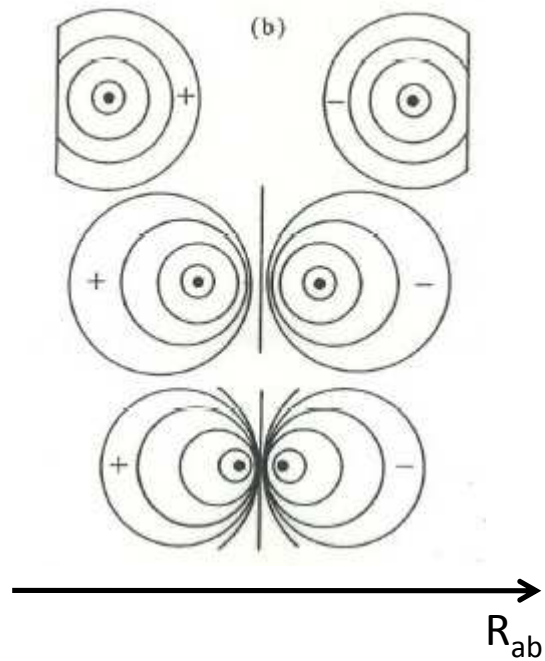
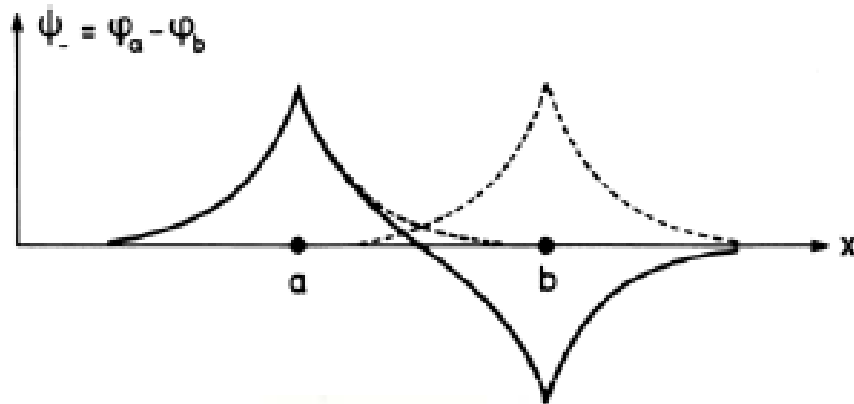
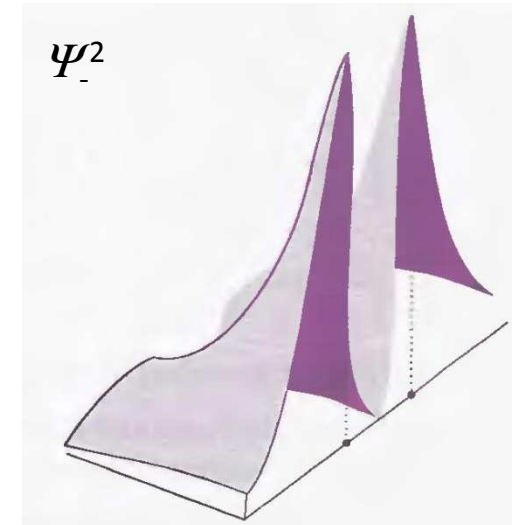


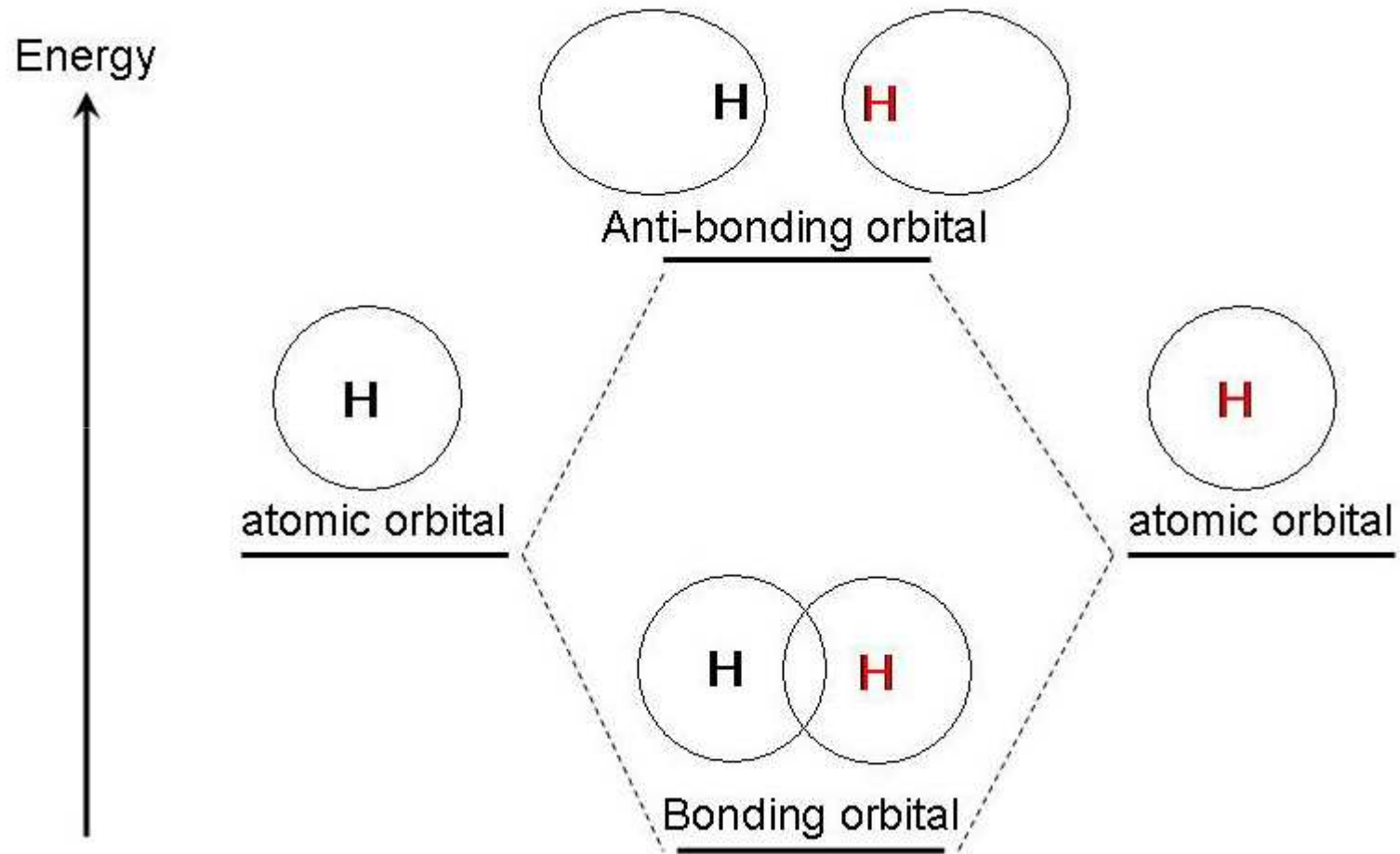
Molecular orbitals

Antibonding orbitals σ^* :

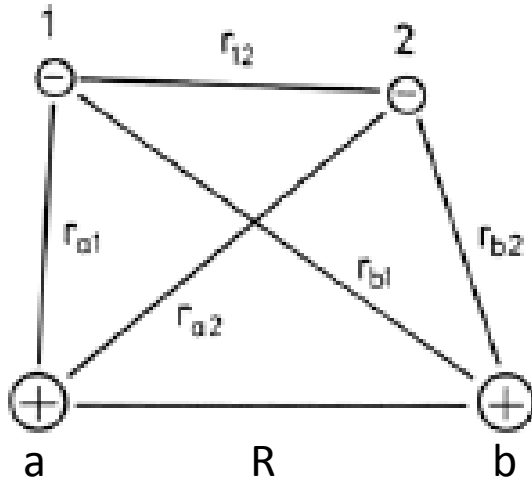
$$\psi_- = c(\varphi_a - \varphi_b)$$



Molecular orbitals: energy level diagram



The H₂ molecule (LCAO)



D_e = dissociation energy

Calc: 3.14 eV

Exp 4.72 eV

r_0 = equilibrium bond length

Calc: 0.80 Å

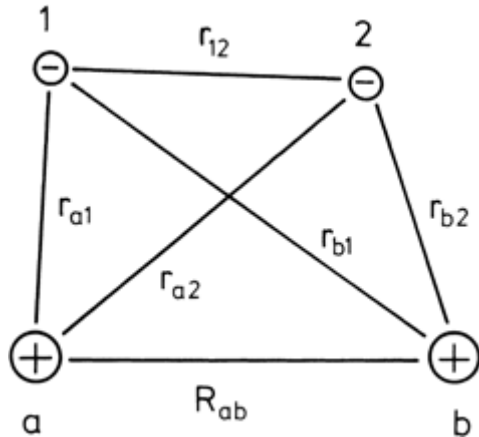
Exp: 0.74 Å

Energy of H₂ molecule:

$$E(R)_{\text{H}_2} = 2E(R)_{\text{H}_2^+} + \frac{e^2}{4\pi\epsilon_0 a_0} \left[\frac{5}{16} - \frac{a_0}{2R} - \frac{a_0}{2R} \left(1 + \frac{11R}{8a_0} + \frac{3R^2}{4a_0^2} + \frac{1R^3}{6a_0^3} \right)^{2R/a_0} \right].$$

The H₂ molecule

Valence –bond theory (VB) / Heitler-London



$$H = -\frac{\hbar^2}{2m_0} \Delta_1 - \frac{e^2}{4\pi\epsilon_0 r_{a1}} - \frac{\hbar^2}{2m_0} \Delta_2 - \frac{e^2}{4\pi\epsilon_0 r_{b2}} - \frac{e^2}{4\pi\epsilon_0 r_{b1}} - \frac{e^2}{4\pi\epsilon_0 r_{a2}} + \frac{e^2}{4\pi\epsilon_0 R_{ab}} + \frac{e^2}{4\pi\epsilon_0 r_{12}} \quad (1)$$

Task: solve $H\Psi(r_1, r_2) = E\Psi(r_1, r_2)$

(2)

R_{ab} large:

$$\left(-\frac{\hbar^2}{2m_0} \Delta_1 - \frac{e^2}{4\pi\epsilon_0 r_{a1}} \right) \varphi_a(r_1) = E_0 \varphi_a(r_1) \quad (3)$$

$$\left(-\frac{\hbar^2}{2m_0} \Delta_2 - \frac{e^2}{4\pi\epsilon_0 r_{b2}} \right) \varphi_b(r_2) = E_0 \varphi_b(r_2) \quad (4)$$

$H = H_1 + H_2$ $\varphi_a(r_1)\varphi_b(r_2)$ trial wavefunction

(5)

Spin wavefunctions: $\alpha(1) \alpha(2)$ up

$\beta(1) \beta(2)$ down

$1/2^{1/2} [\alpha(1) \beta(2) + \alpha(2) \beta(1)]$ symmetric linear combination

$1/2^{1/2} [\alpha(1) \beta(2) - \alpha(2) \beta(1)]$ antisymm. linear combination

The H₂ molecule (VB theory)

Total up wavefunction:

$$\Psi = \varphi_a(r_1)\alpha(1)\varphi_b(r_2)\alpha(2) - \varphi_a(r_2)\alpha(2)\varphi_b(r_1)\alpha(1) = \alpha(1)\alpha(2) \underbrace{[\varphi_a(r_1)\varphi_b(r_2) - \varphi_a(r_2)\varphi_b(r_1)]}_{\Psi_u} \quad (6)$$

Total down wavefunction:

$$\Psi = \beta(1)\beta(2)\Psi_u \quad (7)$$

Total linear combination wavefunctions:

$$\Psi = \frac{1}{\sqrt{2}}[\alpha(1)\beta(2) + \alpha(2)\beta(1)]\Psi_u \quad (8)$$

$$\Psi = \underbrace{[\varphi_a(r_1)\varphi_b(r_2) + \varphi_a(r_2)\varphi_b(r_1)]}_{\Psi_g} [\alpha(1)\beta(2) - \alpha(2)\beta(1)] \quad (9)$$

Ψ_g and Ψ_u are trial solutions of Schrödinger eq. (1).

$$E = \frac{\int \Psi^* H \Psi dV_1 dV_2}{\int \Psi^* \Psi dV_1 dV_2} \quad (10)$$

Denominator: $\iint |\Psi(r_1, r_2)|^2 dV_1 dV_2 \quad \longrightarrow \quad 2(1 \pm S^2)$

$$= \iint [\varphi_a(r_1)\varphi_b(r_2) \pm \varphi_a(r_2)\varphi_b(r_1)]^* \cdot [\varphi_a(r_1)\varphi_b(r_2) \pm \varphi_a(r_2)\varphi_b(r_1)] dV_1 dV_2 \quad (11)$$

The H₂ molecule (VB theory)

Numerator:

$$\iint \varphi_a(r_1)\varphi_b(r_2) \left\{ H_1 + H_2 - \frac{e^2}{4\pi\epsilon_0 r_{b1}} - \frac{e^2}{4\pi\epsilon_0 r_{a2}} + \frac{e^2}{4\pi\epsilon_0 R_{ab}} + \frac{e^2}{4\pi\epsilon_0 r_{12}} \right\} \cdot \varphi_a(r_1)\varphi_b(r_2) dV_1 dV_2 \quad (12)$$



$$\iint \varphi_a(r_1)^2 \varphi_b(r_2)^2 \cdot \left\{ \underbrace{2E_0}_{1)} - \underbrace{\frac{e^2}{4\pi\epsilon_0 r_{b1}}}_{2)} - \underbrace{\frac{e^2}{4\pi\epsilon_0 r_{a2}}}_{3)} + \underbrace{\frac{e^2}{4\pi\epsilon_0 R_{ab}}}_{4)} + \underbrace{\frac{e^2}{4\pi\epsilon_0 r_{12}}}_{5)} \right\} dV_1 dV_2 \quad (13)$$

$2E_0$

$C < 0$ interaction: nucleus b with electron in state a

$C < 0$ interaction: nucleus a with electron in state b

$\frac{e^2}{4\pi\epsilon_0 R_{ab}}$ n-n repulsion

E_{ww} e-e repulsion

$$\hat{E} = 2E_0 + 2C + E_{ww} + \frac{e^2}{4\pi\epsilon_0 R_{ab}} \quad \text{contribution to the total energy} \quad (14)$$

The H₂ molecule (VB theory)

Numerator: $\pm \iint \varphi_b(\mathbf{r}_1)\varphi_a(\mathbf{r}_2)\{ \cdot \mathbf{H} \cdot \} \varphi_b(\mathbf{r}_2)\varphi_a(\mathbf{r}_1)dV_1dV_2$ (15)



$$\pm \iint \varphi_b(\mathbf{r}_1)\varphi_a(\mathbf{r}_2)\varphi_a(\mathbf{r}_1)\varphi_b(\mathbf{r}_2)$$

$$\cdot \left\{ \underbrace{2E_0}_{1)} - \underbrace{\frac{e^2}{4\pi\epsilon_0 r_{b1}}}_{2)} - \underbrace{\frac{e^2}{4\pi\epsilon_0 r_{a2}}}_{3)} + \underbrace{\frac{e^2}{4\pi\epsilon_0 R_{ab}}}_{4)} + \underbrace{\frac{e^2}{4\pi\epsilon_0 r_{12}}}_{5)} \right\} dV_1dV_2$$

$$\pm 2E_0 S^2$$

$$\pm SD$$

$$\pm SD$$

$$\pm S^2 \frac{e^2}{4\pi\epsilon_0 R_{ab}}$$

n-n interaction

$\pm E_{AW}$ e-e interaction

$$\tilde{E} = \pm 2E_0 S^2 \pm 2DS \pm E_{AW} \pm \frac{e^2}{4\pi\epsilon_0 R_{ab}} S^2 \quad \text{contribution to the total energy} \quad (16)$$

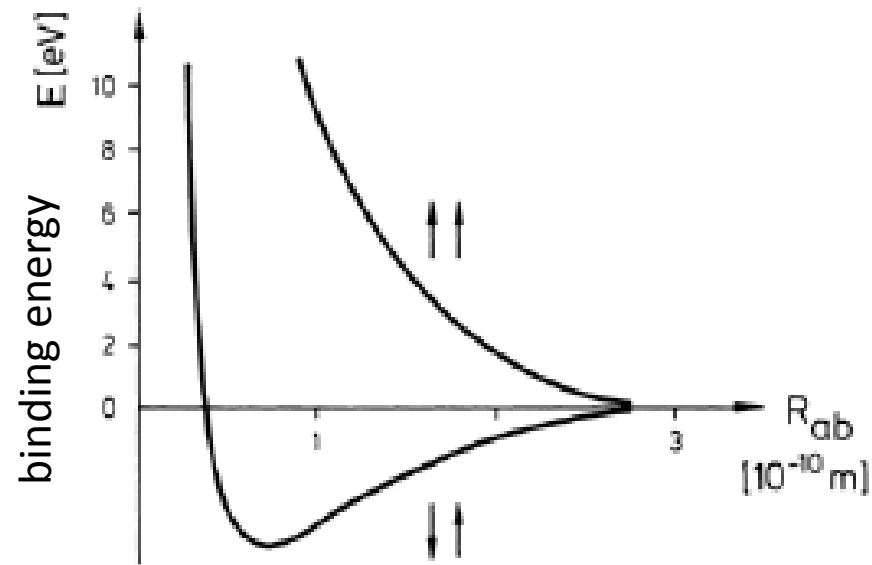
The H₂ molecule (VB theory)

Summing (14) and (16) up:

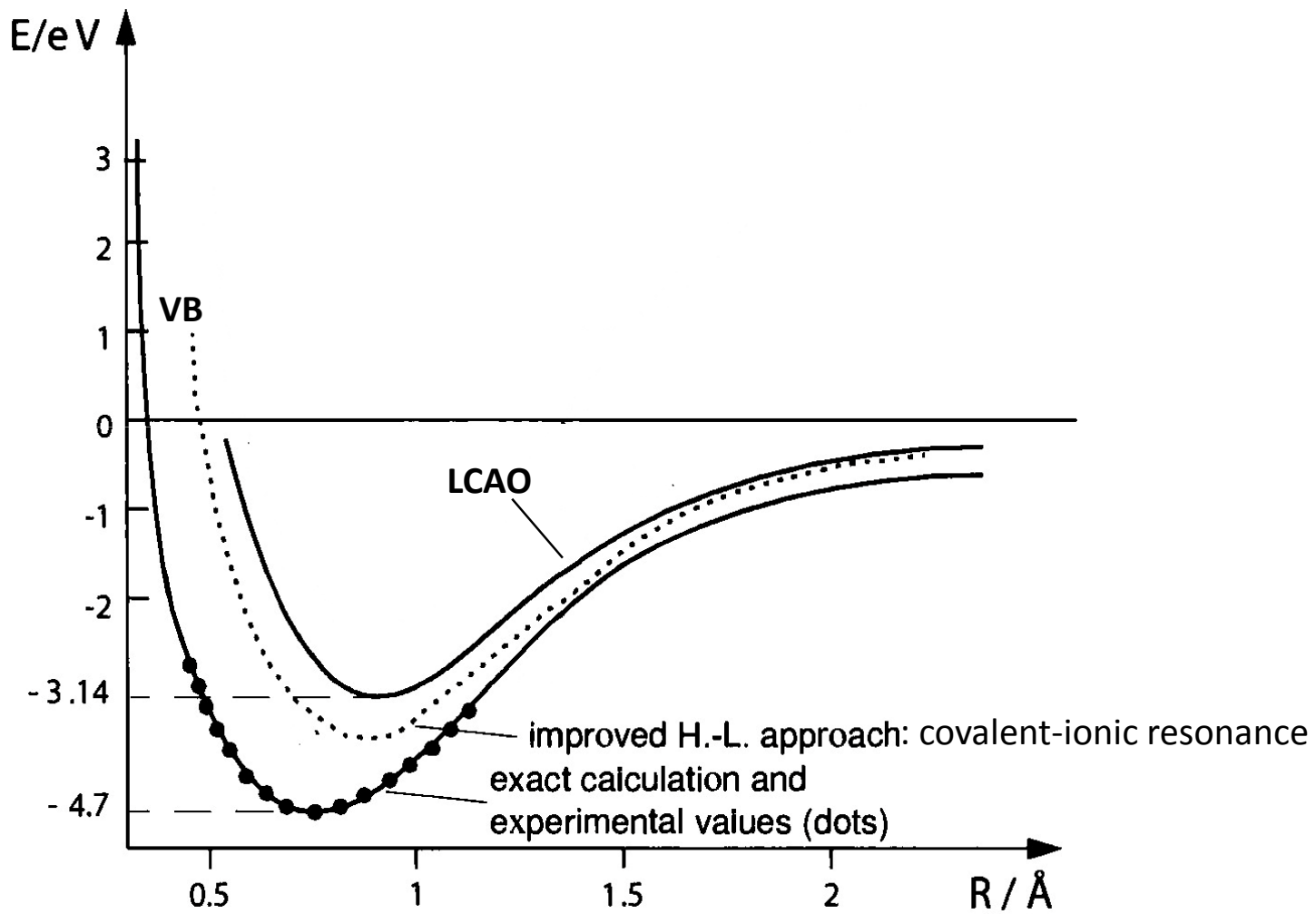
$$E_{g,u} = 2 \frac{\hat{E} \pm \tilde{E}}{\iint |\Psi|^2 dV_1 dV_2}$$

$$E_g = 2E_0 + \frac{2C + E_{WW}}{1 + S^2} + \frac{2DS + E_{AW}}{1 + S^2} + \frac{e^2}{4\pi\epsilon_0 R_{ab}} \quad (17)$$

$$E_u = 2E_0 + \frac{2C + E_{WW}}{1 - S^2} - \frac{2DS + E_{AW}}{1 - S^2} + \frac{e^2}{4\pi\epsilon_0 R_{ab}} \quad (18)$$



The H₂ molecule: comparison of LCAO and VB methods



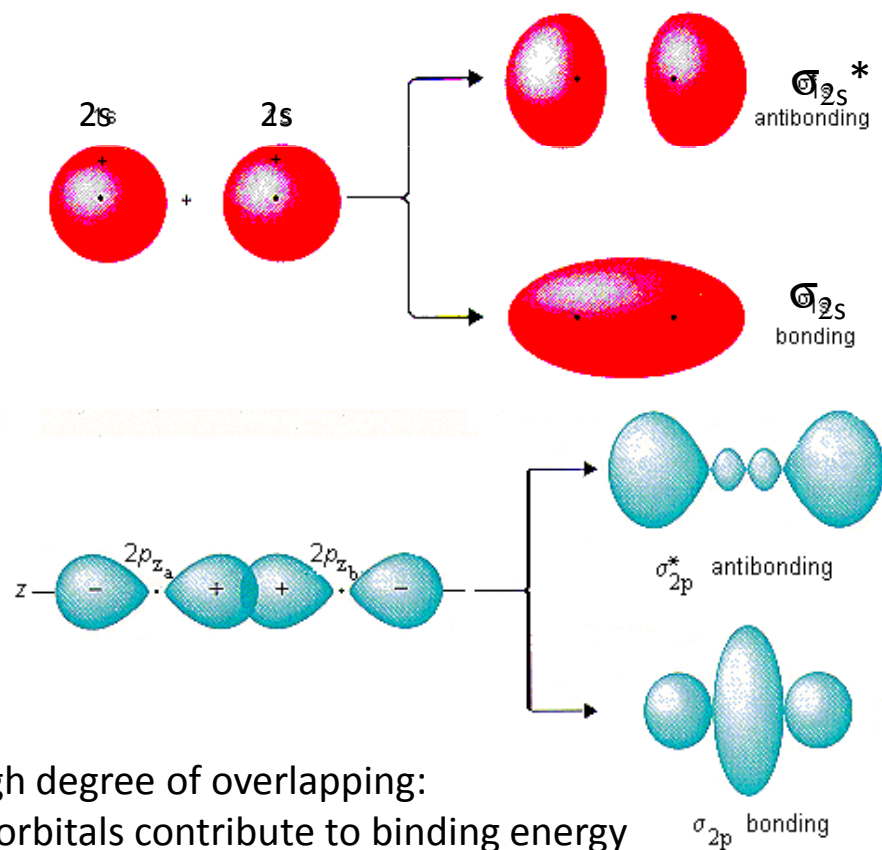
Homonuclear diatomic molecules: orbital formation

Period 2: Li Be B C N O F Ne valence orbitals: 2s 2p

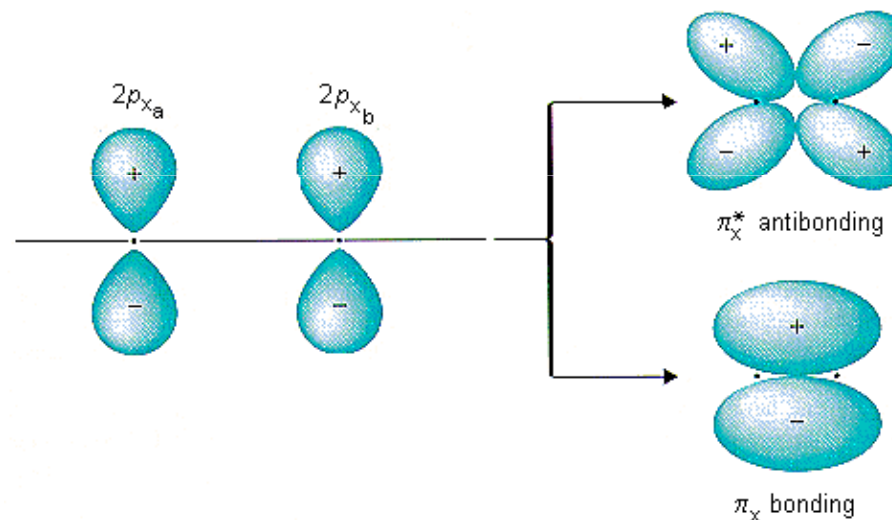
General principle: molecular orbitals are formed from atomic orbitals with the same symmetry.

N: $1s^2(2s^2 2p_x^1 2p_y^1 2p_z^1)$

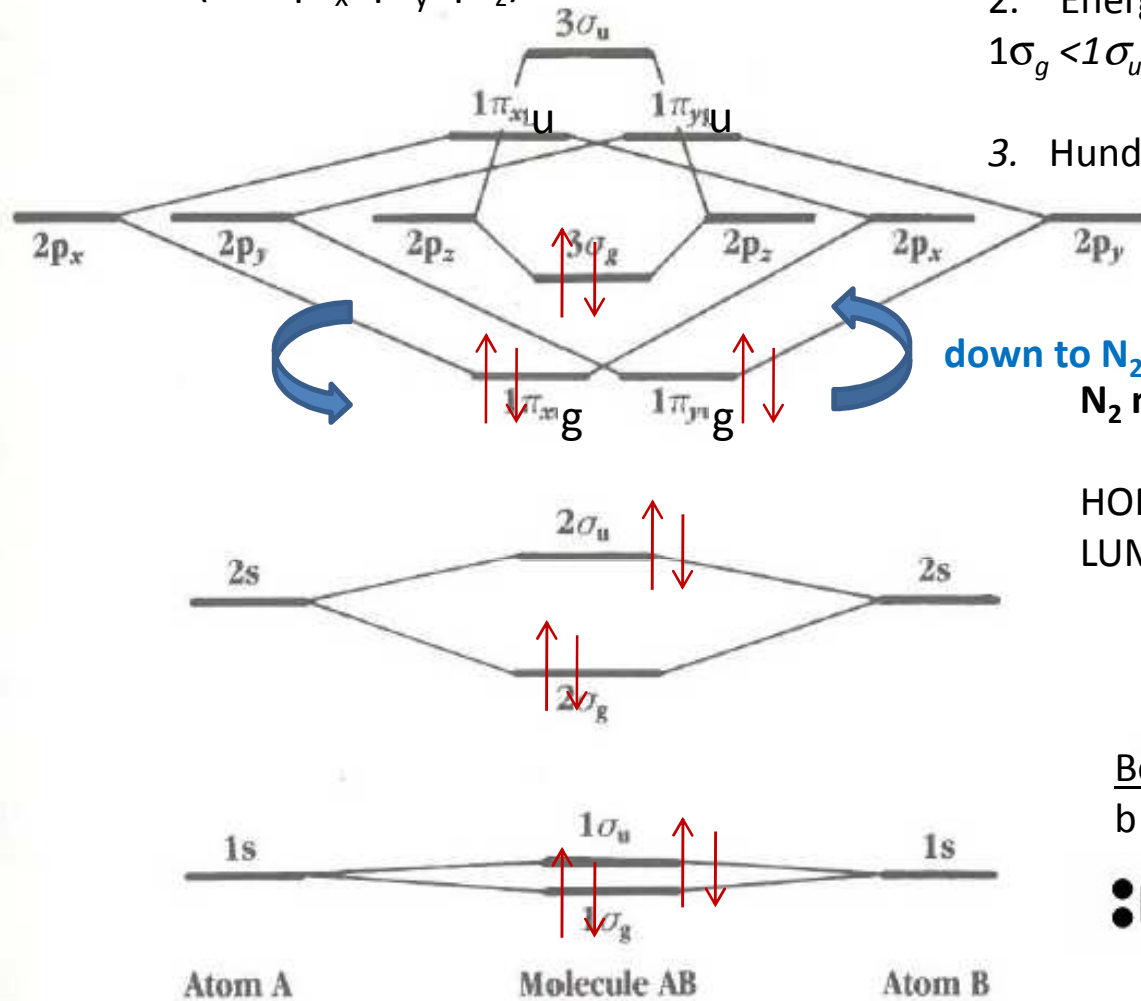
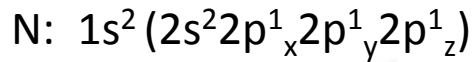
N₂ molecule: σ orbitals



N₂ molecule: π orbitals



Aufbau principle:



1. Pauli exclusion principle

2. Energy ordering:

$$1\sigma_g < 1\sigma_u < 2\sigma_g < 2\sigma_u < 1\pi_g < 3\sigma_g < 1\pi_u < 3\sigma_u < ..$$

3. Hund's rule



HOMO $3\sigma_g$

LUMO $1\pi_u$

Bond order:

$$b = ((\text{bonding el}) - (\text{antibonding el}))/2$$

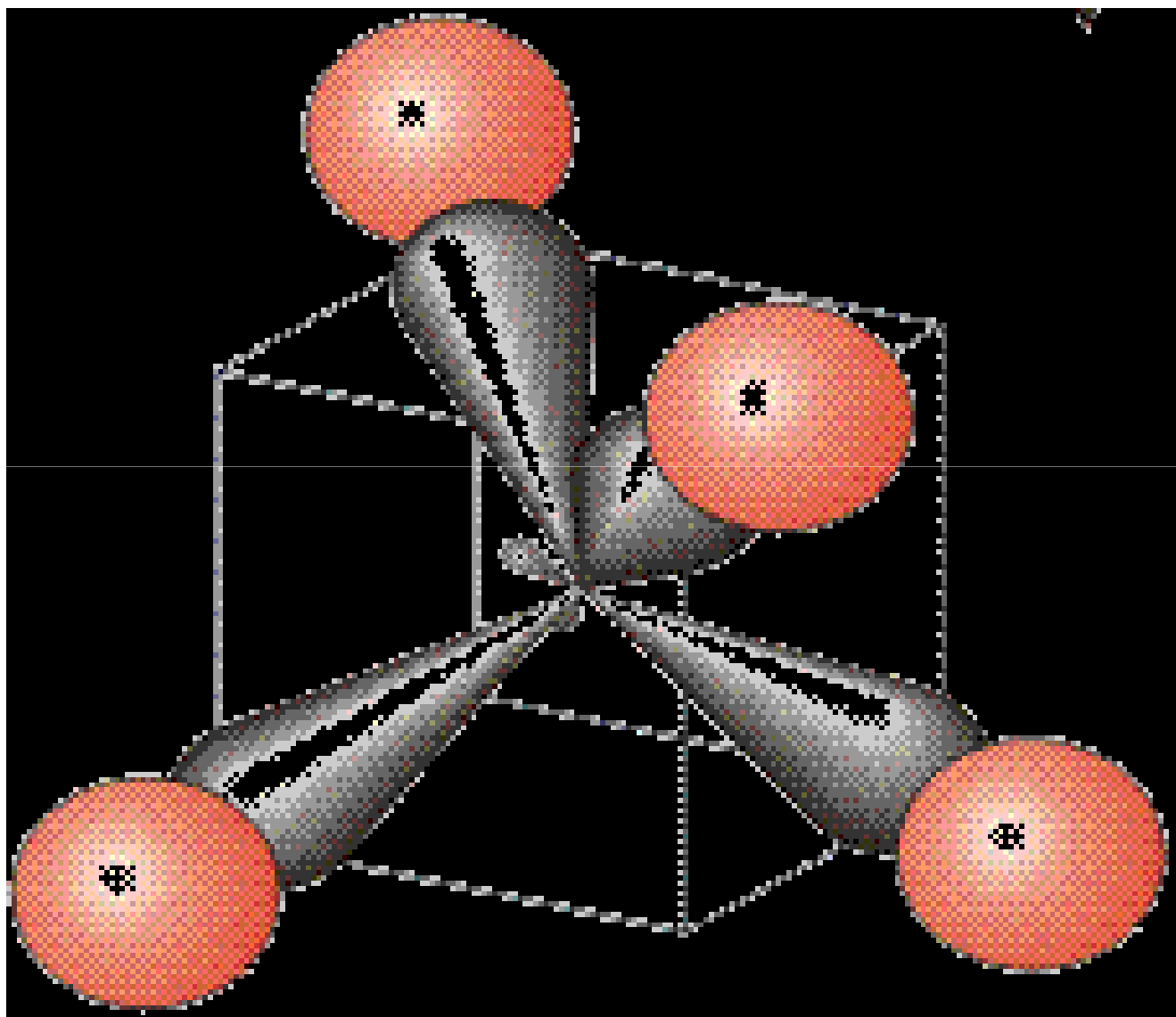


The higher the bond order:

- the shorter the bond
- the stronger the bond

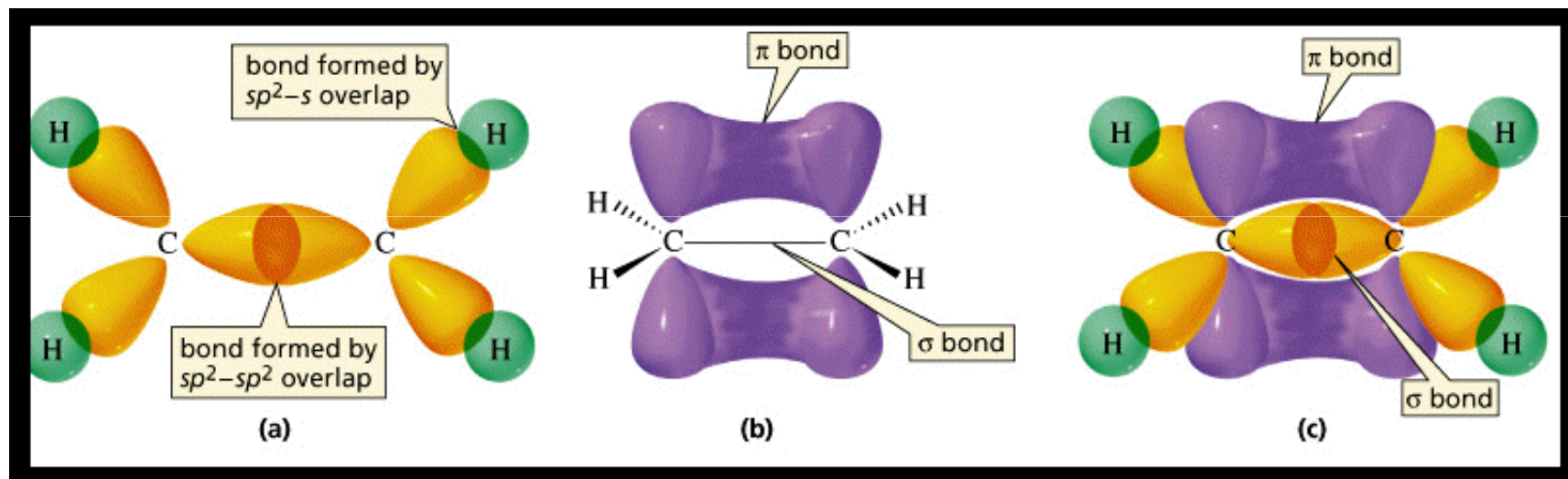
molecular orbital energy level
homonuclear diatomic molecule (up to **N₂**)

CH₄ molecule

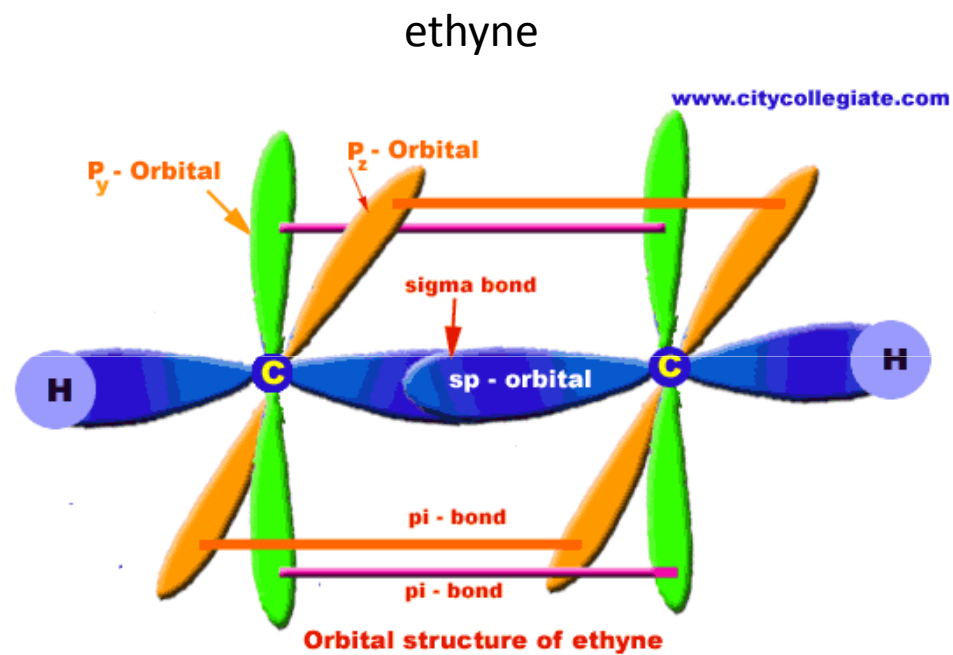
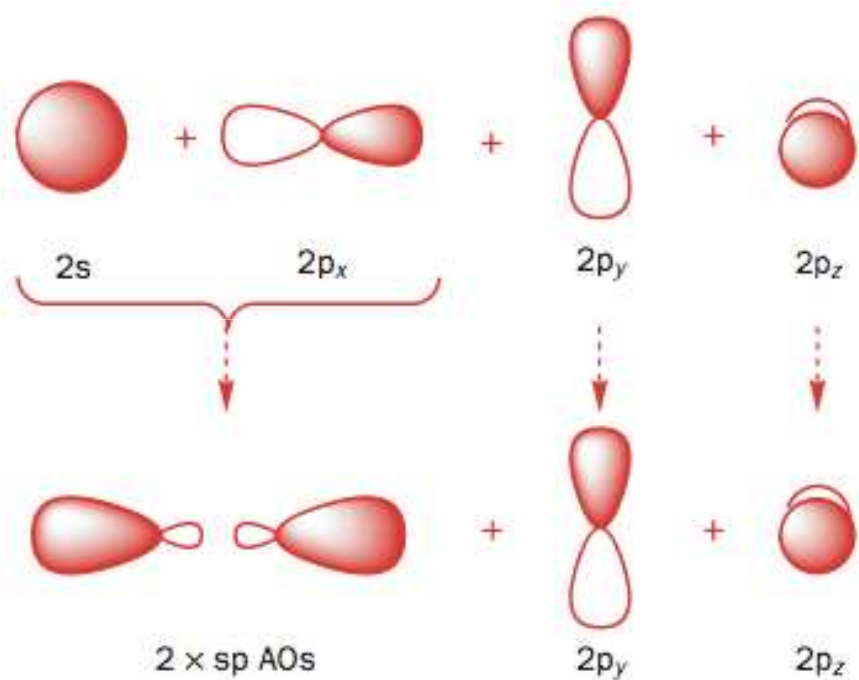


C_2H_4 molecule: sp^2 hybridization

ethene



C₂H₂ molecule: sp hybridization



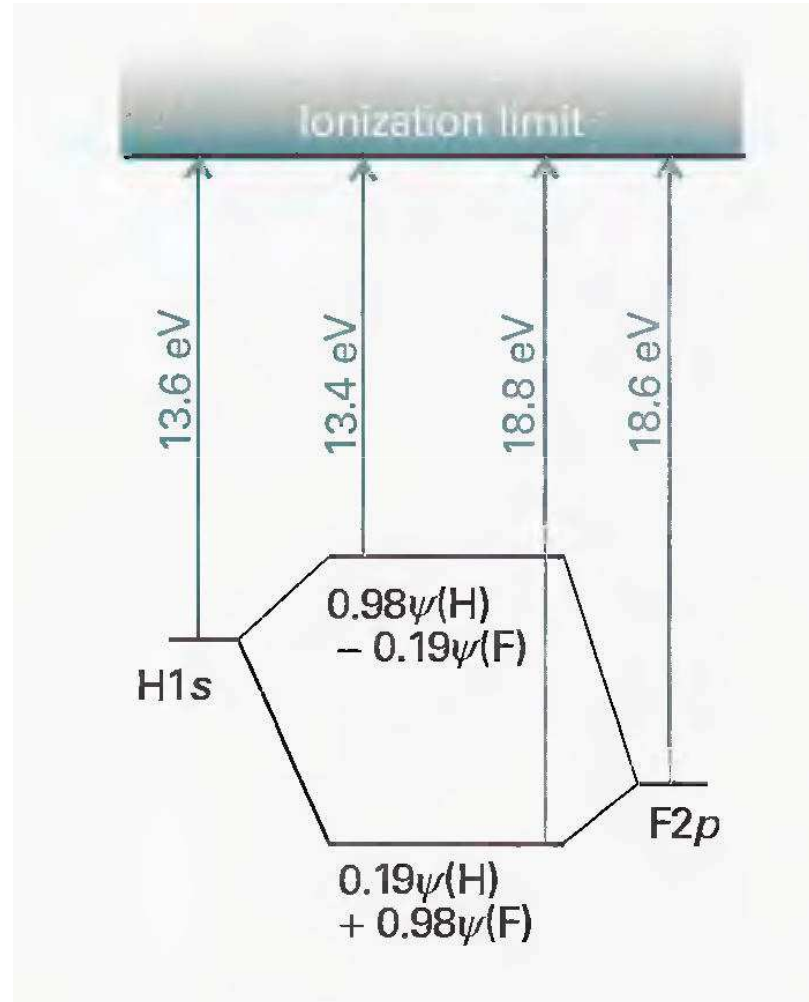
Heteronuclear diatomic molecules (AB)

Ex: HF

H: $1s^1$

F: $1s^2 2s^2 2p^5$

$$\Psi = c_H \phi_H + c_F \phi_F$$



Heteronuclear diatomic molecules: the variational principle

Case 1: $e_A = e_B = e$

The secular determinant: $(e-E)^2 - (D-ES)^2 = 0$

with solutions:

$$E_+ = \frac{e + D}{1 + S} \quad \text{and} \quad \Psi_+ = \frac{1}{\sqrt{2(1+S)}}(\phi_A + \phi_B)$$

$$E_- = \frac{e - D}{1 - S} \quad \text{and} \quad \Psi_- = \frac{1}{\sqrt{2(1-S)}}(\phi_A - \phi_B)$$

Case 2: $S=0$

The secular determinant: $(e_A - E)(e_B - E) - D^2 = 0$

with solutions:

$$E_+ = e_A + D \tan \zeta \quad \text{and} \quad \Psi_+ = \phi_A \cos \zeta + \phi_B \sin \zeta$$

$$E_- = e_B - D \tan \zeta \quad \text{and} \quad \Psi_- = -\phi_A \sin \zeta + \phi_B \cos \zeta$$

where:

$$\zeta = 0.5 \arctan (2D / (e_B - e_A))$$

$e_B - e_A$ large :

- bonding and anti bonding effects are small
- $\Psi_+ \sim \phi_A$ and $\Psi_- \sim \phi_B$ molecular orbitals are almost pure atomic orbitals

Strongest bonding and antibonding effects:
the two atomic orbitals have similar energies.