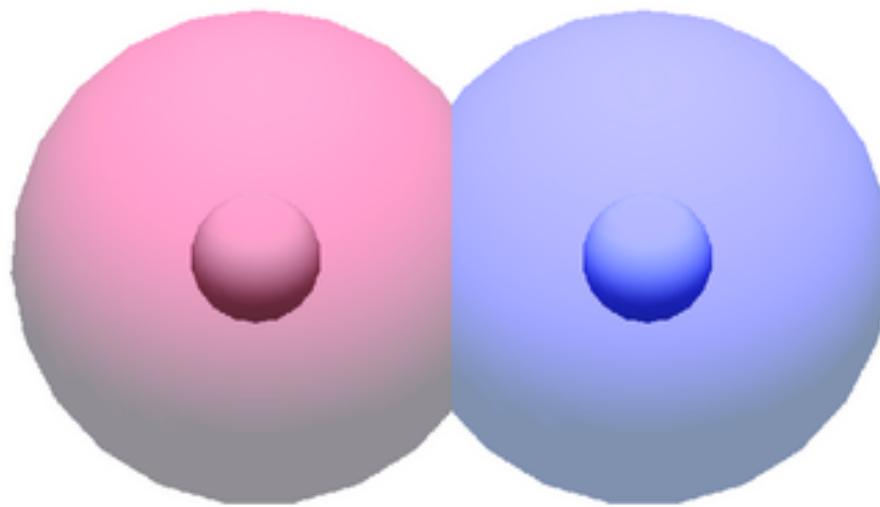
A photograph of a man and a woman standing side-by-side, facing away from the camera. They are holding hands, with their hands meeting in the center. The background is a dramatic sunset or sunrise with orange, yellow, and blue clouds. The silhouettes of the couple are dark against the bright sky.

Molecular Electronic Structure: Bonding

Chemical Bond Formation

Stabilization due to Bond-formation



$$E(4 \text{ charges @ } \infty) - E(2 \text{ H-Atoms}) = \sim 2642 \text{ kJ/mole}$$

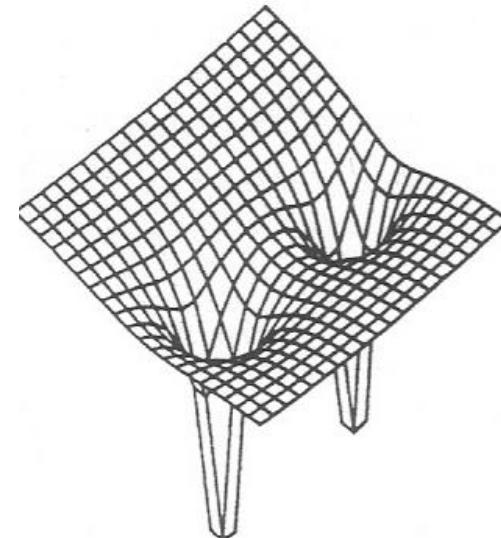
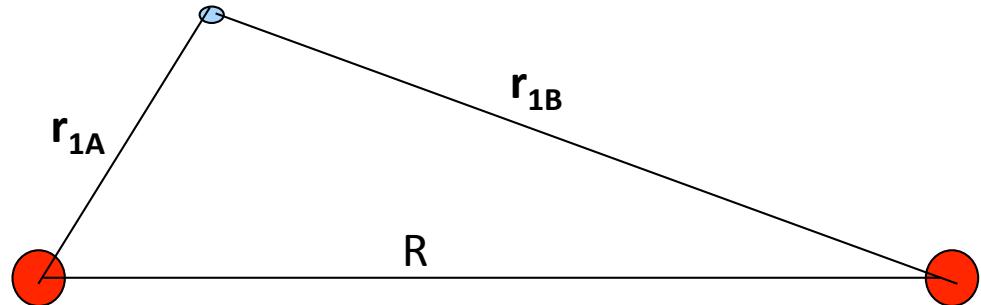
$$E(2 \text{ H-Atoms @ } \infty) - E(\text{H}_2 \text{ molecule}) = \sim 436 \text{ kJ/mole}$$

→ Chemical bond lowers the total energy by only ~17%

Charge distribution in H₂ molecule not very different from Superposition of the charge distribution of individual atoms

Simplest Molecule: H_2^+ - 1 electron

2 Nuclei + 1 Electron



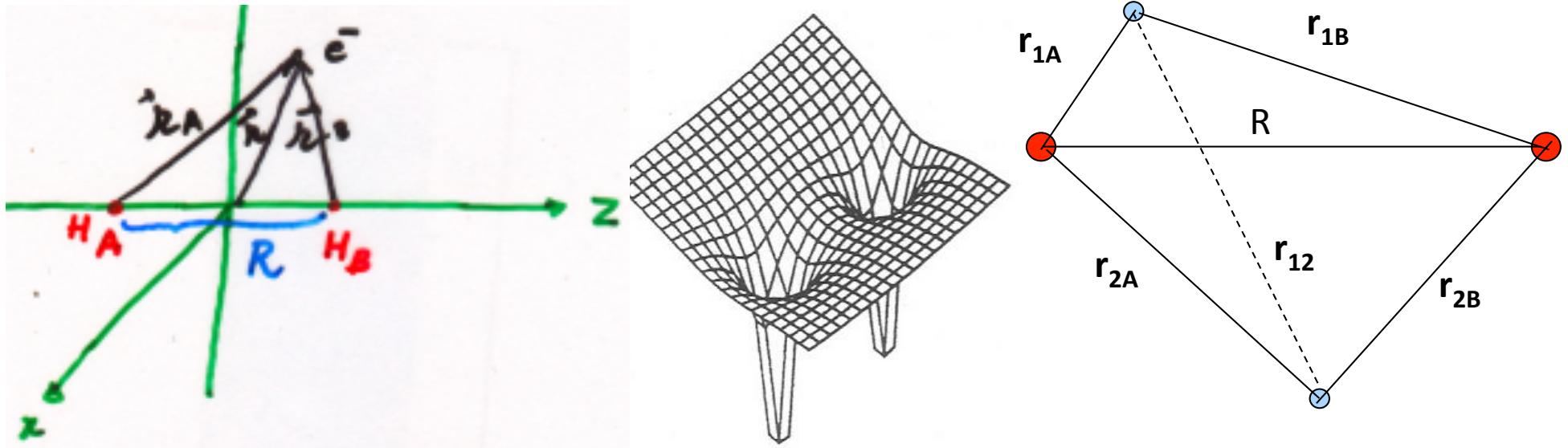
H_2^+ Molecule Ion Exists, Stable (Experimentally)

Bond length $\sim 1\text{\AA}$ ($2a_0$) ; Bond Energy $\sim 270 \text{ kJ/mole}$ ($0.1E_H$)

One more electron complicate matters to great extent!
Just like many electron atoms - So, we need to build a
Model with H_2^+ and get insight into chemical bonding

Then extend model for other multi-electronic
molecules

Simplest Molecules: H_2^+ and H_2



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

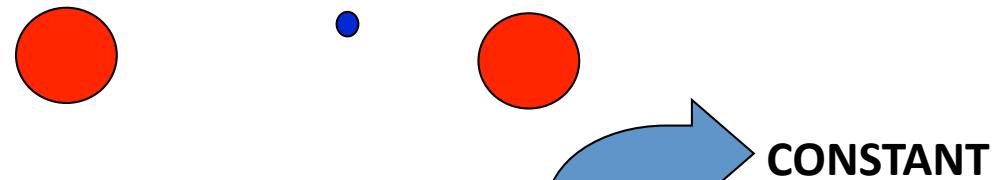
$$\widehat{H}(\text{H}_2^+) \sim \left(-\nabla_A^2 - \nabla_B^2 \right) + \left(-\nabla_{1e}^2 \right) + \left(-\frac{1}{r_{1A}} - \frac{1}{r_{1B}} \right) + \left(\frac{1}{R_{AB}} \right)$$

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



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

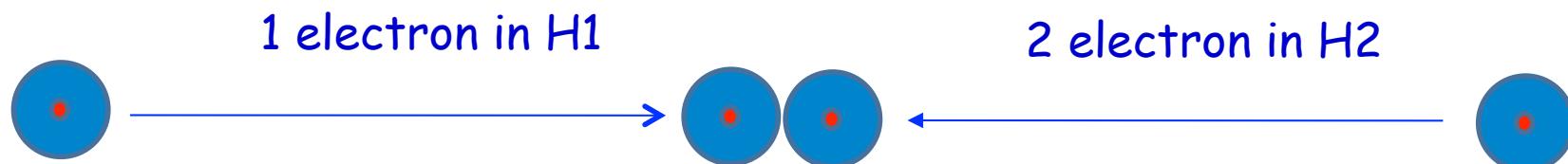
$$\hat{H}_{\text{H}_2^+} \sim \left(-\nabla^2 - \frac{1}{r_{e1A}} \right) + \frac{1}{R_{AB}} - \frac{1}{r_{e1B}} = \hat{H}_{H(1e)} + \frac{1}{R_{AB}} - \frac{1}{r_{eB}}$$

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



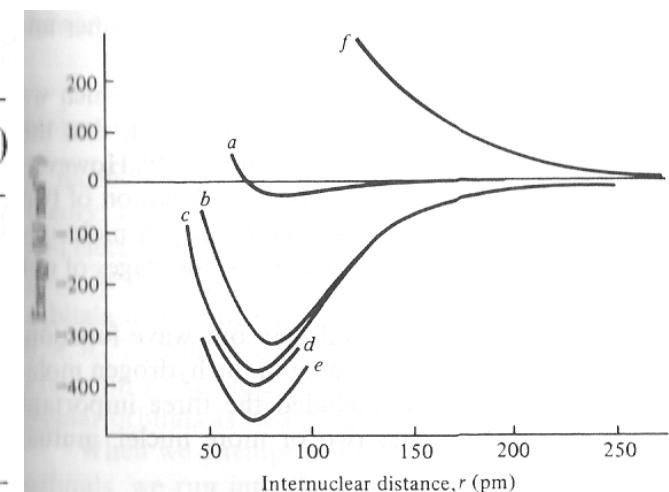
"Resonance"

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

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

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



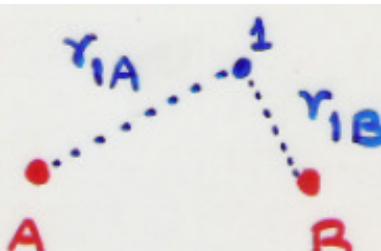
Model 2: Molecular Orbital Theory

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

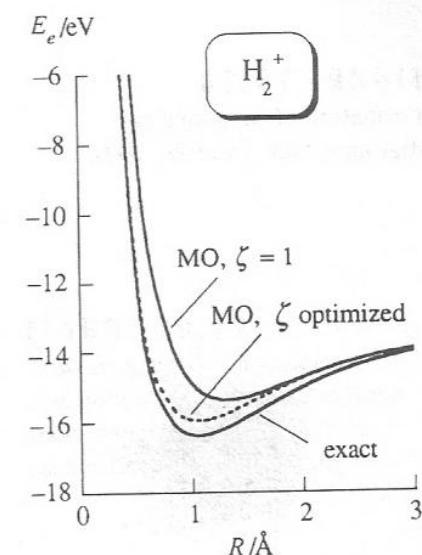


FIGURE 20.7

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)

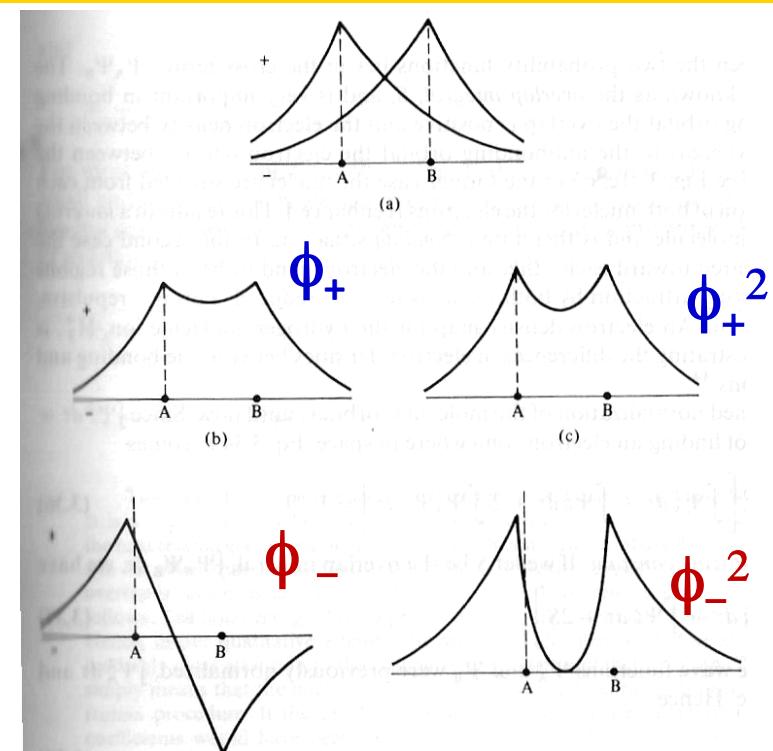
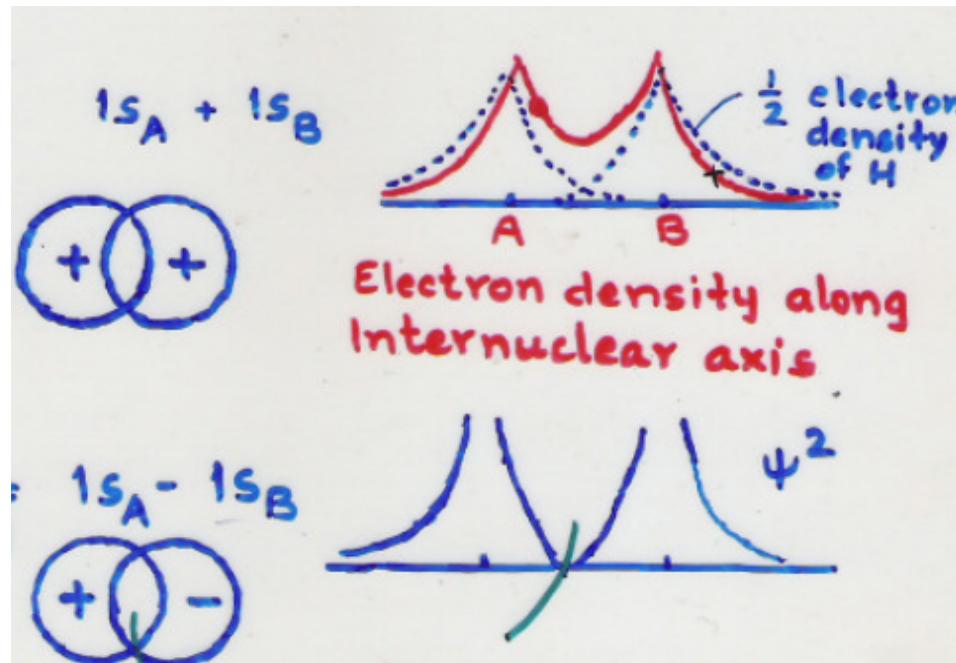
$$\varphi_{MO} = \varphi_{Approx} = c_1\psi_{1s_A} + c_2\psi_{1s_B} = c_1\psi_1 + c_2\psi_2$$

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

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



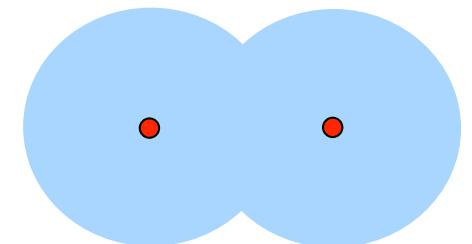




Normalization of Molecular Orbitals

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

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



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

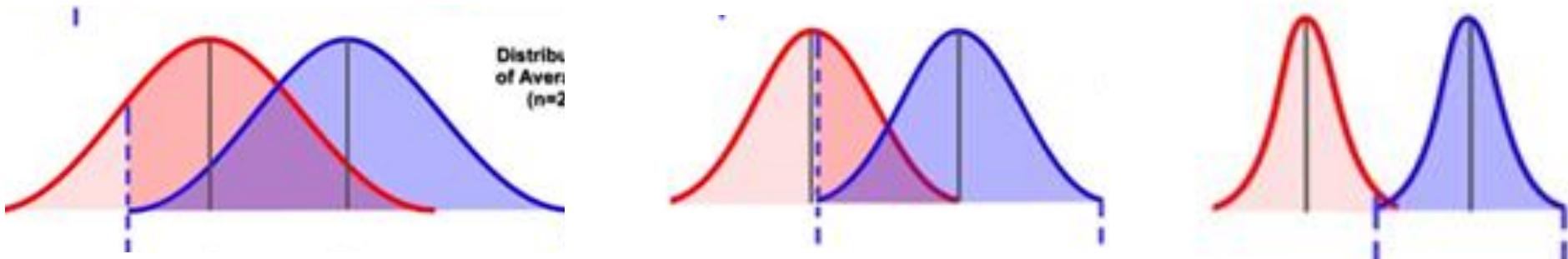
$$c_b = \frac{1}{\sqrt{2 + 2 \langle \psi_1 | \psi_2 \rangle}} \text{ and } c_a = \frac{1}{\sqrt{2 - 2 \langle \psi_1 | \psi_2 \rangle}}$$

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

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

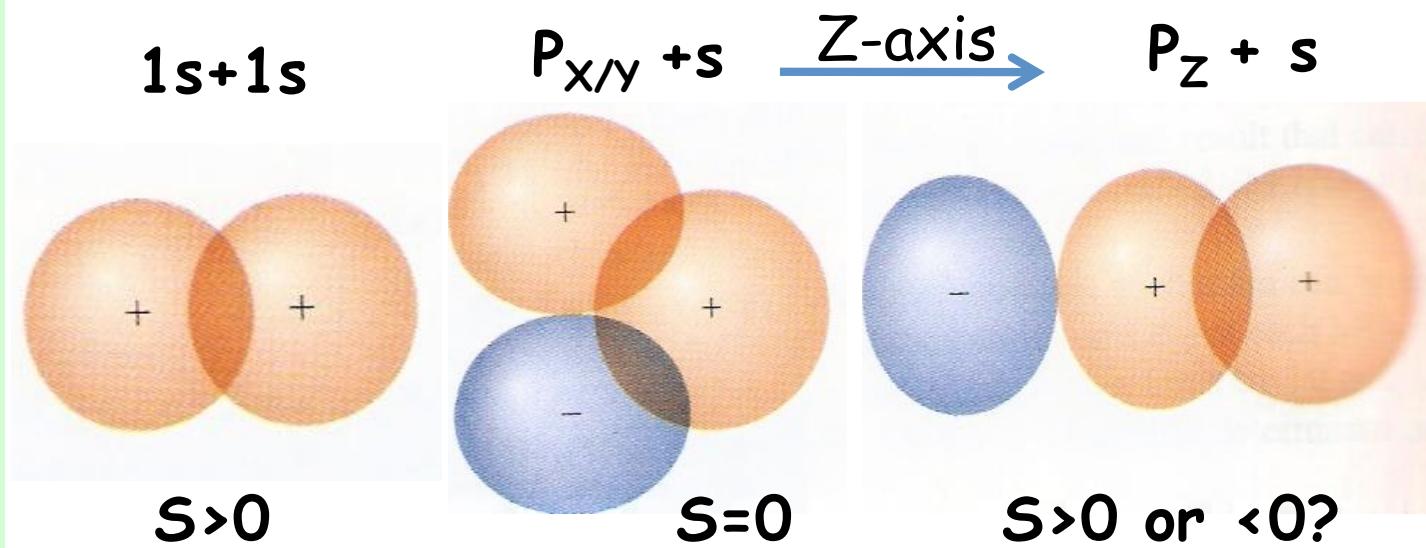
Concept of Overlap Integral

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



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