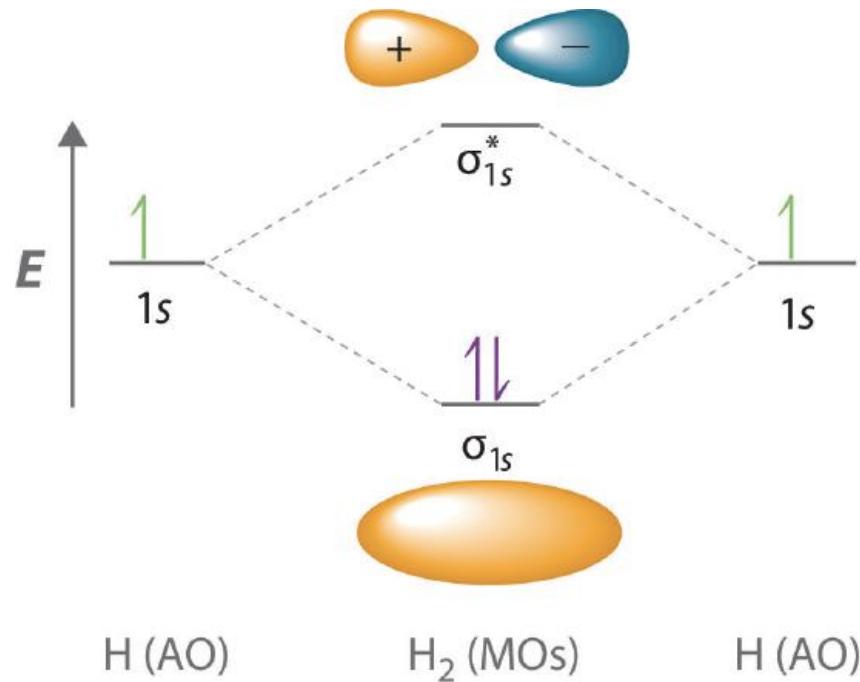
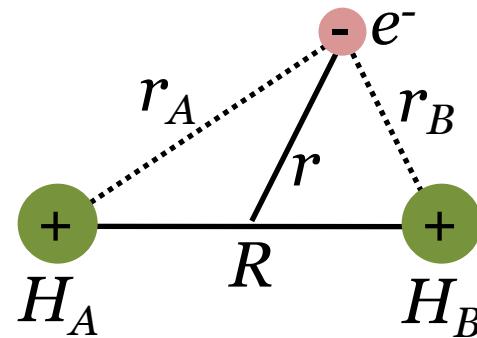


Molecular orbital theory for H_2^\pm



<https://images.app.goo.gl/BYu18Lk8W2aHRMhN8>

Linear combination of appropriate orthonormal functiona



$$\left(-\frac{\hbar^2}{2m_e} \nabla_e^2 - Q \frac{e^2}{r_A} - Q \frac{e^2}{r_B} + Q \frac{e^2}{R} \right) \psi = E \cdot \psi$$

Molecular orbital:

Polycentric one-electron wavefunction

Produced by

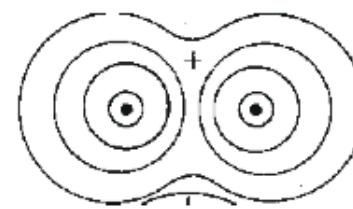
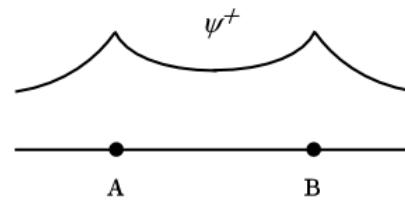
Linear Combination of Atomic Orbitals (LCAO)

$$\text{LCAO-MO: } \psi_{MO} = C_1 \phi_{1s_A} + C_2 \phi_{1s_B}$$

Molecular orbitals

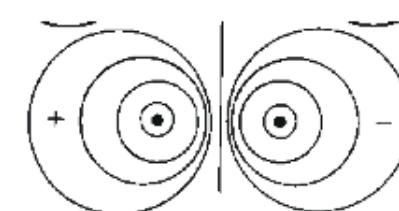
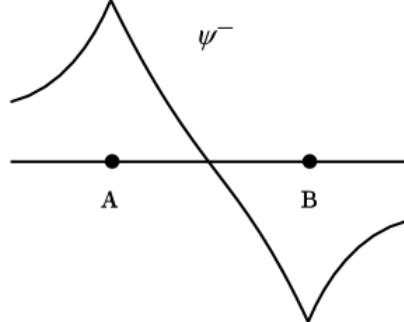
$$\psi_1 = \frac{1}{\sqrt{[2+2S]}} (\phi_{1s_A} + \phi_{1s_B})$$

$$E_1 = \langle \psi_1 | \hat{H} | \psi_1 \rangle$$



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

$$E_2 = \langle \psi_2 | \hat{H} | \psi_2 \rangle$$



Energy of bonding MO

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

Energy of bonding and antibonding MOs

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

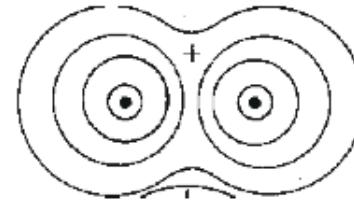
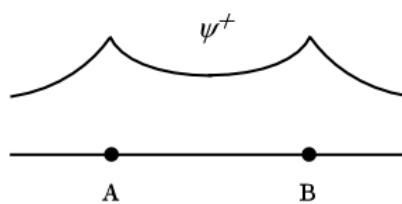
$$E_2 = \left\langle \frac{1}{\sqrt{[2-2S]}} (\phi_{1s_A} - \phi_{1s_B}) \left| \hat{H} \right| \frac{1}{\sqrt{[2+2S]}} (\phi_{1s_A} - \phi_{1s_B}) \right\rangle$$

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

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

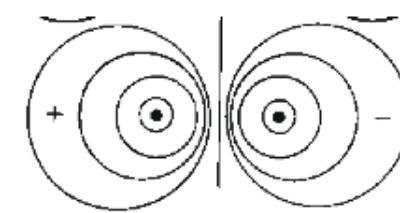
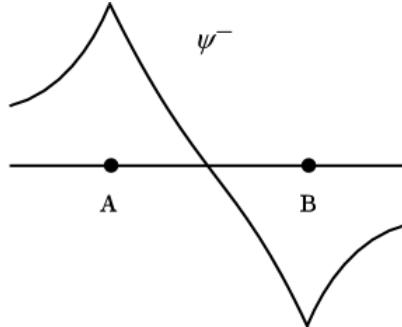
MOT: wavefunctions and energies

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



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

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



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

A closer look at energies

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

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

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

$$\begin{aligned} \left\langle \phi_{1s_i} \left| \hat{H} \right| \phi_{1s_i} \right\rangle &= H_{ii} = H_{jj} = \left\langle \phi_{1s_j} \left| \hat{H} \right| \phi_{1s_j} \right\rangle \\ \left\langle \phi_{1s_i} \left| \hat{H} \right| \phi_{1s_j} \right\rangle &= H_{ij} = H_{ji} = \left\langle \phi_{1s_j} \left| \hat{H} \right| \phi_{1s_i} \right\rangle \\ \left\langle \phi_{1s_i} \left| \phi_{1s_j} \right. \right\rangle &= S_{ij} = S_{ji} = \left\langle \phi_{1s_j} \left| \phi_{1s_i} \right. \right\rangle \end{aligned}$$

\hat{H} is Hermitian

The integral H_{ii}

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

The integral H_{ii}

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

Constant at fixed internuclear distance

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

\Rightarrow Coulomb Integral

The integral H_{ij}

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


Constant

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

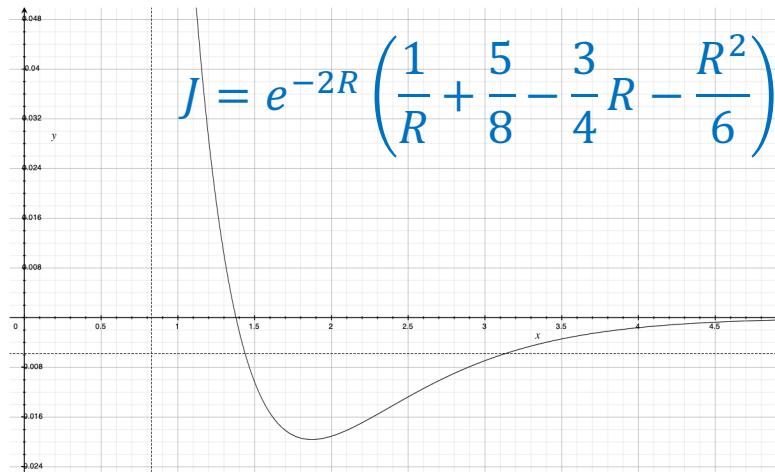
$K \Rightarrow$ Exchange Integral
Resonance Integral

Energies of bonding and antibonding MOs

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

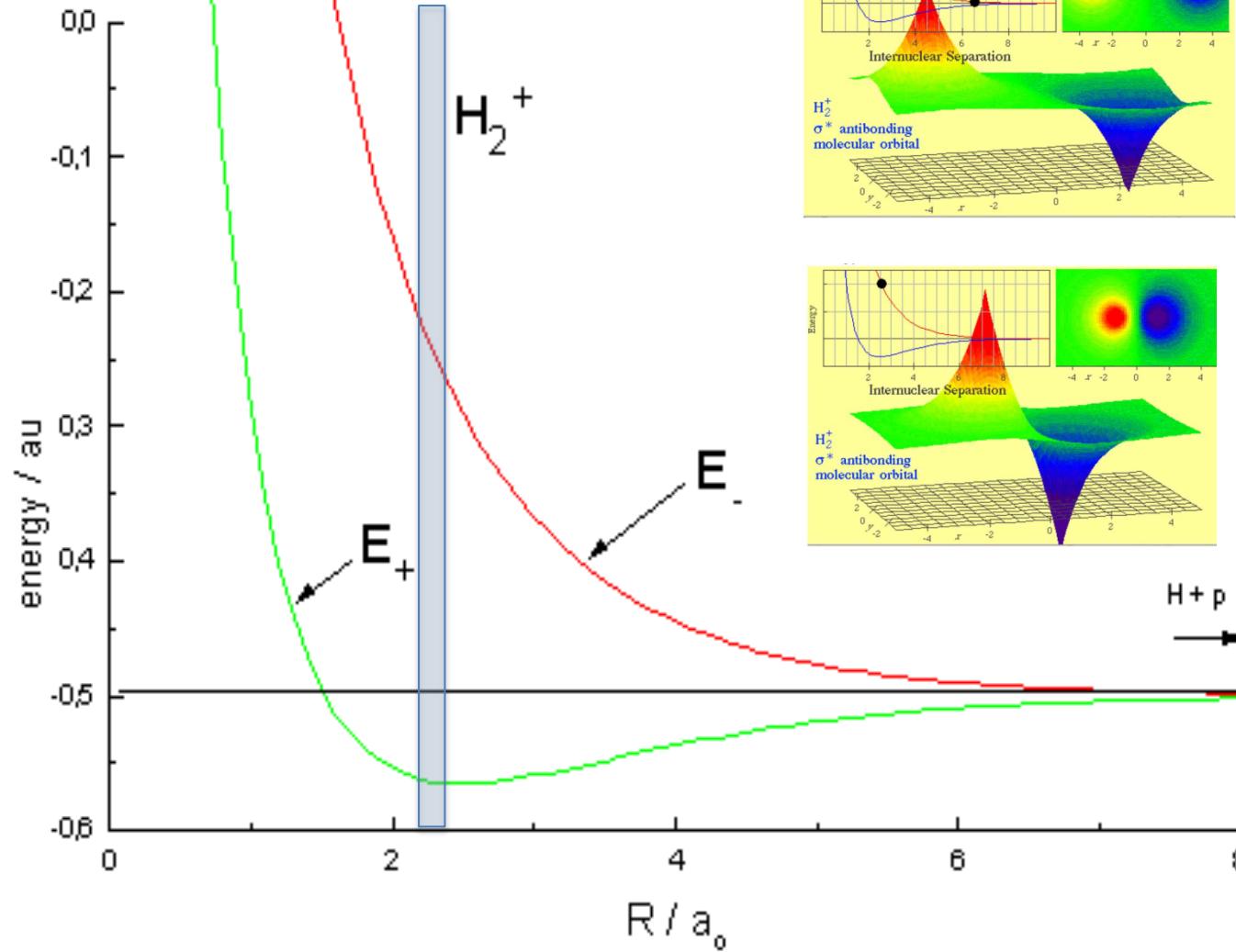
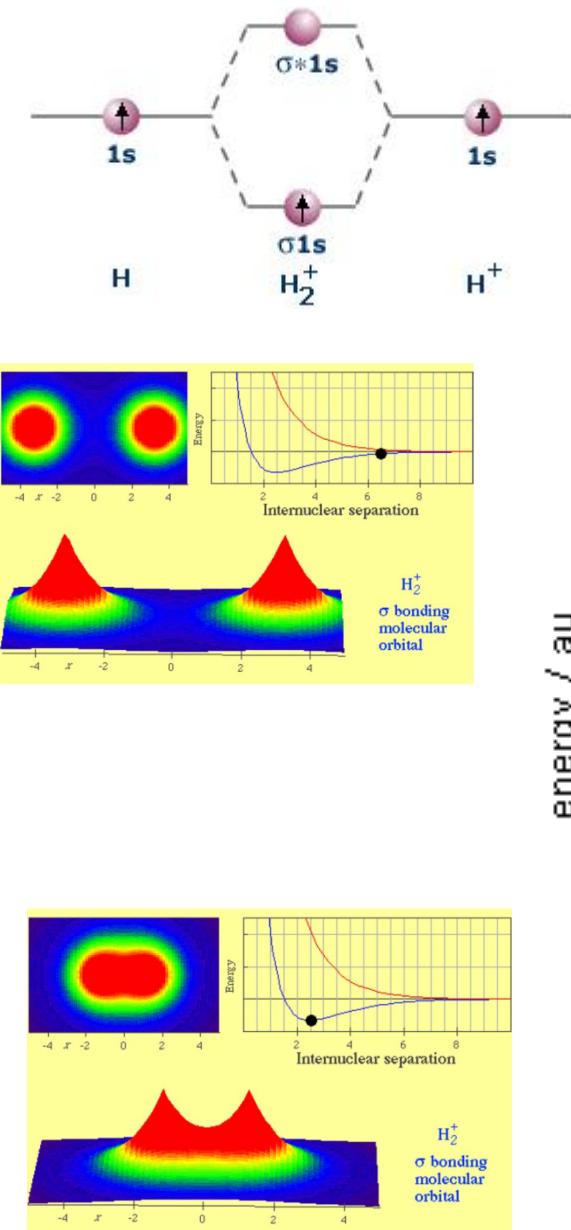
R-dependence of J and K

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

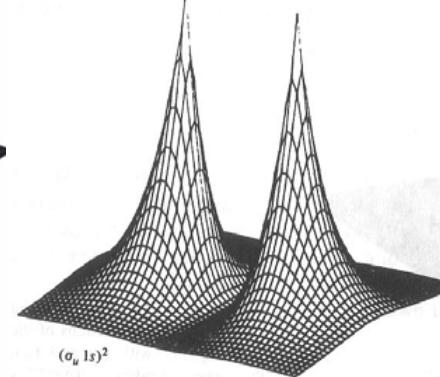
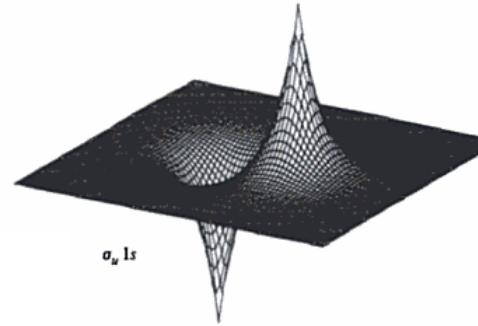
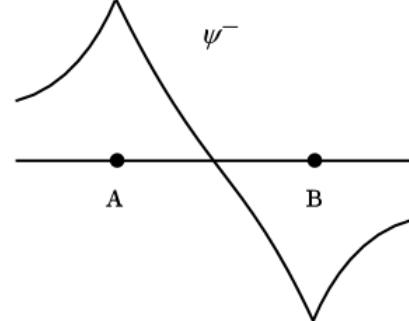
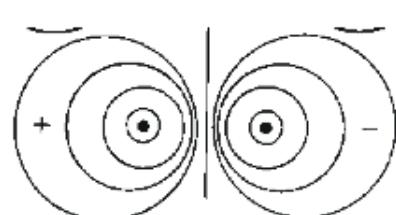
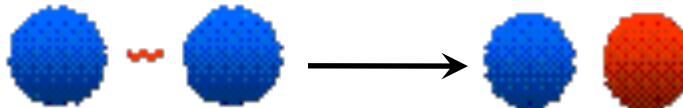
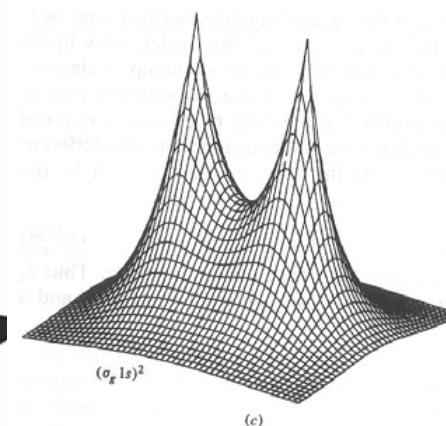
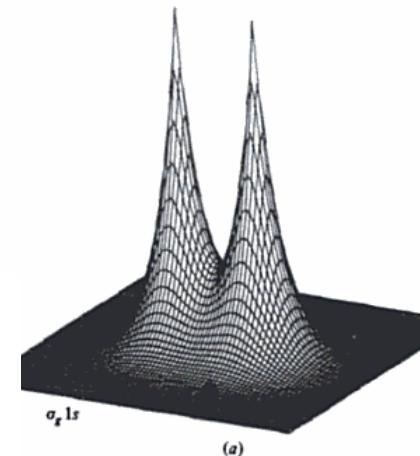
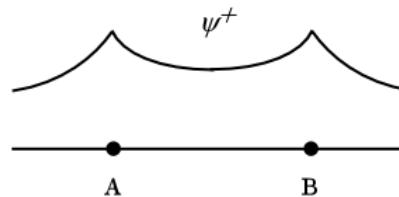
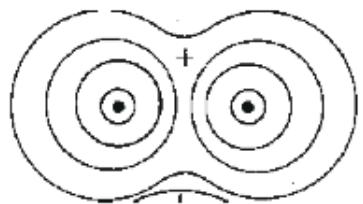
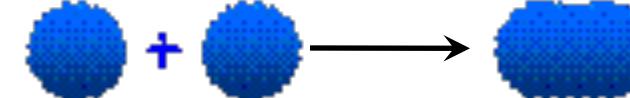


K has similar shape, with deeper minimum

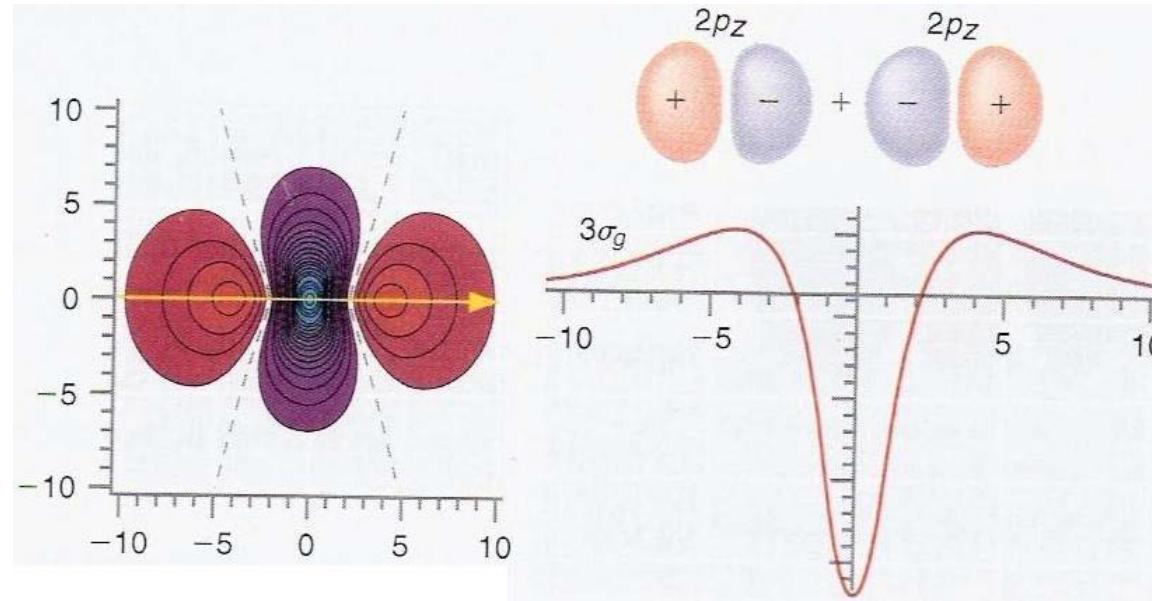
Molecular Orbital energies of H_2^+



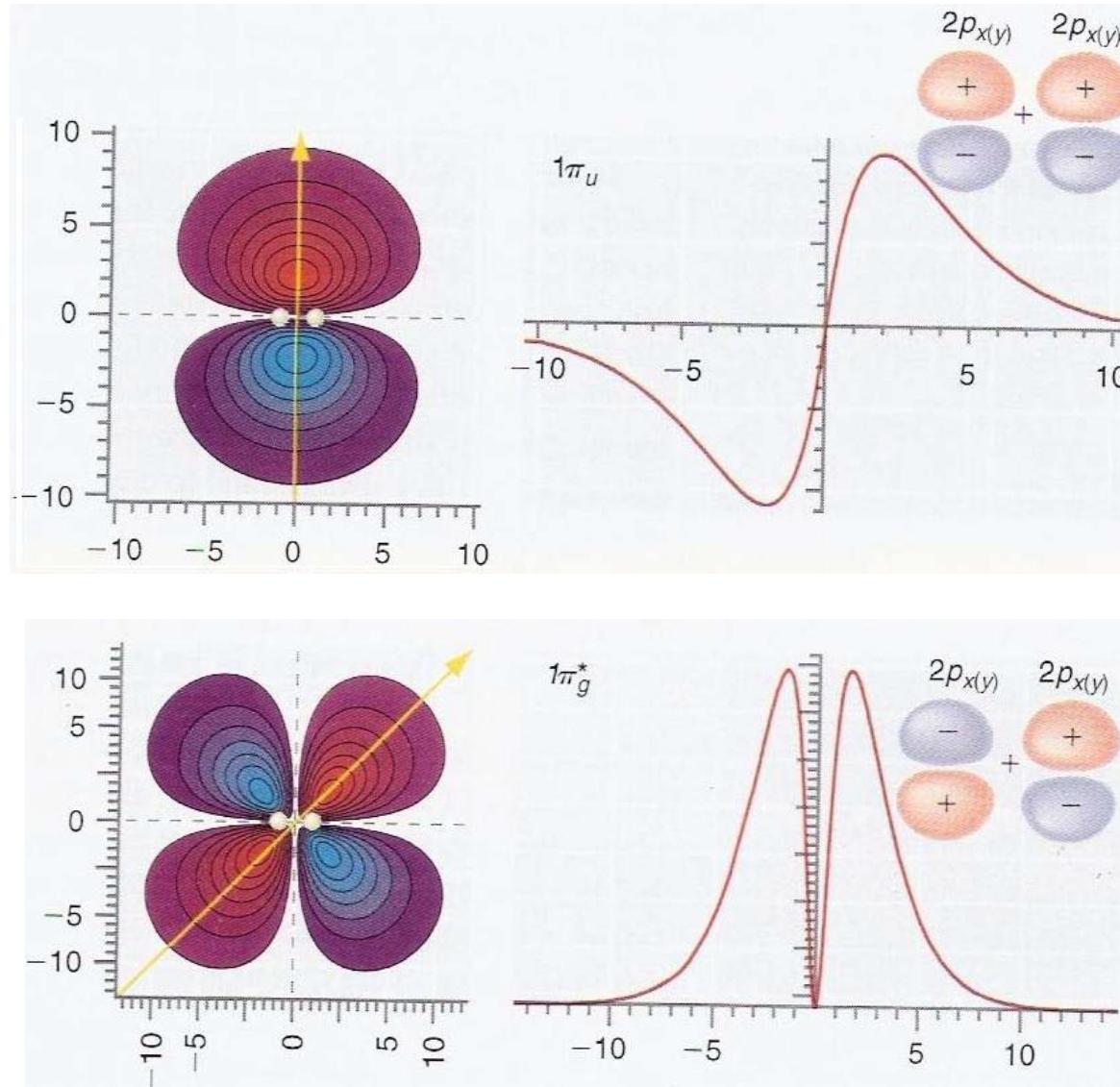
Sigma Bonding with 1s Orbitals



Sigma Bonding with 2p Orbitals



Pi Bonding with 2p Orbitals



Note the signs, symmetries and nodes

Symmetry of Orbitals

Hydrogen molecule ion:

Bonding: Symmetric

$\rightarrow \sigma_g$

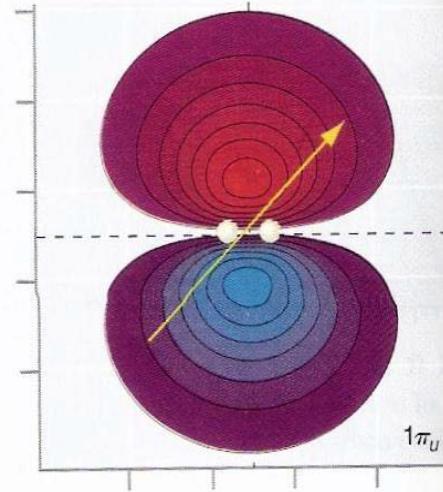
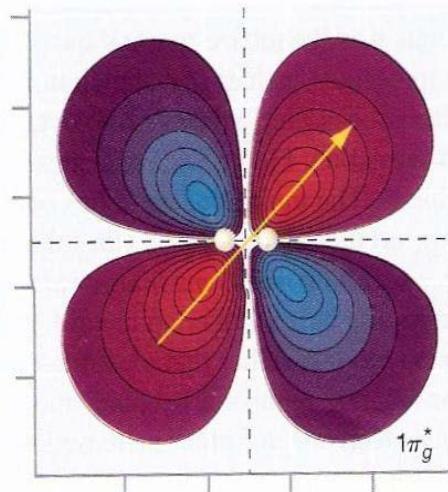
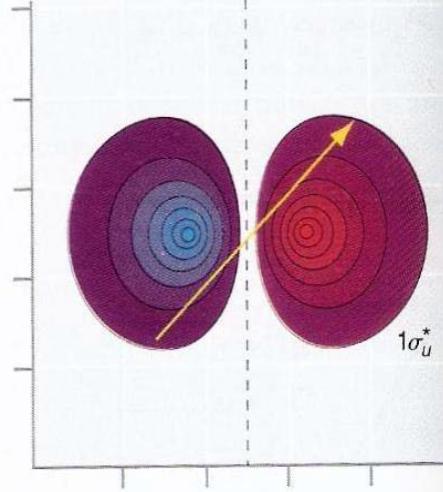
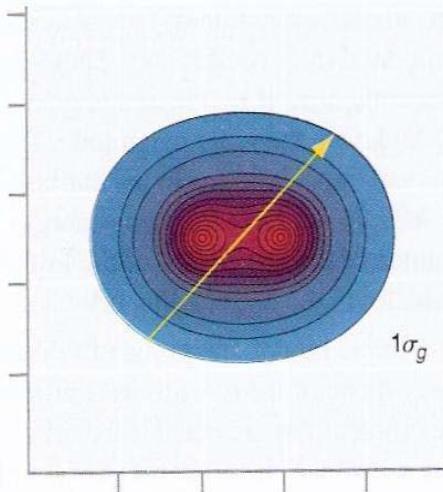
Anti-bonding: Antisymmetric

$\rightarrow \sigma_u$

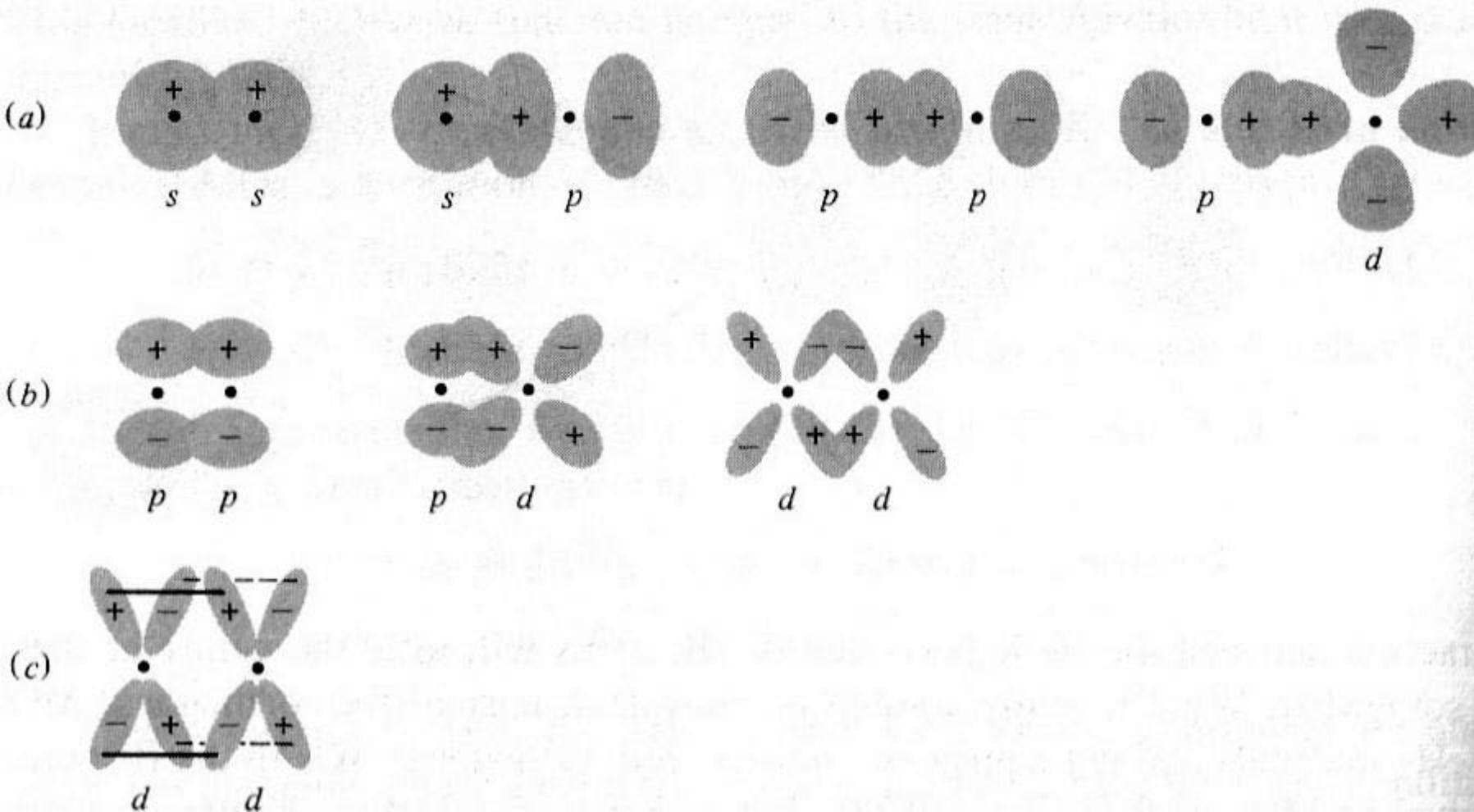
Gerade (g) \rightarrow Symmetric

Ungarade (u) \rightarrow

Antisymmetric



Types of Bonds



Molecular Orbital Theory of H₂

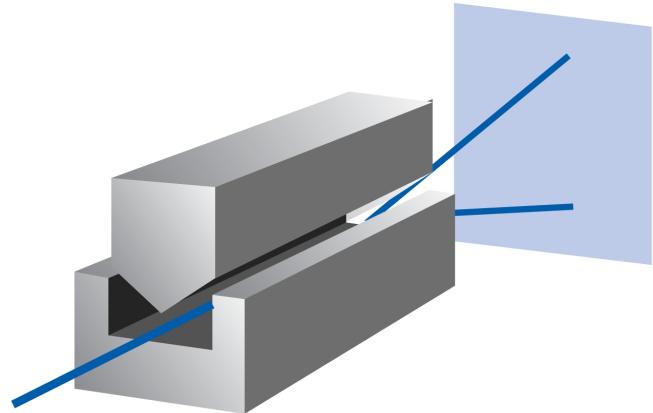
For H₂⁺

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

Place the second electron in the bonding orbital to get H₂ (ground state)

$$\begin{aligned}\psi_{bonding}(H_2) &= \psi_{bonding}(1) \cdot \psi_{bonding}(2) \\ &= \left[\frac{1}{\sqrt{[2+2S]}} (\phi_{1s_A}^{(1)} + \phi_{1s_B}^{(1)}) \right] \cdot \left[\frac{1}{\sqrt{[2+2S]}} (\phi_{1s_A}^{(2)} + \phi_{1s_B}^{(2)}) \right]\end{aligned}$$

“Spin” of an electron



**Stern-Gerlach Experiment
(1922):**

Beam of Ag atoms ($4d^{10} 5s^1$) passed through an inhomogeneous magnetic field: **TWO lines**

Uhlenbeck and Goudsmit (1925):
Two angular momentum states,
Intrinsic to the electron

NOT a result of actual rotation ($v > c$!!)

Spin: $S(\omega)$, ω is an unknown coordinate

Dirac: Relativistic quantum mechanics

Spin Angular Momentum

Spin Angular Momentum “S”

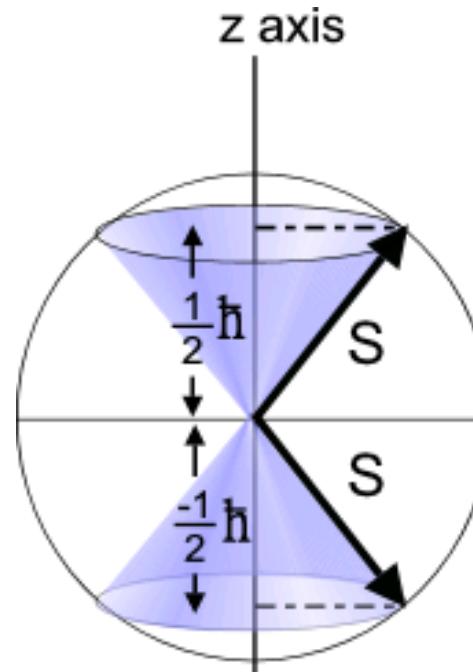
$$|S| = \hbar\sqrt{s(s+1)}$$

s = spin quantum number

$$S_z = m_s \hbar$$

$$m_s = s, s-1, \dots, -s$$

$(2s+1)$ values



For electrons, $s = 1/2$

$$m_s = \frac{1}{2}, -\frac{1}{2}$$

$$S_z = \frac{1}{2} \hbar, -\frac{1}{2} \hbar$$

“spin-up” (or α) and “spin-down” (or β)

Two electron systems

Electron labels: 1 and 2:

✓ $\alpha(1)\alpha(2)$

✓ $\beta(1)\beta(2)$

Which witch is which?

$$\alpha(1)\beta(2) \quad \pm \quad \beta(1)\alpha(2)$$

1 and 2: indistinguishable

Exchange Operator

$$\Psi(1,2) = \pm \Psi(2,1)$$

Linear combination

$$\frac{1}{\sqrt{2}} [\alpha(1)\beta(2) + \beta(1)\alpha(2)]$$

Symmetric

$$\frac{1}{\sqrt{2}} [\alpha(1)\beta(2) - \beta(1)\alpha(2)]$$

Anti-symmetric

6th Postulate of Quantum Mechanics

The complete wavefunction of a system of identical fermions (e.g. electrons) must be anti-symmetric with respect to interchange of all their coordinates (spatial and spin) of any two particles

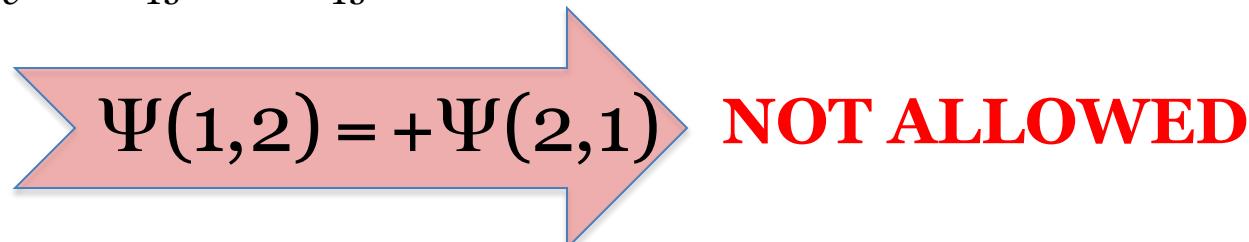
$$\Psi(1,2) = -\Psi(2,1)$$

He atom wavefunction:

$$\psi_{He} = \psi_{1s}(1) \cdot \psi_{1s}(2) \frac{1}{\sqrt{2}} [\alpha(1)\beta(2) - \beta(1)\alpha(2)]$$

What if the two electrons in **1s** orbital had same spin?

$$\psi_{He} = \psi_{1s}(1) \cdot \psi_{1s}(2) \alpha(1)\alpha(2)$$



Pauli exclusion principle

Molecular Orbital Theory of H₂

For H₂⁺

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

Place the second electron in the bonding orbital to get H₂ (ground state)

$$\begin{aligned}\psi_{bonding}(H_2) &= \psi_{bonding}(1) \cdot \psi_{bonding}(2) \\ &= \left[\frac{1}{\sqrt{[2+2S]}} (\phi_{1s_A}^{(1)} + \phi_{1s_B}^{(1)}) \right] \cdot \left[\frac{1}{\sqrt{[2+2S]}} (\phi_{1s_A}^{(2)} + \phi_{1s_B}^{(2)}) \right]\end{aligned}$$

$\alpha(1)\alpha(2)$
 $\beta(1)\beta(2)$
 $\frac{1}{\sqrt{2}} [\alpha(1)\beta(2) \pm \beta(1)\alpha(2)]$

Molecular Orbital Theory of H₂

For H₂⁺

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

Place the second electron in the bonding orbital to get H₂ (ground state)

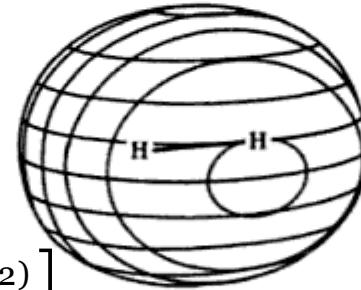
$$\begin{aligned}\psi_{bonding}(H_2) &= \psi_{bonding}(1) \cdot \psi_{bonding}(2) \\ &= \left[\frac{1}{\sqrt{[2+2S]}} (\phi_{1s_A}^{(1)} + \phi_{1s_B}^{(1)}) \right] \cdot \left[\frac{1}{\sqrt{[2+2S]}} (\phi_{1s_A}^{(2)} + \phi_{1s_B}^{(2)}) \right] \left[\frac{1}{\sqrt{2}} [\alpha(1)\beta(2) - \beta(1)\alpha(2)] \right]\end{aligned}$$

Molecular Orbital Theory of H₂

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

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

Spatial Part

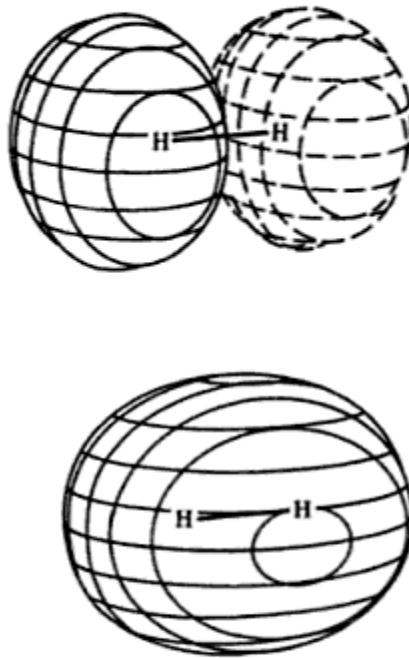
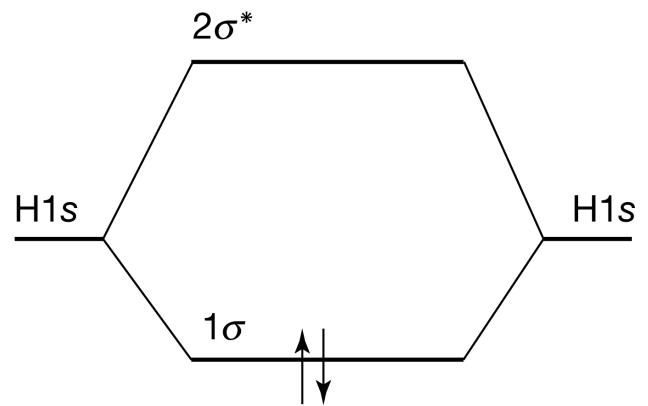


$$\psi_{bonding} = \frac{1}{2[1+S]} \left[\phi_{1s_A}^{(1)} \phi_{1s_A}^{(2)} + \phi_{1s_B}^{(1)} \phi_{1s_B}^{(2)} + \phi_{1s_A}^{(1)} \phi_{1s_B}^{(2)} + \phi_{1s_B}^{(1)} \phi_{1s_A}^{(2)} \right]$$

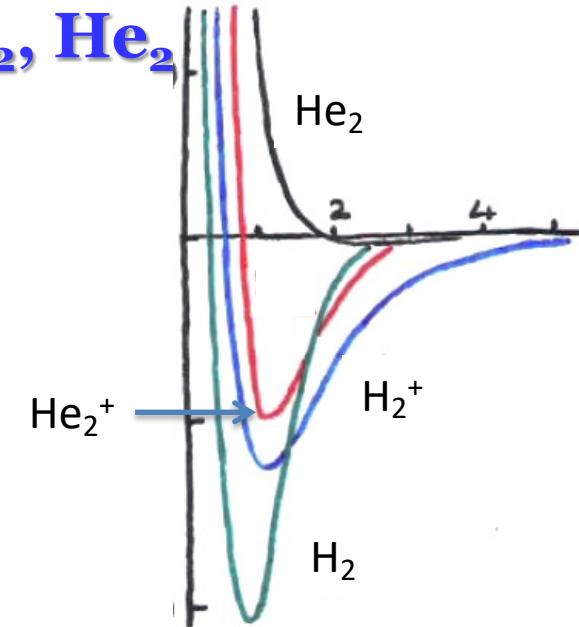
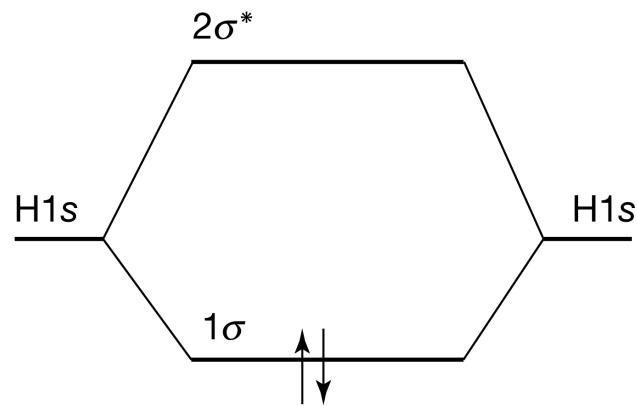
$$= \frac{1}{2[1+S]} \left[1s_A(1) \cdot 1s_A(2) + 1s_B(1) \cdot 1s_B(2) + 1s_A(1) \cdot 1s_B(2) + 1s_B(1) \cdot 1s_A(2) \right]$$

Ionic terms: overemphasized

Molecular Orbital Theory of H₂



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



Species	No. of electrons	Electron config.	Bond order	Bond length (pm)	Binding energy (kJ mol ⁻¹)
H_2^+	1	$(1\sigma)^1$	0.5	106	268
H_2	2	$(1\sigma)^2$	1	74	457
He_2^+	3	$(1\sigma)^2(1\sigma^*)^1$	0.5	108	241
He_2	4	$(1\sigma)^2(1\sigma^*)^2$	0	6000	<<1