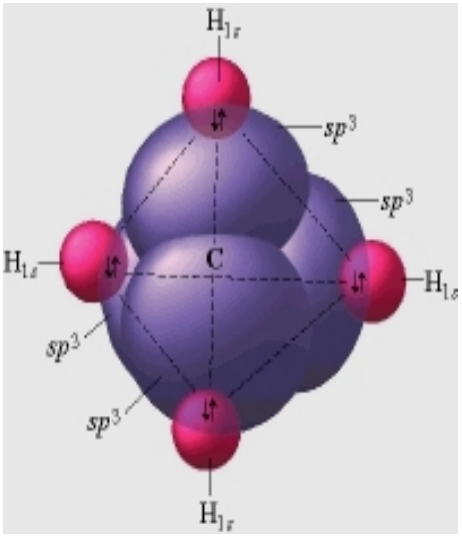
Chemical bond



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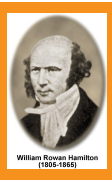


I.A. Hamiltonian

- Atoms combine to form molecules.
- Molecular Hamiltonian

$$\hat{H}(r_i, R_\alpha) = \hat{T}_e(r_i) + \hat{T}_N(R_\alpha) + \hat{V}_{Ne}(r_{\alpha i}) + \hat{V}_{ee}(r_{ij}) + \hat{V}_{NN}(R_{\alpha\beta})$$

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

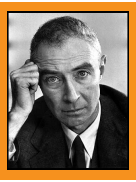
$R_\alpha \Rightarrow$ nuclei $\quad r_{ij} \Rightarrow$ electron-electron

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

- Quantum Chemistry

$$\hat{H}(r_i, R_\alpha)\Psi(r_i, R_\alpha) = E\,\Psi(r_i, R_\alpha)$$

No analytical solution
Numerical solution
Approximate methods

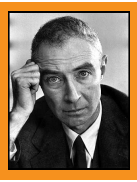


I.B. Born-Oppenheimer approximation

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

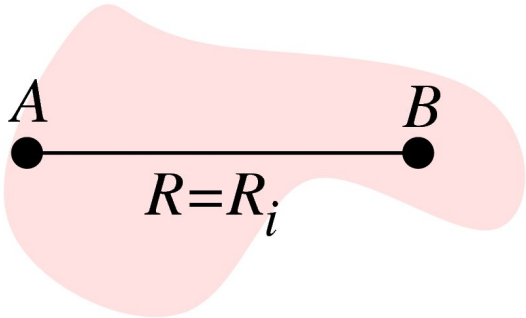
$$\psi(\mathbf{r},\mathbf{R},t) = \underbrace{\phi_j^{\mathrm{BO}}(\mathbf{r},\mathbf{R})}_{\text{electronic}}\,\underbrace{\Omega(\mathbf{R},t)}_{\text{nuclear}} \Rightarrow \frac{\partial \phi^{\mathrm{BO}}}{\partial R_\alpha} = \frac{\partial^2 \phi^{\mathrm{BO}}}{\partial {R_\alpha}^2} = 0$$

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



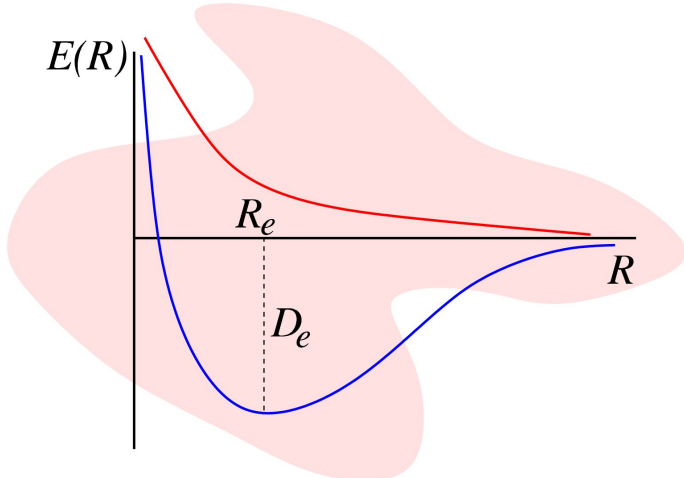
I.B. Born-Oppenheimer approximation

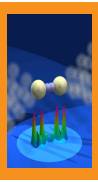
- Grid $\{R_i\}_{i=1}^{N} \Rightarrow \{\varepsilon_j^{\mathrm{BO}}(R_i)\}_{i=1}^{N}$



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

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

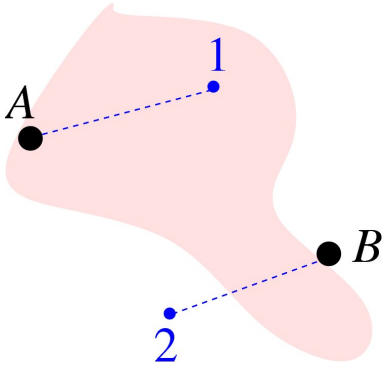


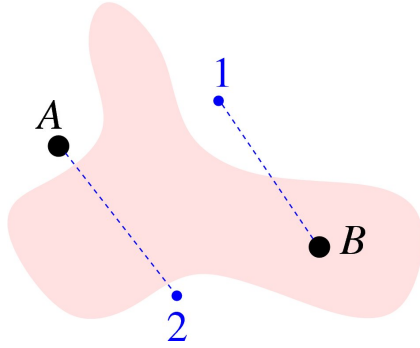


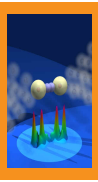
II.A. Hydrogen molecule

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

$$\psi(1,2) = \phi_{H_A,1s}(1)\,\phi_{H_B,1s}(2) \qquad \psi(1,2) = \phi_{H_A,1s}(2)\,\phi_{H_B,1s}(1)$$







II.A. 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 $\Rightarrow S_{11} = S_{22} = 1$
- $S_{12} = \int\int 1s_A^*(1)1s_B^*(2)1s_A(2)1s_B(1)d\tau_1 d\tau_2$
  $= \langle 1s_A(1)|1s_B(1)\rangle \langle 1s_A(2)|1s_B(2)\rangle = S_{AB}^2 \neq 0$
- $S_{21} = S_{12}$

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

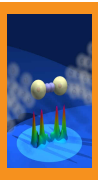
$$\phi_1 = \frac{f_1+f_2}{\sqrt{2(1+S_{12})}} \qquad \phi_2 = \frac{f_1-f_2}{\sqrt{2(1-S_{12})}}$$

II.A. Hydrogen molecule

- Overlap

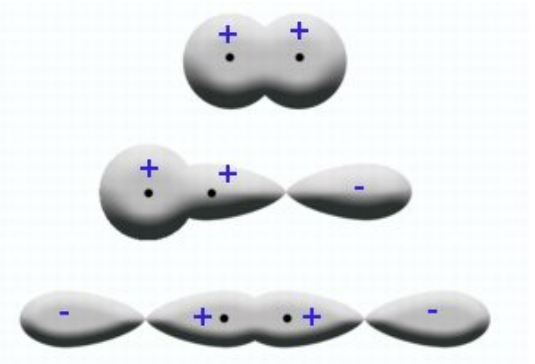
$$\psi(1,2) \propto \left[\phi_{\mathrm{H}_A,1s}(1)\,\phi_{\mathrm{H}_B,1s}(2) + \phi_{\mathrm{H}_A,1s}(2)\,\phi_{\mathrm{H}_B,1s}(1)\right]$$

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



II.A. Hydrogen molecule

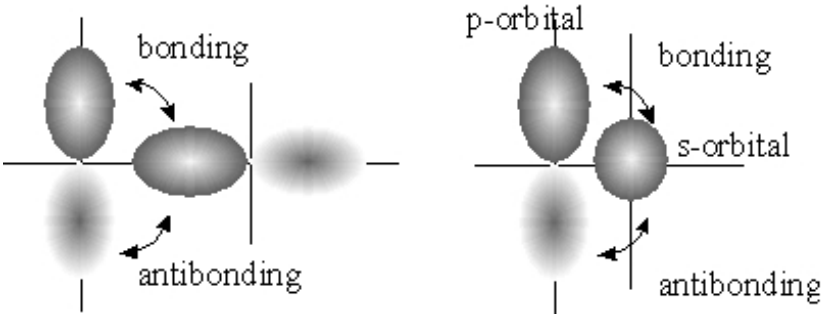
- Cylindrical symmetry $\Rightarrow$ σ bond.



- Plane of symmetry $\Rightarrow$ π bond.

II.A. Hydrogen molecule

- Null overlap $\Rightarrow$ no bond.



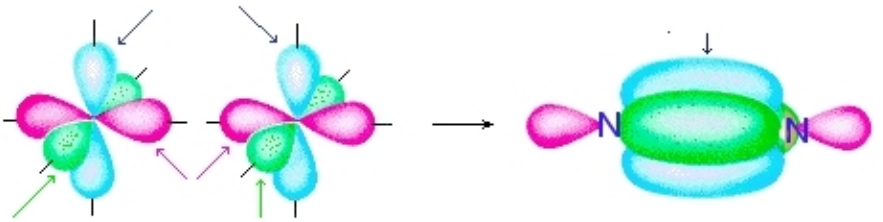
- Extension to polielectronic atoms. Example: N_2 molecule

[N]: $1s^2\,2s^2\,2p^3$

|N≡N|

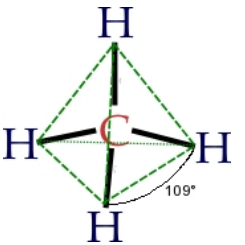
Octect rule

$1\sigma + 2\pi$



II.B. Hybrid orbitals

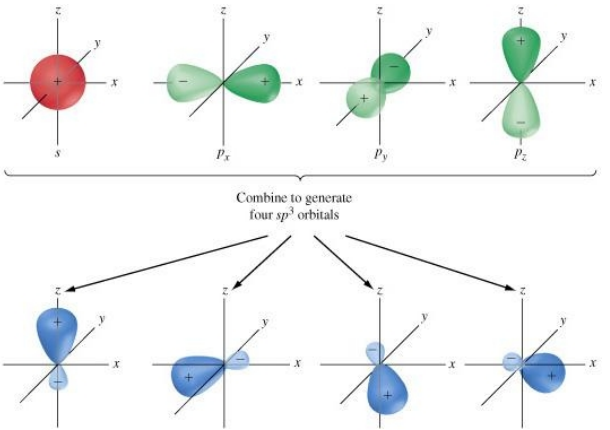
- Molecular geometry. Ej. $CH_4 \Rightarrow$ C-H equiv. $\Rightarrow$



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

- Hibrydization.

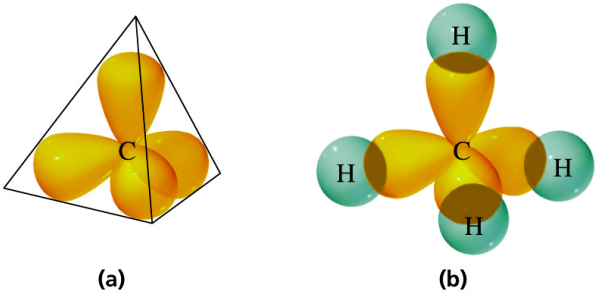
$$h_1 = \tfrac{1}{2}(s+p_x+p_y+p_z)$$
$$h_2 = \tfrac{1}{2}(s-p_x-p_y+p_z)$$
$$h_3 = \tfrac{1}{2}(s-p_x+p_y-p_z)$$
$$h_4 = \tfrac{1}{2}(s+p_x-p_y-p_z)$$



II.B. Hybrid orbitals

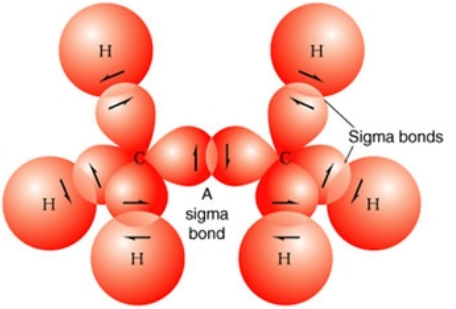
- sp^3 hybrid orbitals $\Rightarrow$ 

  - Thetahedral geometry
  - 4 C-H σ equiv. bonds
  - Minimal repulsion.



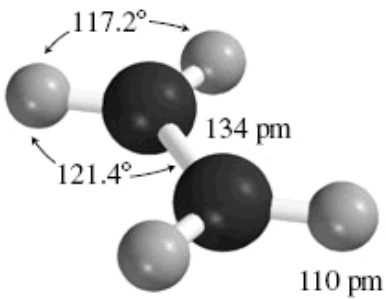
- Ethane $\Rightarrow$ CH_3-CH_3

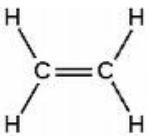
  - [C]: $1s^2\ 2s^2\ 2p^2$; [H]: $1s^1$
  - e^- valence: 4x2+1x6= 14
  - 



II.B. Hybrid orbitals

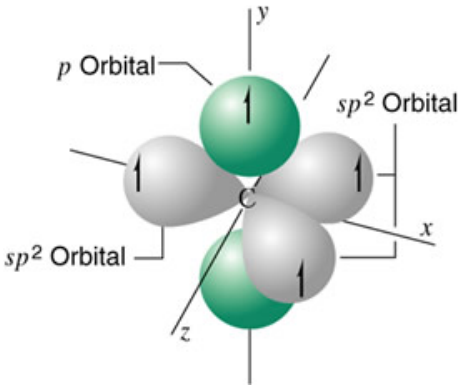
- Ethene $\Rightarrow$ CH_2-CH_2

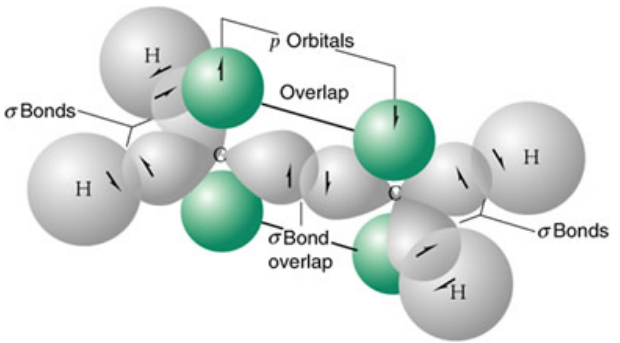




- e^- valence: 4x2+1x4= 12
- sp^2 hybrid orbitals

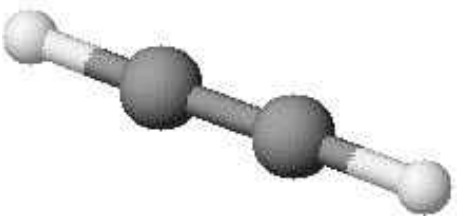
$$h_1 = \frac{1}{\sqrt{3}}\,s + \frac{1}{\sqrt{6}}\,p_x + \frac{1}{\sqrt{2}}\,p_y$$
$$h_2 = \frac{1}{\sqrt{3}}\,s + \frac{1}{\sqrt{6}}\,p_x - \frac{1}{\sqrt{2}}\,p_y$$
$$h_1 = \frac{1}{\sqrt{3}}\,s - \frac{2}{\sqrt{3}}\,p_x$$





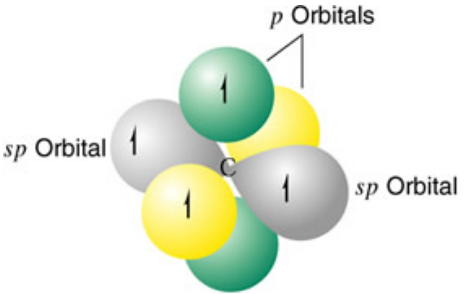
II.B. Hybrid orbitals

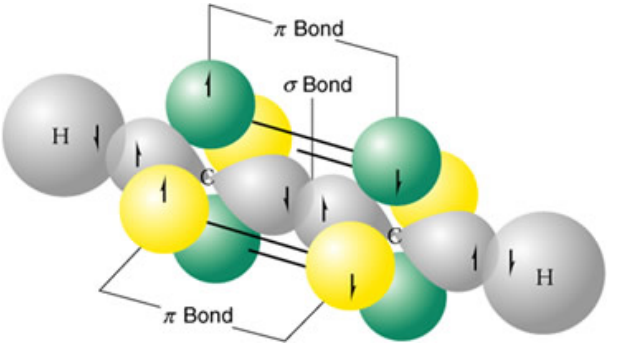
- Acetylene (Ethyne) $\Rightarrow$ CH-CH



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

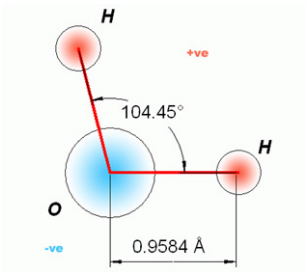
$$h_1 = \frac{1}{\sqrt{2}}(s+p_x)$$
$$h_2 = \frac{1}{\sqrt{2}}(s-p_x)$$



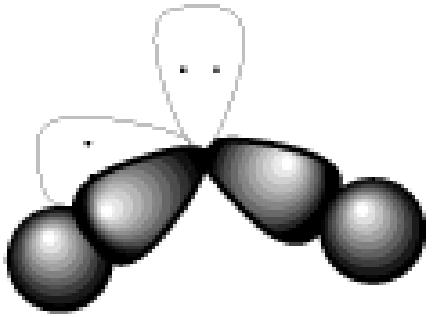


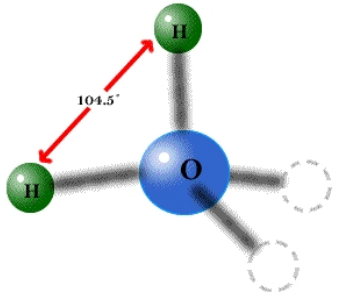
II.B. Hybrid orbitals

- Water $\Rightarrow$ H_2O



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



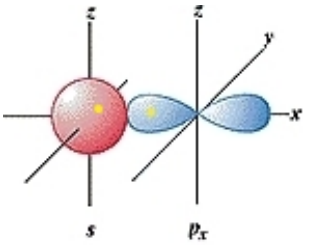


II.C. Covalent and ionic bonds

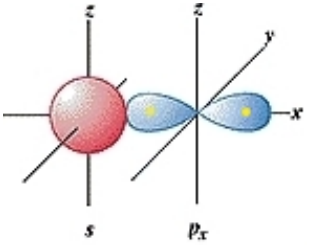
- Homoatomic bonds $\Rightarrow$ Symmetric electronic density
- Heteroatomic bonds. Ex. HCl

  [Cl]: $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^5$; [H]: $1s^1$

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

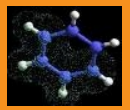


$|\overline{Cl} - H$



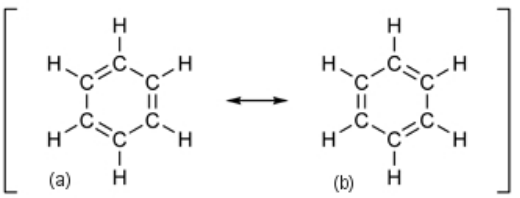
$|\overline{Cl}|^- H^+$

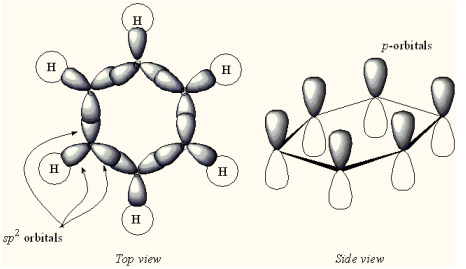
- Resonance $\Rightarrow \Psi_{HCl} = \lambda\,\Psi_{\text{covalent}} + (1-\lambda)\,\Psi_{\text{ionic}};\ \ \lambda \in [0,1]$



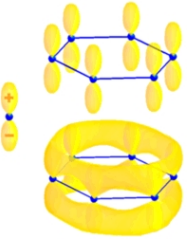
II.D. Resonance

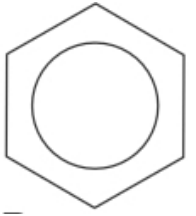
- Resonance hybrids. Ej. Benzene C_6H_6





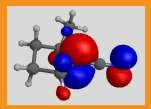
$$\psi = \psi_a + \psi_b \Rightarrow$$





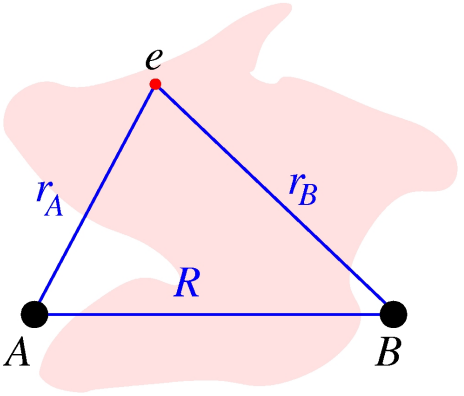
$$d_{\text{C-C}} = 1.54\,\text{Å} > d_{\text{CC}}^{\text{benzene}} = 1.39\,\text{Å} > d_{\text{C=C}} = 1.34\,\text{Å}$$

- Energetic stabilization



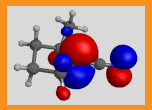
III.A. Definition

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



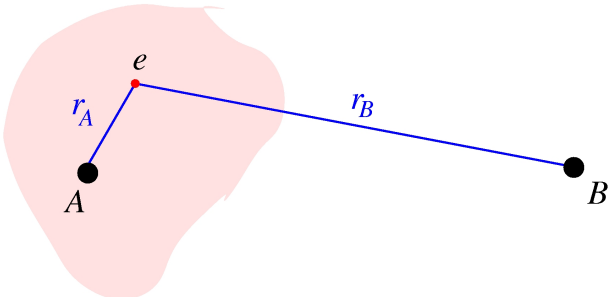
$$\hat{H} = \hat{T} - k\frac{e^2}{r_A} - k\frac{e^2}{r_B} + k\frac{e^2}{R}$$

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

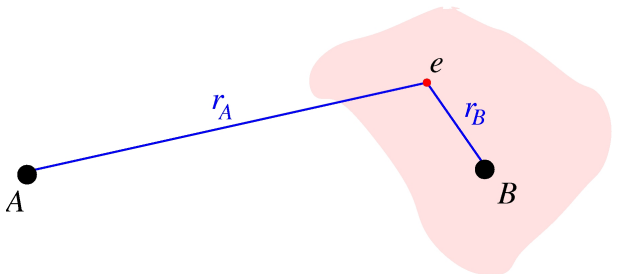


III.A. Definition

- Limiting conditions



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



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

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

- Variational method

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

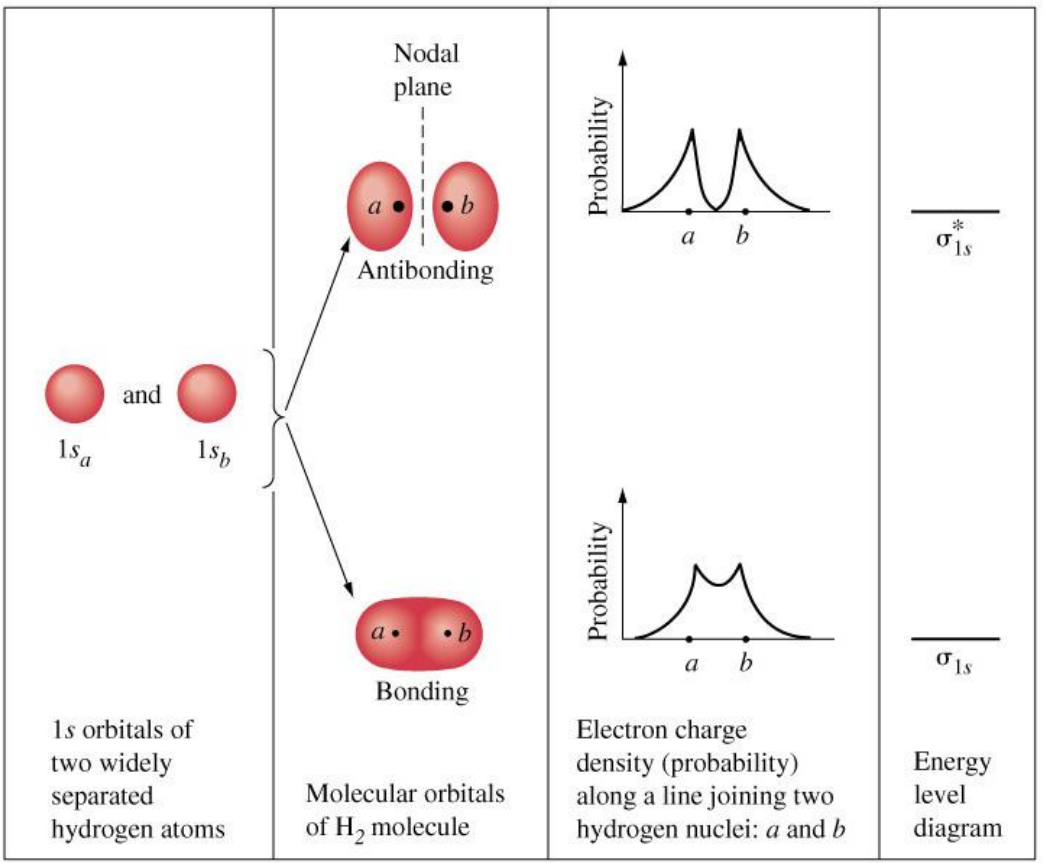
Solutions:

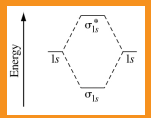
$$c_A = c_B \quad \rightarrow \psi_{\text{OM},1} = c_A \left(\psi_{1s,A} + \psi_{1s,B} \right) \rightarrow E_1 < 2 \cdot E_{\text{atom}}$$
$$c_A = -c_B \rightarrow \psi_{\text{OM},2} = c_A \left(\psi_{1s,A} - \psi_{1s,B} \right) \rightarrow E_2 > 2 \cdot E_{\text{atom}}$$

Probability densities

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

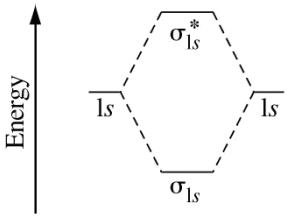
III.A. Definition



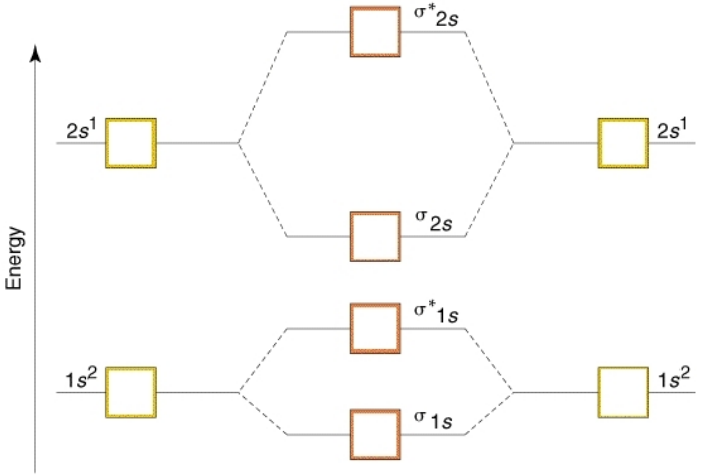


III.B. Energy diagram

- Energy diagram.

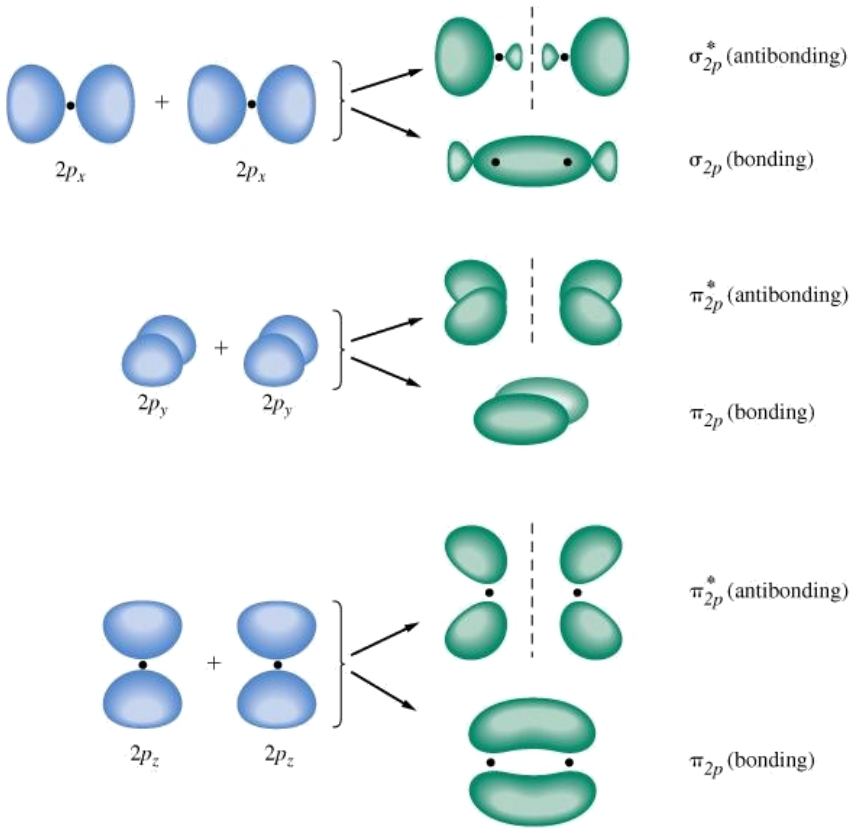


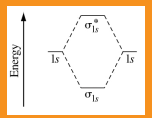
- $2s$ orbitals $\Rightarrow$ idem



III.B. Energy diagram

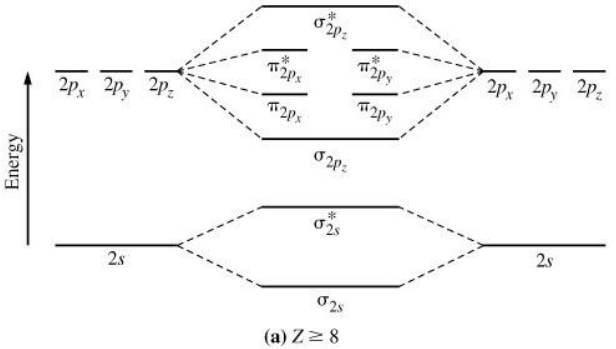
- $2p$ orbitals



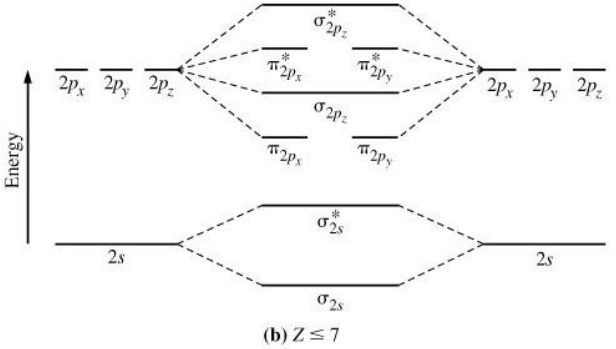


III.B. Energy diagram

- Energy diagram of the second shell



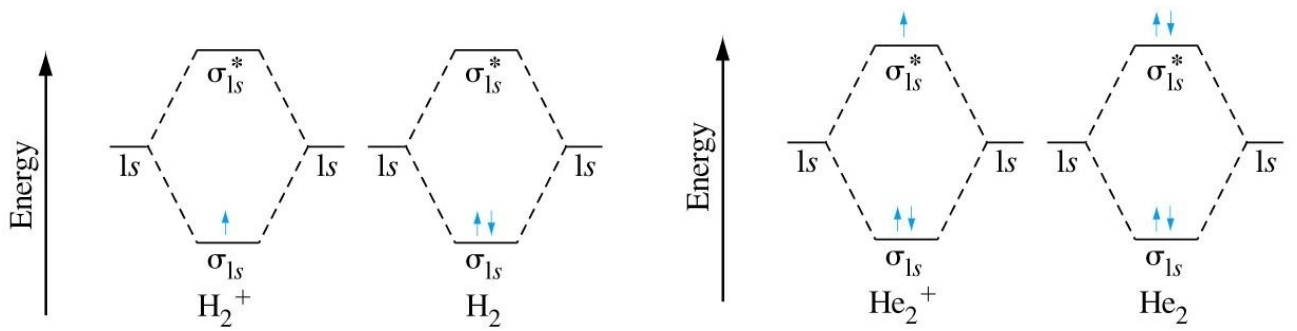
(a) $Z \geq 8$



(b) $Z \leq 7$

III.C. Homonuclear diatomic molecules

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

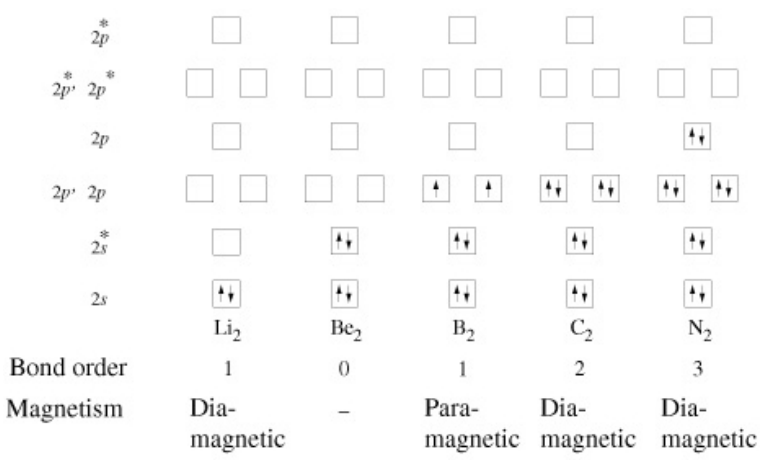


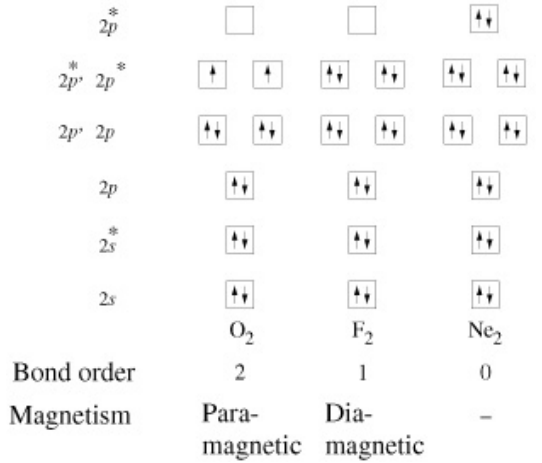
- Bond order $= \frac{1}{2}\left(N_e \text{ bonding} - N_e \text{ antibonding}\right)$

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

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

III.C. Homonuclear diatomic molecules

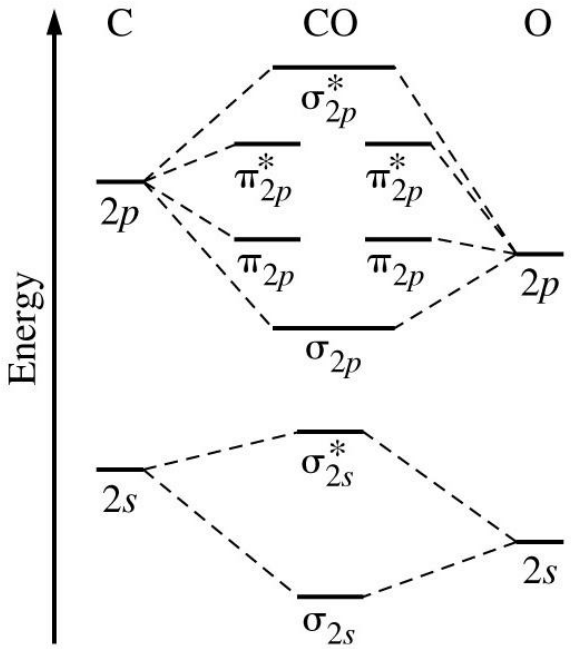


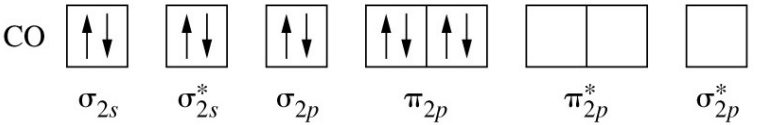


- Paramagnetism $\Rightarrow$ e unpaired.
  VBT $\Rightarrow \langle \mathrm{O}=\mathrm{O} \rangle$ diamagnetic $\Rightarrow$ 
- Distance and energy bond

	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	–

III.D. Heteronuclear diatomic molecules





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

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