

- orbitals are spread over 2 and more atoms – delocalized
- different energies and space distribution of charge than for atomic orbitals
- describe ground and excited states

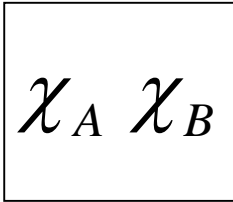
Conditions for orbital combinations:

1. similar energy
2. sufficient overlap
3. equal symmetry

Literature:

G. L. Miessler, P. J. Fischer, D. A. Tarr: Inorganic chemistry 5th ed., chap.5.

Cell containing 2
identical orbitals



$$\varphi_i = \sum_{\mu}^N c_{i\mu} \chi_{\mu}$$

φ_i : molecular orbital, χ_{μ} : atomic orbital

$$\sum_{i=1}^N c_j [H_{ij} - ES_{ij}] = 0$$

$$\chi_A = \chi_B,$$

$$H_{AA} = \int \chi_A^*(R_A) \hat{H} \chi_A(R_A) = H_{BB} = \alpha$$

$$H_{AB} = \int \chi_A^*(R_A) \hat{H} \chi_B(R_B) = \int \chi_B(R_B) \hat{H}^* \chi_A^*(R_A) = H_{BA}^* = \beta$$

$$S_{AB} = \int \chi_A^*(R_A) \chi_B(R_B) = \int \chi_B(R_B) \chi_A^*(R_A) = S_{BA}^* = S$$

$$\begin{pmatrix} H_{AA} - E & H_{AB} - ES_{AB} \\ H_{BA} - ES_{BA} & H_{BB} - E \end{pmatrix} = \begin{pmatrix} \alpha - E & \beta - ES \\ \beta^* - ES^* & \alpha - E \end{pmatrix}$$

$$\det \begin{pmatrix} \alpha - E & \beta - ES \\ (\beta - ES)^* & \alpha - E \end{pmatrix} = (\alpha - E)^2 - (\beta - ES)^2 = 0$$

$$\alpha - E = \pm(\beta - ES) \quad E_{12} = \frac{\alpha \pm \beta}{1 \pm S}, \quad \beta < 0 \Rightarrow E_1 < E_2$$

$$\alpha_1 = \alpha_2$$

$$(\beta < 0, S \ll 1)$$

$$E_2 = \alpha - \beta, \quad \frac{1}{\sqrt{2}}(\varphi_1 - \varphi_2) \quad \text{pink circle} \quad \text{cyan circle}$$

$$E_1 = \alpha + \beta, \quad \frac{1}{\sqrt{2}}(\varphi_1 + \varphi_2) \quad \text{cyan circle} \quad \text{cyan circle}$$

$$\det \begin{pmatrix} \alpha_1 - E & 0 \\ 0 & \alpha_2 - E \end{pmatrix} = (\alpha_1 - E)(\alpha_2 - E) = 0$$

$$E_1 = \alpha_1 \quad E_2 = \alpha_2 \quad \text{pink circle} \quad \text{cyan circle}$$

($\beta = 0, S = 0$)

$$E_2: c_1 [\alpha - (\alpha - \beta)] + c_2 \beta = 0 \rightarrow c_1 \beta + c_2 \beta = 0 \rightarrow c_1 = -c_2$$

$$E_1: c_1 [\alpha - (\alpha + \beta)] + c_2 \beta = 0 \rightarrow c_1 \beta - c_2 \beta = 0 \rightarrow c_1 = c_2$$

$$\sqrt{c_1^2 + c_2^2} = 1$$

$\alpha = \varepsilon$: coulombic energy (energy of AO)

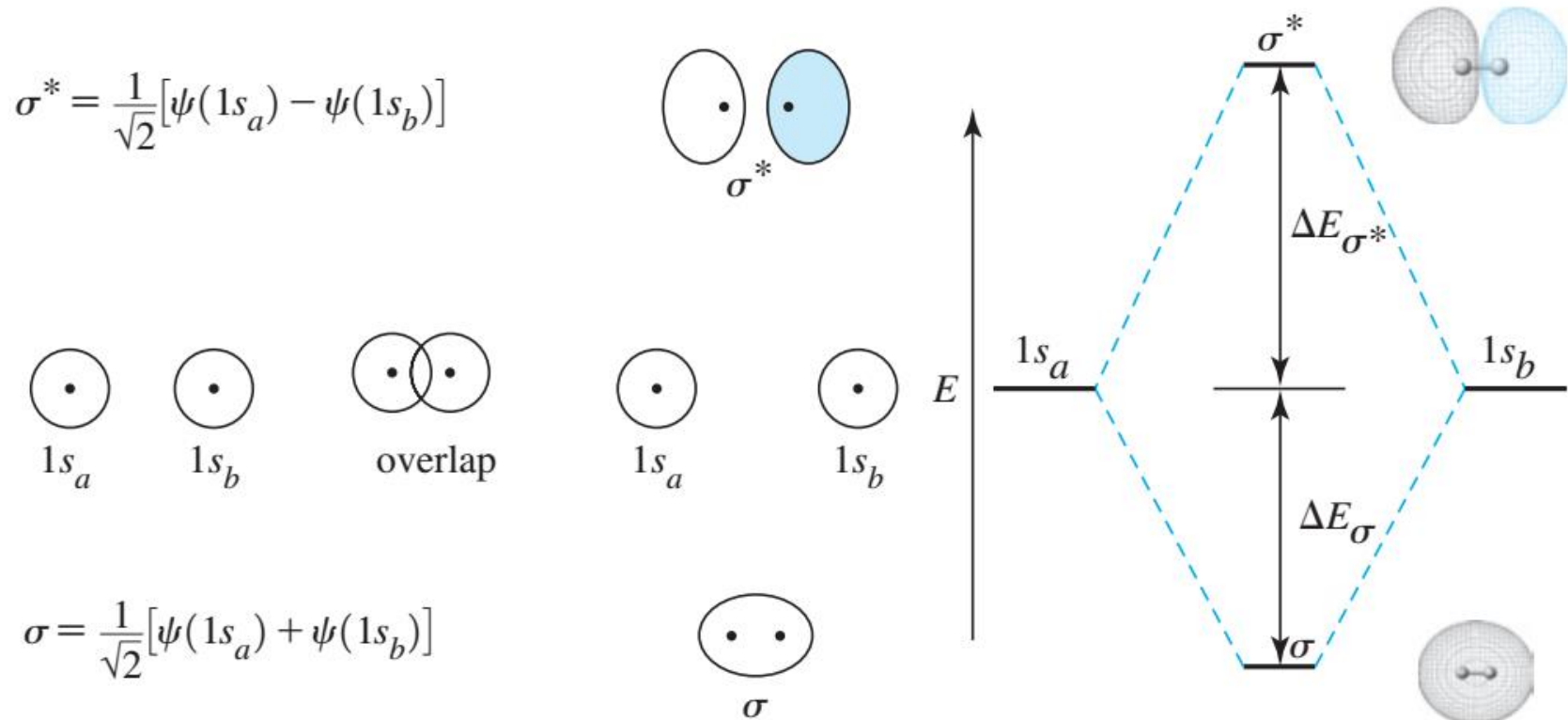
$\beta (< 0) = t$: exchange energy (degree of bonding energy)

$S (0-1)$: overlap integral

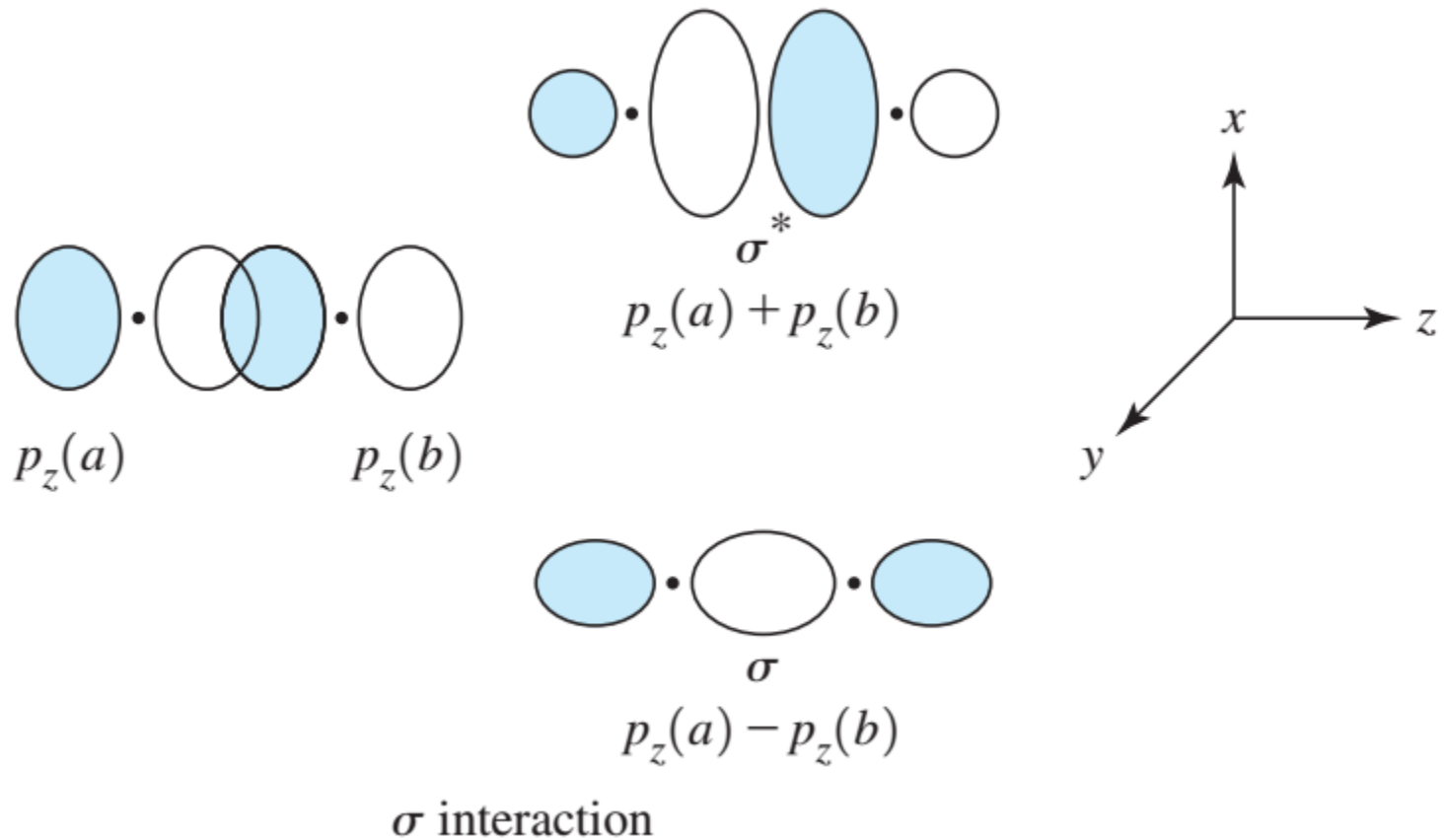
$$\alpha = \int \chi_A^*(R_A) \hat{H} \chi_A(R_A)$$

$$\beta = \int \chi_A^*(R_A) \hat{H} \chi_B(R_B)$$

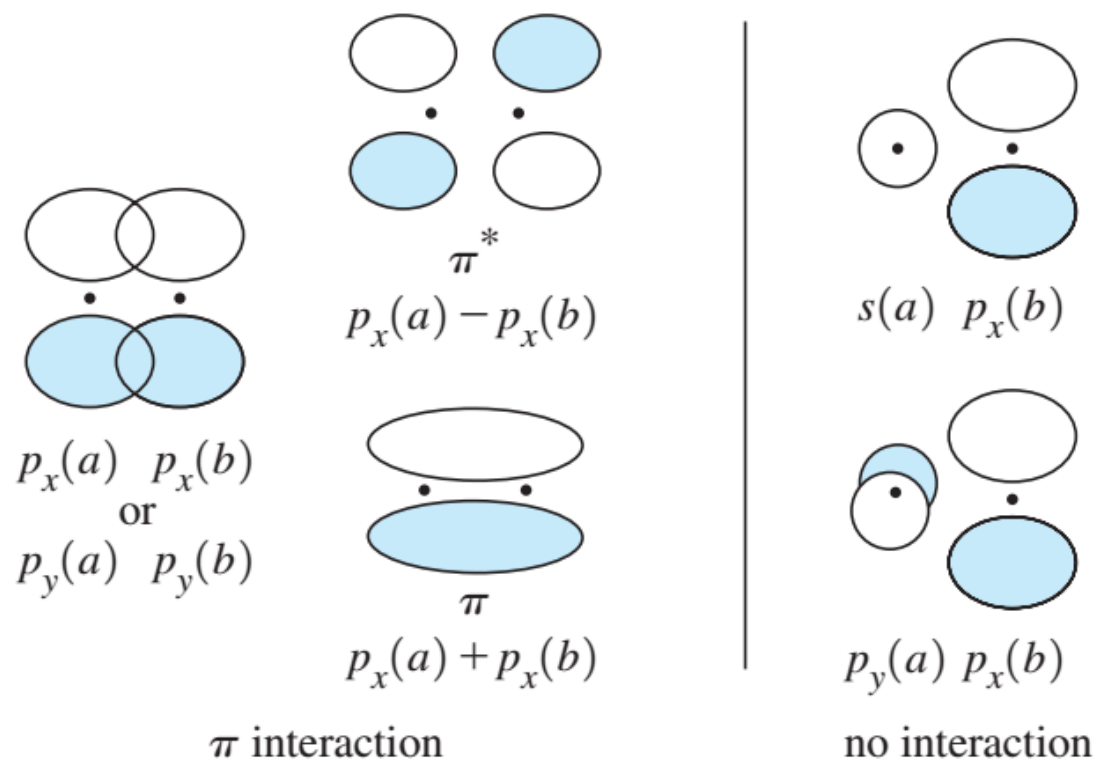
$$S = \int \chi_A^*(R_A) \chi_B(R_B) \quad 3$$



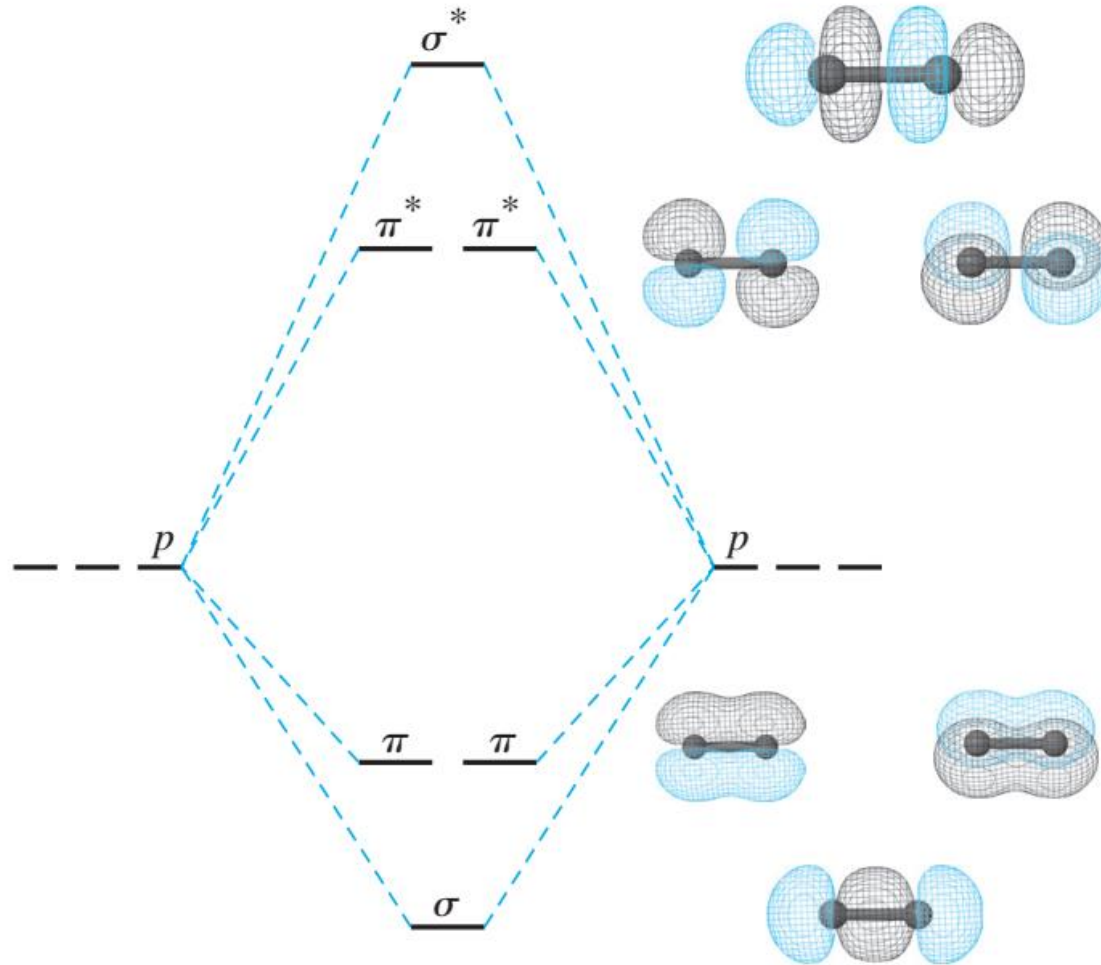
Molecular orbitals from Hydrogen 1s orbitals. The σ molecular orbital is a bonding molecular orbital, and has a lower energy than the original atomic orbitals, since this combination of atomic orbitals results in an increased concentration of electrons between the two nuclei. The σ^* orbital is an antibonding orbital at higher energy since this combination of atomic orbitals results in a node with zero electron density between the nuclei.



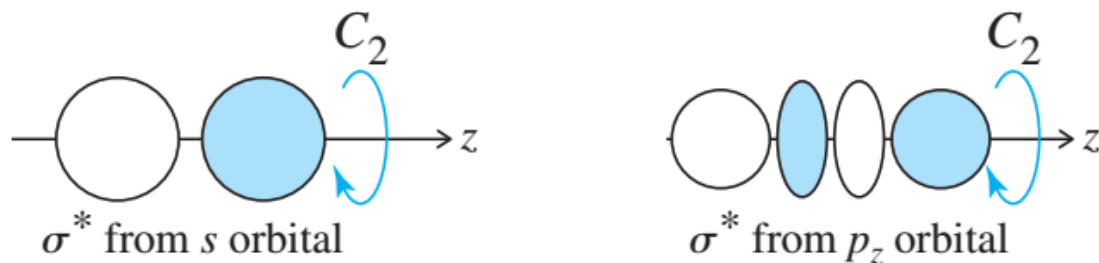
Interactions of p-orbitals – formation of σ molecular orbitals.



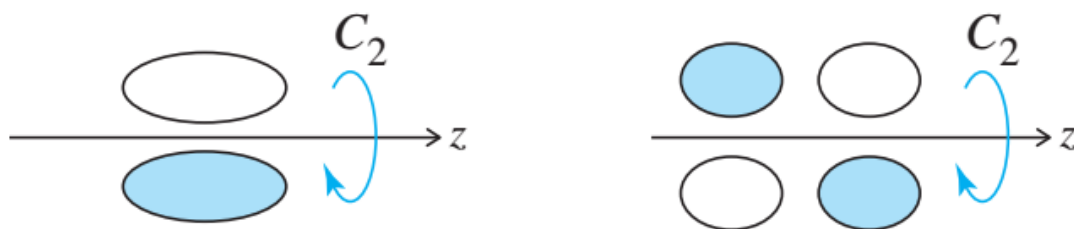
Interactions of p-orbitals – formation of π molecular orbitals and orbitals that do not form molecular orbitals.



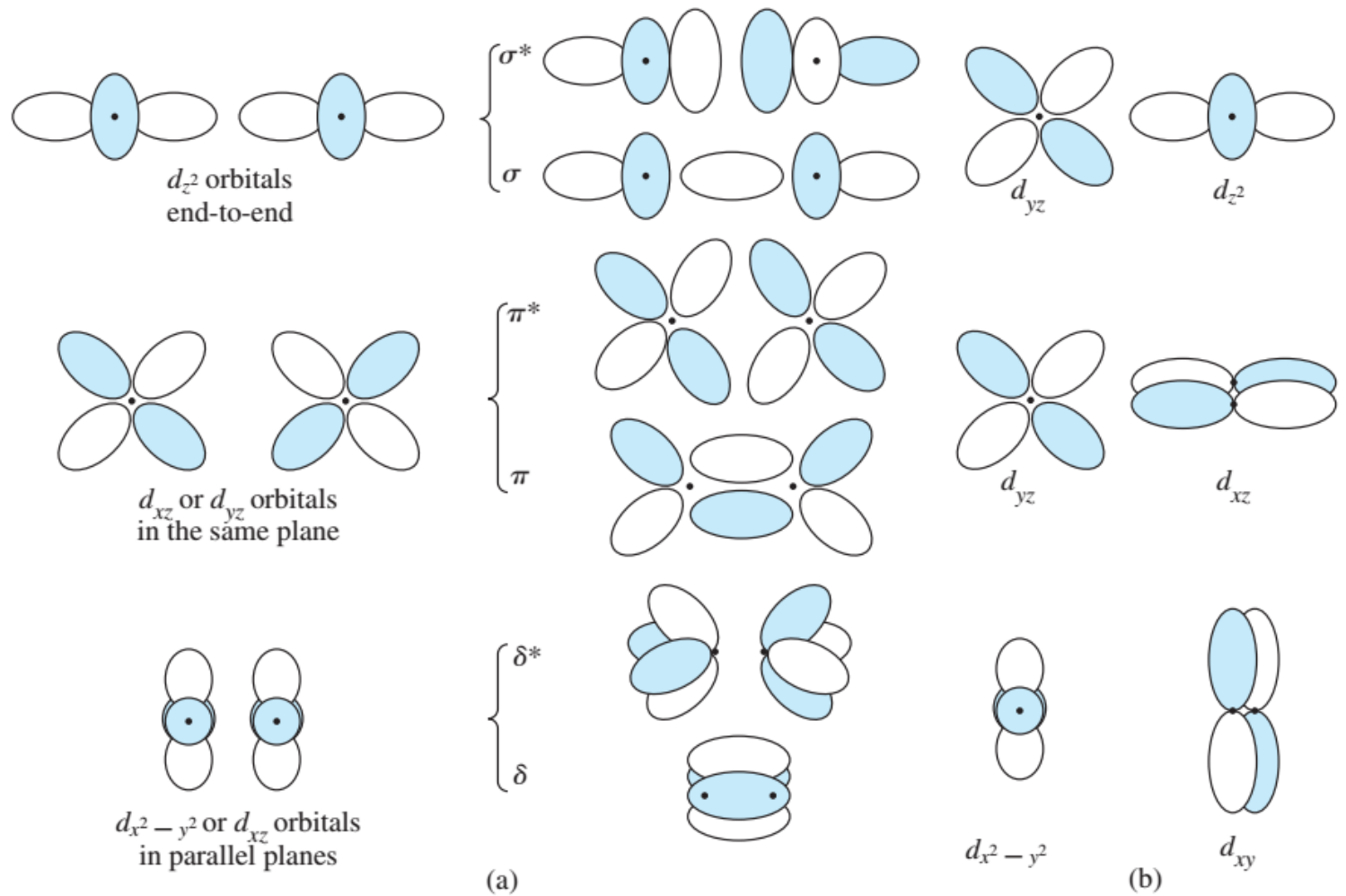
Interactions of p-orbitals – Energy-level diagram.



The σ notation indicates orbitals that are symmetric to rotation about the line connecting the nuclei.

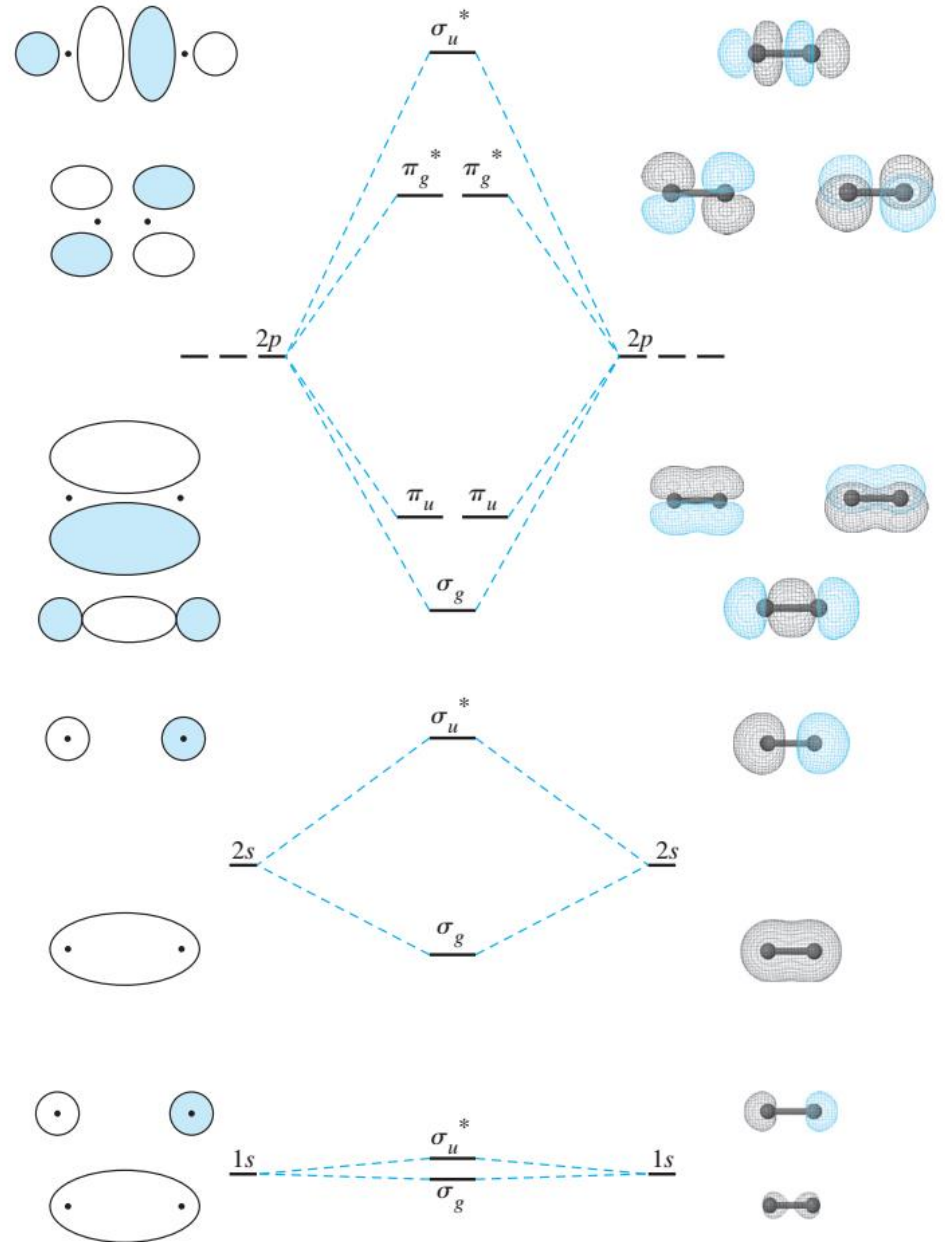


The π notation indicates a change in sign of the wave function with C_2 rotation about the bond axis.



Interactions of d-orbitals: formation of σ , π and δ molecular orbitals.

Molecular orbitals for the first 10 elements, assuming significant interactions only between the valence atomic orbitals of identical energy.



Interaction between molecular orbitals:

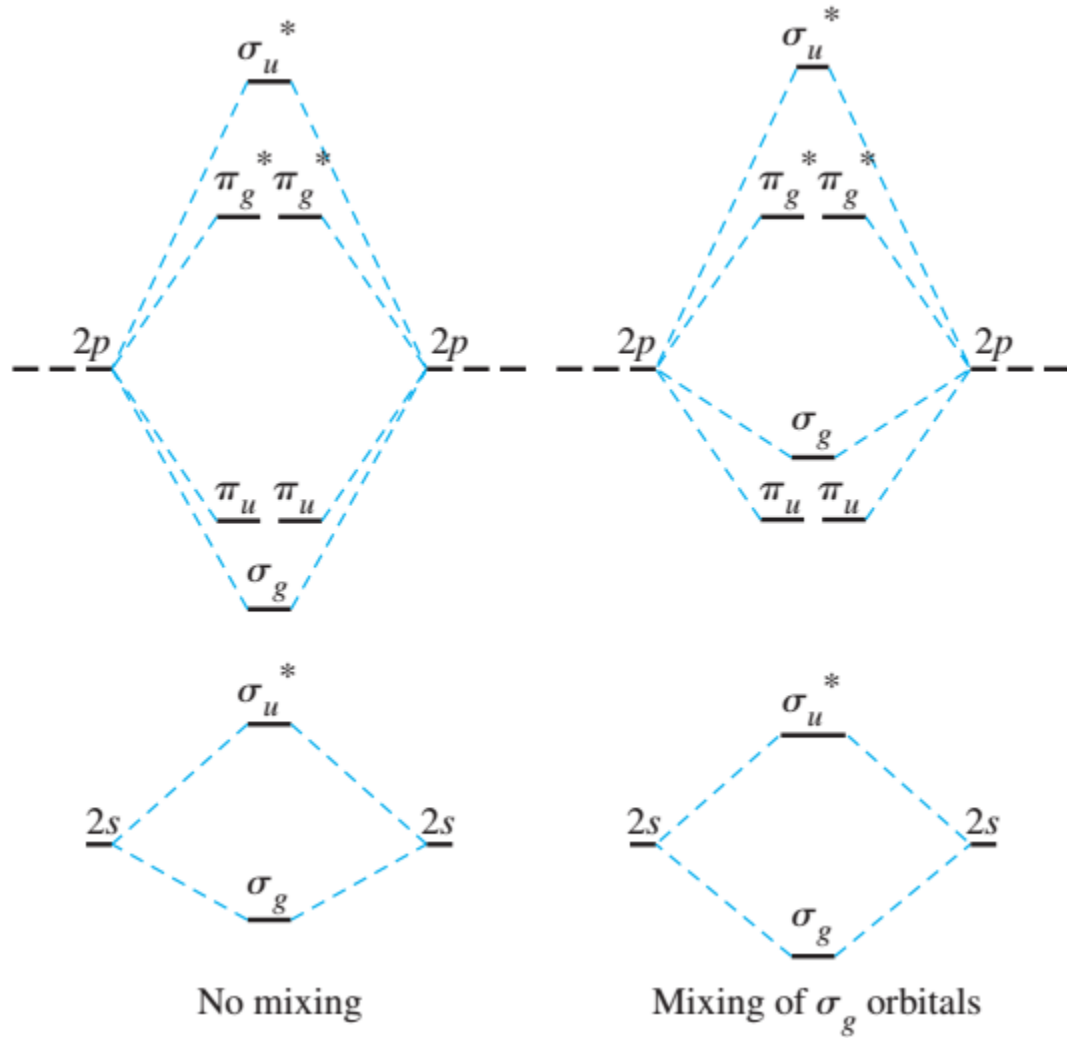
Mixing molecular orbitals of the same symmetry results in a greater energy difference between the orbitals.

When two molecular orbitals of the same symmetry have similar energies, they interact to lower the energy of the lower orbital and raise the energy of the higher orbital.

The $\sigma_g(2s)$ and $\sigma_g(2p)$ orbitals interact to lower the energy of the $\sigma_g(2s)$ and to raise the energy of the $\sigma_g(2p)$. The σ orbitals mix strongly.

Similarly, the $\sigma_u^*(2s)$ and $\sigma_u^*(2p)$ orbitals interact to lower the energy of the $\sigma_u^*(2s)$ and to raise the energy of the $\sigma_u^*(2p)$. The σ^* orbitals differ more in energy and mix weakly.

Mixing results in additional electron stabilization, and enhances the bonding.



Energy levels of the homonuclear diatomics of the second period.
 Mixing of σ_g orbitals for $\text{Li}_2 - \text{N}_2$.

