


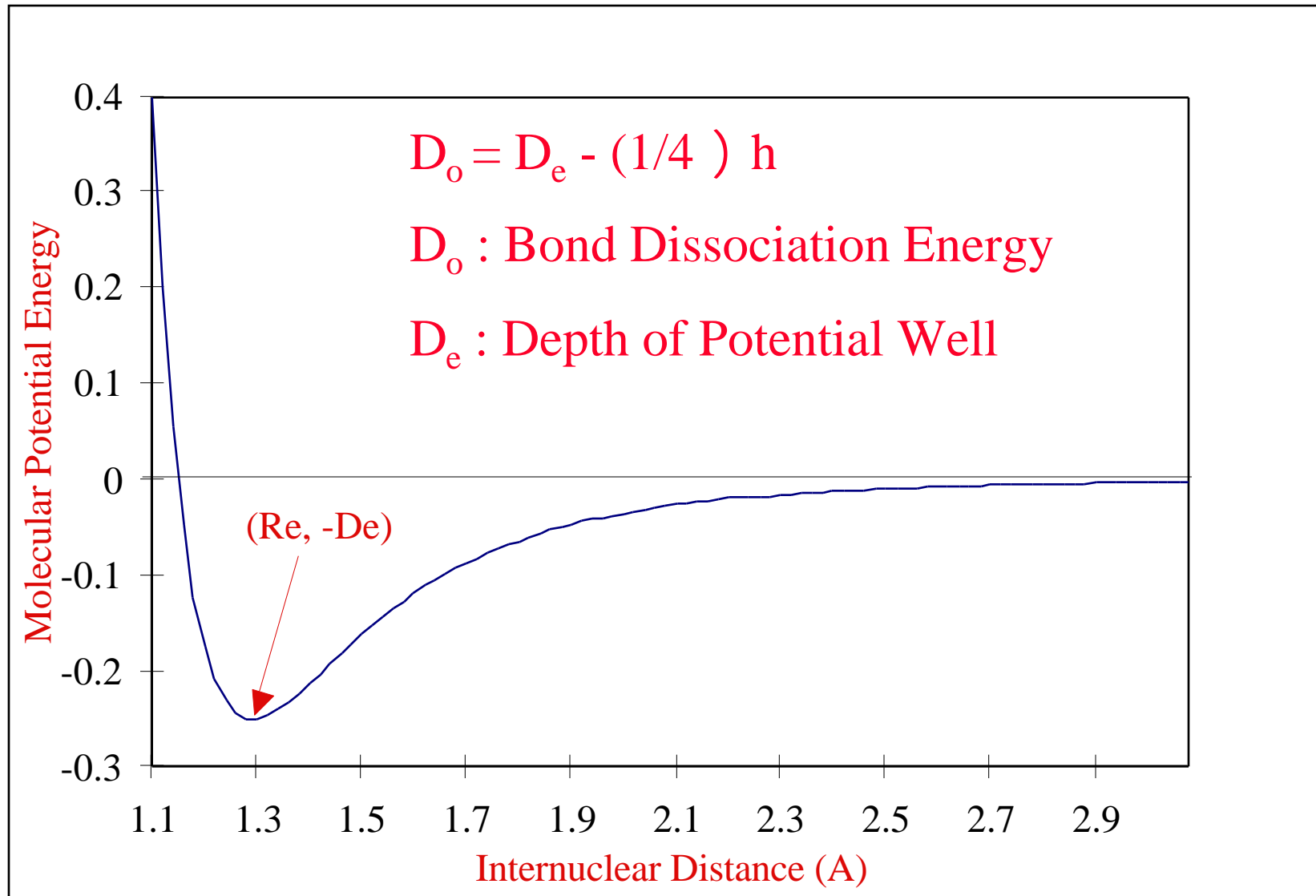
# Molecular Structure

- First Goal: Extend the concept of atomic orbitals to that of molecular orbitals for the description of the electronic configuration of molecules.
- Second Goal: Understand the origin of the “number”, “strength” and “three-dimensional arrangement” of chemical bonds between atoms in a molecule.
- Outcome: Description of Covalent and Ionic Bonding.  
Introduction to Van der Waals and Metallic Bonding.

## Approach:

- By analogy with the study of atomic structures, where we started with **H**, we begin the study of molecular structures with  $\text{H}_2^+$ . In either case, we are dealing with a **one-electron system**.
- Consider the **Born-Oppenheimer Approximation**: Nuclei are stationary while the electrons move relative to them (inertia of nuclei that are heavier than electrons).
- Solve the Schrodinger Equation for an arbitrary separation distance between the two nuclei (i.e calculate energy levels and associated wave functions for the molecular ion for that separation distance). Repeat the calculation for different distances between nuclei.
-  Explore the energy of molecules as a function of bond length : Molecular Potential Energy Curve (Kinetic energy of the molecular ion was ignored).

# Molecular Potential Energy Curve



# Molecular Orbital Theory

- **Valence Bond Theory** (see Atkins 5th ed. pages 463-468): Electrons are shared between atoms making a given bond. The electron “Valence Bond” wave function is localized between the nuclei that define the bond.
- **Molecular Orbital Theory** is an alternative to the Valence Bond Theory : In the MO theory electrons in the molecule do not belong to specific bonds but their wave function (e-cloud) spreads over the whole molecule.  
➔ **Molecular Orbital**
- M.O. Theory applicable for the description of solids, metals.

$$\hat{H}\psi = -\frac{\hbar^2}{2m_r} \nabla^2\psi + V(r).\psi = E.\psi \quad V(r) = -\frac{e^2}{4\pi\epsilon_0} \left( \frac{1}{r_{A1}} + \frac{1}{r_{B1}} \right)$$

- The Schrodinger Equation for one electron and two nuclei can be solved exactly to yield the one-electron wave functions (**molecular orbitals**) and the associated molecular orbital energies. **However, the results are very complex ...**
- An Excellent Approximation: **MO LCAO**  
The approximation will consist in describing **Molecular Orbitals** as **Linear Combination of Atomic Orbitals**.

**Justification:**

electron close to  $H_A$  then  $1/r_{A1} \gg 1/r_{B1}$  and  $\psi = \psi(H_A)$

electron close to  $H_B$  then  $1/r_{B1} \gg 1/r_{A1}$  and  $\psi = \psi(H_B)$

Then, we define the electron wave function by a linear combination of atomic orbitals for  $H_A$  and  $H_B$  as:

$$\psi = a \psi(H_A) + b \psi(H_B)$$

where a and b are constants.

## Determination of the Normalization Constants for the Molecular Orbital Wave Function

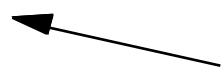
- Symmetry considerations impose:  $a=b$
- The wave functions  $\psi_{1s}(H_A)$ ,  $\psi_{1s}(H_B)$  must be normalized.

$$\int \psi_{1s}(H_A) \psi_{1s}^*(H_A) dV = 1$$

$$\int \psi_{1s}(H_B) \psi_{1s}^*(H_B) dV = 1$$

$$\int \psi \psi^* dV = 1$$

$$a^2 \int \psi_{1s}(H_A) \psi_{1s}^*(H_A) dV + \int \psi_{1s}(H_B) \psi_{1s}^*(H_B) dV + 2 \int \psi_{1s}(H_A) \psi_{1s}^*(H_B) dV = 1$$



S=overlap integral

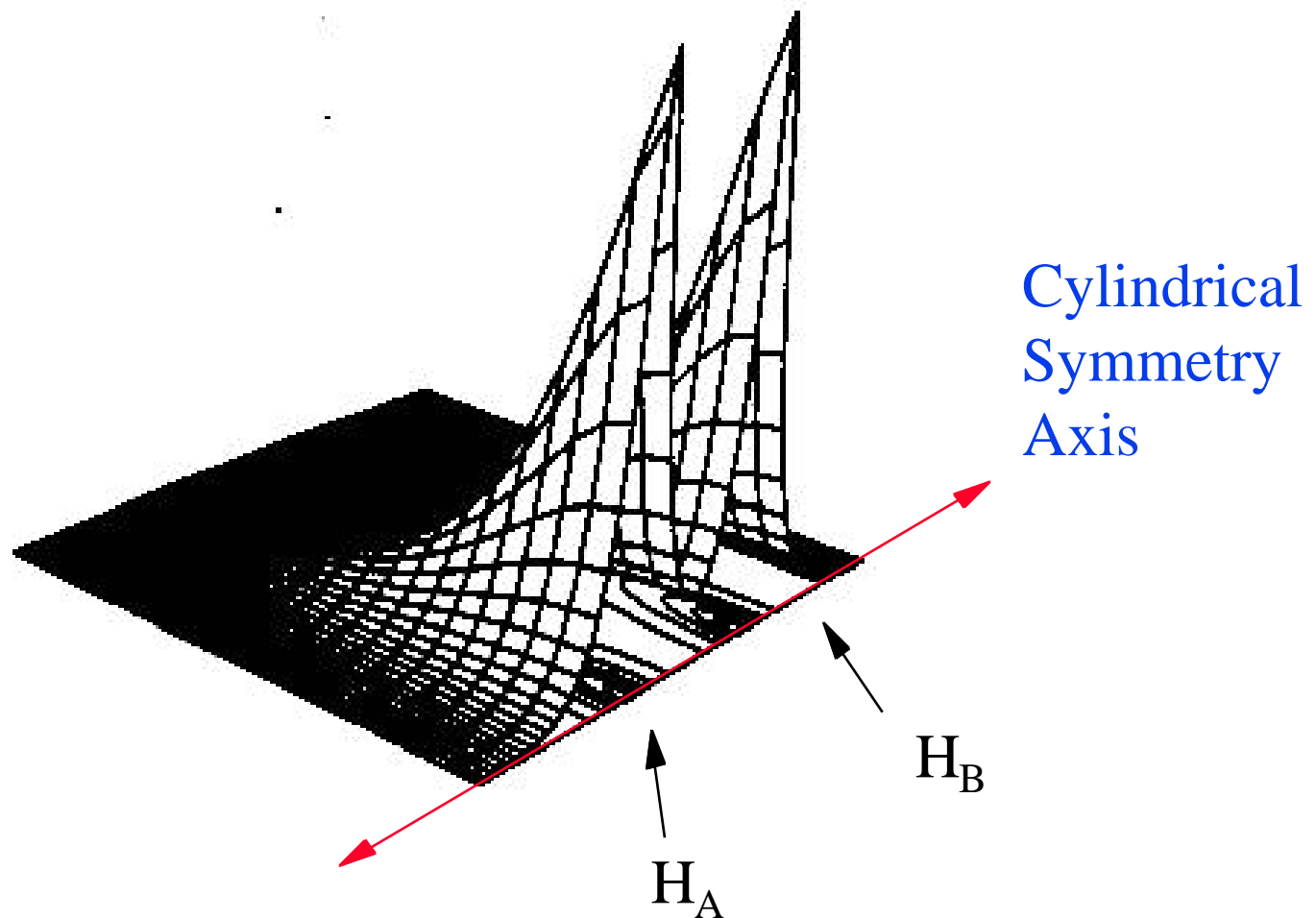
$$a = \frac{1}{\sqrt{2(1+S)}}$$

## Bonding Molecular Orbital

- The Overlap Integral  $S$  accounts for the enhancement of electron density between the two nuclei over what would be expected if only one nucleus were present. This increase in electron density arises from the **constructive interference** between the atomic wave functions in the internuclear region (physically speaking: electrons like to be where they can interact favorably with both nuclei). Energy of the molecule is lower than that of the separate atoms.
- A Molecular Orbital that has **cylindrical symmetry** about the internuclear axis is called a **orbital**. Electronic configuration is  $1\sigma_g^2$  for  $H_2^+$  in this lowest energy state.
- This Molecular Orbital is called a **bonding orbital** because in such orbital there is an increase in electron density between the nuclei.

# Bonding Molecular Orbital

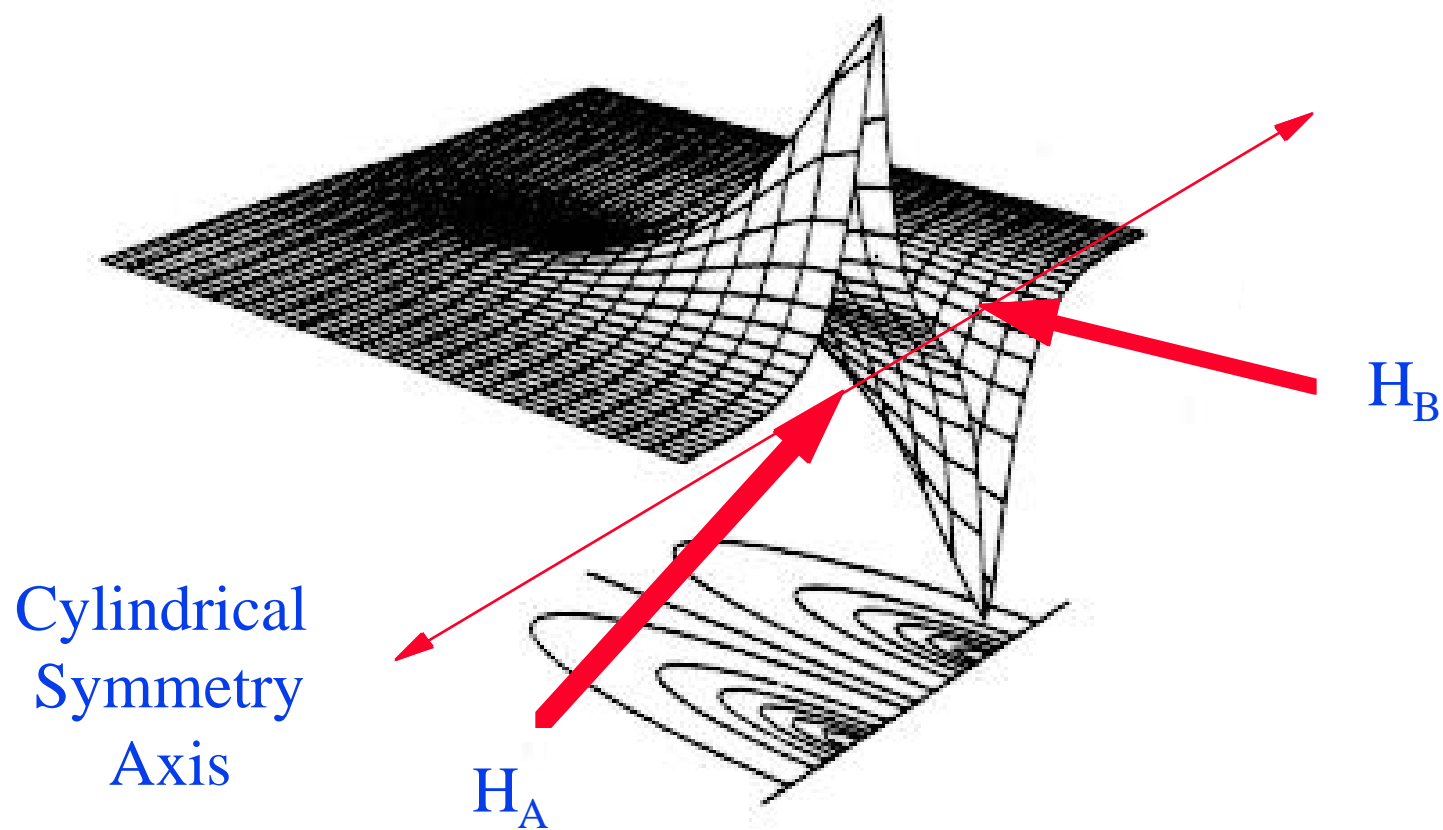
$$\psi = \frac{1}{\sqrt{2}} (\psi_A + \psi_B)$$



## Antibonding Molecular Orbital

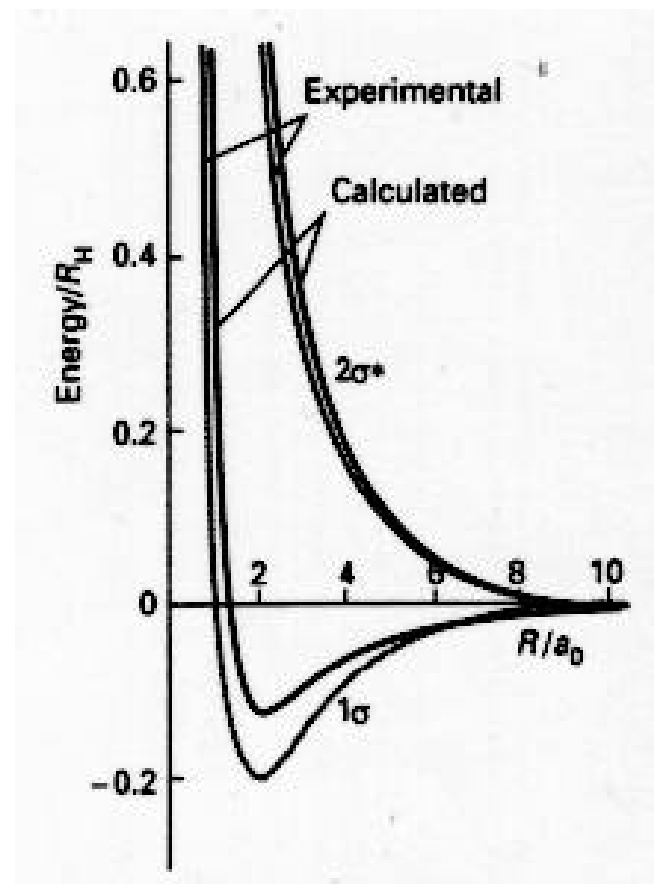
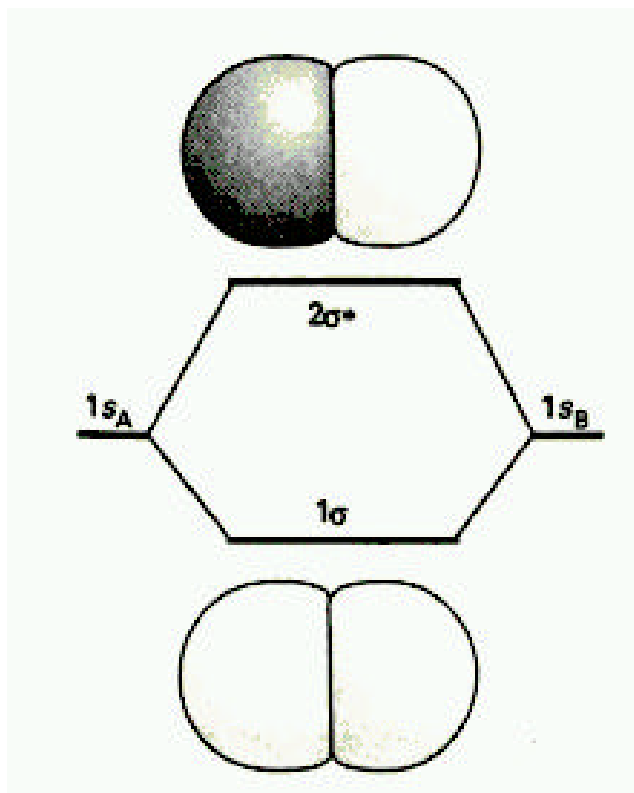
- When we wrote  $\psi = a(\psi_A) + b(\psi_B)$  with  $a^2 = b^2 = \frac{1}{2(1+S)}$  we actually assumed  $a = b$
- A second solution would be given by  $b = -a$ , which leads to:
  - $\psi = a(\psi_A) - b(\psi_B)$  and
  - $a^2 = b^2 = \frac{1}{2(1-S)}$
- In this case, the overlap integral **S** is subtracted from the electron density associated with  $\psi_A$  and  $\psi_B$  alone. This decrease in electron density arises from the **destructive interference** between the atomic wave functions in the internuclear region. Energy of the molecule associated with this wave function is higher than that of the separate atoms.
- This Molecular Orbital is called a **antibonding orbital** because in such orbital there is an decrease in electron density between the nuclei. The electronic configuration is  $\sigma_{2p}^1$  for  $\text{O}_2^+$  in this high energy state

## Antibonding 2 Molecular Orbital



# Molecular Orbital Energy Level Diagram

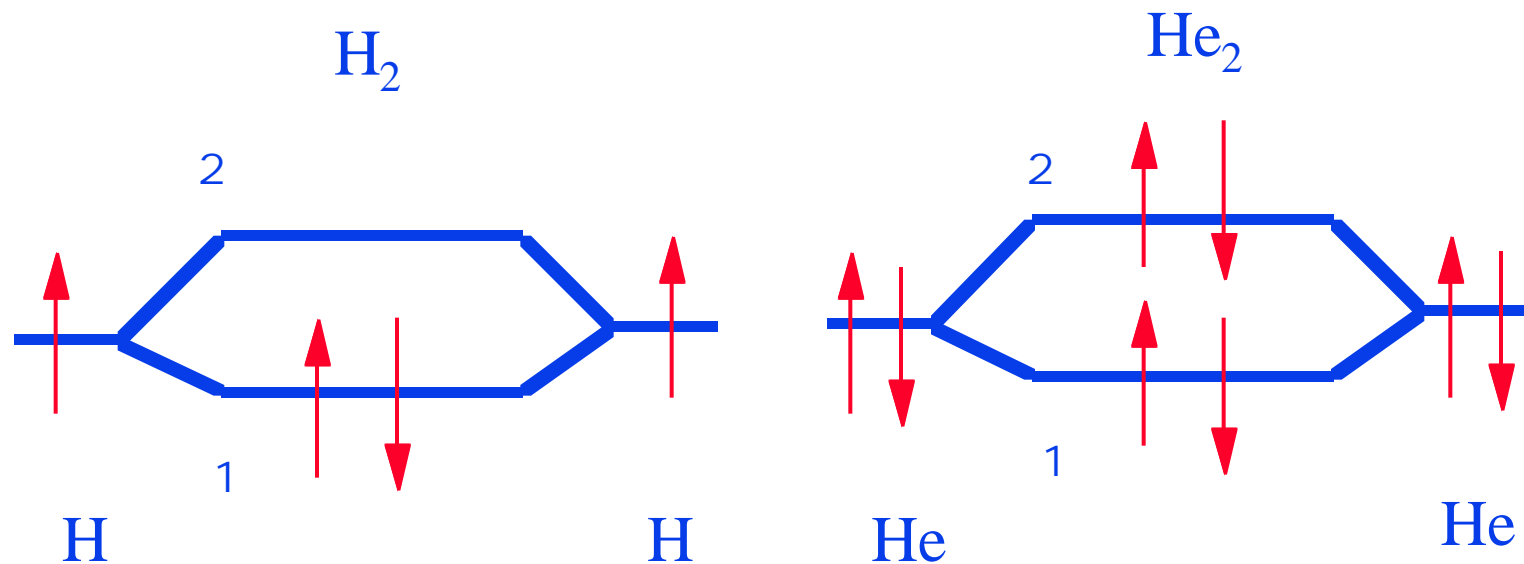
$$\psi_2 = a (\psi_A) - b (\psi_B)$$



$$\psi_1 = a (\psi_A) + b (\psi_B)$$

## Diatomic Homonuclear Molecules: Symmetrical Polyelectronic Diatomic Molecules

- From  $N$  atomic orbitals we construct  $N$  molecular orbitals
- First Period: Hydrogen  $H_2$  and Helium  $He_2$  Molecules



$$\text{Bond Order} = b = \frac{1}{2}(n - n^*)$$

$$b(H_2) = 1$$

$$b(He_2) = 0$$

## Some Remarks

- The greater the bond order, the stronger the bond, the shorter the bond.
- The antibonding molecular orbital is more antibonding than the bonding orbital is bonding. This implies that molecules with bond order equal to 0 do not exist ( $\text{He}_2$ ).

$$1/2(E(\sigma^*) + E(\sigma)) > E(\text{AO})$$

For  $\text{H}_2^+$

$$E(1\sigma) = E_{\text{H}} - \frac{V_1 + V_2}{1 + S} + \frac{e^2}{4\pi\epsilon_0 R}$$

$V_1$ : attractive potential between e at one nucleus and charge of other nucleus

$$E(2\sigma^*) = E_{\text{H}} - \frac{V_1 - V_2}{1 - S} + \frac{e^2}{4\pi\epsilon_0 R}$$

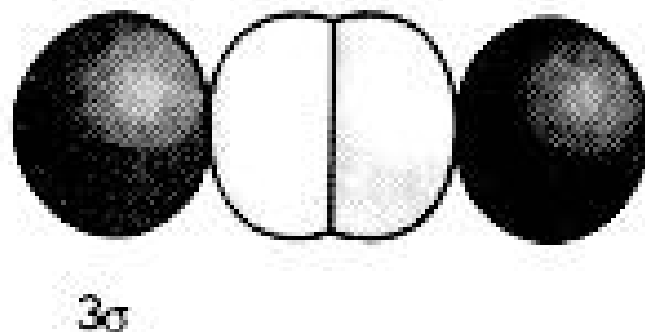
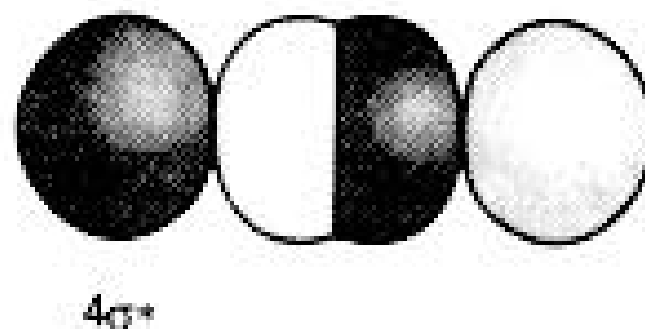
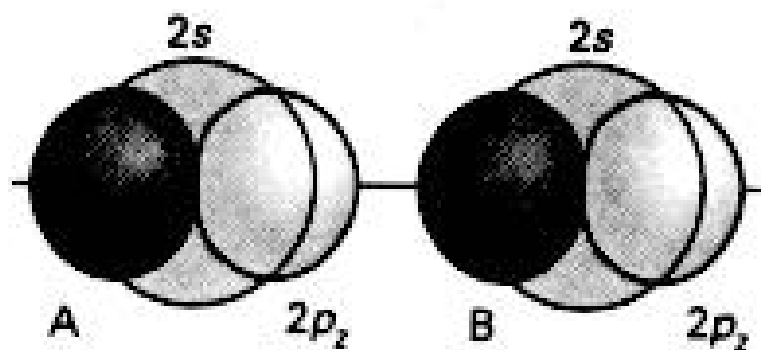
$V_2$ : attraction between overlap density and one of the nuclei

## Period 2 Diatomic Homonuclear Molecules

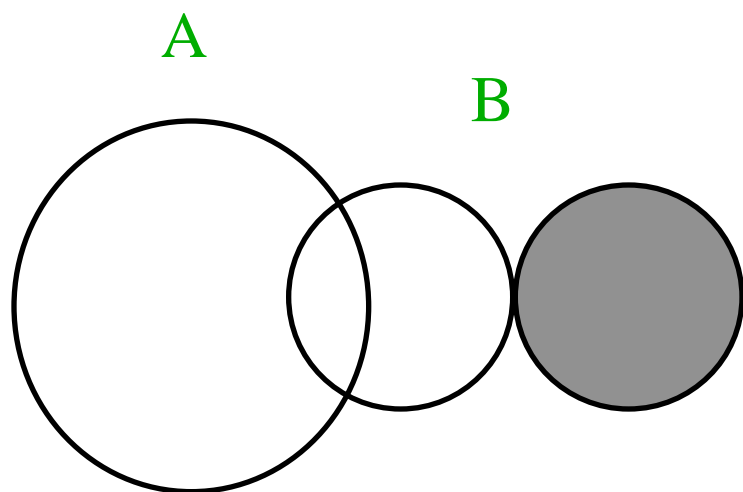
(Assume the z-axis to be the internuclear axis)

- When constructing Molecular Orbitals, one considers only the valence atomic orbitals, as the core orbitals are too compact.
- One assumes that only the orbitals having the appropriate symmetry can contribute to the molecular orbital.
  - ➔ Only orbitals which exhibit a significant overlap contribute to the molecular orbital.
- The Molecular Orbitals are obtained by linear combination of atomic orbitals that have “at least” cylindrical symmetry about the internuclear axis. Atomic orbitals of different energies are generally considered separately (for instance  $2s(A)$  with  $2s(B)$ ,  $2p_z(A)$  with  $2p_z(B)$ ).

## Molecular Orbitals Formed from $2s$ and $2p_z$ Atomic Orbitals

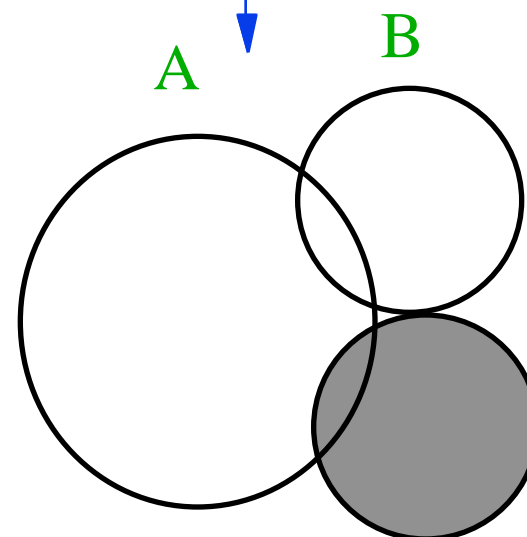


# Overlap Integral $S$ Measures the Extent of Overlap Between Two Orbitals



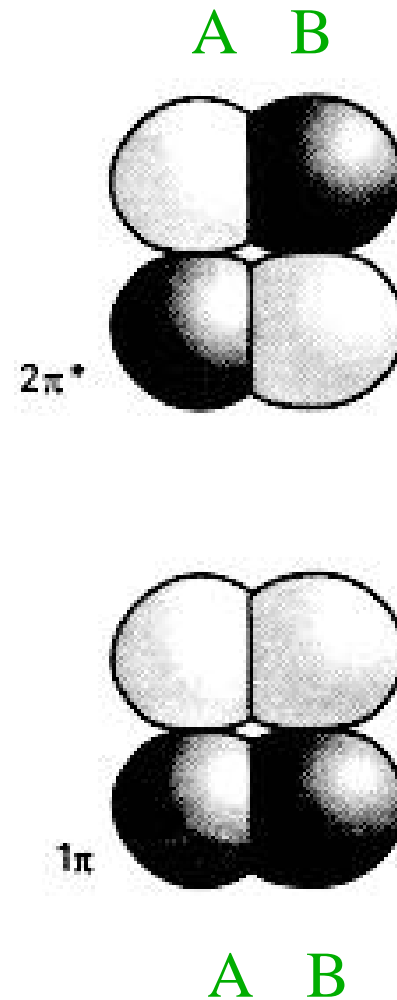
End-on overlap between an “s” and a “ $p_z$ ” orbital leads to a “ ” (non-zero overlap)

Broadside overlap between an “s” and a “ $p_y$ ” orbital leads to no MO. (zero net overlap)



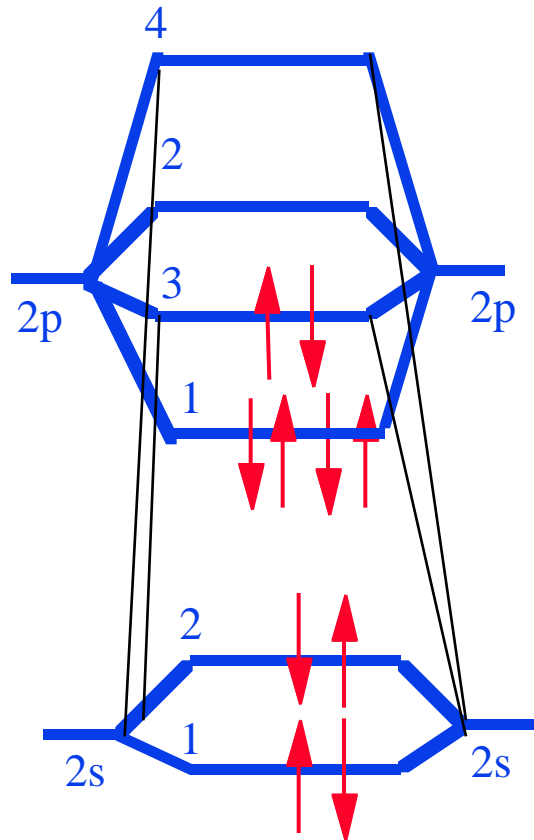
## orbitals

- The **orbitals** are formed by broad-side overlap of atomic orbitals such as  $p_x$ ,  $p_y$ .  
orbitals can be bonding if there is a constructive interference between AO or antibonding ( ) if the interference is destructive.  $p_x$ ,  $p_y$  lead to degenerate  $\pi$ ,  $\pi^*$

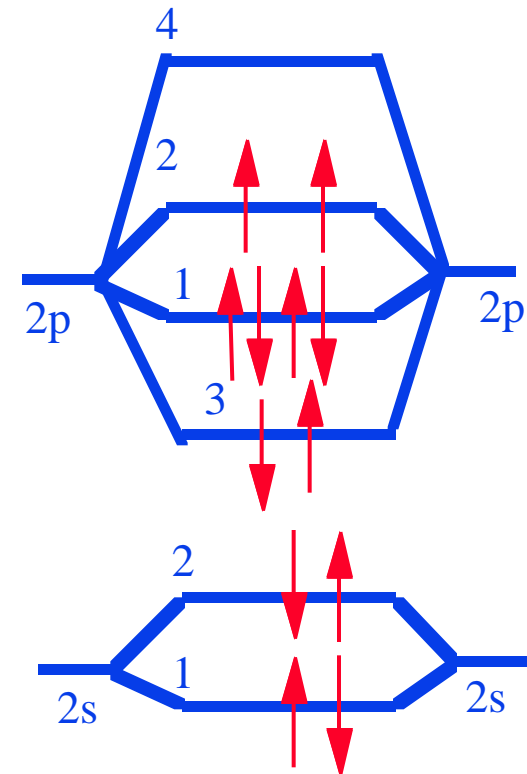


# Molecular Orbital Energy Level Diagram for Homonuclear Diatomic Molecules

For  $\text{Li}_2$ ,  $\text{Be}_2$ ,  $\text{B}_2$ ,  $\text{C}_2$  &  $\text{N}_2$



For  $\text{O}_2$  and  $\text{F}_2$



# Variation in the Molecular Orbital Energies for Period-2 Diatomics

