Molecular Orbital Theory of H_2^+

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

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

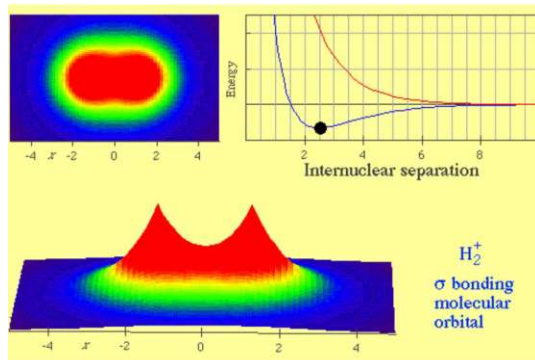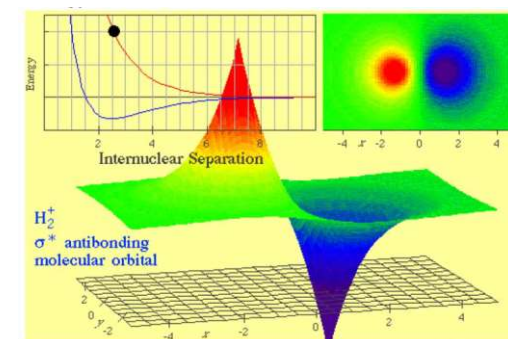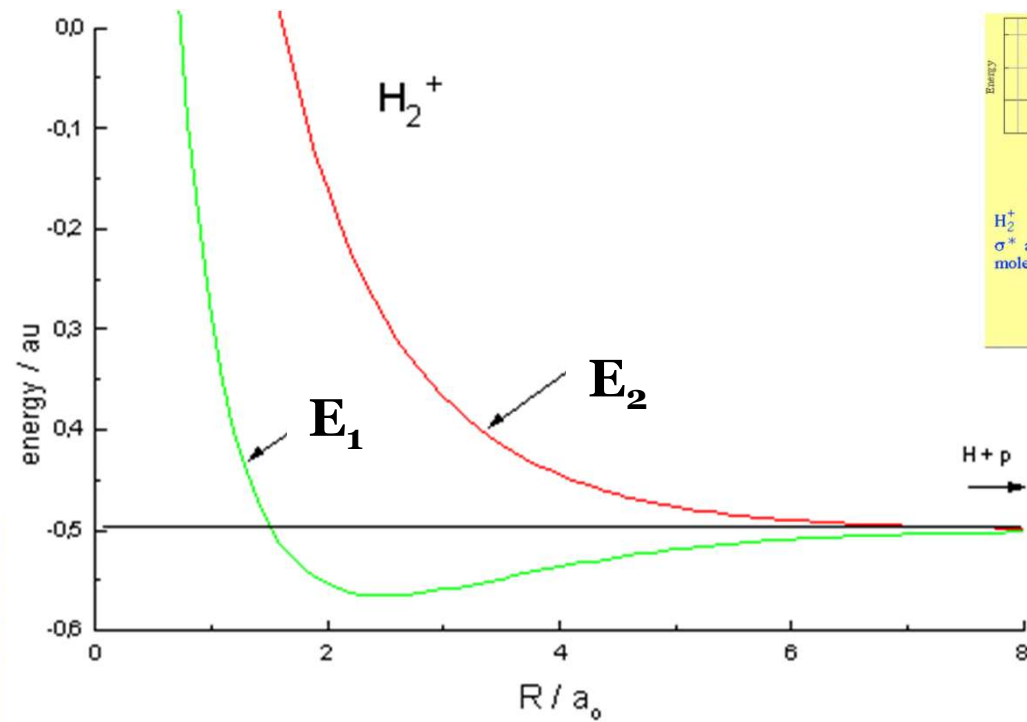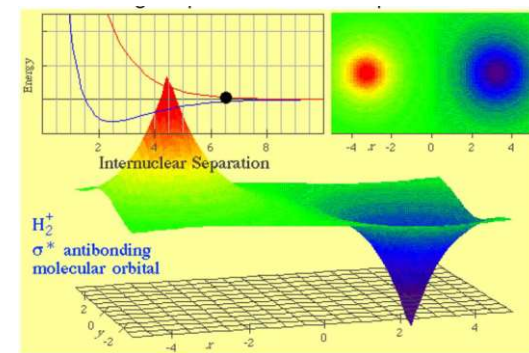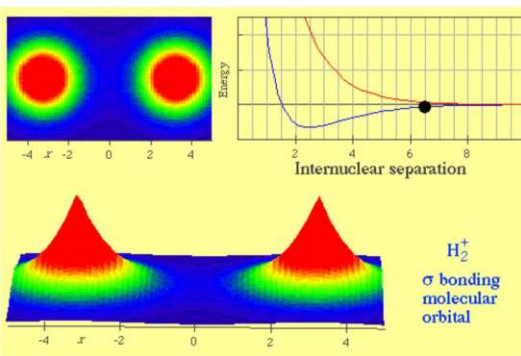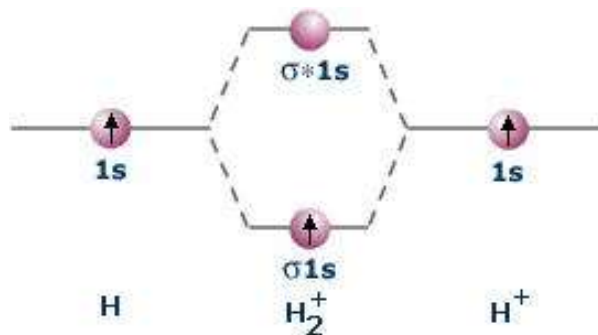$$0 \leq |S| \leq 1; J < 0 \ \& \ K < 0$$

J - **Coulomb integral - interaction of electron in 1s orbital around A with a nucleus at B**

K - **Exchange integral – exchange (resonance) of electron between the two nuclei.**

Destabilization of Anti-bonding orbital is more than **Stabilization of Bonding** orbital

Molecular Orbital Theory of H_2^+

Sigma Bonding with 1s Orbitals
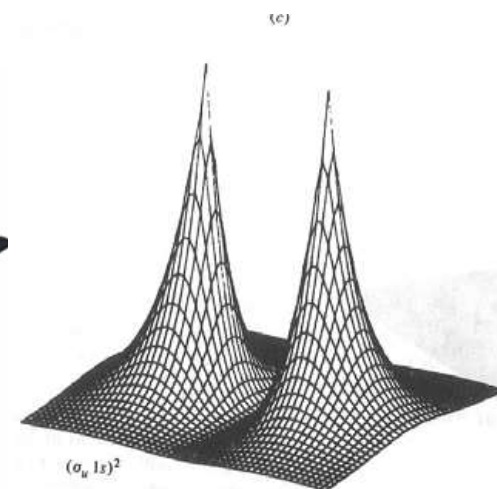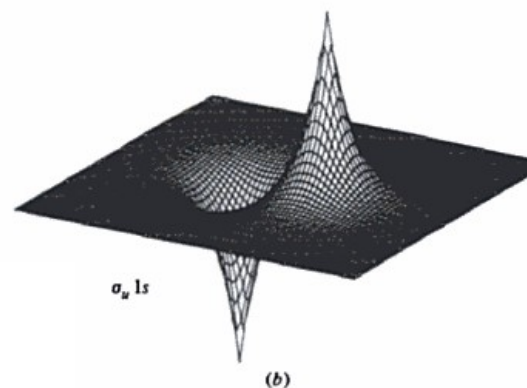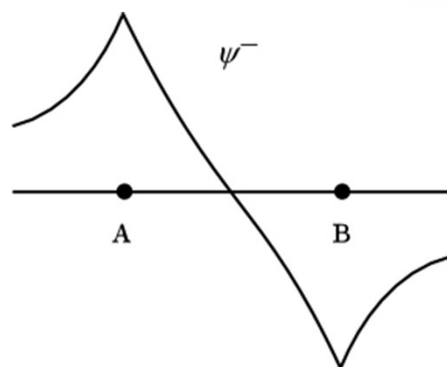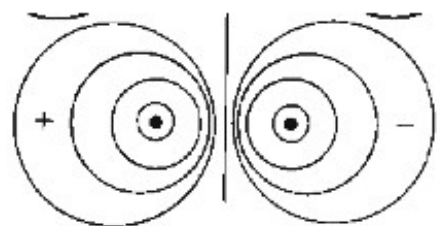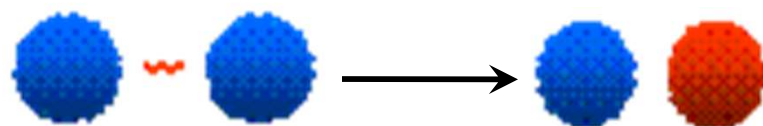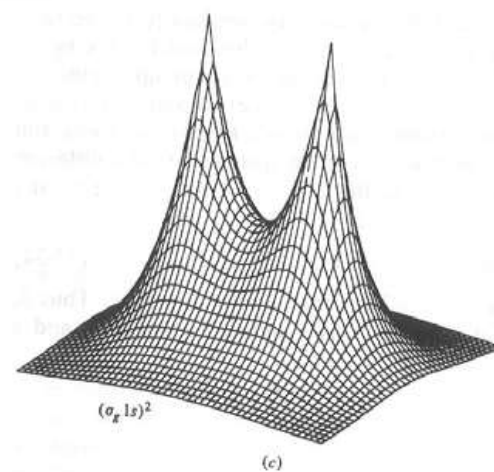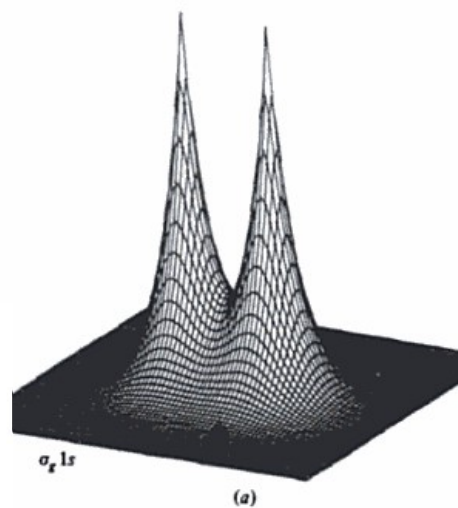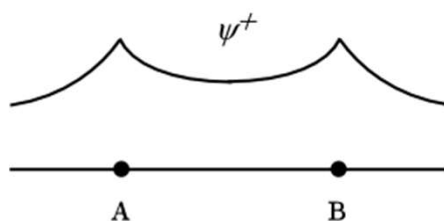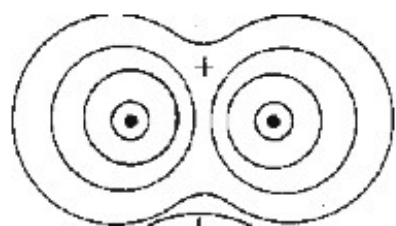
Bonding with 2p Orbitals
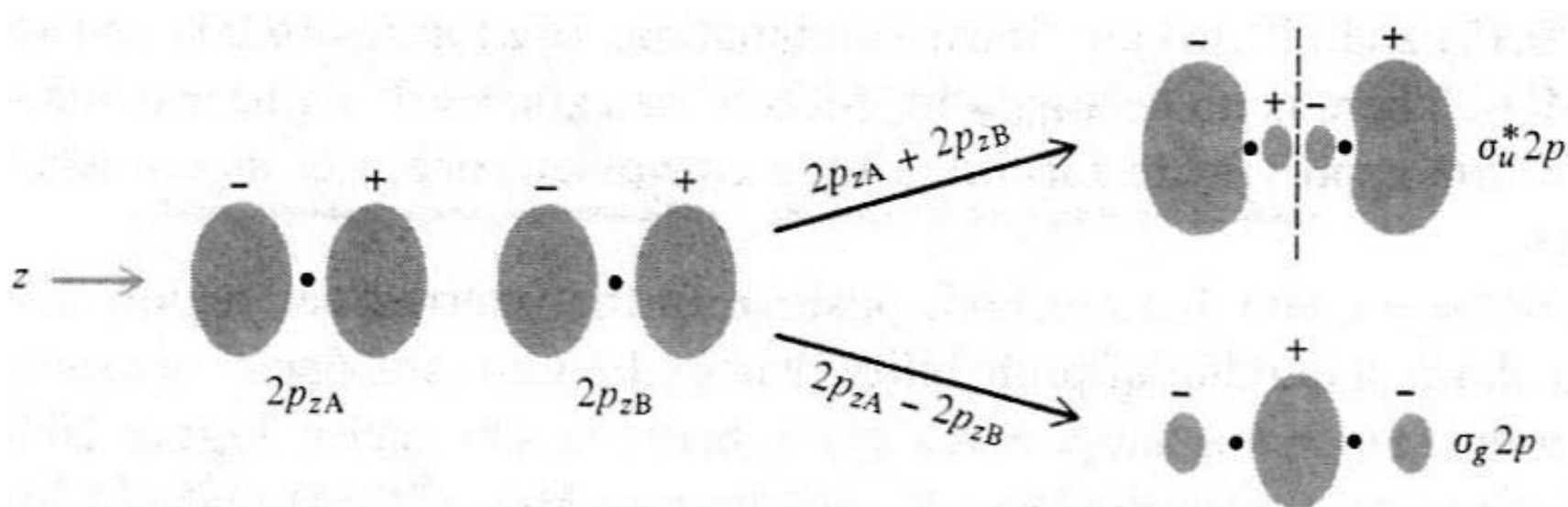
Note the signs, symmetries and nodes

Sigma Bonding with 2p Orbitals

Pi Bonding with 2p Orbitals

Note the signs, symmetries and nodes

Symmetry of Orbitals

Hydrogen molecule ion:

Bonding: Symmetric
→ σ_g
Anti-bonding: Antisymmetric
→ σ_u

Gerade (g) → Symmetric
Ungarade (u) →
Antisymmetric
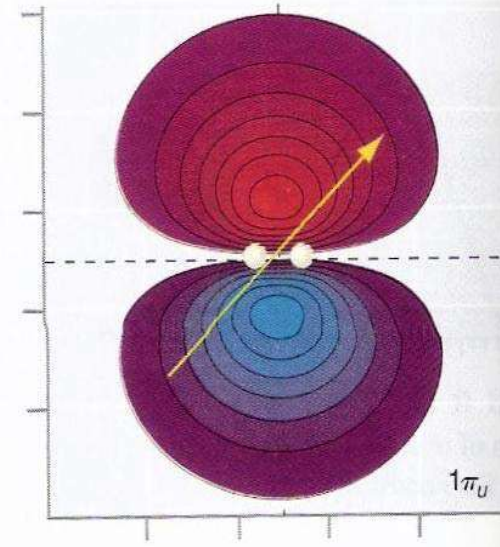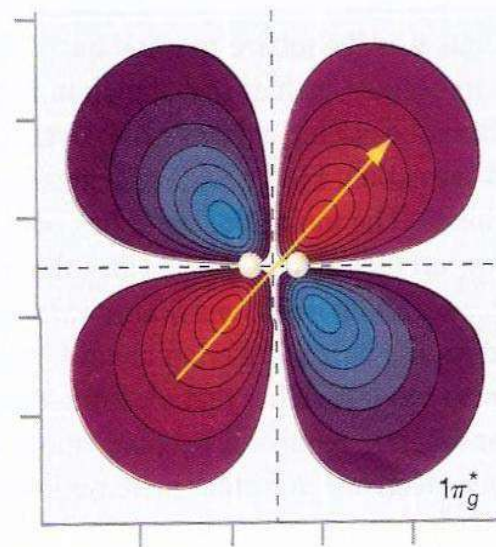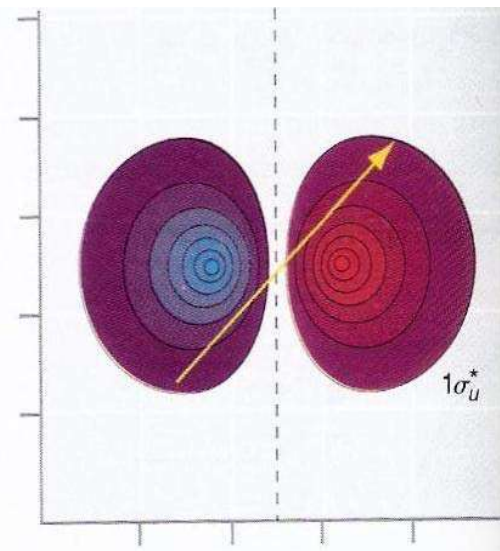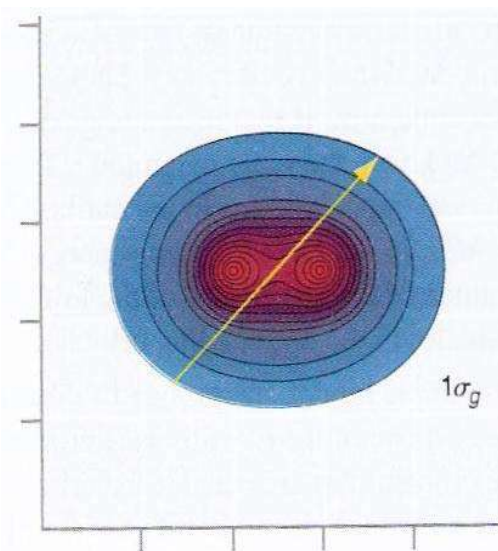
Types of Bonds
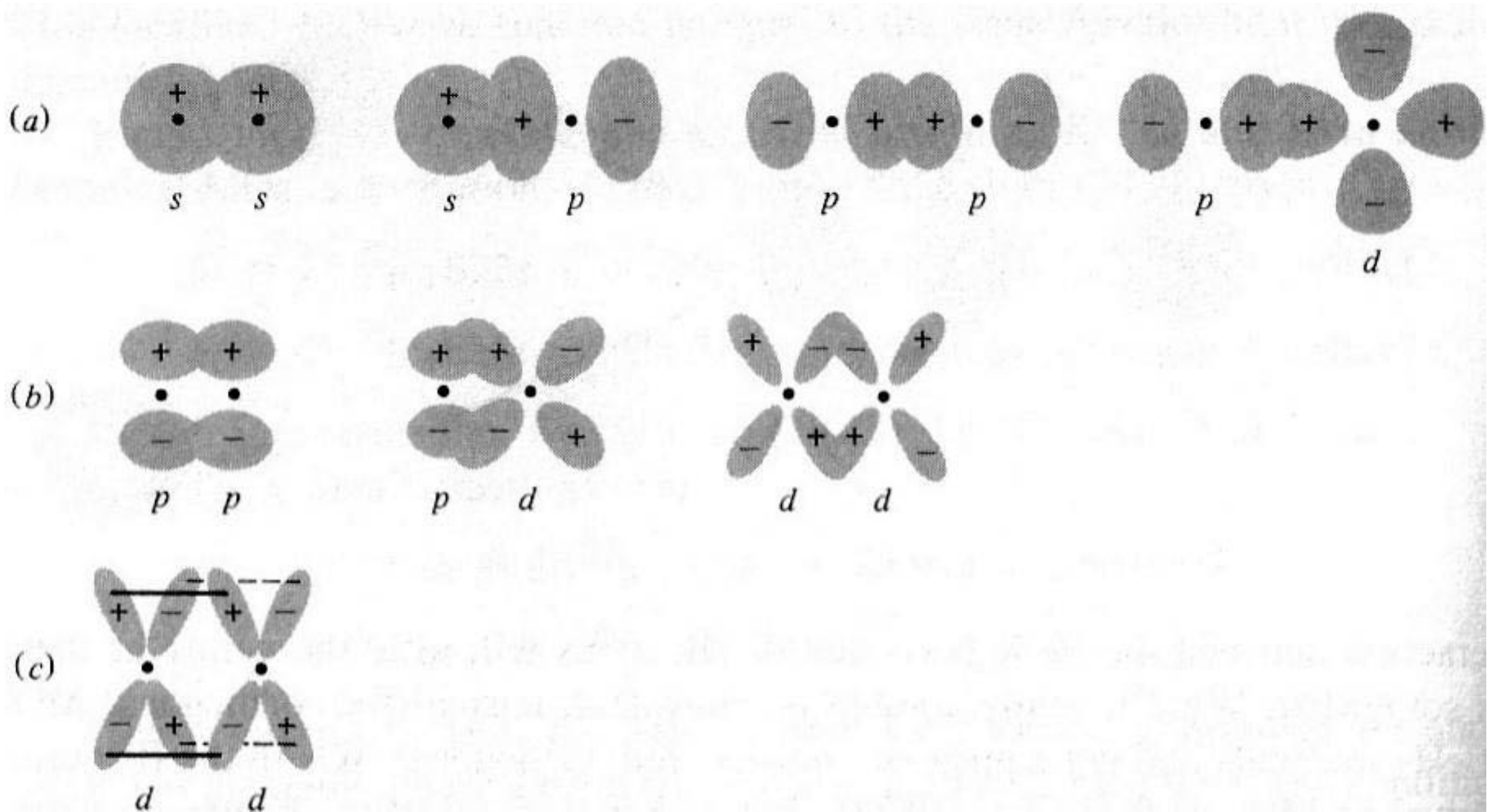
Molecular Orbital Theory of H₂

$$\widehat{H}(H_2) = \underbrace{-\frac{\hbar^2}{2m_A}\nabla_A^2 - \frac{\hbar^2}{2m_B}\nabla_B^2}_{\text{ignore}} - \frac{\hbar^2}{2m_e}\nabla_{e1}^2 - \frac{\hbar^2}{2m_e}\nabla_{e2}^2$$

$$-Q\frac{e^2}{r_{1A}} - Q\frac{e^2}{r_{1B}} Q\frac{e^2}{r_{2A}} - Q\frac{e^2}{r_{2B}} + Q\frac{e^2}{r_{12}} + Q\frac{e^2}{R}$$

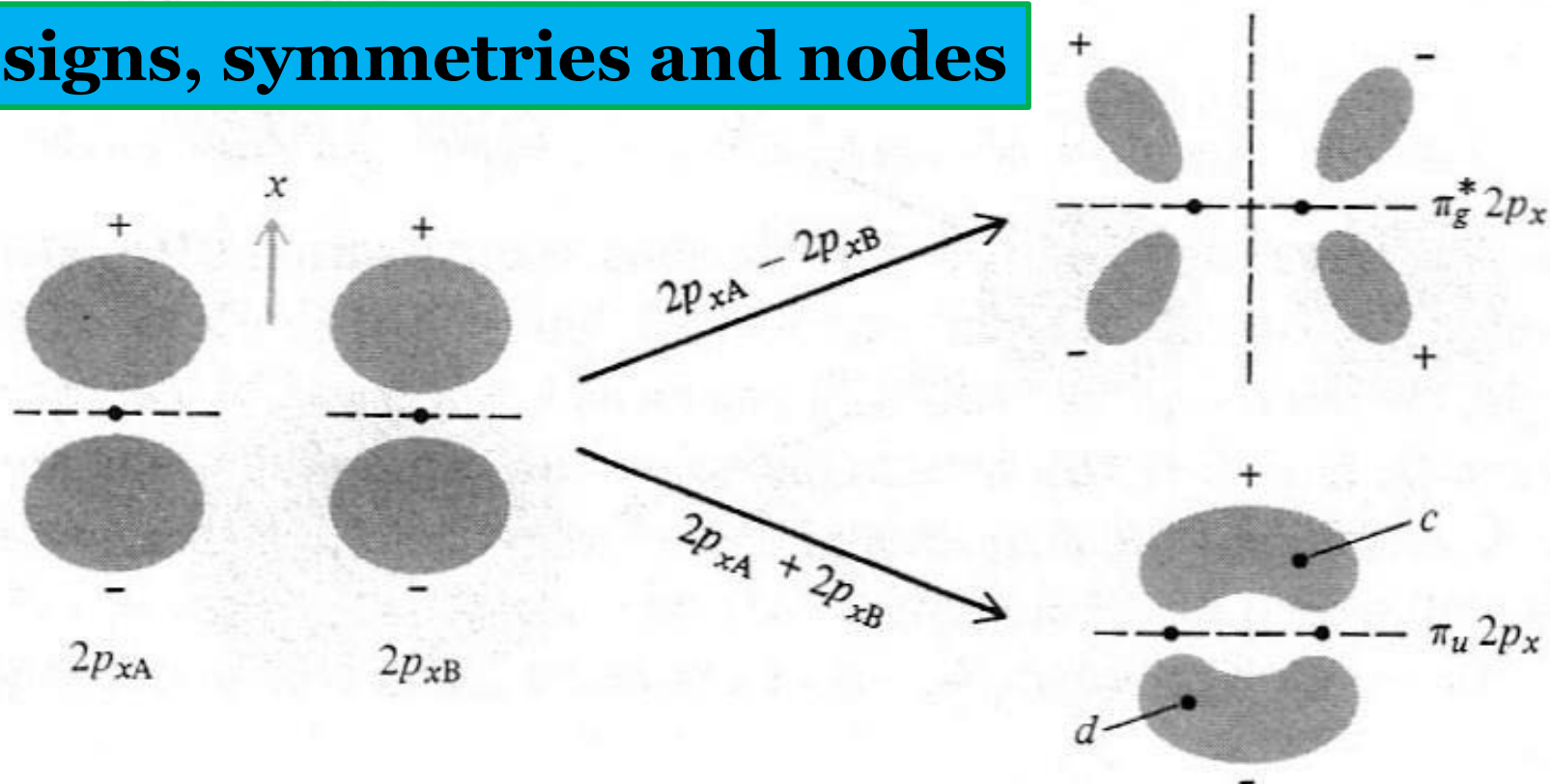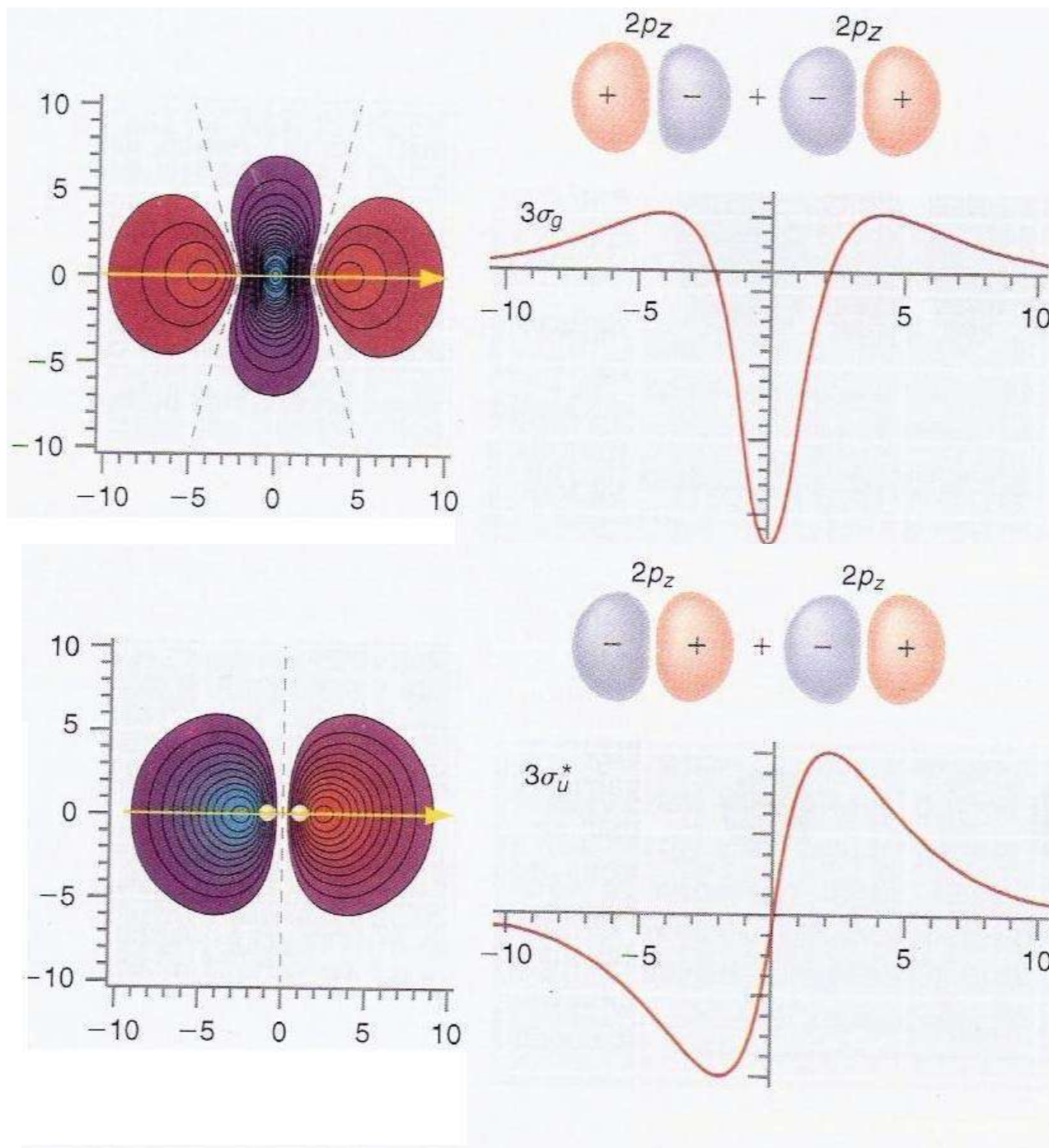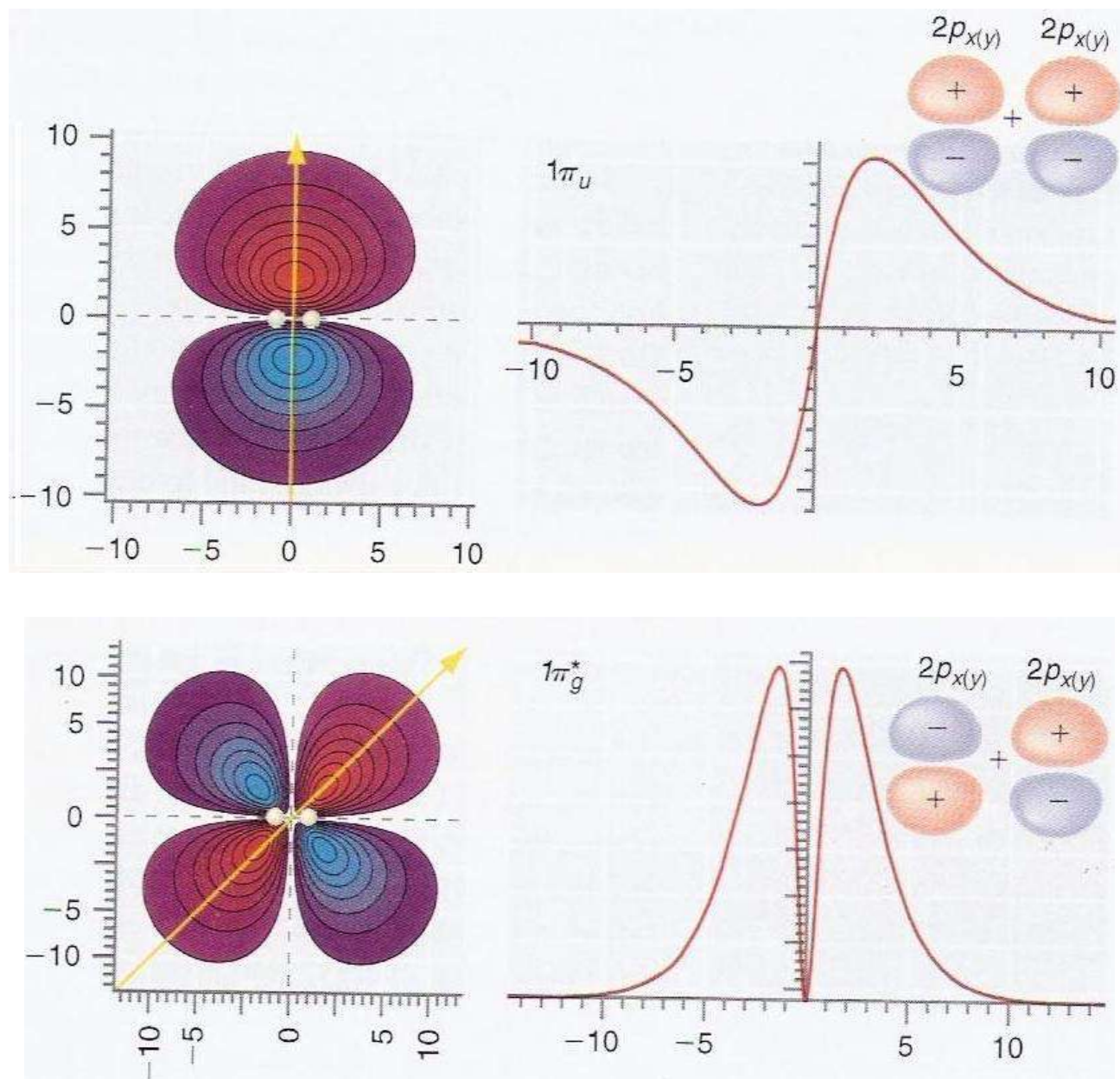$$\widehat{H}(H_2) = -\frac{\hbar^2}{2m_e}\nabla_{e1}^2 - \frac{\hbar^2}{2m_e}\nabla_{e2}^2 - Q\frac{e^2}{r_{1A}} - Q\frac{e^2}{r_{1B}} Q\frac{e^2}{r_{2A}} - Q\frac{e^2}{r_{2B}} + Q\frac{e^2}{r_{12}} + Q\frac{e^2}{R}$$

$$\widehat{H}(H_2) = -\left[\frac{\hbar^2}{2m_e}\nabla_{e1}^2 + Q\frac{e^2}{r_{1A}}\right] - \left[\frac{\hbar^2}{2m_e}\nabla_{e2}^2 + Q\frac{e^2}{r_{2B}}\right] - Q\frac{e^2}{r_{1B}} Q\frac{e^2}{r_{2A}} + Q\frac{e^2}{r_{12}} + Q\frac{e^2}{R}$$

$$\widehat{H}(H_2) = \widehat{H}(H_{1e}) + \widehat{H}(H_{2e}) - -Q\frac{e^2}{r_{1B}} Q\frac{e^2}{r_{2A}} + Q\frac{e^2}{r_{12}} + Q\frac{e^2}{R} \quad \boxed{\text{Cannot be Solved}}$$

Molecular Orbital Theory of H_2

For H_2^+

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

Place the second electron in the bonding orbital to get H_2

$$\psi_{bonding}(H_2) = \psi_1 \cdot \psi_2$$

$$= \left[\frac{1}{\sqrt{[2+2S]}}\left(\phi_{1s_A}^1 + \phi_{1s_B}^1\right)\right] \cdot \left[\frac{1}{\sqrt{[2+2S]}}\left(\phi_{1s_A}^2 + \phi_{1s_B}^2\right)\right]\left[\frac{1}{\sqrt{2}}\left[\alpha(1)\beta(2) - \beta(1)\alpha(2)\right]\right]$$

Molecular Orbital Theory of H$_2$

$$\psi_{bonding}(H_2)$$

$$= \frac{1}{2[1+S]}\left[\left(\phi^1_{1s_A}+\phi^1_{1s_B}\right)\right]\cdot\left[\left(\phi^2_{1s_A}+\phi^2_{1s_B}\right)\right]\left[\frac{1}{\sqrt{2}}\left[\alpha(1)\beta(2)-\beta(1)\alpha(2)\right]\right]$$

Spatial Part

$$\psi_{bonding}=\frac{1}{2[1+S]}\left[\phi^1_{1s_A}\phi^2_{1s_A}+\phi^1_{1s_B}\phi^2_{1s_B}+\phi^1_{1s_A}\phi^2_{1s_B}+\phi^1_{1s_B}\phi^2_{1s_A}\right]$$

$$\frac{1}{2[1+S]}\left[1s_A(1)\cdot 1s_A(2)+1s_B(1)\cdot 1s_B(2)+1s_A(1)\cdot 1s_B(2)+1s_B(1)\cdot 1s_A(2)\right]$$
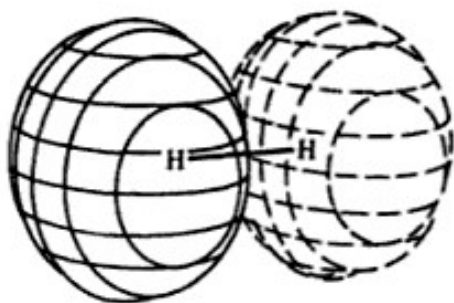
Molecular Orbital Theory of H₂

$$\psi_{anti-bonding}(H_2)$$

$$= \frac{1}{2[1-S]}\left[\left(\phi^1_{1s_A} - \phi^1_{1s_B}\right)\right]\cdot\left[\left(\phi^2_{1s_A} - \phi^2_{1s_B}\right)\right]\left[\frac{1}{\sqrt{2}}\left[\alpha(1)\beta(2) - \beta(1)\alpha(2)\right]\right]$$

Spatial Part

$$\psi_{anti-bonding} = \frac{1}{2[1-S]}\left[\phi^1_{1s_A}\phi^2_{1s_A} + \phi^1_{1s_B}\phi^2_{1s_B} - \phi^1_{1s_A}\phi^2_{1s_B} - \phi^1_{1s_B}\phi^2_{1s_A}\right]$$

$$\frac{1}{2[1-S]}\left[1s_A(1)\cdot 1s_A(2) + 1s_B(1)\cdot 1s_B(2) - 1s_A(1)\cdot 1s_B(2) - 1s_B(1)\cdot 1s_A(2)\right]$$

Molecular Orbital Theory of H_2

$$\psi_{anti-bonding} = \frac{1}{2[1-S]}\left[\phi^1_{1s_A}\phi^2_{1s_A} + \phi^1_{1s_B}\phi^2_{1s_B} - \phi^1_{1s_A}\phi^2_{1s_B} - \phi^1_{1s_B}\phi^2_{1s_A}\right]$$

$$\frac{1}{2[1-S]}\left[1s_A(1)\cdot 1s_A(2) + 1s_B(1)\cdot 1s_B(2) - 1s_A(1)\cdot 1s_B(2) - 1s_B(1)\cdot 1s_A(2)\right]$$

$$\psi_{bonding} = \frac{1}{2[1+S]}\left[\phi^1_{1s_A}\phi^2_{1s_A} + \phi^1_{1s_B}\phi^2_{1s_B} + \phi^1_{1s_A}\phi^2_{1s_B} + \phi^1_{1s_B}\phi^2_{1s_A}\right]$$
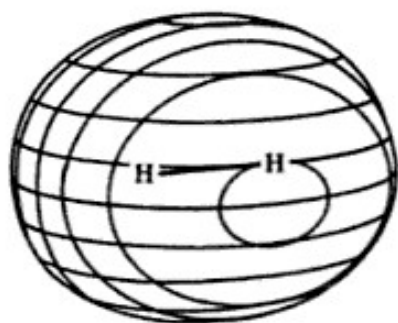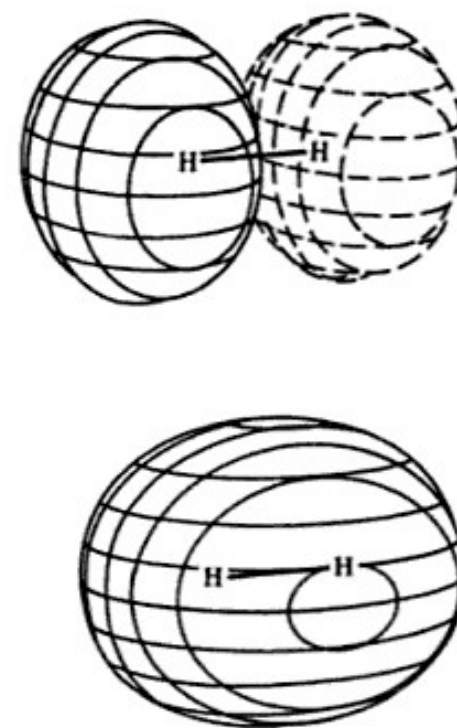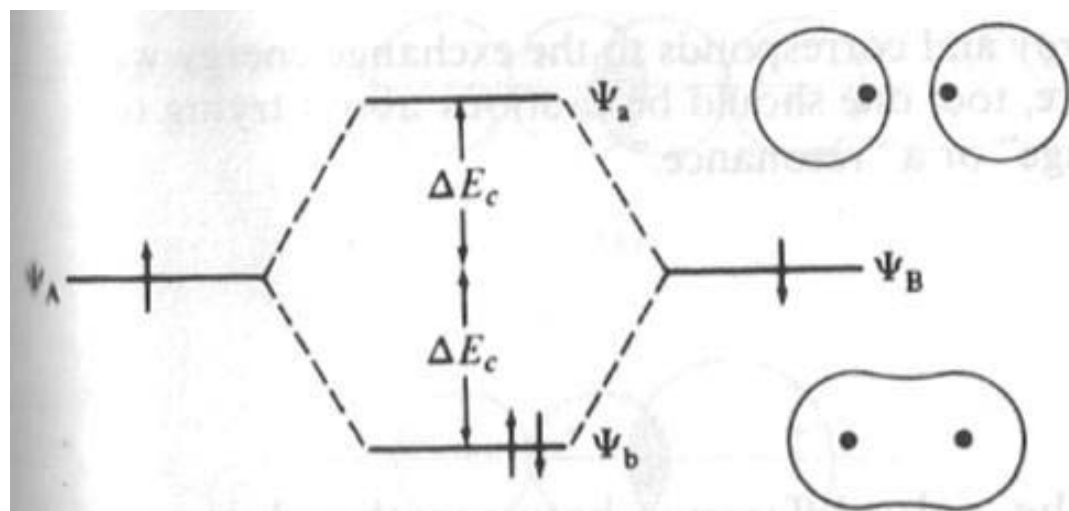
$$\frac{1}{2[1+S]}\left[1s_A(1)\cdot 1s_A(2) + 1s_B(1)\cdot 1s_B(2) + 1s_A(1)\cdot 1s_B(2) + 1s_B(1)\cdot 1s_A(2)\right]$$
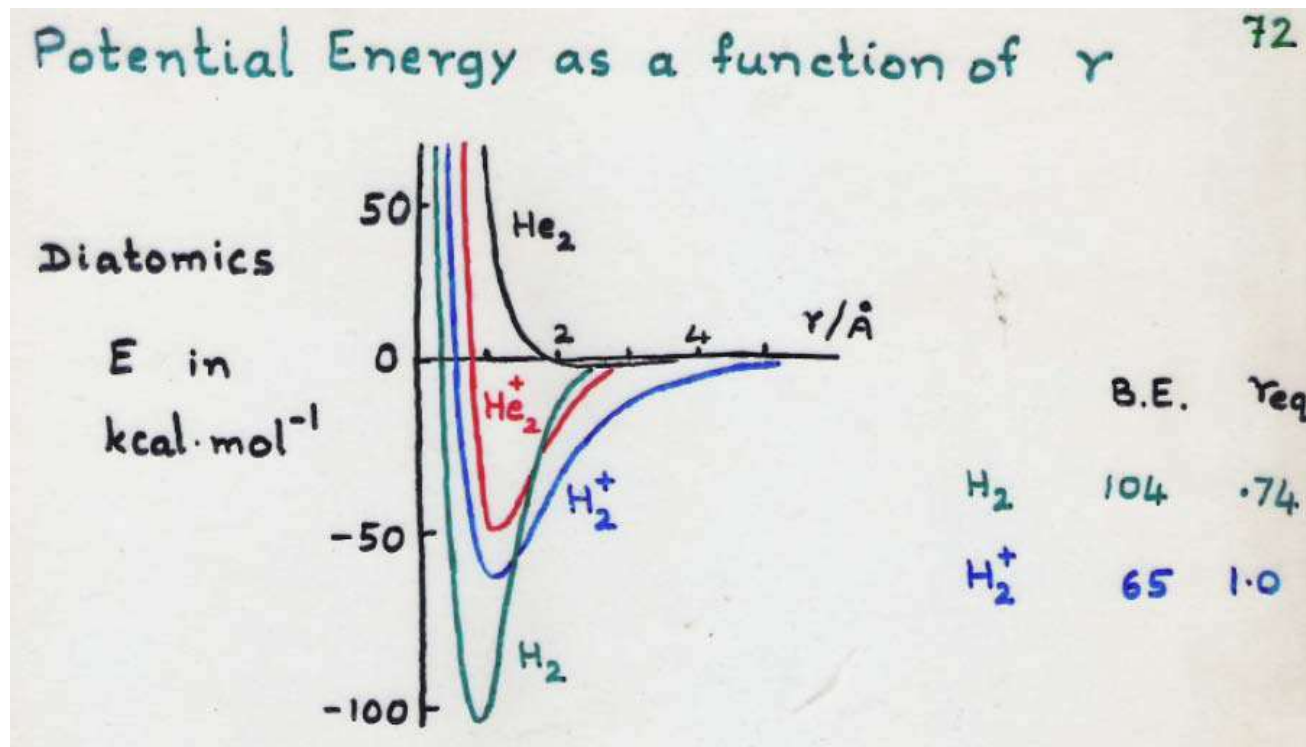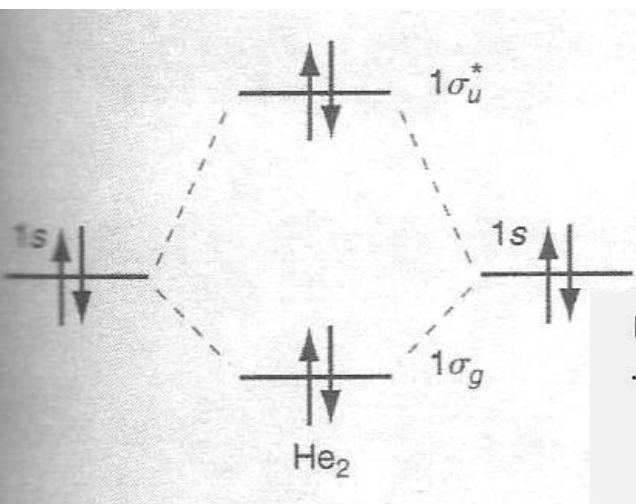
Molecular Orbital Theory of H_2

Effective nuclear charge changes the absolute energy
Levels and the size of orbitals!

Matching of energies of AOs important for LCAO-MO
If energies are not close to each other, they would
Not interact to form MOs.

Diatoms of First Row: H_2^+, H_2, He_2, He_2^+

H₂ MO diagram

He₂ MO diagram

Potential Energy as a function of r

	B.E.	r_{eq}
H_2	104	.74
H_2^+	65	1.0

Molecular properties of H_2^+, H_2, He_2^+, and He_2.

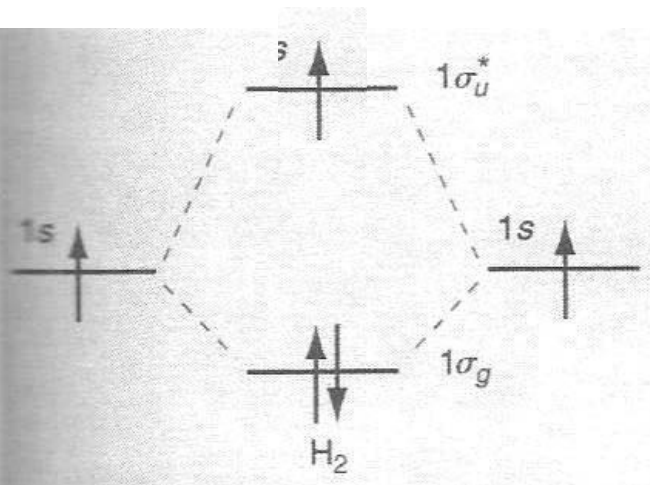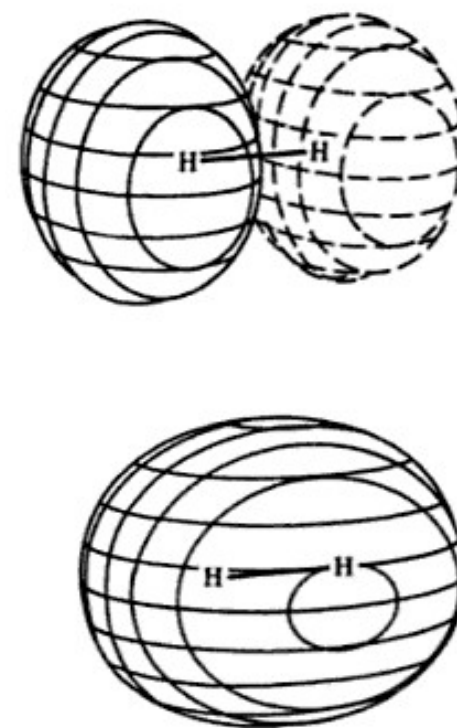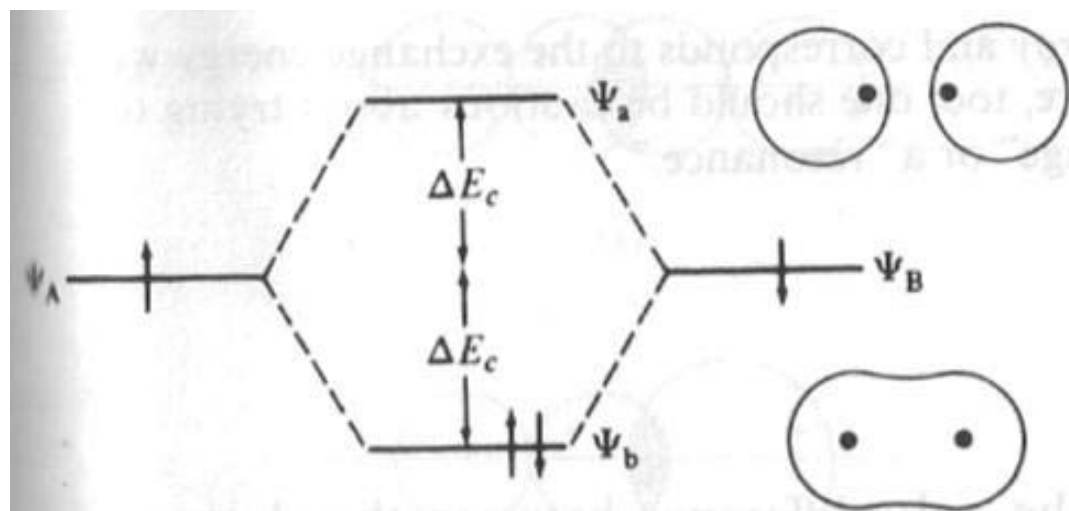| Species	Number of electrons	Ground-state electron configuration	Bond order	Bond length/pm	Binding energy/ kJ·mol⁻¹
H_2^+	1	$(\sigma_g 1s)^1$	1/2	106	268
H_2	2	$(\sigma_g 1s)^2$	1	74	457
He_2^+	3	$(\sigma_g 1s)^2(\sigma_u 1s)^1$	1/2	108	241
He_2	4	$(\sigma_g 1s)^2(\sigma_u 1s)^2$	0	≈ 6000	≪ 1

Molecular Orbital Theory of H_2

Effective nuclear charge changes the absolute energy levels and the size of orbitals!

Matching of energies of AOs important for LCAO-MO, if the energies of two Aos are not close they will not interact to form MOs.