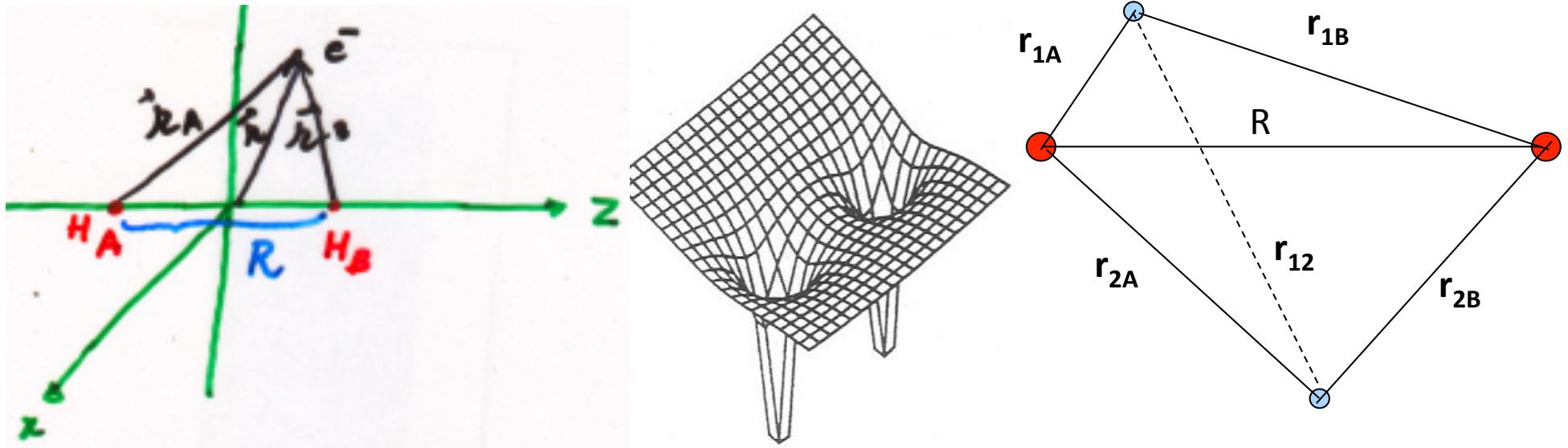


Simplest Molecules: H_2^+ and H_2



H_2^+ Molecule Ion (2 Nuclei + 1 Electron)

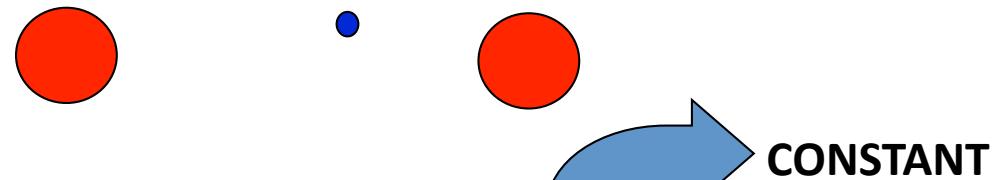
$$\widehat{H}(\text{H}_2^+) \sim \left(-\nabla_A^2 - \nabla_B^2 \right) + \left(-\nabla_{1e}^2 \right) + \left(-\frac{1}{r_{1A}} - \frac{1}{r_{1B}} \right) + \left(\frac{1}{R_{AB}} \right)$$

For H_2 Molecule (2 Nuclei + 2 Electrons):

$$\widehat{H}(\text{H}_2) \sim \left(-\nabla_A^2 - \nabla_B^2 \right) + \left(-\nabla_{1e}^2 - \nabla_{2e}^2 \right) + \left(-\frac{1}{r_{1A}} - \frac{1}{r_{2A}} - \frac{1}{r_{1B}} - \frac{1}{r_{2B}} \right) + \left(\frac{1}{R_{AB}} + \frac{1}{r_{12}} \right)$$

Born-Oppenheimer Approximation

Nuclei are stationary
wrt electronic motion



$$\hat{H}(\text{H}_2^+) \sim \cancel{\left(-\nabla_{AB}^2 \right)} + \left(-\nabla_{1e}^2 \right) + \left(-\frac{1}{r_{1A}} - \frac{1}{r_{1B}} \right) + \left(\frac{1}{R_{AB}} \right)$$

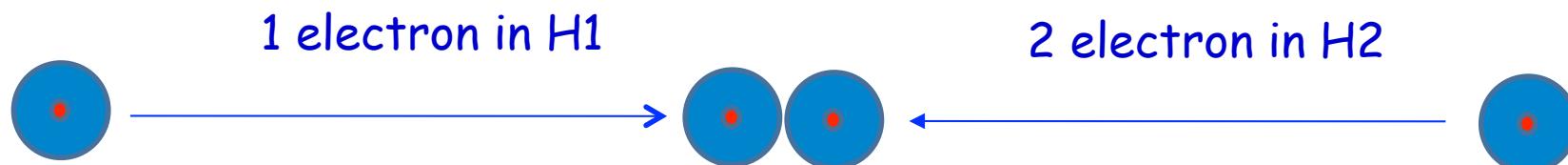
$$\hat{H}_{\text{H}_2^+} \sim \left(-\nabla^2 - \frac{1}{r_{e1A}} \right) + \frac{1}{R_{AB}} - \frac{1}{r_{e1B}} = \hat{H}_{H(1e)} + \frac{1}{R_{AB}} - \frac{1}{r_{eB}}$$

TISE for H_2^+

$$\widehat{H}_{\text{H}_2^+}(\vec{r}, R) \Psi_{\text{H}_2^+}(\vec{r}, R) = E_{\text{H}_2^+}(R) \Psi_{\text{H}_2^+}(\vec{r}, R)$$

Very difficult, but possible to solve the TISE under elliptical polar coordinates. Numerically easier!

Model 1: Valence Bond Theory (VBT)



$$\Psi = \Psi_{A(1)} \Psi_{B(2)}$$

$$\Psi = \Psi_{A(1)} \Psi_{B(2)} + \Psi_{A(2)} \Psi_{B(1)}$$

$$\Psi = \Psi_{A(1)} \Psi_{B(2)}$$

Inclusion of ionic terms



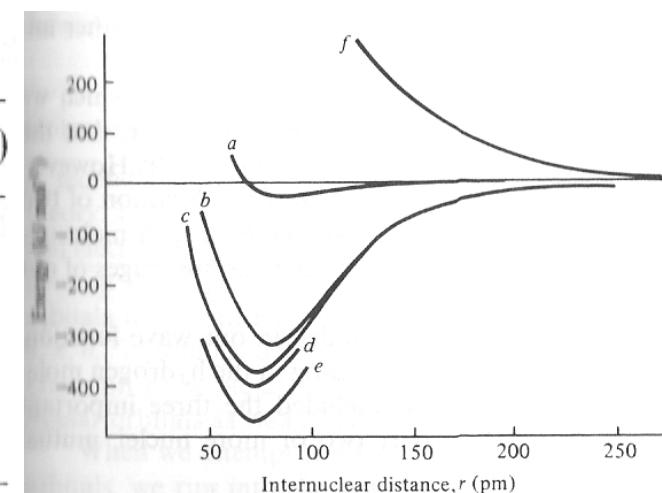
"Resonance"

$$\Psi = \Psi_{A(1)} \Psi_{B(2)} + \Psi_{A(2)} \Psi_{B(1)} + \lambda \Psi_{A(1)} \Psi_{A(2)} + \lambda \Psi_{B(1)} \Psi_{B(2)}$$

$$\Psi = \Psi_{\text{cov}} + \lambda' \Psi_{\text{H}^+\text{H}^-} + \lambda' \Psi_{\text{H}^-\text{H}^+}$$

Table 3.7 Energies and equilibrium distances for VB wave functions

Type of wave function	Energy (kJ mol^{-1})	Distance (pm)
Uncorrected, $\Psi = \Psi_A \Psi_B$	24	90
"Heitler-London"	303	86.9
Addition of shielding	365	74.3
Addition of ionic contributions	388	74.9
(Observed values)	458.0	74.1



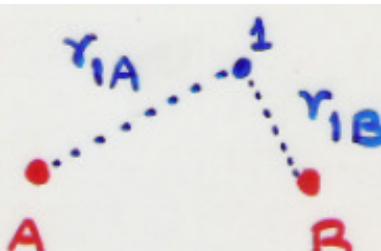
Model 2: Molecular Orbital Theory

A MO [one electron function like an AO] spreads throughout the molecule
ie, it is a polycentric one electron function,

eg: Linear Combination of Atomic Orbitals [LCAO-MO]

eg: H_2^+

$$\left[-\frac{\hbar^2}{2m_e} \nabla_i^2 - \frac{e^2}{r_{1A}} - \frac{e^2}{r_{1B}} \right] \psi = E \psi$$



$$\psi_1 = \phi_A(r_{1A}) + \phi_B(r_{1B})$$

$$\psi_2 = \phi_A(r_{1A}) - \phi_B(r_{1B})$$

Function of the coordinates
of an electron

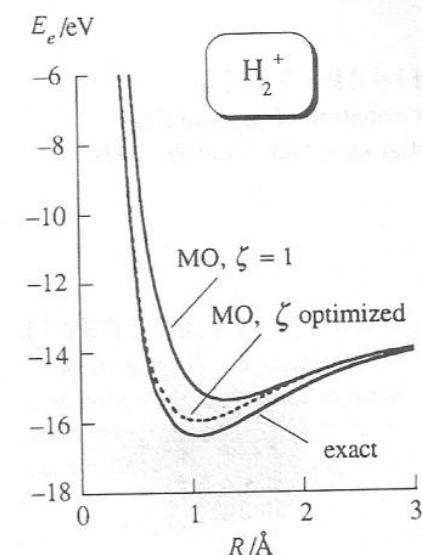


FIGURE 20.7

Electronic energy including internuclear repulsion for the H_2^+ ground electronic state. The curves are calculated from the exact wave function, from the LCAO MO function with optimized orbital exponent ζ , and from the LCAO MO function with $\zeta = 1$ (as in the lower curve in Fig. 20.6).

Both VBT and MOT are used frequently - each of them work good for certain systems, respectively, and often are not so good for other systems!

Molecular Orbital Theory: LCAO

Linear Combination of Atomic Orbitals (LCAO)

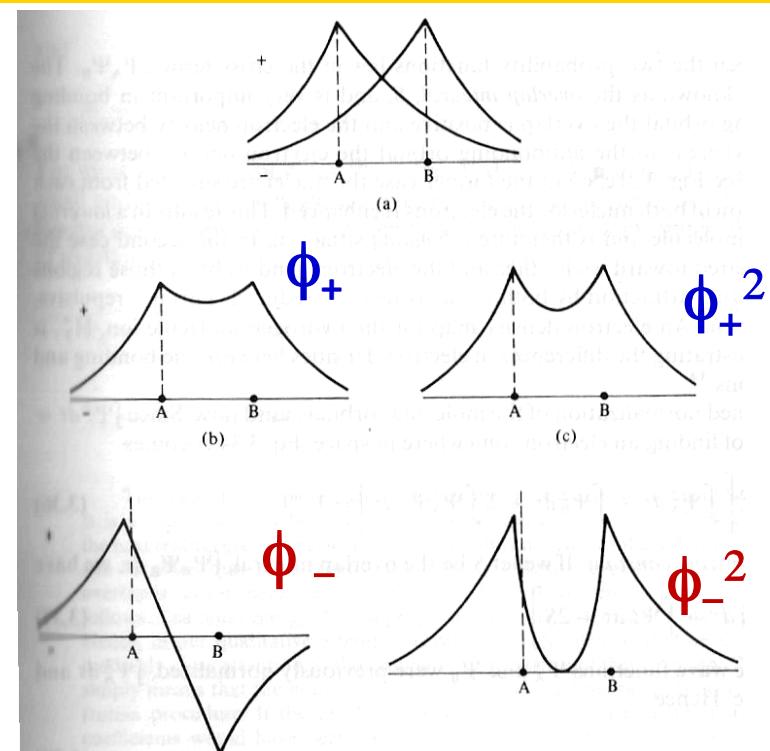
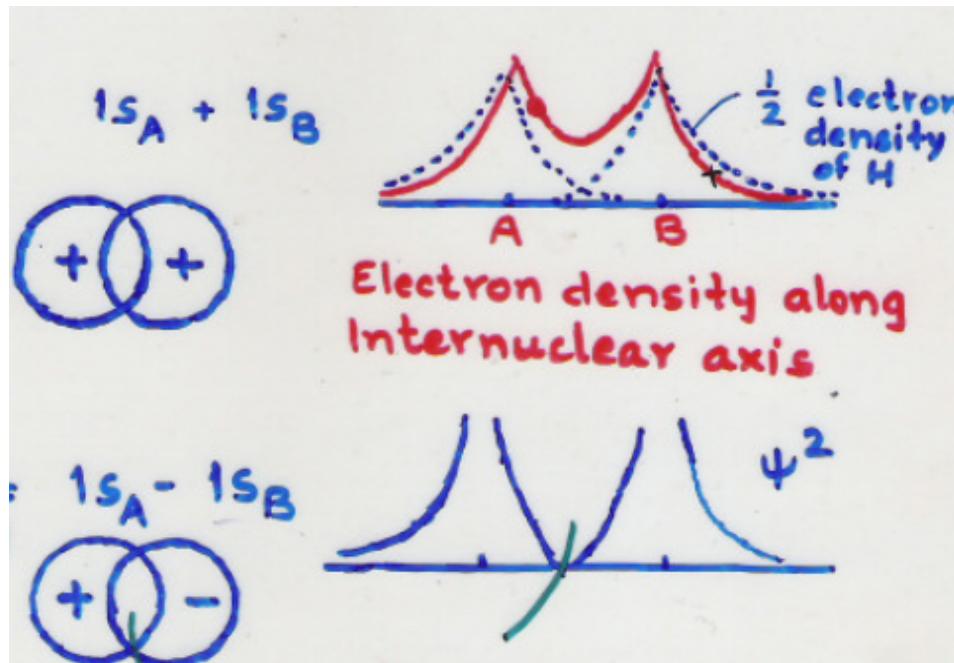
$$\varphi_{MO} = \varphi_{Approx} = c_1\psi_{1s_A} + c_2\psi_{1s_B} = c_1\psi_1 + c_2\psi_2$$

$$\varphi_{MO}^2 = c_1^2\psi_1^2 + c_2^2\psi_2^2 + 2c_1c_2\psi_1\psi_2$$

symmetry: $c_1^2 = c_2^2, \Rightarrow c_1 = \pm c_2$

for $c_1 = c_2 = c_b, \quad \varphi_b^2 = c_b^2(\psi_1 + \psi_2)^2 \Rightarrow \varphi_b = \pm c_b(\psi_1 + \psi_2) \sim 1s_A + 1s_B$

for $c_2 = -c_1 = -c_a, \quad \varphi_a^2 = c_a^2(\psi_1 - \psi_2)^2 \Rightarrow \varphi_a = \pm c_a(\psi_1 - \psi_2) \sim 1s_A - 1s_B$



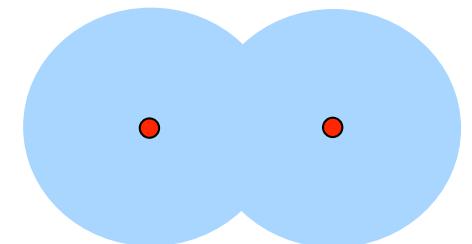




Normalization of Molecular Orbitals

$$\varphi_{a/-} = \pm c_a (\psi_1 - \psi_2) \sim 1s_A - 1s_B$$

$$\varphi_{b/+} = \pm c_b (\psi_1 + \psi_2) \sim 1s_A + 1s_B$$



How to find out c_a and c_b ? Normalize!

$$1 = \langle \varphi_{b/+} | \varphi_{b/+} \rangle = c_b^2 \langle (\psi_1 + \psi_2) | (\psi_1 + \psi_2) \rangle$$
$$1 = c_b^2 \left[\boxed{\langle \psi_1 | \psi_1 \rangle} + \boxed{\langle \psi_2 | \psi_2 \rangle} + \boxed{\cancel{\langle \psi_1 | \psi_2 \rangle}} + \boxed{\cancel{\langle \psi_2 | \psi_1 \rangle}} \right]$$

1 1 Same integral

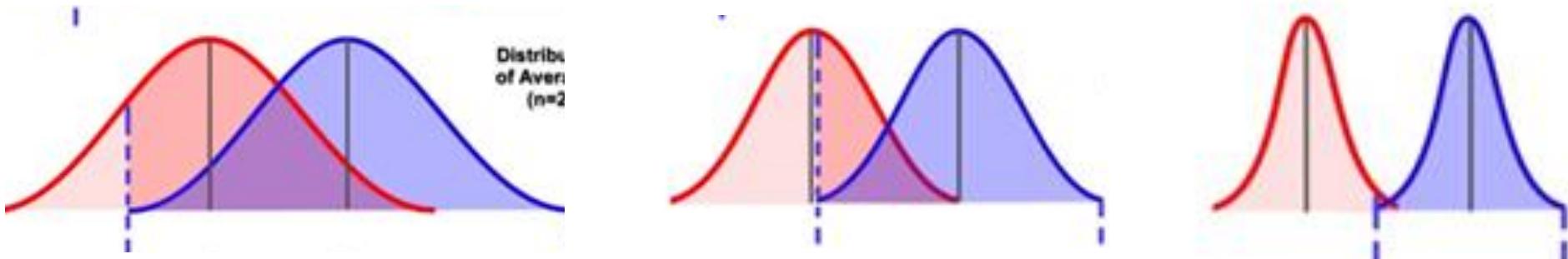
$$c_b = \frac{1}{\sqrt{2 + 2 \langle \psi_1 | \psi_2 \rangle}} \text{ and } c_a = \frac{1}{\sqrt{2 - 2 \langle \psi_1 | \psi_2 \rangle}}$$

$$\langle \psi_1 | \psi_2 \rangle = \langle \psi_2 | \psi_1 \rangle \rightarrow S \Leftrightarrow \text{Overlap Integral}$$

$$\varphi_{a/-} = \frac{1}{\sqrt{2 - 2S}} (\psi_1 - \psi_2); \quad \varphi_{b/+} = \frac{1}{\sqrt{2 + 2S}} (\psi_1 + \psi_2)$$

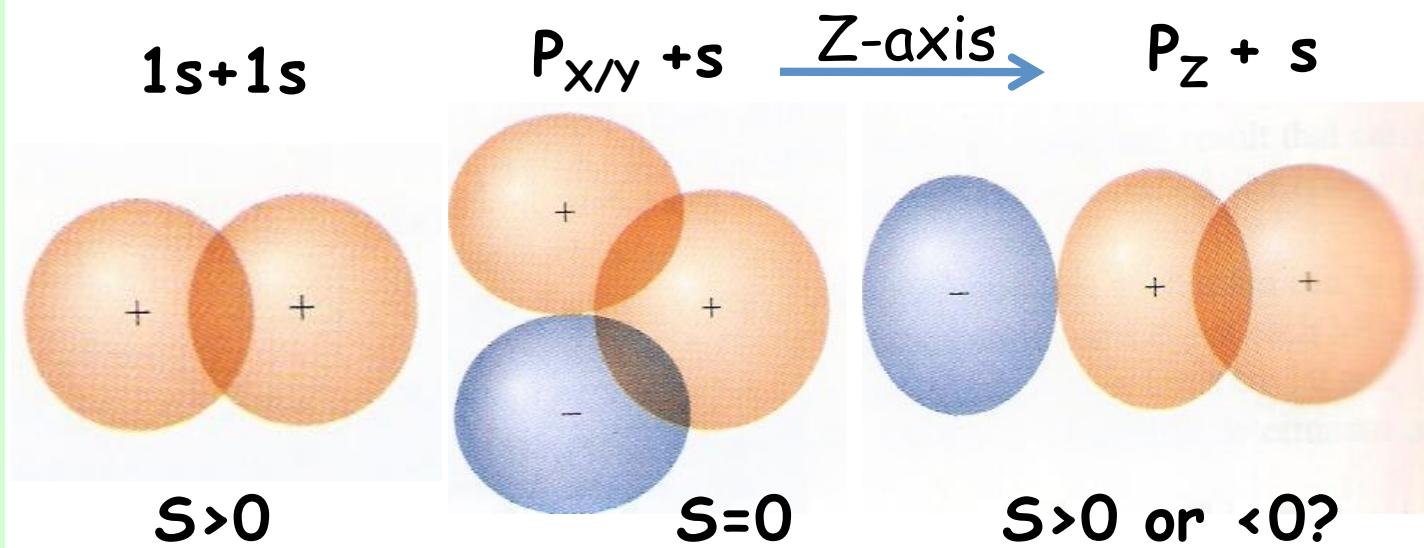
Concept of Overlap Integral

$$\text{Overlap Integral } S_{AB}(R) = \langle \psi_1 | \psi_2 \rangle = \int \psi_1 \psi_2 dt$$



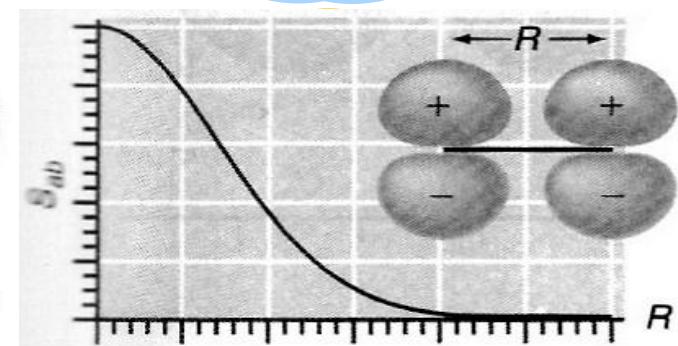
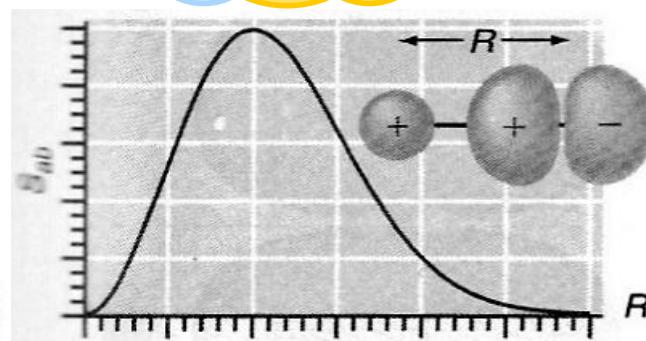
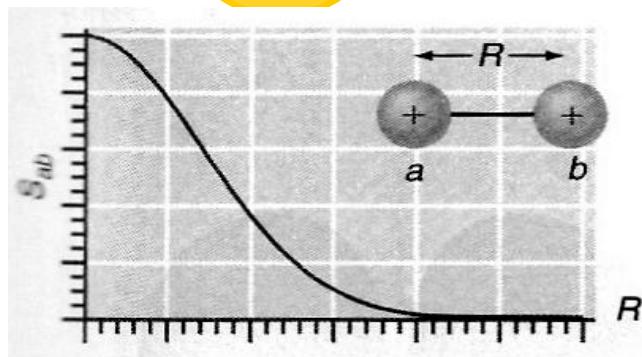
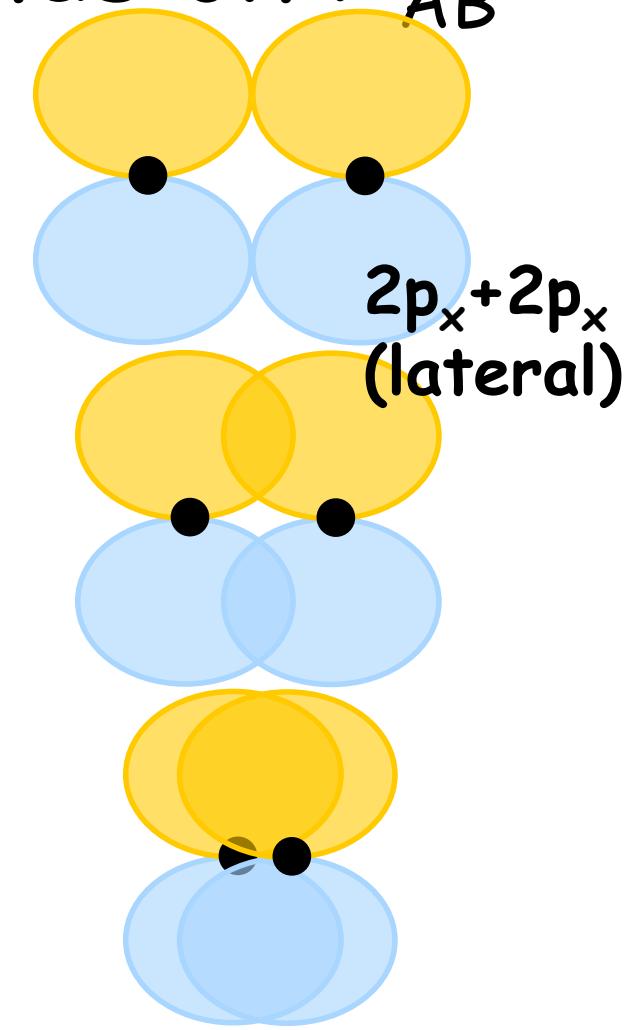
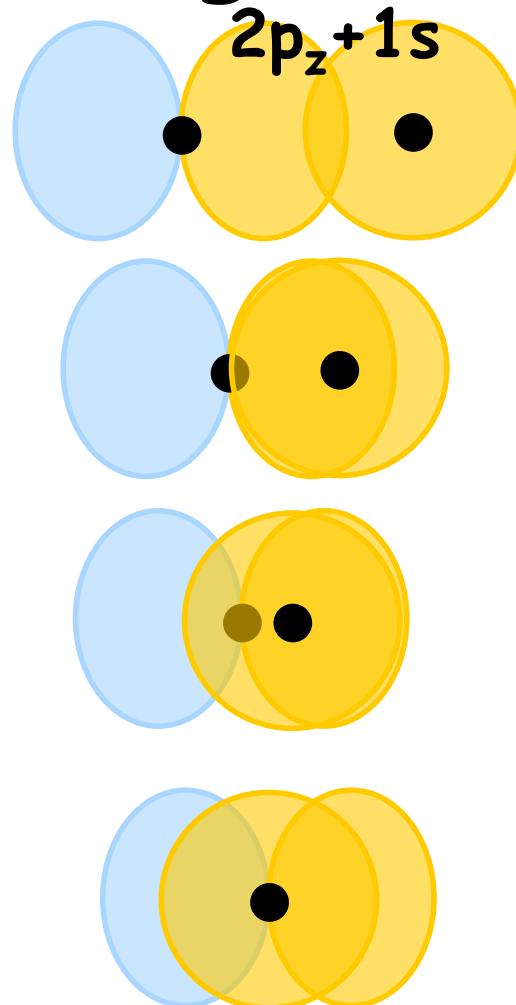
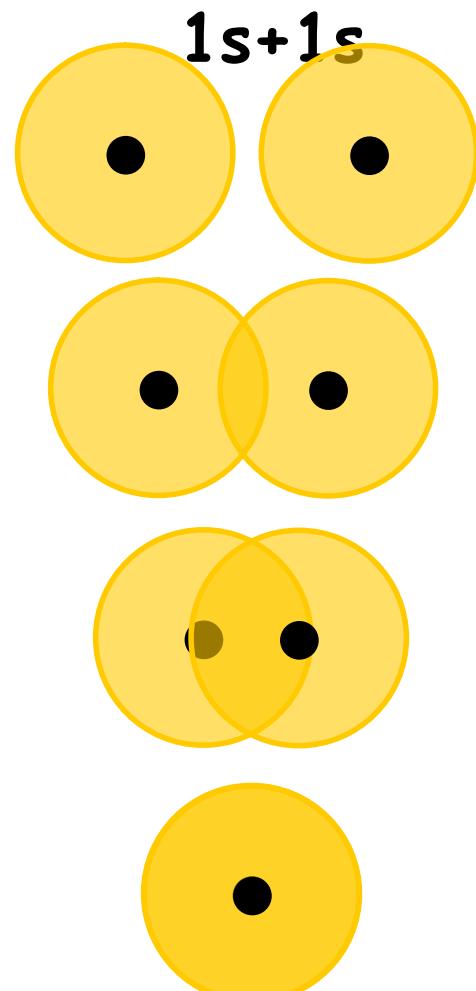
Overlapped area of 2 Wave-functions (can have +/- values)

Have to consider extent (amount) of both positive and negative contributions!

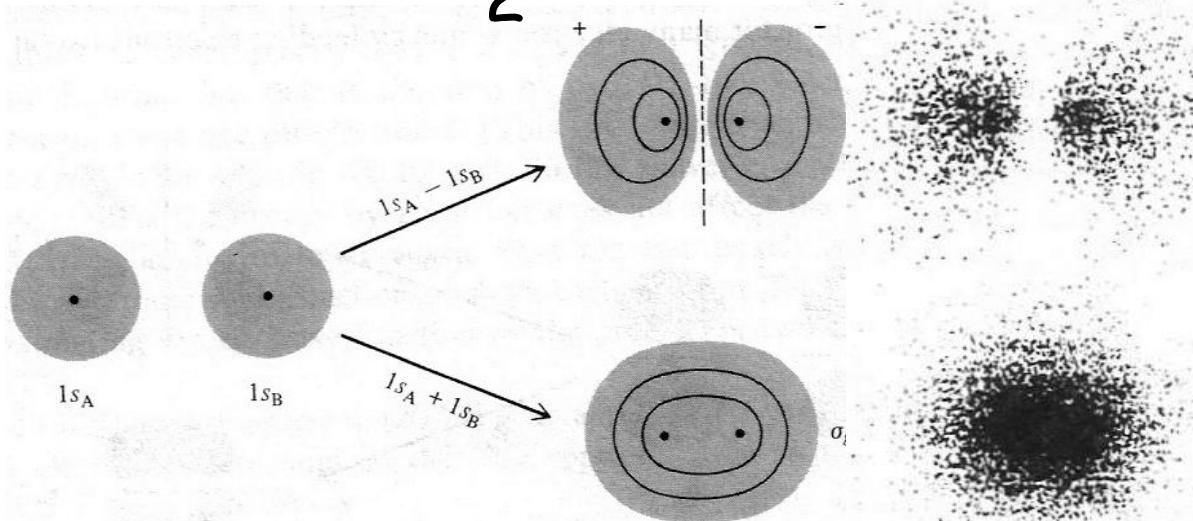


→ S is a qualitative measure of bond strength
→ $S(R) = 0 \rightarrow$ bond formation cannot occur

Overlap Integral depends on R_{AB}



H_2^+ Molecular Orbitals



$$\varphi_- = \frac{1}{\sqrt{2 - 2S(R)}} (\psi_{1s_A} - \psi_{1s_B})$$

$$\varphi_+ = \frac{1}{\sqrt{2 + 2S(R)}} (\psi_{1s_A} + \psi_{1s_B})$$

$$\langle E \rangle_+ = \langle \varphi_+ | \hat{H} | \varphi_+ \rangle = \left\langle \frac{1}{\sqrt{2 + 2S}} (\psi_{1s_A} + \psi_{1s_B}) \middle| \hat{H}_{H_2^+} \middle| \frac{1}{\sqrt{2 + 2S}} (\psi_{1s_A} + \psi_{1s_B}) \right\rangle$$

$$\langle E \rangle_+ = \frac{1}{2(1+S)} \left[\langle \psi_{1s_A} | \hat{H} | \psi_{1s_A} \rangle + \langle \psi_{1s_B} | \hat{H} | \psi_{1s_B} \rangle + \langle \psi_{1s_A} | \hat{H} | \psi_{1s_B} \rangle + \langle \psi_{1s_B} | \hat{H} | \psi_{1s_A} \rangle \right]$$

Let $H_{ii} = \langle \psi_{1s_i} | \hat{H} | \psi_{1s_i} \rangle$ and $H_{ij} = \langle \psi_{1s_i} | \hat{H} | \psi_{1s_j} \rangle$

$$\Rightarrow \langle E \rangle_+ = \frac{H_{ii} + H_{ij}}{1+S_{ij}} \text{ and } \langle E \rangle_- = \frac{H_{ii} - H_{ij}}{1-S_{ij}}$$

Stabilization due to Bond Formation

$$\hat{H} \sim \left(-\nabla^2 - \frac{1}{r_{eA}} \right) + \frac{1}{R_{AB}} - \frac{1}{r_{eB}} = \hat{H}_{H(1e)} + \frac{1}{R_{AB}} - \frac{1}{r_{eB}}$$

$$\langle E \rangle_+ = \frac{\frac{H_{ii} + H_{jj}}{2}}{1+S_{..}}; \langle E \rangle_- = \frac{\frac{H_{ii} - H_{jj}}{2}}{1-S_{..}}$$

$$H_{ii} = \langle \psi_{1S_A} | \hat{H} | \psi_{1S_A} \rangle = \left[\langle \psi_{1S_A} | \hat{H}_{H(1e)} | \psi_{1S_A} \rangle + \frac{1}{R_{AB}(\text{const.})} \langle \psi_{1S_A} | \psi_{1S_A} \rangle - \langle \psi_{1S_A} | \frac{1}{r_{eB}} | \psi_{1S_A} \rangle \right]$$

$$H_{ii} (\text{or } H_{AA} = H_{BB}) = E_{1S(1e)} + \frac{1}{R_{AB}} - J \quad \text{where } J = \langle \psi_{1S_A} | \frac{1}{r_{eB}} | \psi_{1S_A} \rangle \Rightarrow \text{Coulomb Integral}$$

Interaction energy viewed as a -ve charge cloud with a +ve charged nucleus

$$H_{ij} = \langle \psi_{1S_B} | \hat{H} | \psi_{1S_A} \rangle = \left[\langle \psi_{1S_B} | \hat{H}_{H(1e)} | \psi_{1S_A} \rangle + \frac{1}{R_{AB}(\text{const.})} \langle \psi_{1S_B} | \psi_{1S_A} \rangle - \langle \psi_{1S_B} | \frac{1}{r_{eB}} | \psi_{1S_A} \rangle \right]$$

$$H_{ij} (\text{or } H_{BA}) = \langle \psi_{1S_B} | E_{1S(1e)} | \psi_{1S_A} \rangle + \frac{1}{R_{AB}} \langle \psi_{1S_B} | \psi_{1S_A} \rangle - \langle \psi_{1S_B} | \frac{1}{r_{eB}} | \psi_{1S_A} \rangle$$

$$H_{ij} = E_{1S(1e)} S + \frac{S}{R_{AB}} - K, \quad \text{where } K = \langle \psi_{1S_B} | \frac{1}{r_{eB}} | \psi_{1S_A} \rangle$$

$K \Rightarrow$ Exchange Integral or Resonance Integral:
Lowering of energy leads to bond formation.

K is purely quantum-mechanical concept:
No Classical analogue

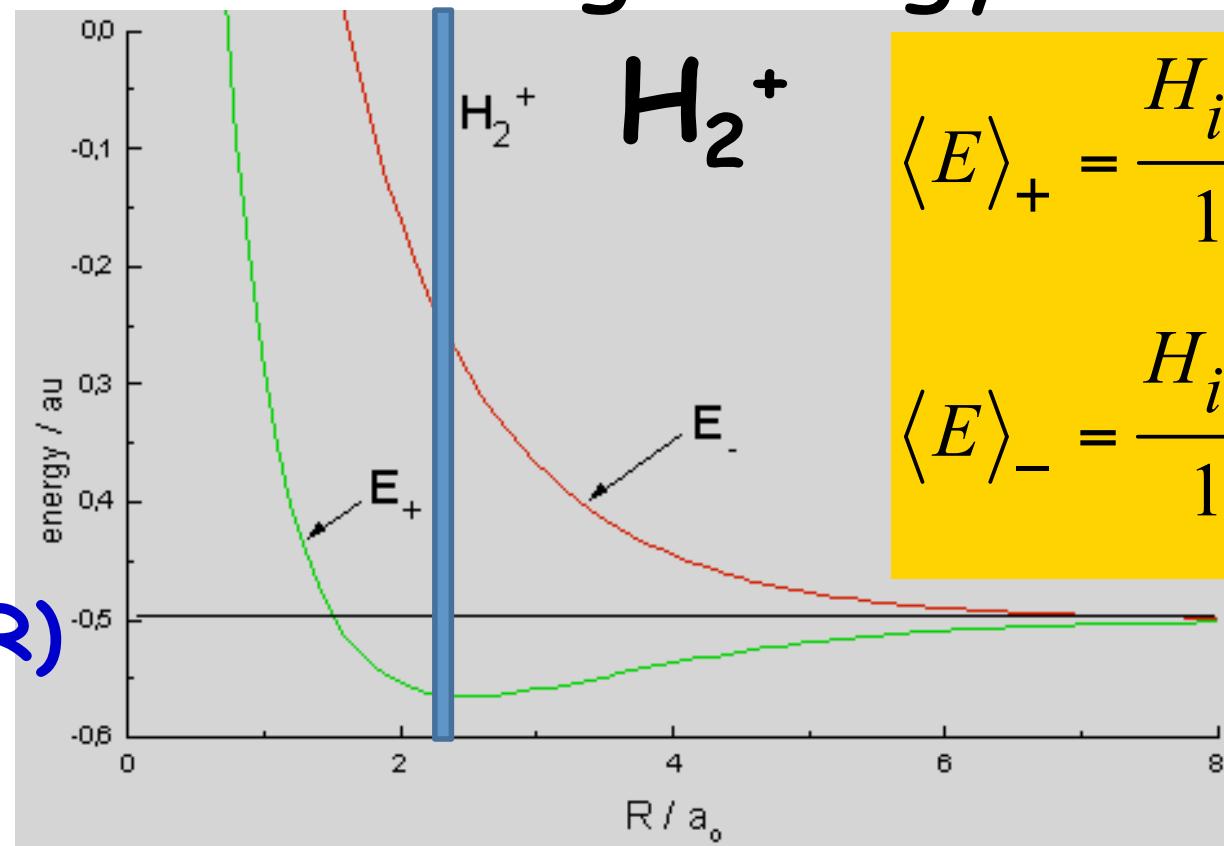
Bonding/Anti-bonding energy is $f(R_{AB})$

$$S = f(R)$$

$$H_{ii} = H_{ii}(R)$$

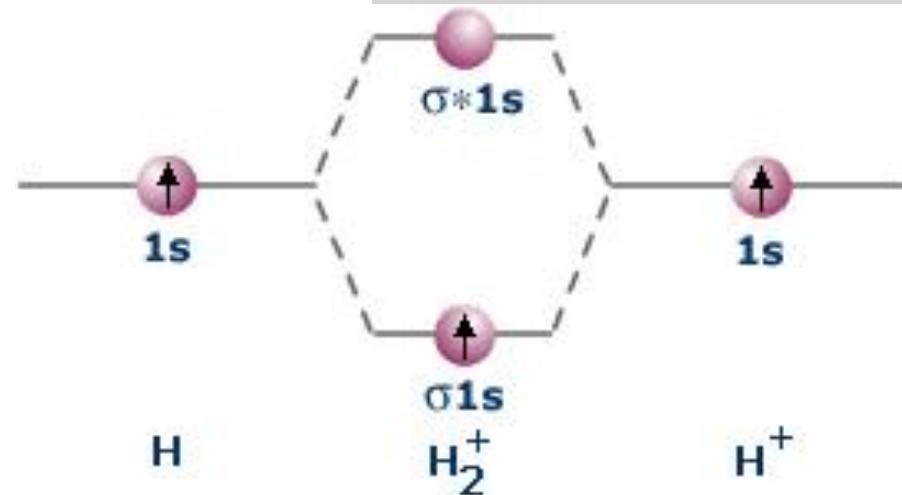
$$H_{ij} = H_{ij}(R)$$

$$\text{Energy} = E(R)$$



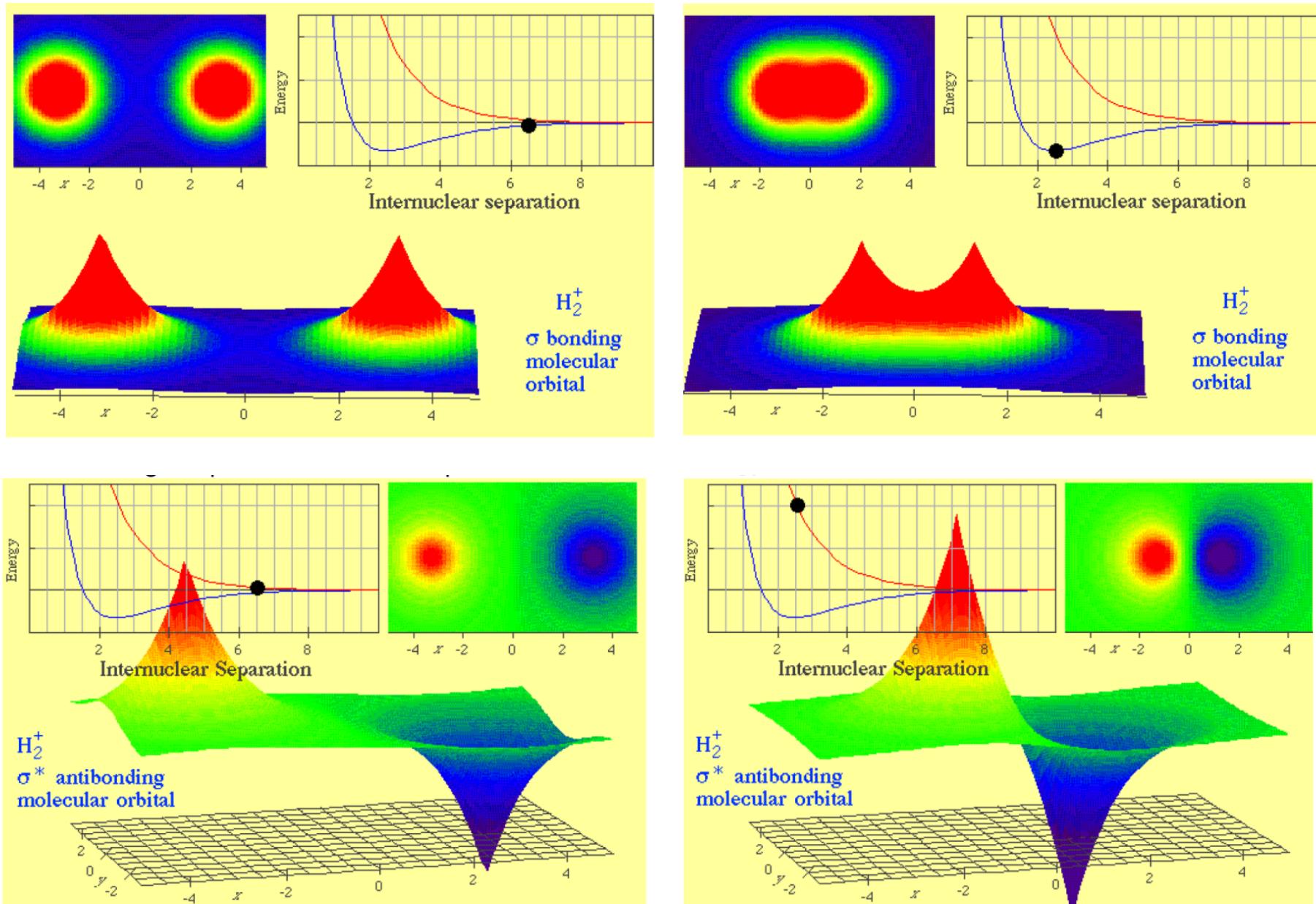
$$\langle E \rangle_+ = \frac{H_{ii} + H_{ij}}{1 + S_{ij}}$$

$$\langle E \rangle_- = \frac{H_{ii} - H_{ij}}{1 - S_{ij}}$$

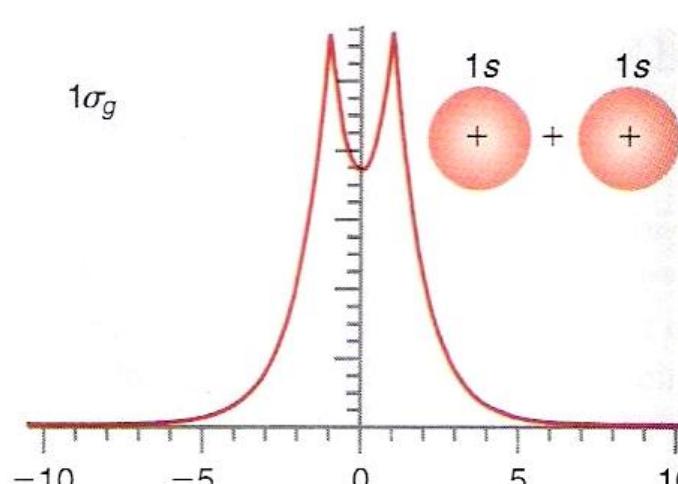
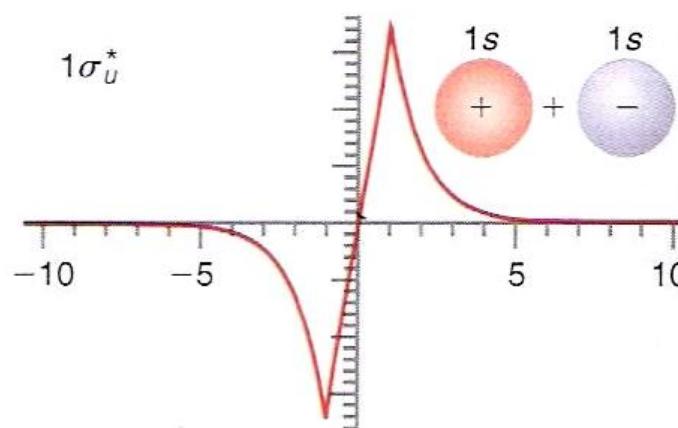
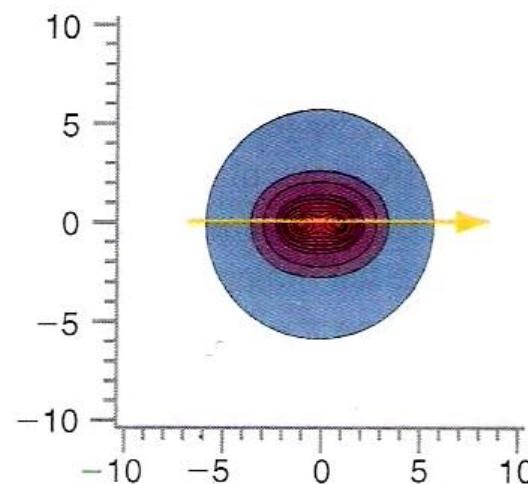
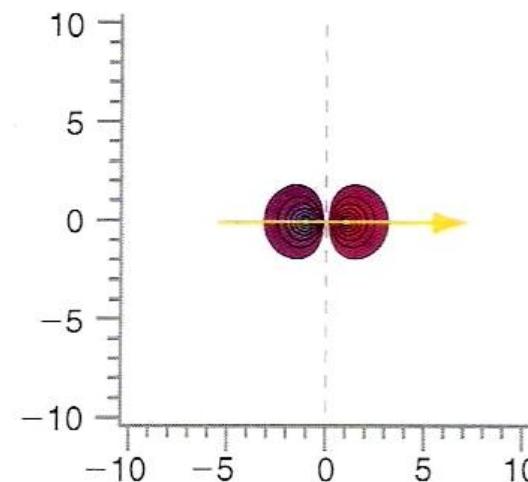


Represents the energies of bonding and anti-bonding levels at equilibrium R_{AB}

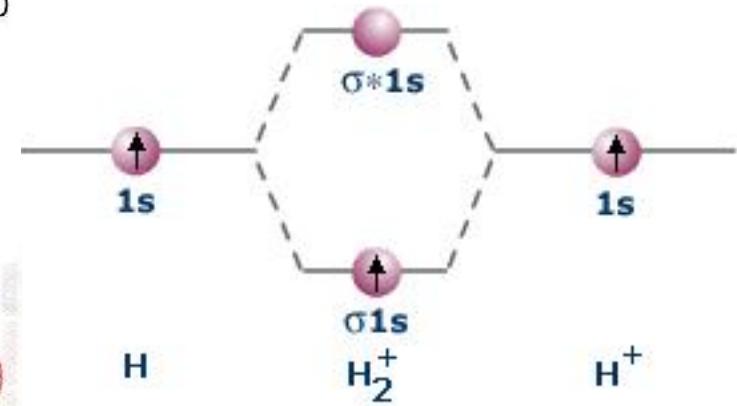
Electron Density and Energy: $f(R_{AB})$



H_2^+ σ -bonds: Electron Density/Energy at Equilibrium Bond distance (R_{Eq})



At R_{Eq} Anti-Bonding:
Electron density = 0
At midpoint between
nuclei, i.e., Nodal
plane present

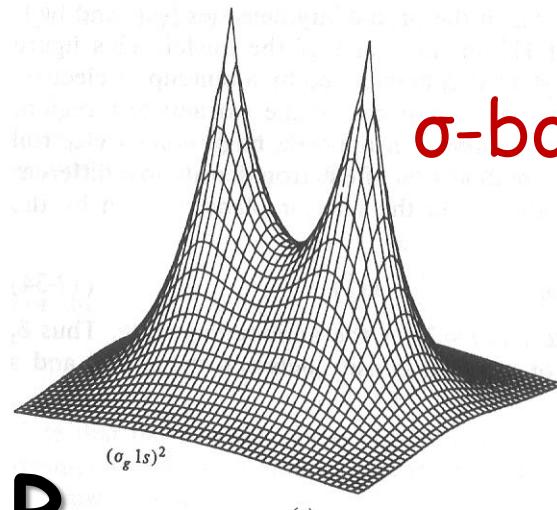


At R_{Eq} Bonding state:
Electron density non-
Zero at midpoint
between nuclei \rightarrow No
nodal plane!

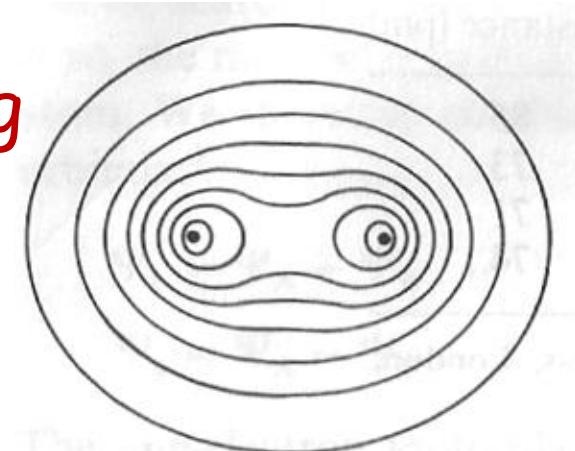
Surface/Contours of electron density

$\varphi_{Bonding}$

$$= \psi_{1S_A} + \psi_{1S_B}$$



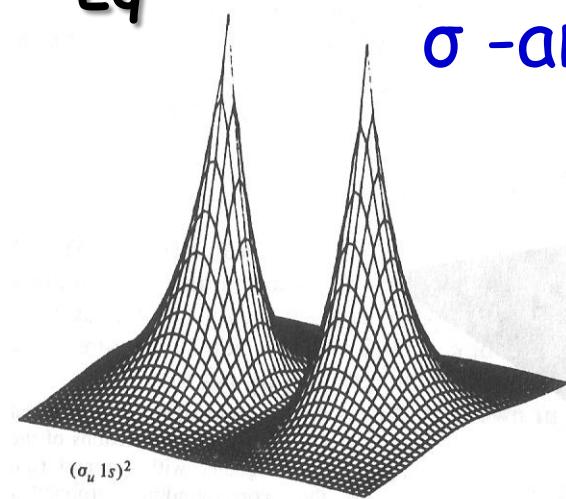
σ -bonding



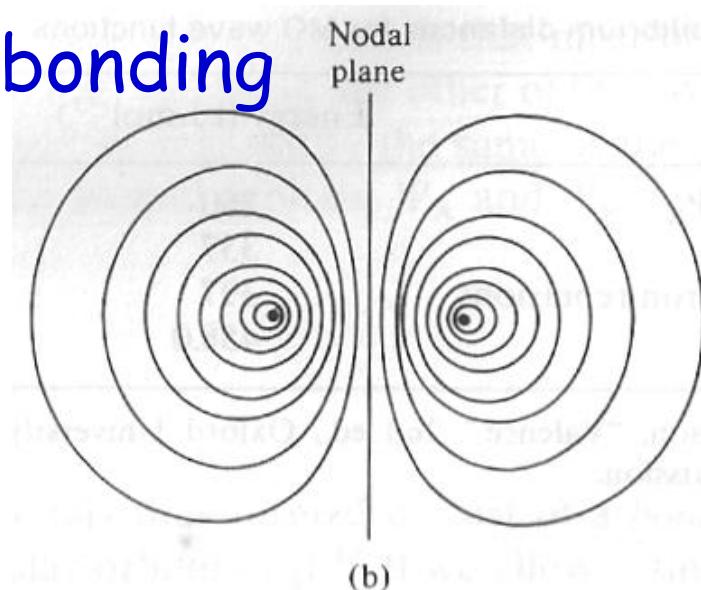
At R_{Eq}

$\varphi_{Anti-bonding}$

$$= \psi_{1S_A} - \psi_{1S_B}$$



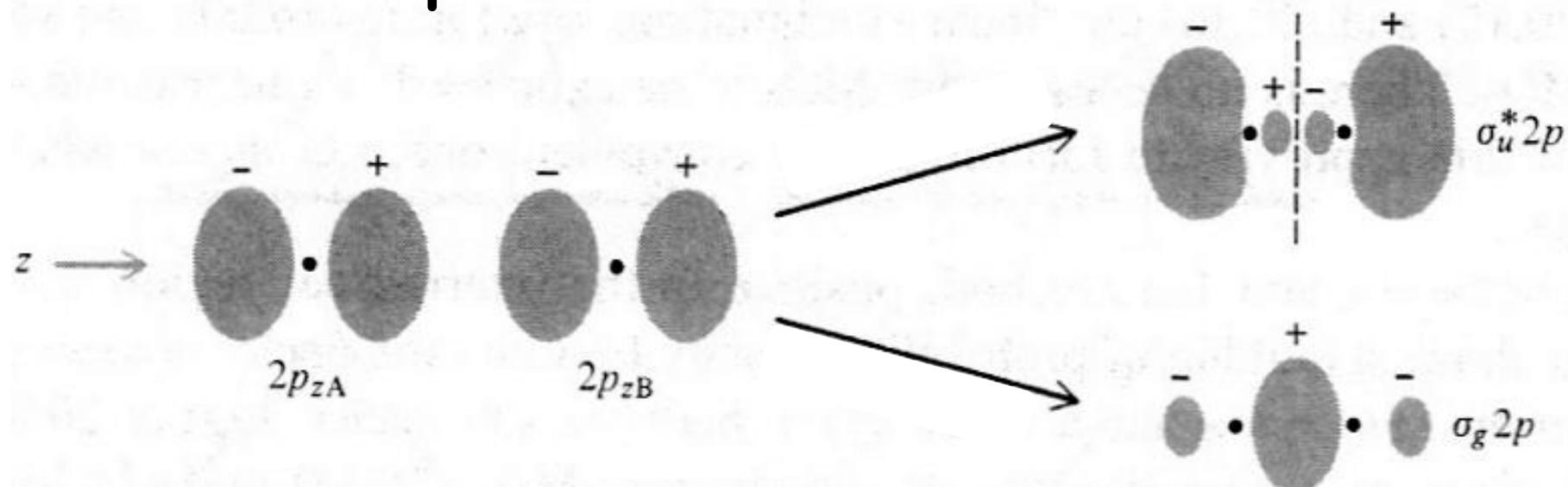
σ -antibonding



(b)

Electron density delocalized over entire molecule
Localized in different manner for bonding and antibonding

LCAO of p-orbitals: σ - and π - bonds



Note the signs, symmetries and nodes

