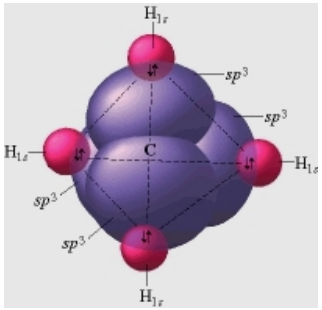

Chemical bond

Adolfo Bastida

Facultad de Química

Physical Chemistry I

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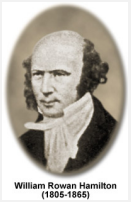


Hamiltonian

- Atoms combine to form molecules.
- Molecular Hamiltonian

$$\hat{H}(r_i, R_\alpha) = \hat{T}_e(r_i) + \hat{T}_N(R_\alpha) + \hat{V}_{N\,e}(r_{\alpha\,i}) + \hat{V}_{e\,e}(r_{i\,j}) + \hat{V}_{N\,N}(R_{\alpha\,\beta})$$

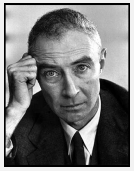
$r_i \Rightarrow$ electrons $\qquad r_{\alpha\,i} \Rightarrow$ nuclei-electrons

$R_\alpha \Rightarrow$ nuclei $\qquad r_{i\,j} \Rightarrow$ electron-electron

$R_{\alpha\,\beta} \Rightarrow$ nucleus-nucleus

- Quantum Chemistry

$$\hat{H}(r_i, R_\alpha)\Psi(r_i, R_\alpha) = E\,\Psi(r_i, R_\alpha) \begin{cases} \text{No analytical solution} \\ \text{Numerical solution} \\ \text{Approximate methods} \end{cases}$$

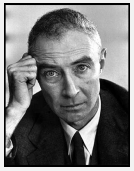


Born-Oppenheimer approximation

- Molecular Hamiltonian $\Rightarrow \hat{H}(\mathrm{r},\mathrm{R}) = \hat{T}_{\mathrm{e}}(\mathrm{r}) + \hat{T}_{\mathrm{N}}(\mathrm{R}) + \hat{V}(\mathrm{r},\mathrm{R})$
- $m_e \ll m_\alpha \Rightarrow e^-$ move faster than nuclei
- BO approximation:

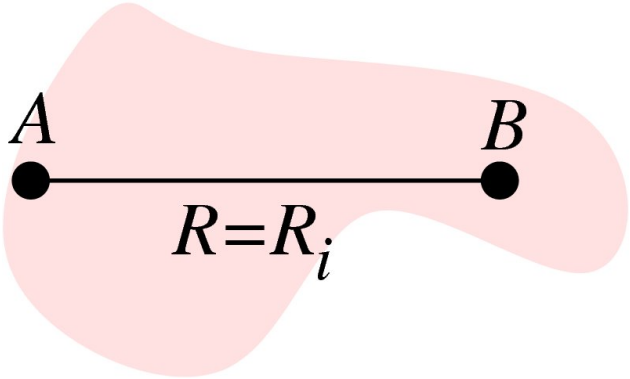
$$\psi(\mathrm{r},\mathrm{R},t) = \underbrace{\phi_j^{\mathrm{BO}}(\mathrm{r},\mathrm{R})}_{\text{electronic}}\,\underbrace{\Omega(\mathrm{R},t)}_{\text{nuclear}} \Rightarrow \frac{\partial\phi^{\mathrm{BO}}}{\partial R_\alpha} = \frac{\partial^2\phi^{\mathrm{BO}}}{\partial R_\alpha^2} = 0$$

$$\begin{cases} \left[\hat{T}_{\mathrm{e}}(\mathrm{r}) + \hat{V}(\mathrm{r},\mathrm{R})\right]\phi_j^{\mathrm{BO}}(\mathrm{r},\mathrm{R}) = \epsilon_j^{\mathrm{BO}}(\mathrm{R})\,\phi_j^{\mathrm{BO}}(\mathrm{r},\mathrm{R}) \\ i\hbar\frac{\partial\Omega(\mathrm{R},t)}{\partial t} = \left[\hat{T}_{\mathrm{N}}(\mathrm{R}) + \epsilon_j^{\mathrm{BO}}(\mathrm{R})\right]\Omega(\mathrm{R},t) \end{cases}$$



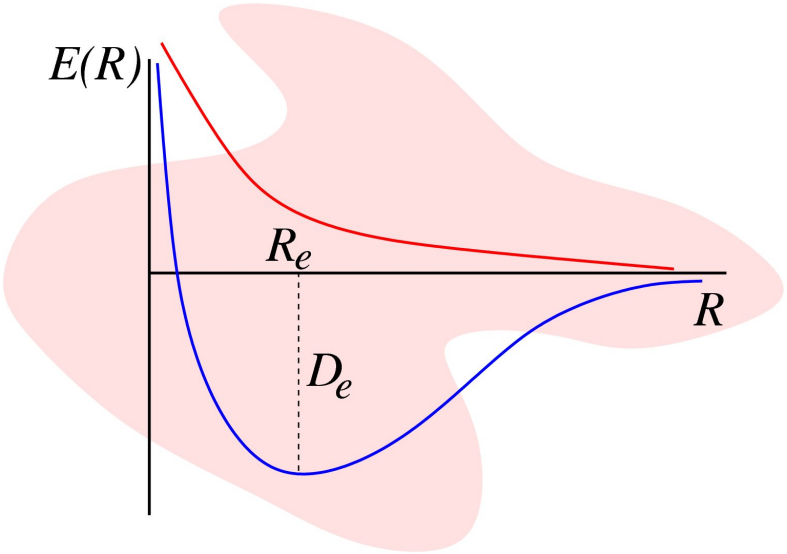
Born-Oppenheimer approximation

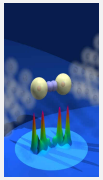
- Grid $\{R_i\}_{i=1}^{N} \Rightarrow \{\epsilon_j^{\mathrm{BO}}(R_i)\}_{i=1}^{N}$



$$\langle \phi | \hat{H} | \phi \rangle = E(R_1)$$
$$\langle \phi | \hat{H} | \phi \rangle = E(R_2)$$
$$\vdots \quad = \quad \vdots$$

- unbonded states
- bonded states
  - Dissociation Energy $\Rightarrow D_e$
  - Equilirium internuclear distance $\Rightarrow R_e$ (bond distance)

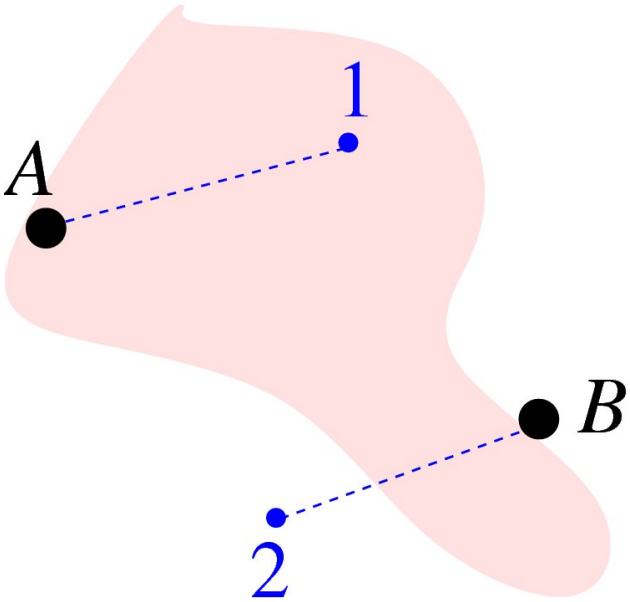


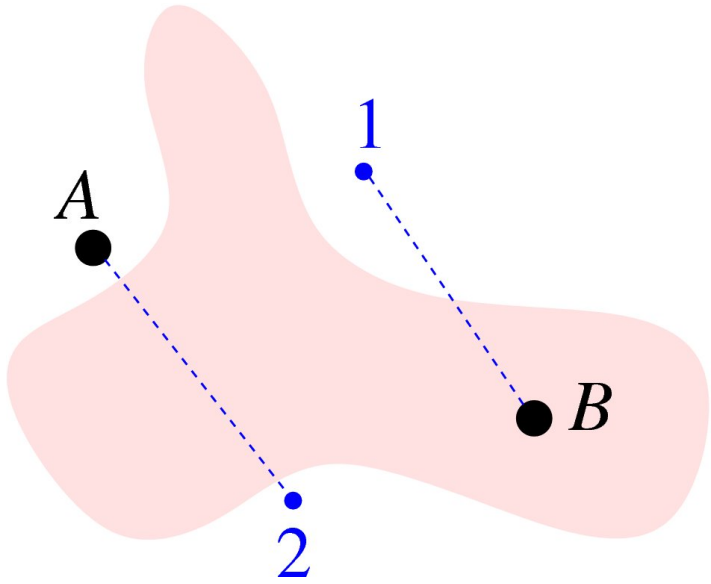


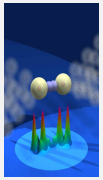
Hydrogen molecule

- Chemical bond $\Rightarrow$ sharing of electrons.
- Valence electrons $\Rightarrow$ external, higher energy, less attracted, ...
- H_2 molecule

$$\psi(1,2) = \phi_{\mathrm{H}_A,1s}(1)\,\phi_{\mathrm{H}_B,1s}(2) \qquad \psi(1,2) = \phi_{\mathrm{H}_A,1s}(2)\,\phi_{\mathrm{H}_B,1s}(1)$$







Hydrogen molecule

- Variational treatment

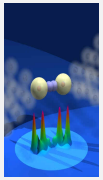
$$\psi = c_1 f_1 + c_2 f_2 = c_1 1s_A(1)1s_B(2) + c_2 1s_A(2)1s_B(1)$$

$$\begin{vmatrix} H_{11}-W & H_{12}-WS_{12} \\ H_{12}-WS_{12} & H_{22}-W \end{vmatrix} = 0$$

- $\hat{H}$ hermitian $\Rightarrow H_{12} = H_{21}$
- Normalization $\Rightarrow S_{11} = S_{22} = 1$
- $S_{12} = \int\int 1s_A^*(1)1s_B^*(2)1s_A(2)1s_B(1)d\tau_1 d\tau_2$
  $= \langle 1s_A(1)|1s_B(1)\rangle \langle 1s_A(2)|1s_B(2)\rangle = S_{AB}^2 \neq 0$
- $S_{21} = S_{12}$

$$W_1 = \frac{H_{11} + H_{12}}{1 + S_{12}} \qquad W_2 = \frac{H_{11} - H_{12}}{1 - S_{12}}$$

$$\phi_1 = \frac{f_1 + f_2}{\sqrt{2(1 + S_{12})}} \qquad \phi_2 = \frac{f_1 - f_2}{\sqrt{2(1 - S_{12})}}$$

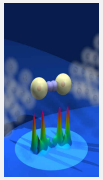


Hydrogen molecule

- Overlap

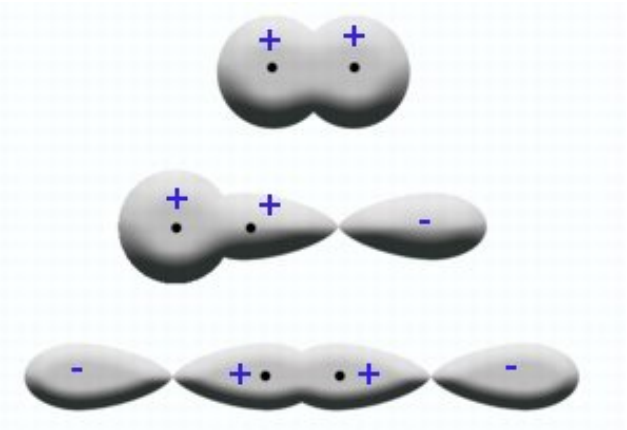
$$\psi(1,2) \propto \left[\phi_{\mathrm{H}_A,1s}(1)\,\phi_{\mathrm{H}_B,1s}(2) + \phi_{\mathrm{H}_A,1s}(2)\,\phi_{\mathrm{H}_B,1s}(1)\right]$$

$$|\psi(1,2)|^2 \propto \left[|\phi_{\mathrm{H}_A,1s}(1)\,\phi_{\mathrm{H}_B,1s}(2)|^2 + |\phi_{\mathrm{H}_A,1s}(2)\,\phi_{\mathrm{H}_B,1s}(1)|^2\right] + 2\mathrm{Re}\left[\phi^*_{\mathrm{H}_A,1s}(1)\,\phi^*_{\mathrm{H}_B,1s}(2)\,\phi_{\mathrm{H}_A,1s}(2)\,\phi_{\mathrm{H}_B,1s}(1)\right]$$

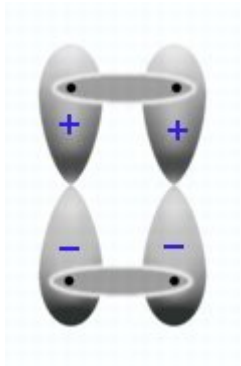


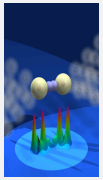
Hydrogen molecule

- Cylindrical symmetry $\Rightarrow$ σ bond.



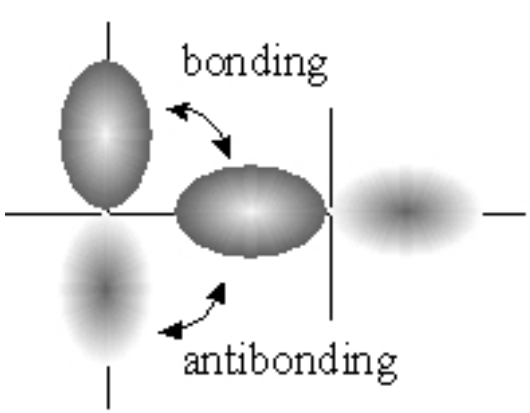
- Plane of symmetry $\Rightarrow$ π bond.

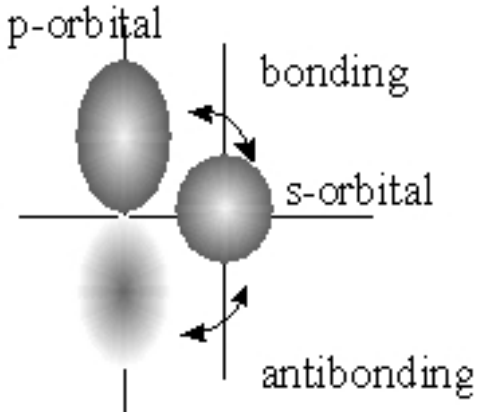




Hydrogen molecule

- Null overlap $\Rightarrow$ no bond.

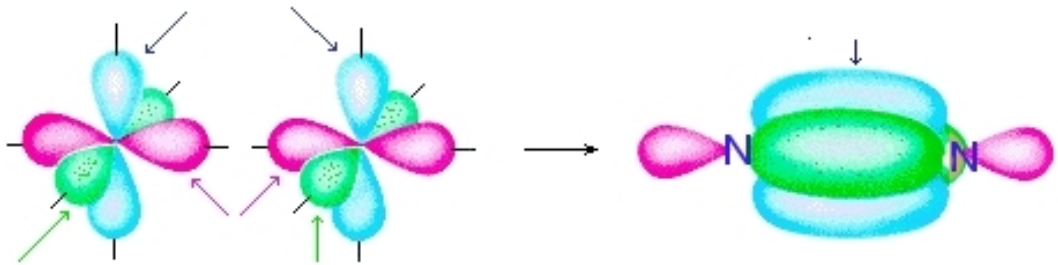


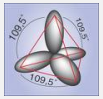


- Extension to polielectronic atoms. Example: N_2 molecule

[N]: $1s^2\,2s^2\,2p^3$ |N≡N|

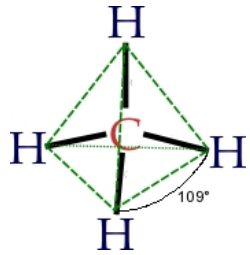
Octect rule $1\,\sigma + 2\,\pi$





Hybrid orbitals

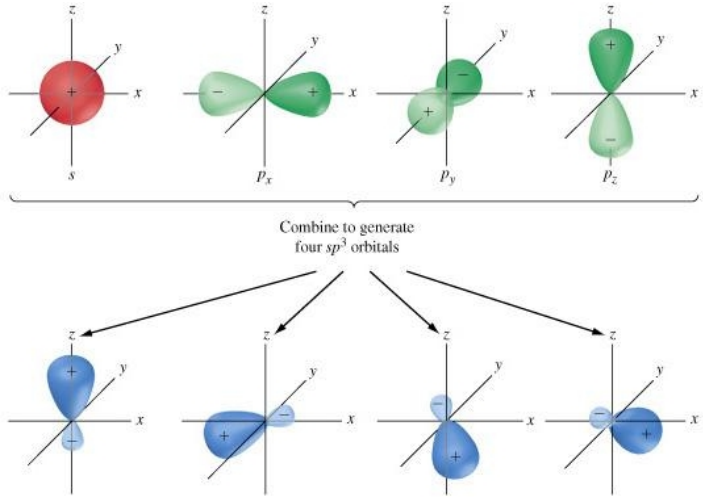
- Molecular geometry. Ej. $CH_4 \Rightarrow$ C-H equiv. $\Rightarrow$

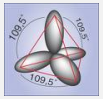


[C]: $1s^2\,2s^2\,2p^2 \Rightarrow$ Valence shell $2s$ y $2p$.

- Hibrydization.

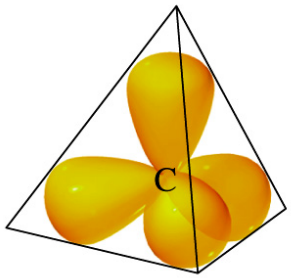
$$h_1 = \tfrac{1}{2}(s+p_x+p_y+p_z)$$
$$h_2 = \tfrac{1}{2}(s-p_x-p_y+p_z)$$
$$h_3 = \tfrac{1}{2}(s-p_x+p_y-p_z)$$
$$h_4 = \tfrac{1}{2}(s+p_x-p_y-p_z)$$



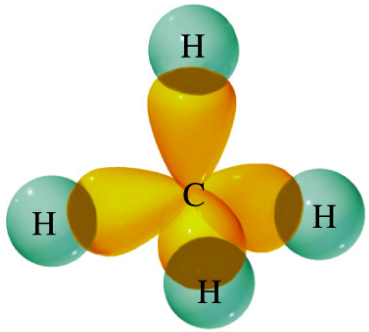


Hybrid orbitals

- sp^3 hybrid orbitals $\Rightarrow$ 
  - Thetahedral geometry
  - 4 C-H σ equiv. bonds
  - Minimal repulsion.

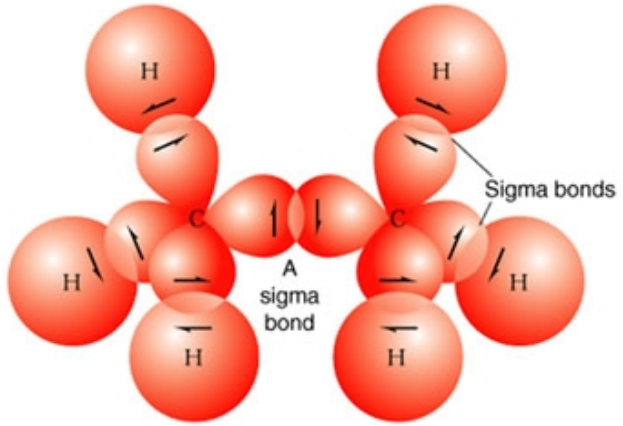


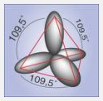
(a)



(b)

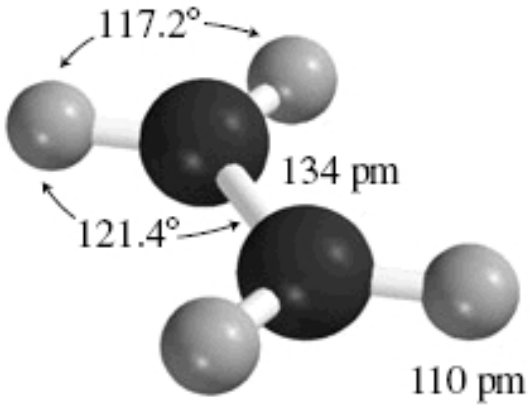
- Ethane $\Rightarrow$ CH_3-CH_3
  - [C]: $1s^2$ $2s^2$ $2p^2$; [H]: $1s^1$
  - e^- valence: 4x2+1x6= 14
  - 



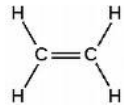


Hybrid orbitals

- Ethene $\Rightarrow$ CH_2-CH_2



- e^- valence: 4x2+1x4= 12

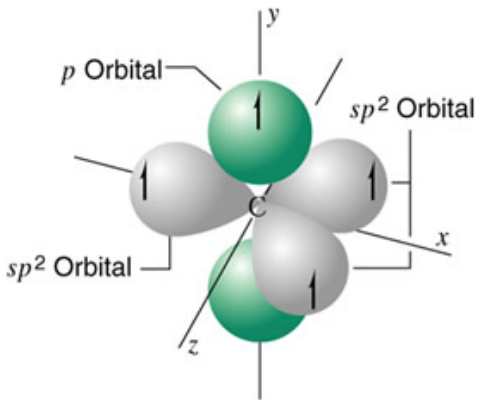


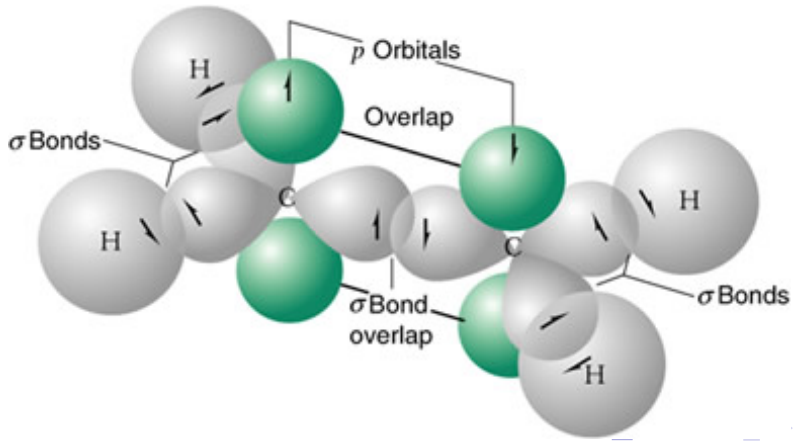
- sp^2 hybrid orbitals

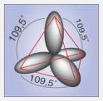
$$h_1 = \frac{1}{\sqrt{3}}\, s + \frac{1}{\sqrt{6}}\, p_x + \frac{1}{\sqrt{2}}\, p_y$$

$$h_2 = \frac{1}{\sqrt{3}}\, s + \frac{1}{\sqrt{6}}\, p_x - \frac{1}{\sqrt{2}}\, p_y$$

$$h_1 = \frac{1}{\sqrt{3}}\, s - \frac{2}{\sqrt{3}}\, p_x$$

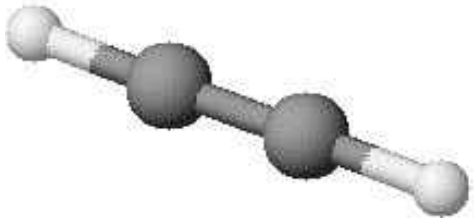






Hybrid orbitals

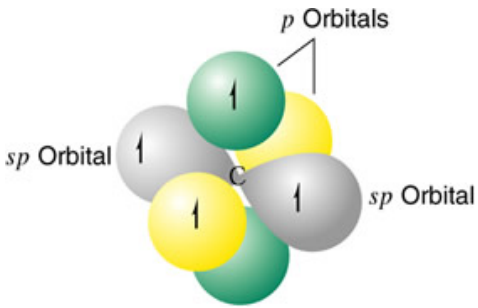
- Acetylene (Ethyne) $\Rightarrow$ CH-CH

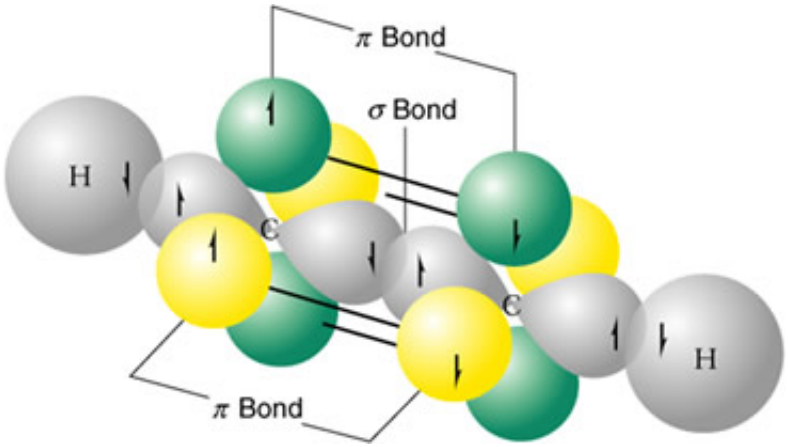


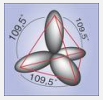
- e^- valence: 4x2+1x2= 10
- H−C≡C−H
- *sp* hybrid orbital

$$h_1 = \frac{1}{\sqrt{2}}(s+p_x)$$

$$h_2 = \frac{1}{\sqrt{2}}(s-p_x)$$

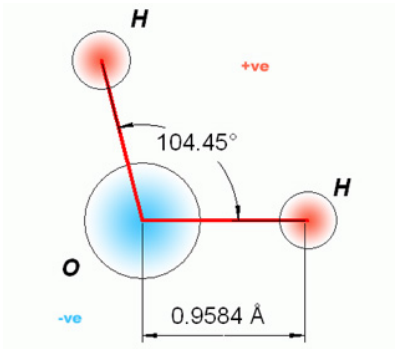




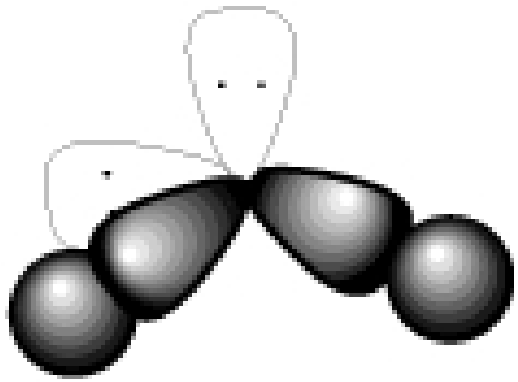


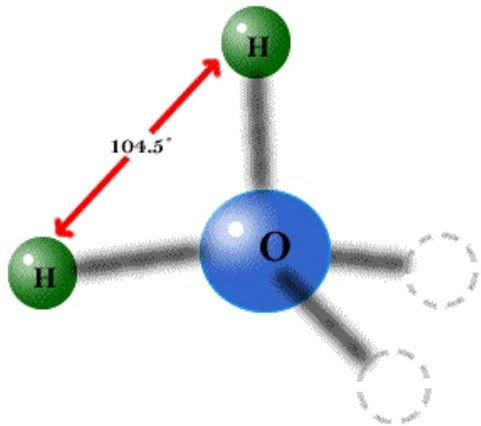
Hybrid orbitals

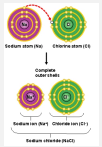
- Water $\Rightarrow$ H_2O



- [O]: $1s^2$ $2s^2$ $2p^4$; [H]: $1s^1$
- e^- valence: 6x1+1x2= 8
- H$-\overline{\underline{\text{O}}}-$H
- e^- repulsion $\Rightarrow$ sp^3





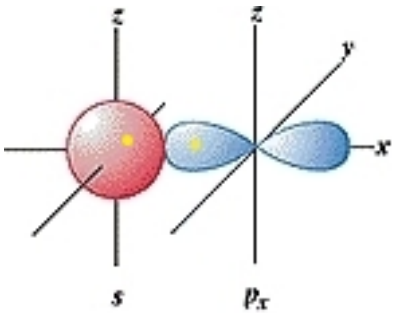


Covalent and ionic bonds

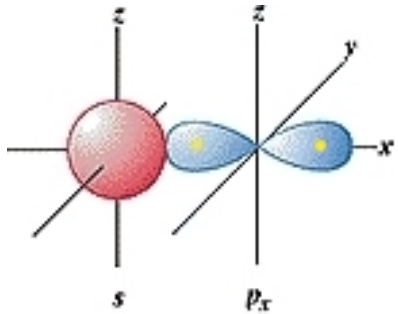
- Homoatomic bonds $\Rightarrow$ Symmetric electronic density
- Heteroatomic bonds. Ex. HCl
  [Cl]: $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^5$; [H]: $1s^1$

$$\psi_{\text{covalent}} = \phi_{\text{H},1s}(1)\,\phi_{\text{Cl},3p}(2) + \phi_{\text{H},1s}(2)\,\phi_{\text{Cl},3p}(1)$$

$$\psi_{\text{ionic}} = \phi_{\text{Cl},3p}(1)\,\phi_{\text{Cl},3p}(2)$$

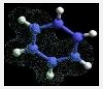


$|\overline{\text{Cl}} - \text{H}$



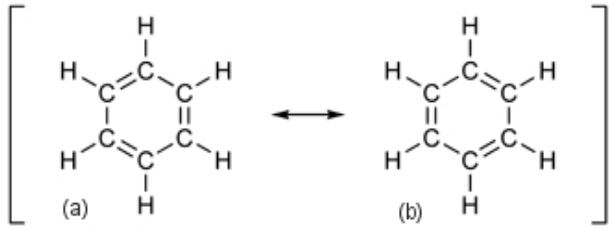
$|\overline{\text{Cl}}|^- \ \text{H}^+$

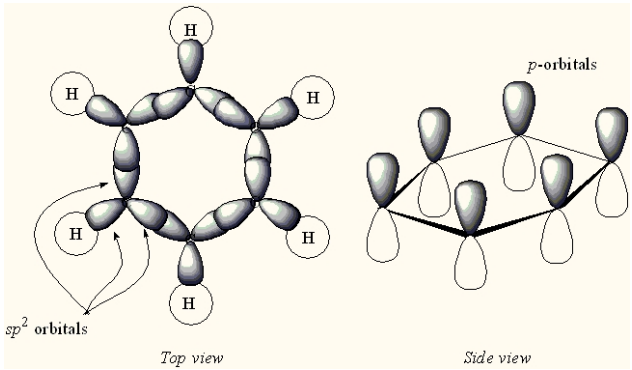
- Resonance $\Rightarrow \psi_{\text{HCl}} = \lambda\,\psi_{\text{covalent}} + (1-\lambda)\,\psi_{\text{ionic}};\quad \lambda \in [0,1]$



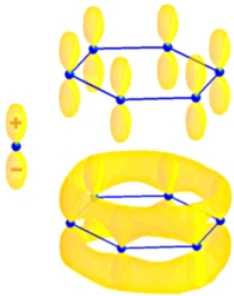
Resonance

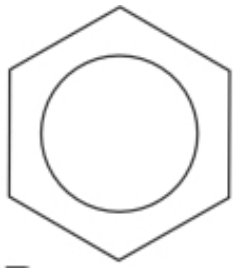
- Resonance hybrids. Ej. Benzene C_6H_6





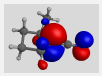
$$\psi = \psi_a + \psi_b \quad \Rightarrow$$





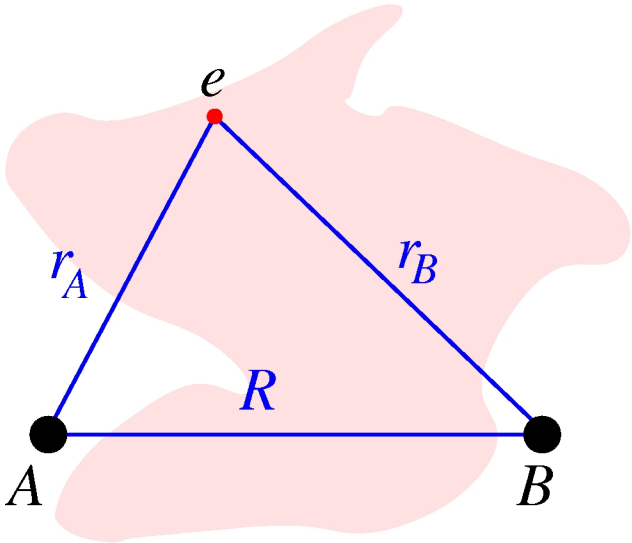
$$d_{C\text{-}C} = 1.54\,\text{Å} > d_{CC}^{\text{benzene}} = 1.39\,\text{Å} > d_{C=C} = 1.34\,\text{Å}$$

- Energetic stabilization



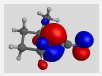
Definition

- Orbitals delocalized through the molecule
- Standard approximation in Quantum Chemistry calculations.
- Simplest diatomic molecule $\Rightarrow H_2^+$



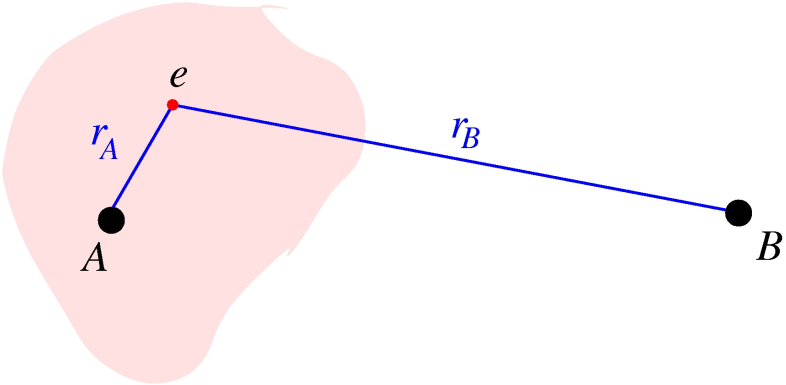
$$\hat{H} = \hat{T} - k\frac{e^2}{r_A} - k\frac{e^2}{r_B} + k\frac{e^2}{R}$$

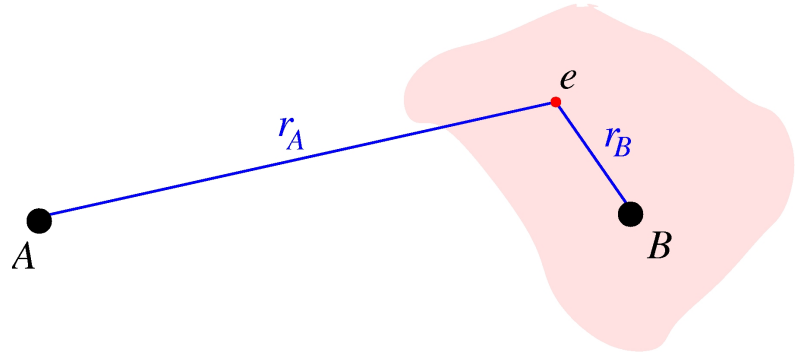
$$\hat{H}\psi_{\mathrm{OM}} = E\,\psi_{\mathrm{OM}}$$



Definition

- Limiting conditions

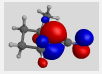




$r_B \gg r_A \Rightarrow \psi_{\mathrm{OM}} \sim \psi_{1s,A}$

$r_A \gg r_B \Rightarrow \psi_{\mathrm{OM}} \sim \psi_{1s,B}$

$$\psi_{\mathrm{OM}} = c_A\,\psi_{1s,A} + c_B\,\psi_{1s,B} = N\left(c_A\,e^{-r_A/a_0} + c_B\,e^{-r_B/a_0}\right)$$



Definition

- Variational method

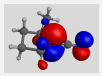
$$E_{\text{approx}} = \langle \psi_{\text{OM}} | \hat{H} | \psi_{\text{OM}} \rangle \Rightarrow \frac{\partial E_{\text{approx}}}{\partial c_A} = \frac{\partial E_{\text{approx}}}{\partial c_B} = 0$$

Solutions:

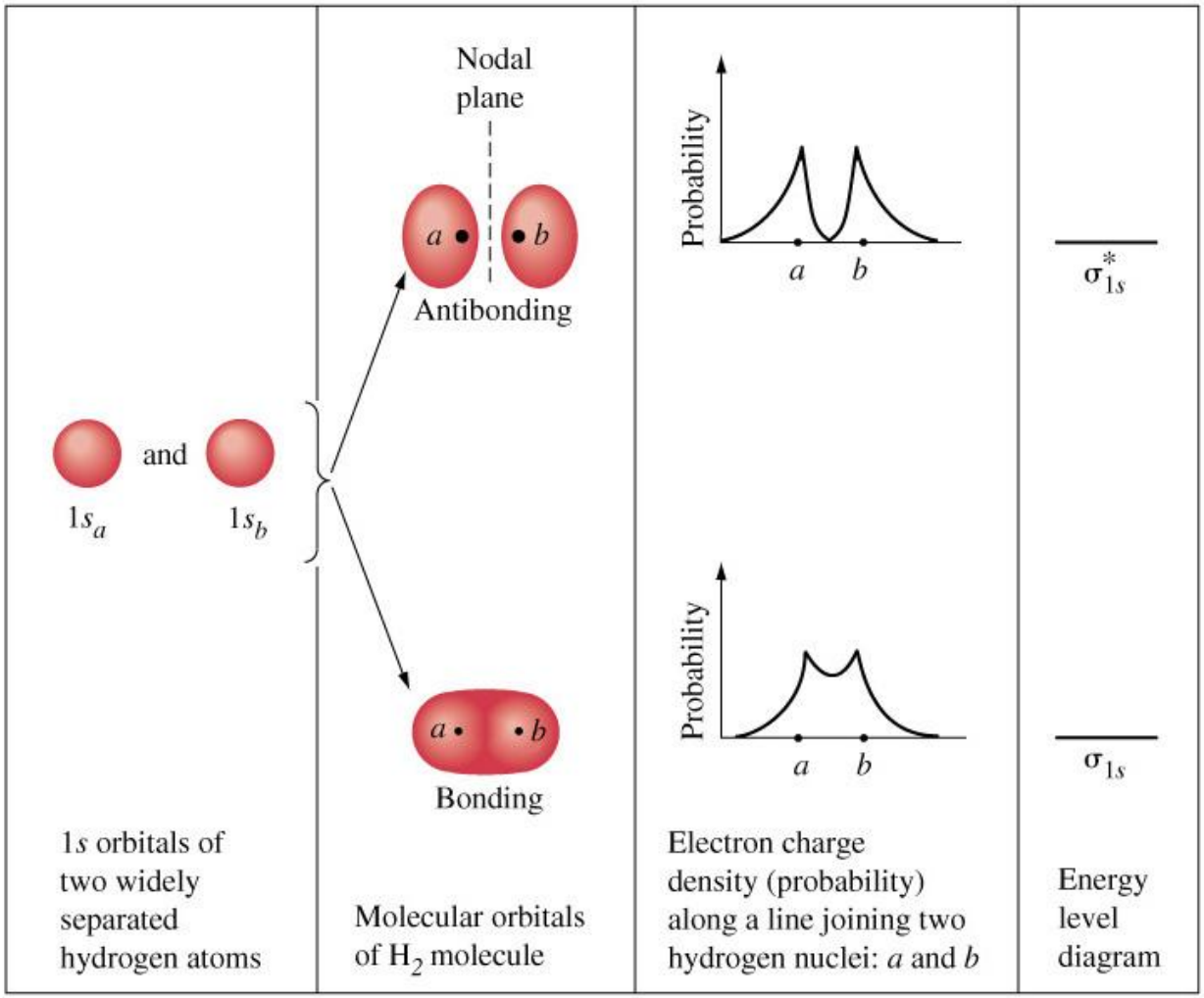
$$\begin{aligned} c_A = c_B \quad &\rightarrow \psi_{\text{OM},1} = c_A\left(\psi_{1s,A} + \psi_{1s,B}\right) \quad \rightarrow E_1 < 2 \cdot E_{\text{atom}} \\ c_A = -c_B \quad &\rightarrow \psi_{\text{OM},2} = c_A\left(\psi_{1s,A} - \psi_{1s,B}\right) \quad \rightarrow E_2 > 2 \cdot E_{\text{atom}} \end{aligned}$$

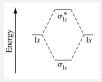
Probability densities

$$\begin{aligned} |\psi_{\text{OM},1}|^2 &= |c_A|^2\left(|\psi_{1s,A}|^2 + |\psi_{1s,B}|^2 + 2\,Re\left\{\psi^*_{1s,A}\psi_{1s,B}\right\}\right) \\ |\psi_{\text{OM},2}|^2 &= |c_A|^2\left(|\psi_{1s,A}|^2 + |\psi_{1s,B}|^2 - 2\,Re\left\{\psi^*_{1s,A}\psi_{1s,B}\right\}\right) \end{aligned}$$



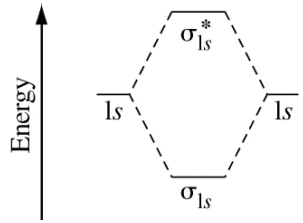
Definition


Nodal plane
a
b
Antibonding
and
1s_a
1s_b
Bonding
Probability
a
b
σ*_1s
σ_1s
1s orbitals of two widely separated hydrogen atoms
Molecular orbitals of H2 molecule
Electron charge density (probability) along a line joining two hydrogen nuclei: a and b
Energy level diagram

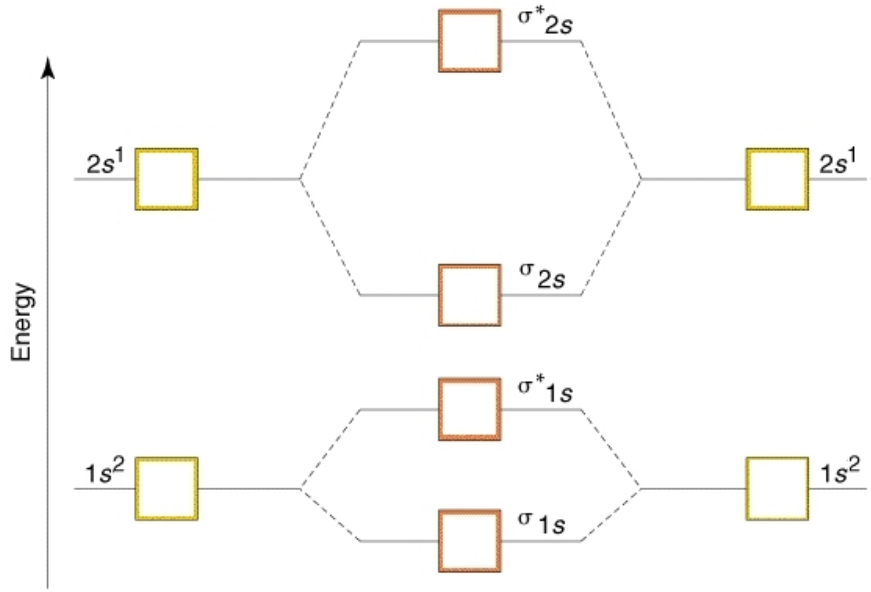


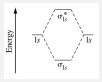
Energy diagram

- Energy diagram.



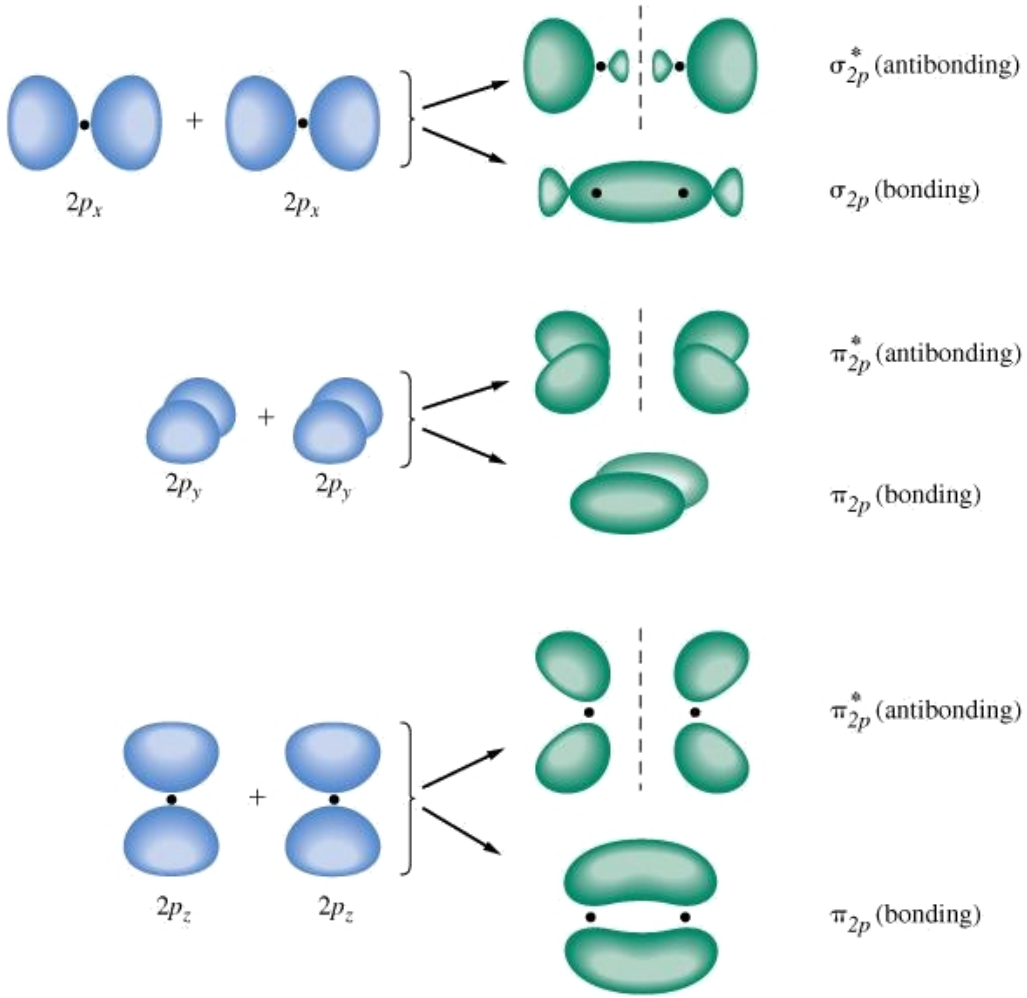
- 2s orbitals $\Rightarrow$ idem

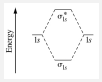




Energy diagram

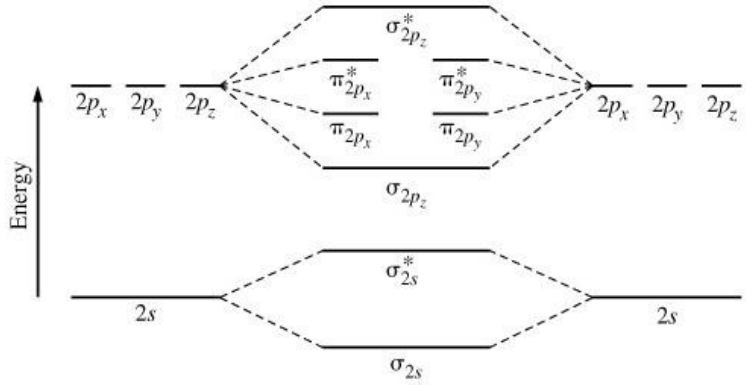
- $2p$ orbitals



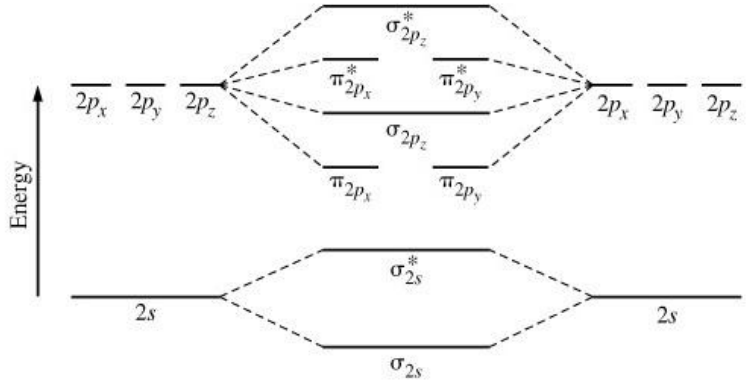


Energy diagram

- Energy diagram of the second shell



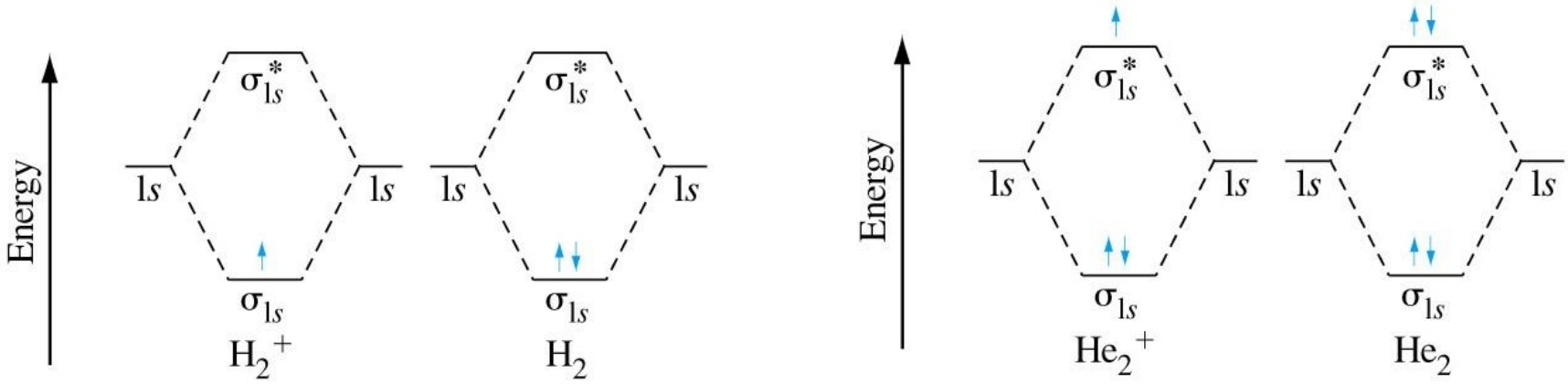
(a) $Z \geq 8$



(b) $Z \leq 7$

Homonuclear diatomic molecules

- Representative elements
- Pauli exclusion principle and Hund's rule

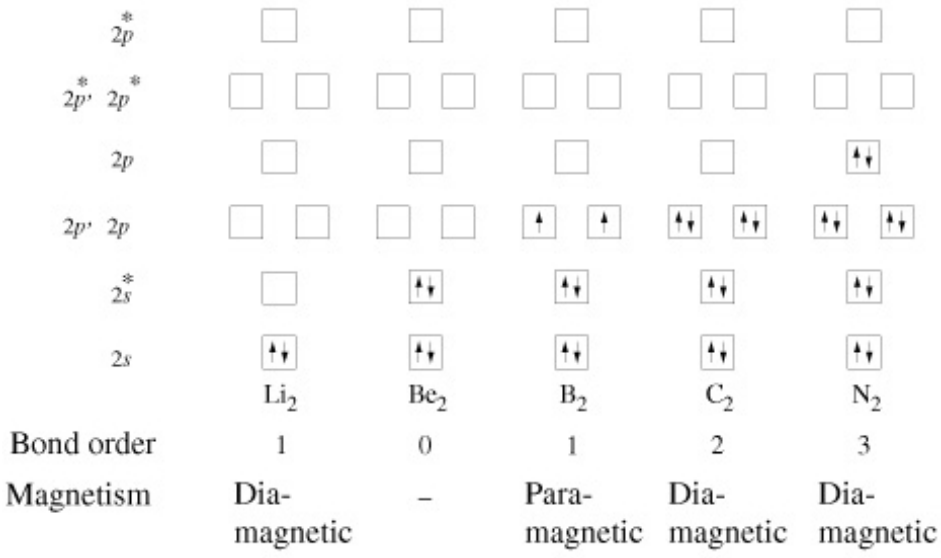


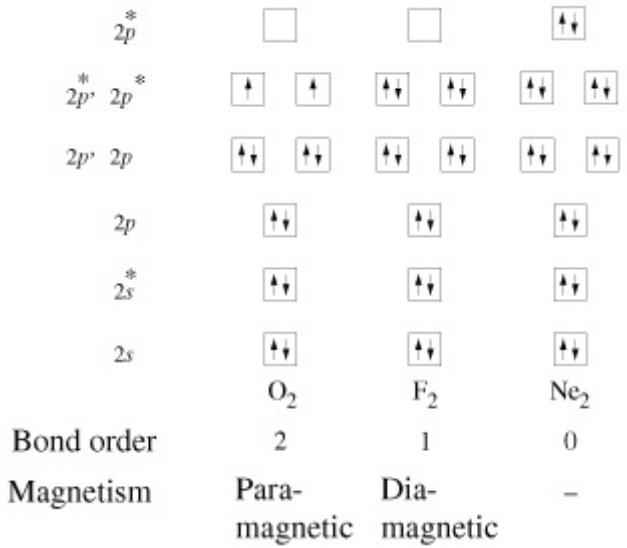
- Bond order $= \frac{1}{2}\left(N_{e\ \text{bonding}} - N_{e\ \text{antibonding}}\right)$

$$\text{OE}_{H_2^+} = \frac{1}{2}(1-0) = 0.5 \qquad \text{OE}_{He_2^+} = \frac{1}{2}(2-1) = 0.5$$

$$\text{OE}_{H_2} = \frac{1}{2}(2-0) = 1 \qquad \text{OE}_{He_2} = \frac{1}{2}(2-2) = 0$$

Homonuclear diatomic molecules



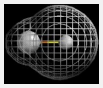


- Paramagnetism $\Rightarrow$ *e* unpaired.

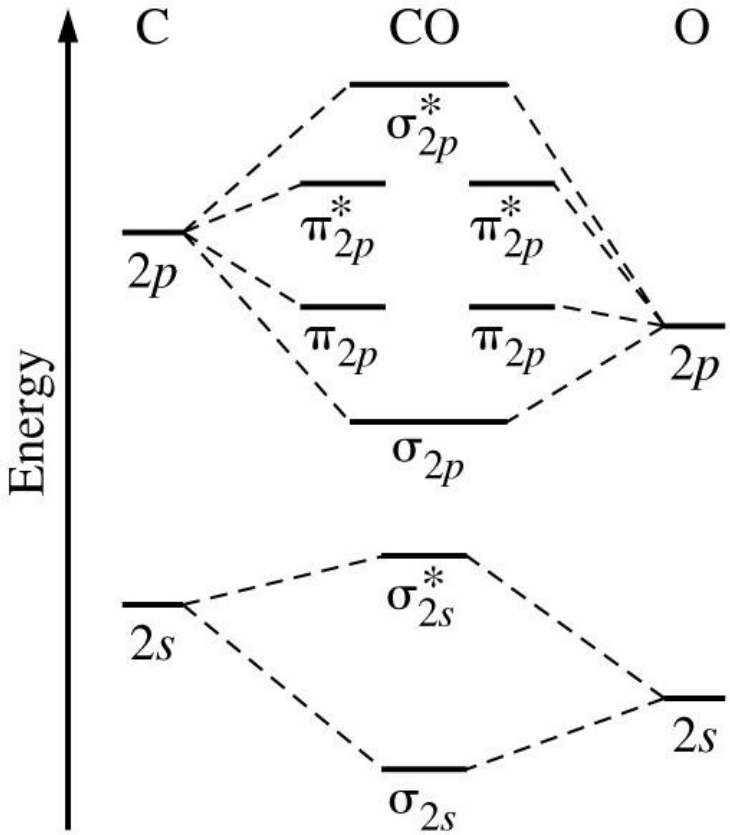
  VBT $\Rightarrow \langle \mathrm{O}=\mathrm{O} \rangle$ diamagnetic $\Rightarrow$ 👎

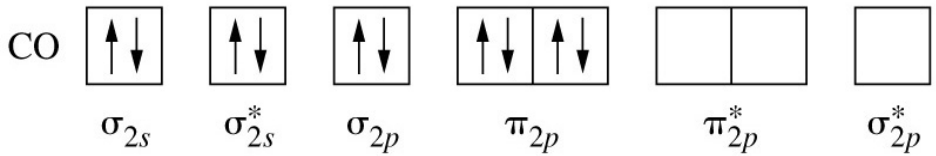
- Distance and energy bond

	B_2	C_2	N_2	O_2	F_2	Ne_2
D_e (kJ/mol)	290	620	941	495	155	–
R_e (Å)	1.59	1.31	1.10	1.21	1.43	–



Heteronuclear diatomic molecules





$$\psi_{\sigma_{2s}} = a\,\psi_{2s,\mathrm{C}} + b\,\psi_{2s,\mathrm{O}} \rightarrow |a| < |b|$$

$$\psi_{\sigma^*_{2s}} = c\,\psi_{2s,\mathrm{C}} + d\,\psi_{2s,\mathrm{O}} \rightarrow |c| > |d|$$