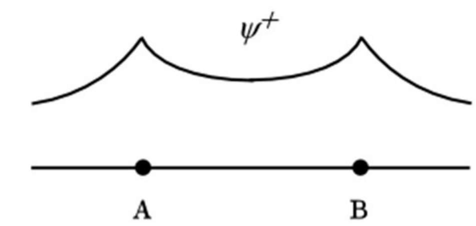
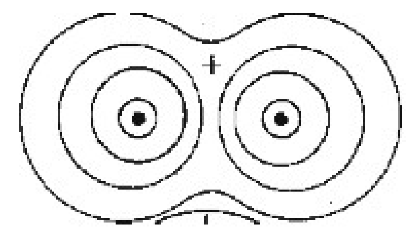
Molecular Orbital Theory- $H2^+$

$$\psi_1 = \frac{1}{\sqrt{[2+2S]}}\left(\phi_{1s_A} + \phi_{1s_B}\right)$$

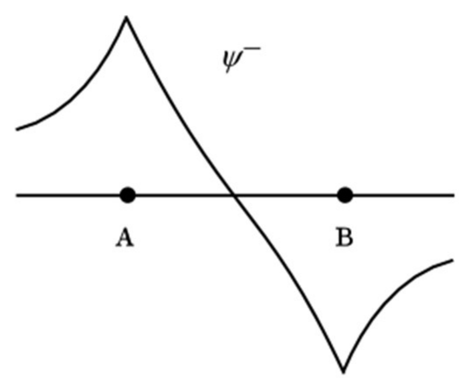
$$\boxed{E_1 = \left\langle \psi_1 \middle| \hat{H} \middle| \psi_1 \right\rangle}$$

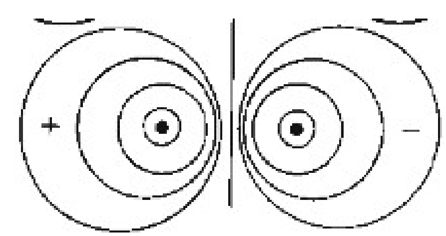




$$\psi_2 = \frac{1}{\sqrt{[2-2S]}}\left(\phi_{1s_A} - \phi_{1s_B}\right)$$

$$\boxed{E_2 = \left\langle \psi_2 \middle| \hat{H} \middle| \psi_2 \right\rangle}$$





Molecular Orbital Theory- H2$^+$

$$E_1 = \left\langle \psi_1 \middle| \widehat{H} \middle| \psi_1 \right\rangle$$

$$E_1 = \left\langle \frac{1}{\sqrt{[2+2S]}}\left(\phi_{1s_A} + \phi_{1s_B}\right) \middle| \widehat{H} \middle| \frac{1}{\sqrt{[2+2S]}}\left(\phi_{1s_A} + \phi_{1s_B}\right) \right\rangle$$

$$E_1 = \frac{1}{[2+2S]}\left\langle \left(\phi_{1s_A} + \phi_{1s_B}\right) \middle| \widehat{H} \middle| \left(\phi_{1s_A} + \phi_{1s_B}\right) \right\rangle$$

$$E_1 = \frac{1}{[2+2S]}\left[\left\langle \phi_{1s_A} \middle| \widehat{H} \middle| \phi_{1s_A} \right\rangle + \left\langle \phi_{1s_B} \middle| \widehat{H} \middle| \phi_{1s_B} \right\rangle + \left\langle \phi_{1s_A} \middle| \widehat{H} \middle| \phi_{1s_B} \right\rangle + \left\langle \phi_{1s_B} \middle| \widehat{H} \middle| \phi_{1s_A} \right\rangle\right]$$

Molecular Orbital Theory- $H2^+$

$$E_2 = \left\langle \psi_2 \middle| \widehat{H} \middle| \psi_2 \right\rangle$$

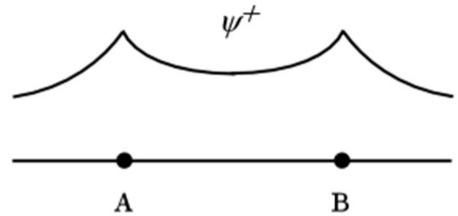
$$E_2 = \left\langle \frac{1}{\sqrt{[2-2S]}} \left(\phi_{1s_A} - \phi_{1s_B}\right) \middle| \widehat{H} \middle| \frac{1}{\sqrt{[2+2S]}} \left(\phi_{1s_A} - \phi_{1s_B}\right) \right\rangle$$

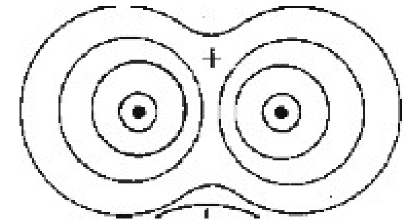
$$E_2 = \frac{1}{[2-2S]} \left\langle \left(\phi_{1s_A} - \phi_{1s_B}\right) \middle| \widehat{H} \middle| \left(\phi_{1s_A} - \phi_{1s_B}\right) \right\rangle$$

$$E_2 = \frac{1}{[2-2S]} \left[\left\langle \phi_{1s_A} \middle| \widehat{H} \middle| \phi_{1s_A} \right\rangle + \left\langle \phi_{1s_B} \middle| \widehat{H} \middle| \phi_{1s_B} \right\rangle - \left\langle \phi_{1s_A} \middle| \widehat{H} \middle| \phi_{1s_B} \right\rangle - \left\langle \phi_{1s_B} \middle| \widehat{H} \middle| \phi_{1s_A} \right\rangle \right]$$

Molecular Orbital Theory- $H2^{+}$

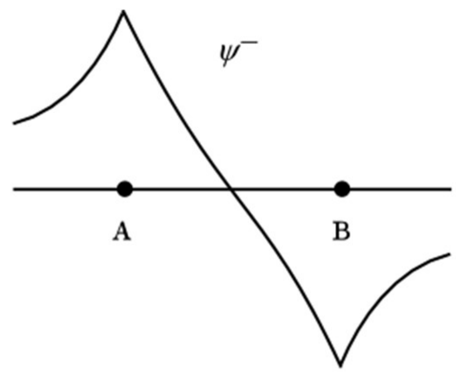
$$\psi_1 = \frac{1}{\sqrt{\left[2+2S\right]}}\left(\phi_{1s_A} + \phi_{1s_B}\right)$$

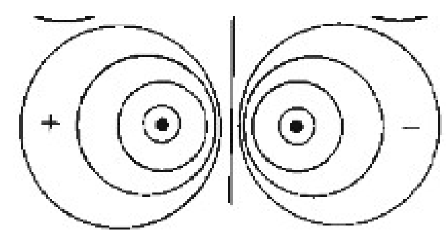




$$E_1 = \frac{1}{\left[2+2S\right]}\left[\left\langle \phi_{1s_A} \middle| \widehat{H} \middle| \phi_{1s_A} \right\rangle + \left\langle \phi_{1s_B} \middle| \widehat{H} \middle| \phi_{1s_B} \right\rangle + \left\langle \phi_{1s_A} \middle| \widehat{H} \middle| \phi_{1s_B} \right\rangle + \left\langle \phi_{1s_B} \middle| \widehat{H} \middle| \phi_{1s_A} \right\rangle\right]$$

$$\psi_2 = \frac{1}{\sqrt{\left[2-2S\right]}}\left(\phi_{1s_A} - \phi_{1s_B}\right)$$





$$E_2 = \frac{1}{\left[2-2S\right]}\left[\left\langle \phi_{1s_A} \middle| \widehat{H} \middle| \phi_{1s_A} \right\rangle + \left\langle \phi_{1s_B} \middle| \widehat{H} \middle| \phi_{1s_B} \right\rangle - \left\langle \phi_{1s_A} \middle| \widehat{H} \middle| \phi_{1s_B} \right\rangle - \left\langle \phi_{1s_B} \middle| \widehat{H} \middle| \phi_{1s_A} \right\rangle\right]$$

Molecular Orbital Theory- H2$^+$

$$E_1 = \frac{1}{\left[2+2S\right]}\left[\left\langle \phi_{1s_A}\middle|\widehat{H}\middle|\phi_{1s_A}\right\rangle + \left\langle \phi_{1s_B}\middle|\widehat{H}\middle|\phi_{1s_B}\right\rangle + \left\langle \phi_{1s_A}\middle|\widehat{H}\middle|\phi_{1s_B}\right\rangle + \left\langle \phi_{1s_B}\middle|\widehat{H}\middle|\phi_{1s_A}\right\rangle\right]$$

$$E_2 = \frac{1}{\left[2-2S\right]}\left[\left\langle \phi_{1s_A}\middle|\widehat{H}\middle|\phi_{1s_A}\right\rangle + \left\langle \phi_{1s_B}\middle|\widehat{H}\middle|\phi_{1s_B}\right\rangle - \left\langle \phi_{1s_A}\middle|\widehat{H}\middle|\phi_{1s_B}\right\rangle - \left\langle \phi_{1s_B}\middle|\widehat{H}\middle|\phi_{1s_A}\right\rangle\right]$$

$$E_1 = \frac{2H_{ii} + 2H_{ij}}{\left[2+2S_{ij}\right]} = \frac{H_{ii} + H_{ij}}{\left[1+S_{ij}\right]}$$

$$\left\langle \phi_{1s_i}\middle|\widehat{H}\middle|\phi_{1s_i}\right\rangle = H_{ii} = H_{jj} = \left\langle \phi_{1s_j}\middle|\widehat{H}\middle|\phi_{1s_j}\right\rangle$$

$$\left\langle \phi_{1s_i}\middle|\widehat{H}\middle|\phi_{1s_j}\right\rangle = H_{ij} = H_{ji} = \left\langle \phi_{1s_j}\middle|\widehat{H}\middle|\phi_{1s_i}\right\rangle$$

$$\left\langle \phi_{1s_i}\middle|\phi_{1s_j}\right\rangle = S_{ij} = S_{ji} = \left\langle \phi_{1s_j}\middle|\phi_{1s_i}\right\rangle$$

$\hat{\boldsymbol{H}}$ is Hermitian

Molecular Orbital Theory- H2⁺

$$\widehat{H} = -\frac{\hbar^2}{2m_e}\nabla_e^2 - Q\frac{e^2}{r_i} - Q\frac{e^2}{r_j} + Q\frac{e^2}{R}$$

$$\widehat{H} = \left(-\frac{\hbar^2}{2m_e}\nabla_e^2 - Q\frac{e^2}{r_i}\right) - Q\frac{e^2}{r_j} + Q\frac{e^2}{R}$$

$$\boxed{\widehat{H} = \widehat{H}_{1e} - Q\frac{e^2}{r_j} + Q\frac{e^2}{R}}$$

Molecular Orbital Theory of H_2^+ : H_{ii}

$$H_{ii}(\text{or } H_{AA} = H_{BB}) = \left\langle \phi_{1s_i} \middle| \hat{H} \middle| \phi_{1s_i} \right\rangle$$

Constant at fixed internuclear distance

$$H_{ii} = \left\langle \phi_{1s_i} \middle| \hat{H}_{1e} \middle| \phi_{1s_i} \right\rangle + Qe^2 \left\langle \phi_{1s_i} \middle| \frac{1}{R} \middle| \phi_{1s_i} \right\rangle - Qe^2 \left\langle \phi_{1s_i} \middle| \frac{1}{r_j} \middle| \phi_{1s_i} \right\rangle$$

$J \Rightarrow$ Coulomb Integral

$J \Rightarrow$ Interaction E of the e- (-) charge cloud with the + nucleus at some distance

Molecular Orbital Theory of H_2^+ : H_{ij}

$$H_{ij}(\text{or } H_{AB} = H_{BA}) = \left\langle \phi_{1s_i} \middle| \widehat{H} \middle| \phi_{1s_j} \right\rangle$$

Constant

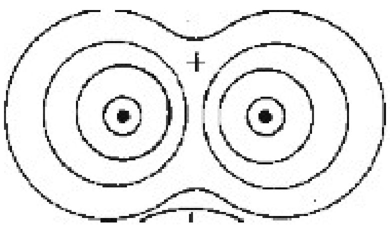
K is purely a quantum mechanical concept. There is no classical counterpart

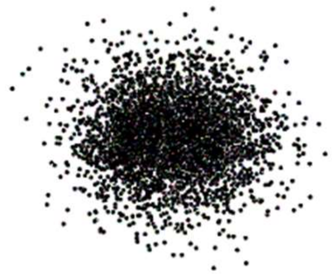
K $\Rightarrow$ Exchange Integral
Resonance Integral

Molecular Orbital Theory- H2$^+$

$$E_1 = \frac{H_{ii} + H_{ij}}{\left[1 + S_{ij}\right]} = \frac{1}{\left[1 + S\right]}\left[\qquad \right]$$

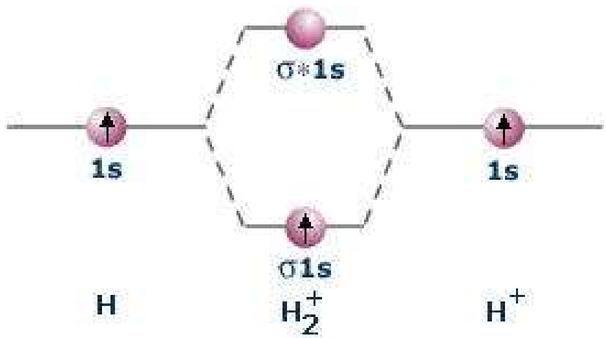
Molecular Orbital Theory- H2$^+$

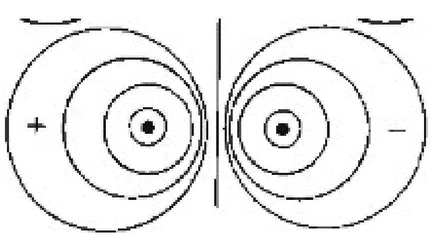




$$\psi_1 = \frac{1}{\sqrt{[2+2S]}}\left(\phi_{1s_A} + \phi_{1s_B}\right)$$

$$E_1 = E_{1s} + \frac{Qe^2}{R} - \frac{Qe^2[J+K]}{[1+S]}$$

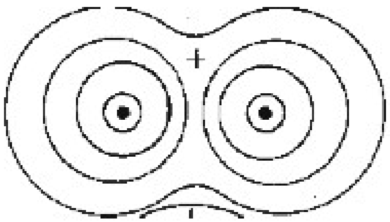


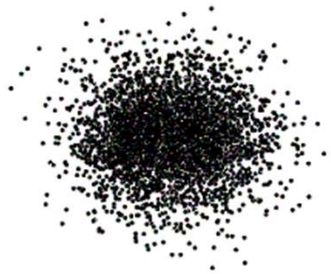


$$\psi_2 = \frac{1}{\sqrt{[2-2S]}}\left(\phi_{1s_A} - \phi_{1s_B}\right)$$

$$E_2 = E_{1s} + \frac{Qe^2}{R} - \frac{Qe^2[J-K]}{[1-S]}$$

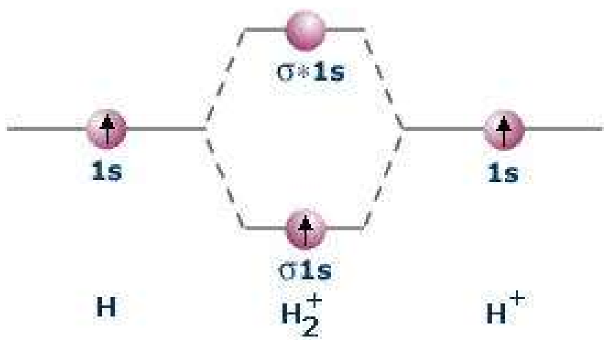
Molecular Orbital Theory- H2$^+$

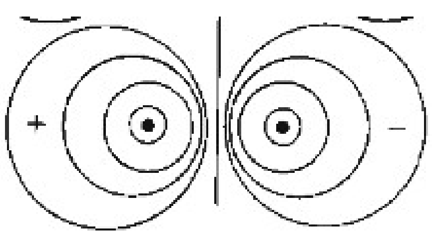




$$\psi_1 = \frac{1}{\sqrt{2+2S}}\left(\phi_{1s_A} + \phi_{1s_B}\right)$$

$$E_1 = E_{1s} + \frac{Qe^2}{R} - \frac{Qe^2\left[J+K\right]}{\left[1+S\right]}$$





$$\psi_2 = \frac{1}{\sqrt{2-2S}}\left(\phi_{1s_A} - \phi_{1s_B}\right)$$

$$E_2 = E_{1s} + \frac{Qe^2}{R} - \frac{Qe^2\left[J-K\right]}{\left[1-S\right]}$$

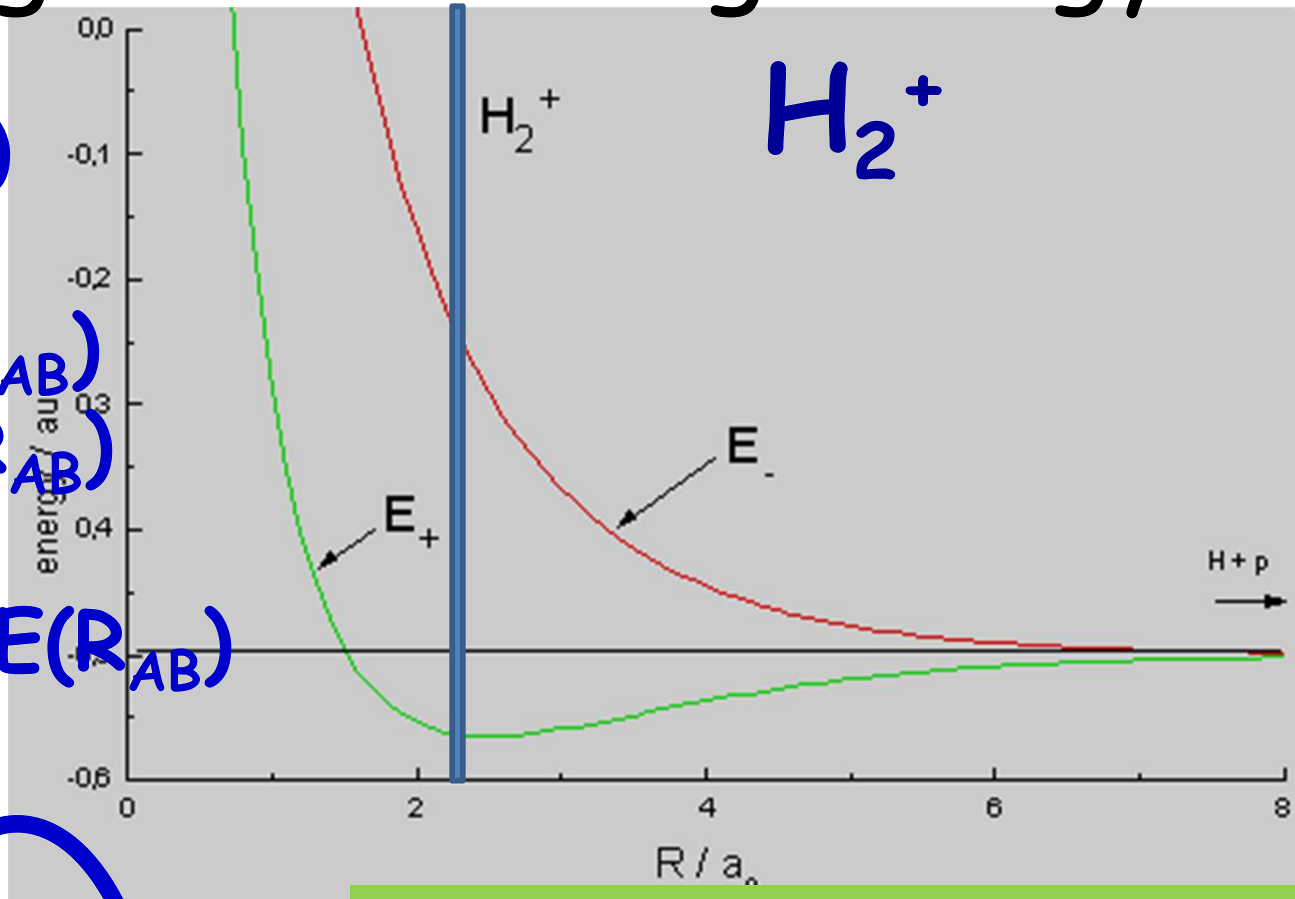
Bonding/Antibonding energy is $f(R_{AB})$

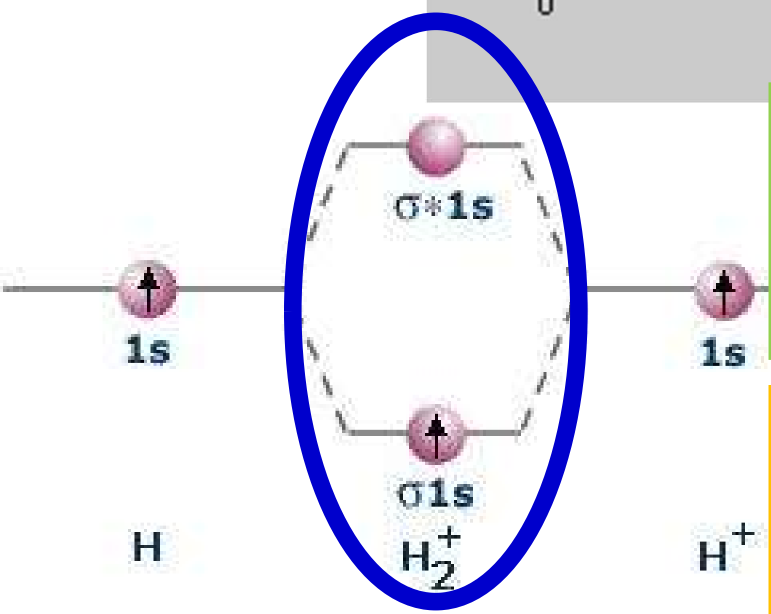
$S = f(R_{AB})$

$H_{ii} = H_{ii}(R_{AB})$

$H_{ij} = H_{ij}(R_{AB})$

$\text{Energy} = E(R_{AB})$

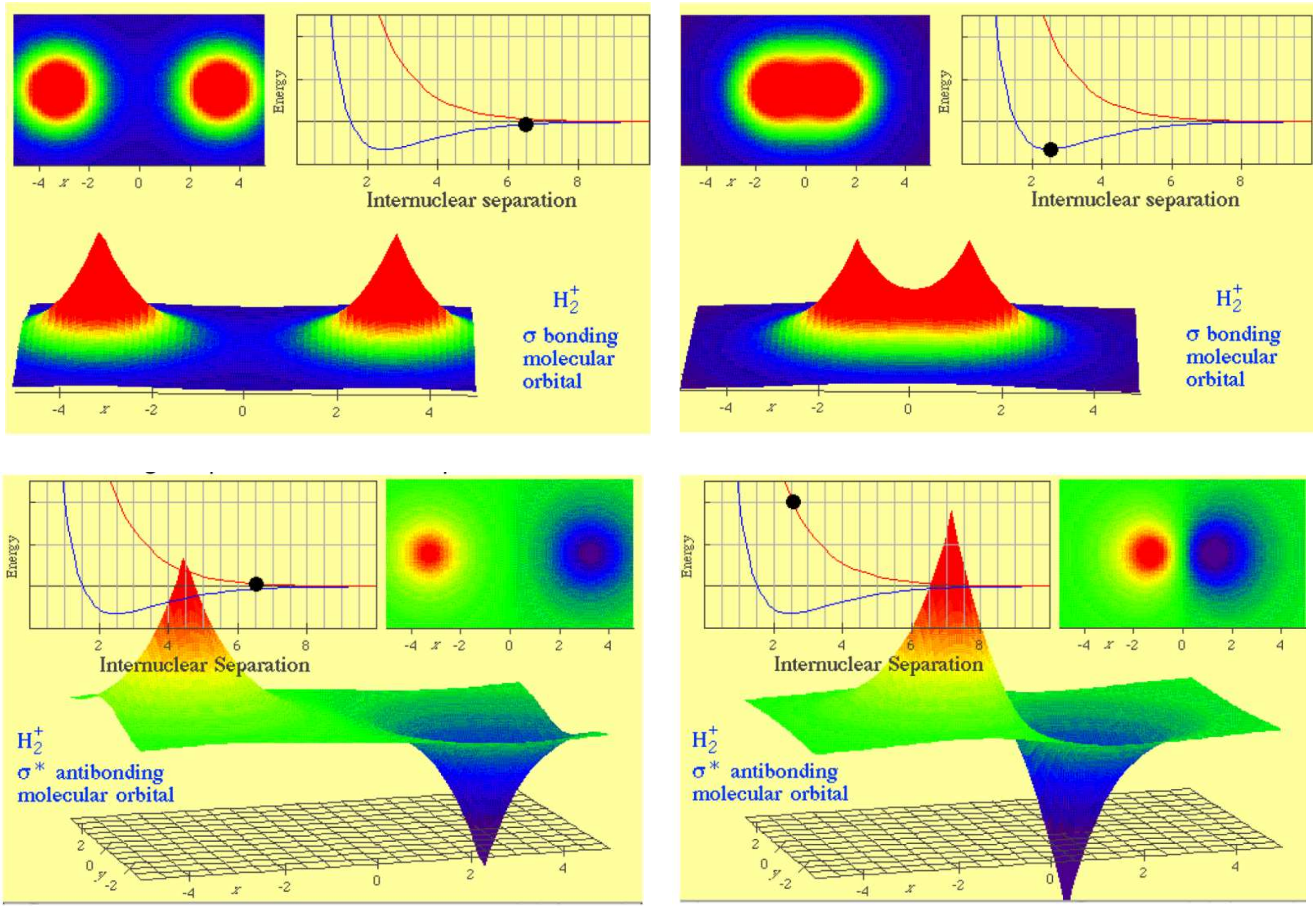


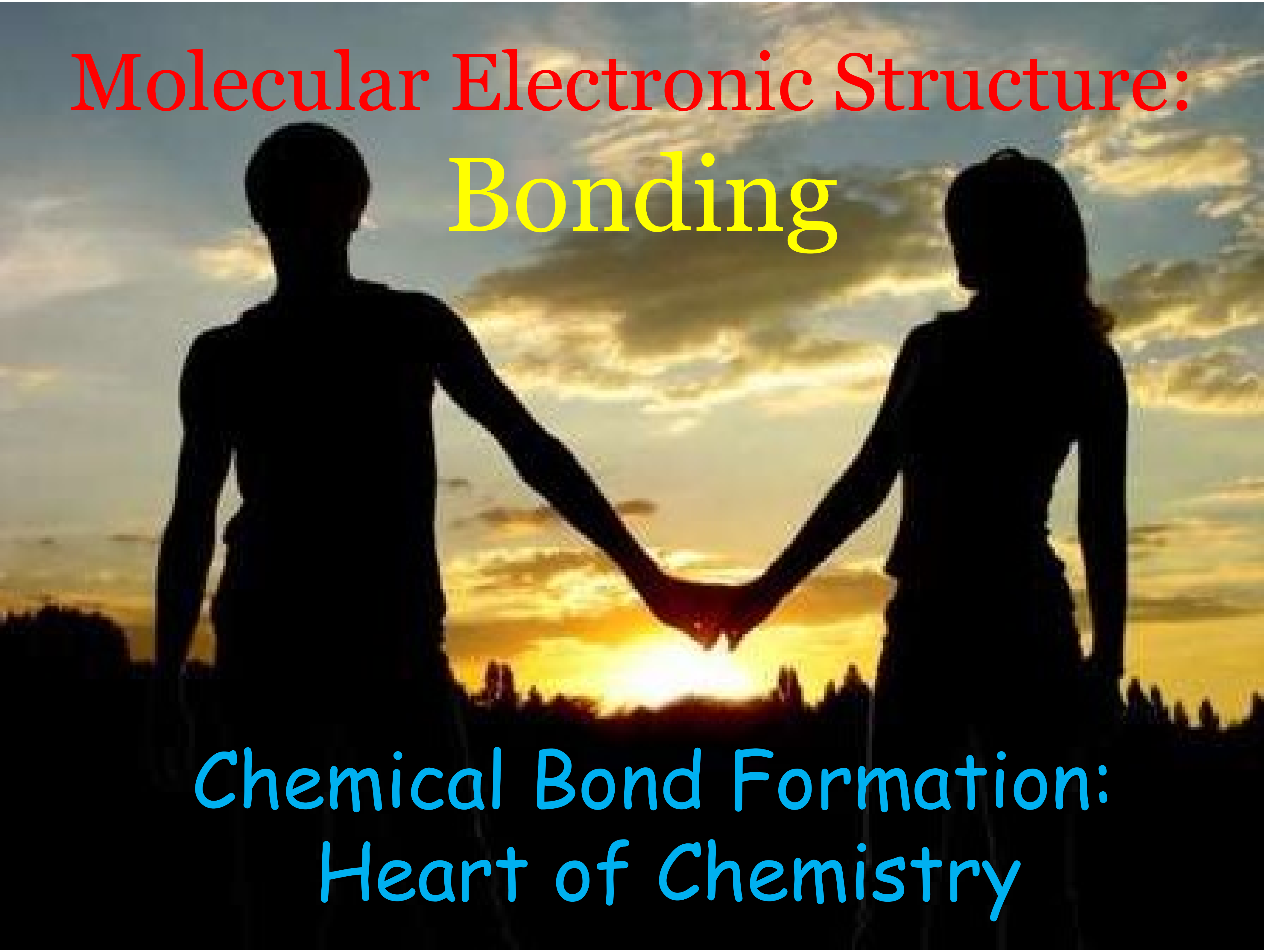


Calculate energies as a function
Of internuclear separation, R_{AB}:
A bound state and an unbound state

Textbook pictures: Represents
energies of bonding and anti-bonding
levels at equilibrium R_{AB}

Electron Densities and Energy: f(R_{AB})




Molecular Electronic Structure:
Bonding
Chemical Bond Formation:
Heart of Chemistry

Sigma Bonding with 1s Orbitals