

# Tema 11.- Estructura Electrónica Molecular

11.1. Aproximación de Born-Oppenheimer

11.2. La molécula de  $H_2^+$

11.3. Concepto de orbital molecular

11.4. Combinación de orbitales atómicos para formar orbitales moleculares

11.5 Orbitales para moléculas biatómicas homonucleares

11.6 Orden de enlace, energía de enlace y longitud de enlace

11.7 Moléculas biatómicas heteronucleares

Hamiltoniano Molecular:  $\hat{H}(\vec{r}_1, \vec{r}_2, \vec{r}_3, \dots, \vec{r}_n, \vec{R}_A, \vec{R}_B, \dots, \vec{R}_M)$

$$\hat{H} \Psi(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_n, \vec{R}_A, \vec{R}_B, \dots, \vec{R}_M) = E \Psi(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_n, \vec{R}_A, \vec{R}_B, \dots, \vec{R}_M)$$

Términos del Hamiltoniano Molecular:

$$\hat{H} = \hat{T}_e + \hat{T}_n + \hat{V}_{e-n} + \hat{V}_{e-e} + \hat{V}_{n-n}$$

Aproximación Born-Oppenheimer: Separar Movimiento Nuclear del Electrónico

1ª Etapa:  $\hat{T}_n = 0$ ,  $\hat{V}_{n-n} = de = \sum_A \sum_{B \neq A} \frac{Z_A \cdot Z_B e^2}{4\pi\epsilon_0 R_{AB}}$

$$\hat{H}^{elec} = \hat{T}_e + \hat{V}_{e-n} + \hat{V}_{e-e}$$

$$\hat{H}^{elec} \Psi^{elec}(\{\vec{r}_i\}; \{\vec{R}_A\}) = E^{elec} \Psi^{elec}(\{\vec{r}_i\}; \{\vec{R}_A\})$$

$$U = E^{elec} + V_{n-n} = U(\{\vec{R}_A\})$$

2ª Etapa: Movimiento nuclear:

$$\hat{H}_n = \hat{T}_n + \hat{U}$$

$$\hat{H}_n \Psi_n(\{\vec{R}_A\}) = E \Psi_n(\{\vec{R}_A\})$$

# Aproximación Born-Oppenheimer

Molécula de  $H_2^+$

término constante mientras se resuelve el problema electrónico

$$\hat{H} = -\frac{\hbar^2}{2m_p}(\nabla_a^2 + \nabla_b^2) - \frac{\hbar^2}{2m_e}\nabla_e^2 - \frac{e^2}{4\pi\epsilon_0}\left(\frac{z_a}{r_a} + \frac{z_b}{r_b}\right) + \frac{e^2}{4\pi\epsilon_0}\frac{1}{R}$$

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Molécula AB con un solo electrón

$$-\frac{\hbar^2}{2m_e}\nabla_e^2 - \frac{e^2}{4\pi\epsilon_0}\left(\frac{z_a}{r_a} + \frac{z_b}{r_b}\right)$$

Desacoplando el movimiento electrónico del nuclear

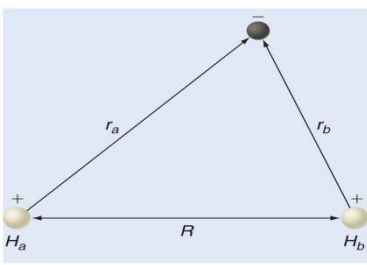
$$U = E_{el} + \frac{e^2 z_a z_b}{4\pi\epsilon_0 R}$$

Factorización de la función de ondas



$$\Psi = \Psi^{elec}(\{r_i\}; \{R_A\}) \cdot \Psi_n(\{R_A\})$$

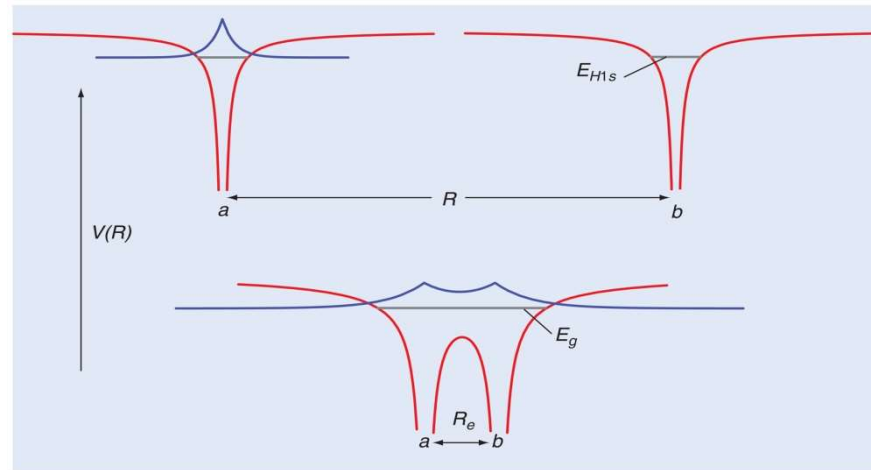
# La Molécula $H_2^+$



$$\hat{H} = -\frac{\hbar^2}{2m_p} (\nabla_a^2 + \nabla_b^2) - \frac{\hbar^2}{2m_e} \nabla_e^2 - \frac{e^2}{4\pi\epsilon_0} \left( \frac{1}{r_a} + \frac{1}{r_b} \right) + \frac{e^2}{4\pi\epsilon_0} \frac{1}{R}$$

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La energía potencial de  $H_2^+$  para 2 valores distintos de  $R$



$R$  grande:  $H + H^+$

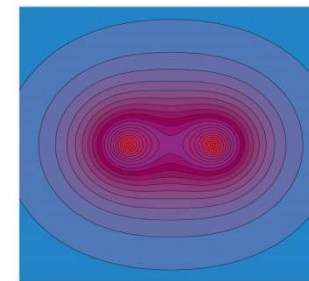
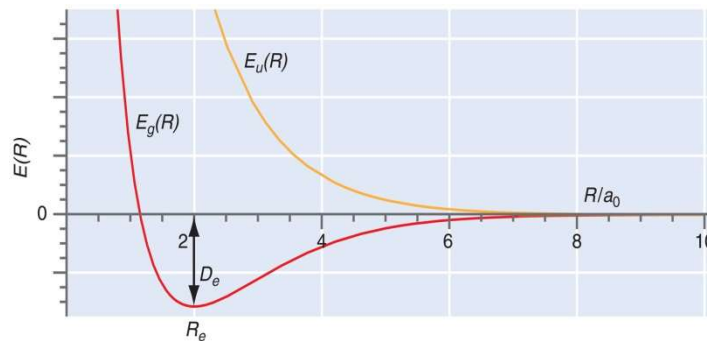
$R$  pequeña:  $H_2^+$

**Orbitales Moleculares** son las distribuciones espaciales sobre la molécula donde se definen los electrones.

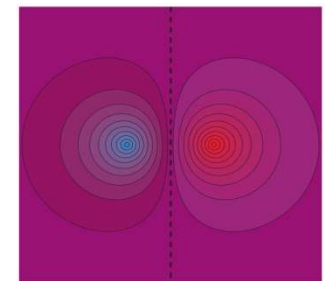
$$\psi_g = c_g(\phi_{H1s_a} + \phi_{H1s_b})$$

$$\psi_u = c_u(\phi_{H1s_a} - \phi_{H1s_b})$$

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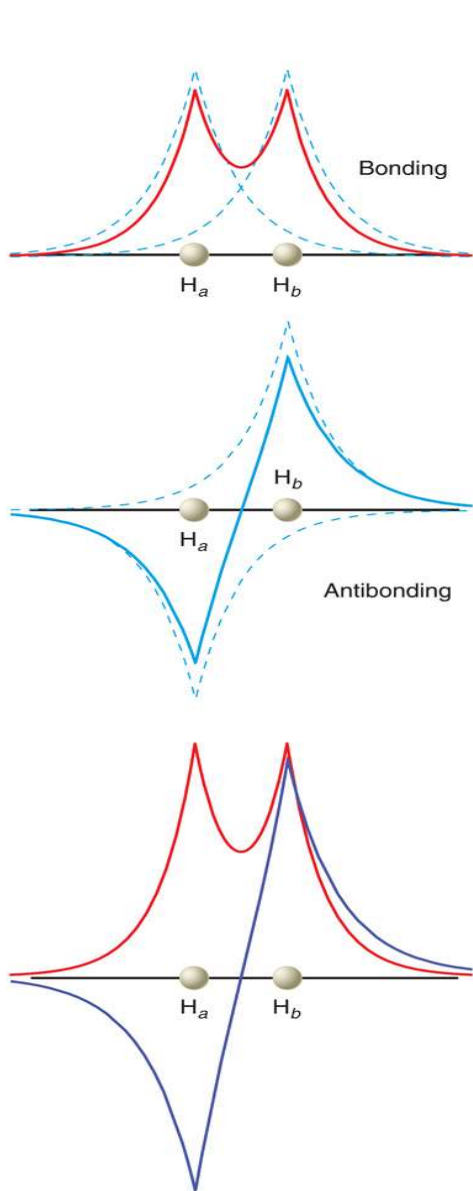


$\Psi_g$

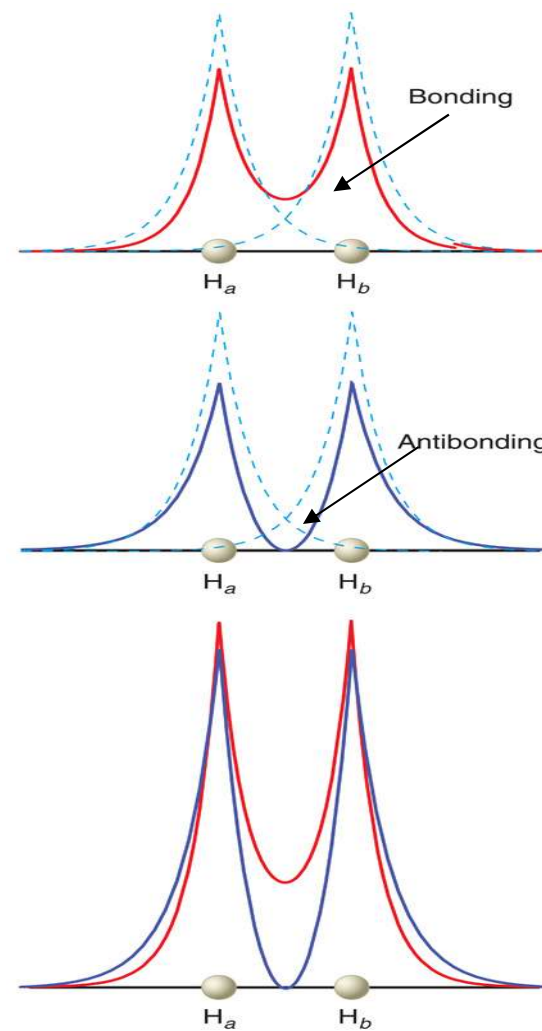


$\Psi_u$

**Modelo LCAO-MO**



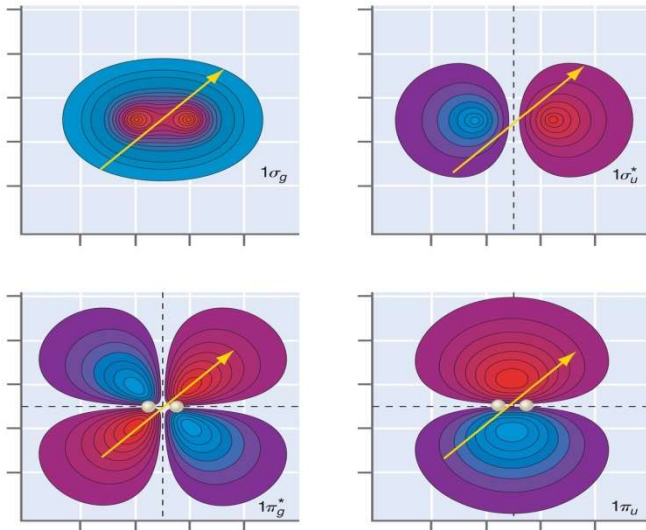
Funciones de ondas moleculares para  $\Psi_g$  y  $\Psi_u$  y su comparación. (las líneas discontinuas representan Las funciones tomando los OA 1s del H)



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Densidades de probabilidad para para  $\Psi_g^2$  y  $\Psi_u^2$  y su comparación. (las líneas discontinuas representan Las funciones tomando los OA 1s del H)

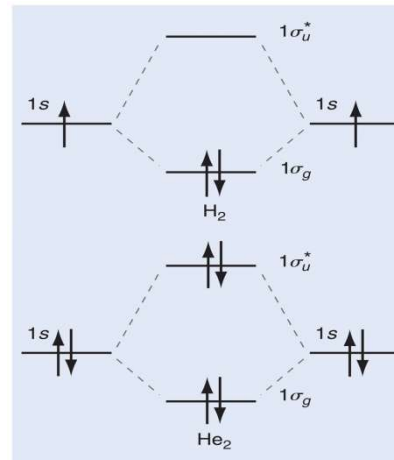
# Moléculas Diatómicas Homonucleares



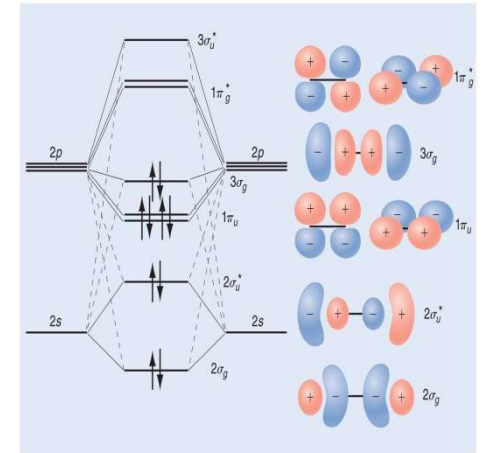
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Representaciones de contorno para varios OM enlazantes y antienlazantes de  $H_2^+$

Aplicación del principio Aufbau para relleno de LCAO-MO



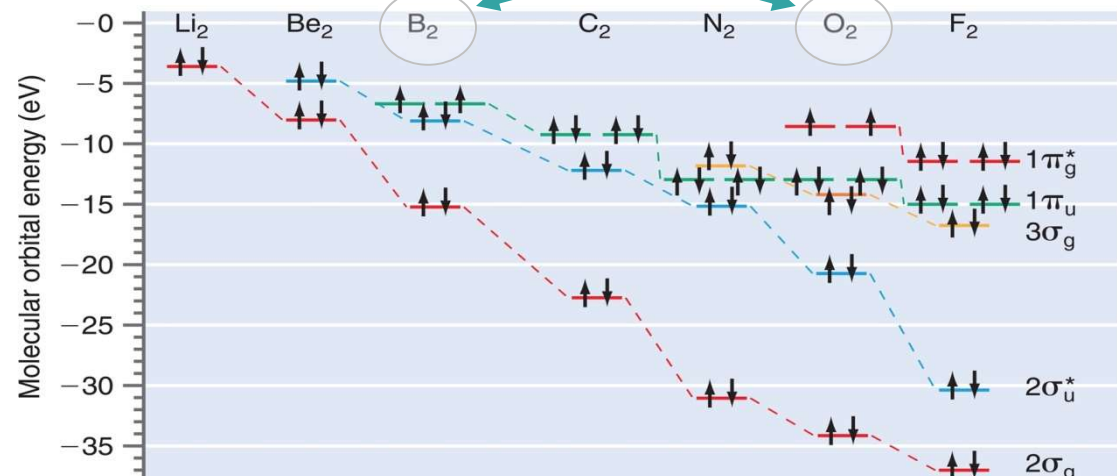
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Diagrama CLOA-OM para  $N_2$

## Moléculas paramagnéticas



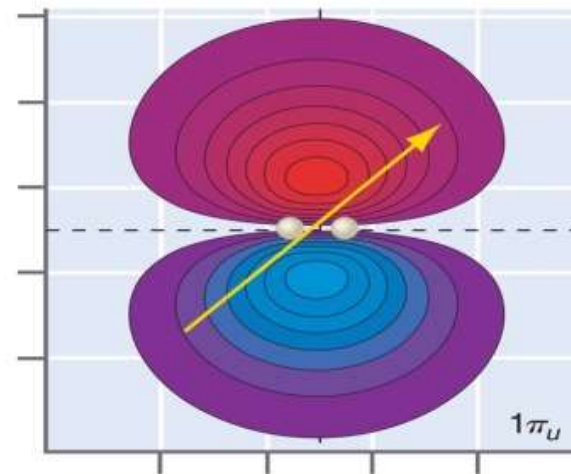
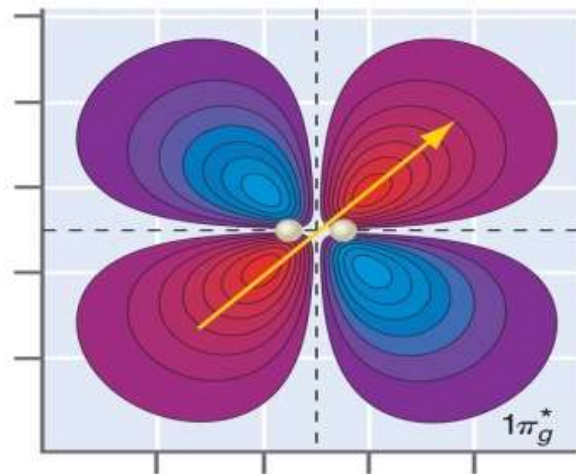
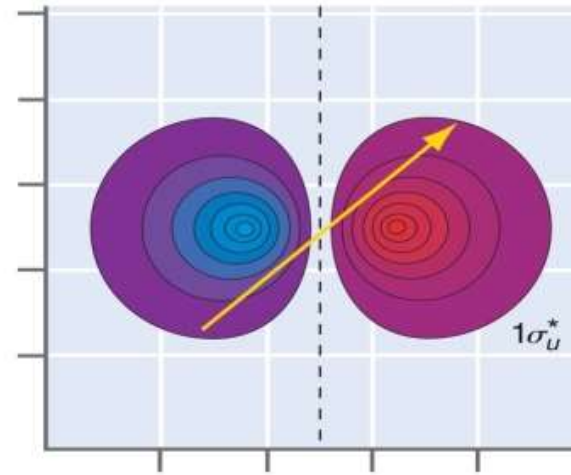
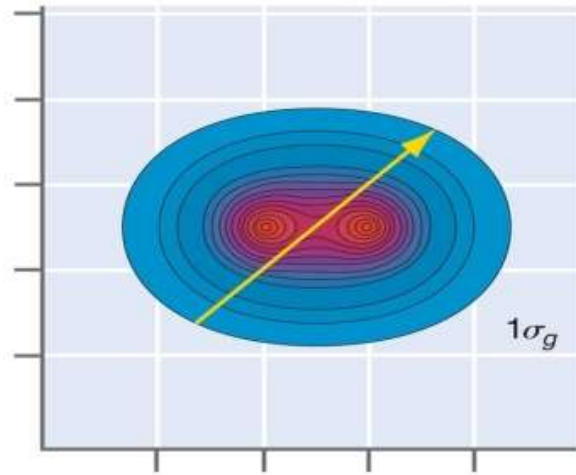
Niveles de energía de OM ocupados para  $X_2$  (2° Período)

TABLE 23.2 MOLECULAR ORBITALS USED TO DESCRIBE CHEMICAL BONDING IN HOMONUCLEAR DIATOMIC MOLECULES

MO Designation	Alternate	Character	Atomic Orbitals
$1\sigma_g$	$\sigma_g(1s)$	Bonding	1s
$1\sigma_u^*$	$\sigma_u^*(1s)$	Antibonding	1s
$2\sigma_g$	$\sigma_g(2s)$	Bonding	2s (2p <sub>z</sub> )
$2\sigma_u^*$	$\sigma_u^*(2s)$	Antibonding	2s (2p <sub>z</sub> )
$3\sigma_g$	$\sigma_g(2p_z)$	Bonding	2p <sub>z</sub> (2s)
$3\sigma_u^*$	$\sigma_u^*(2p_z)$	Antibonding	2p <sub>z</sub> (2s)
$1\pi_u$	$\pi_u(2p_x, 2p_y)$	Bonding	2p <sub>x}, 2p_y</sub>
$1\pi_g^*$	$\pi_g^*(2p_x, 2p_y)$	Antibonding	2p <sub>x}, 2p_y</sub>

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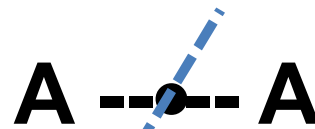


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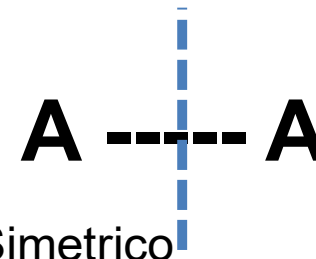
Centro de inversión



Simetrico  $\sigma$   
Antisimétrico  $\pi$



Simetrico  $g$   
Antisimétrico  $u$



Simetrico (enlazante)  
Antisimétrico \* (antienlazante)

# Las Partes por el Todo: Orden de Enlace, Energía de Enlace y Longitud de Enlace

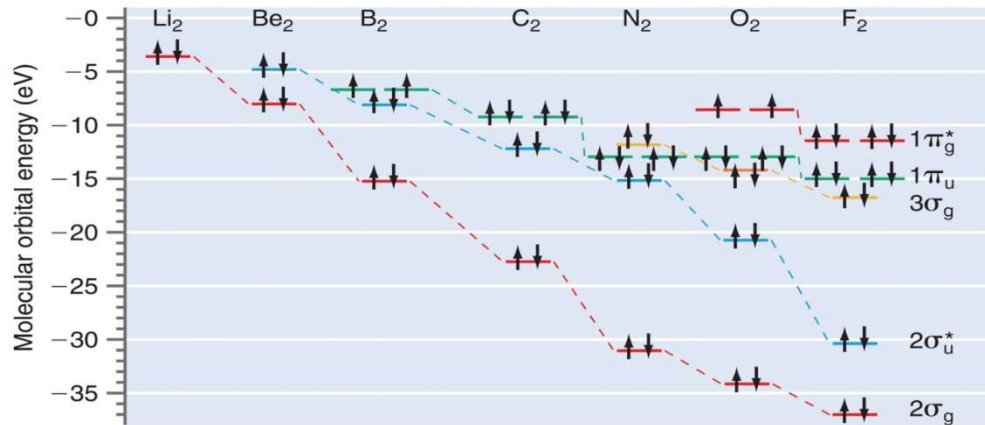
## Aproximación orbital

función de ondas  
polielectrónica

orbitales moleculares

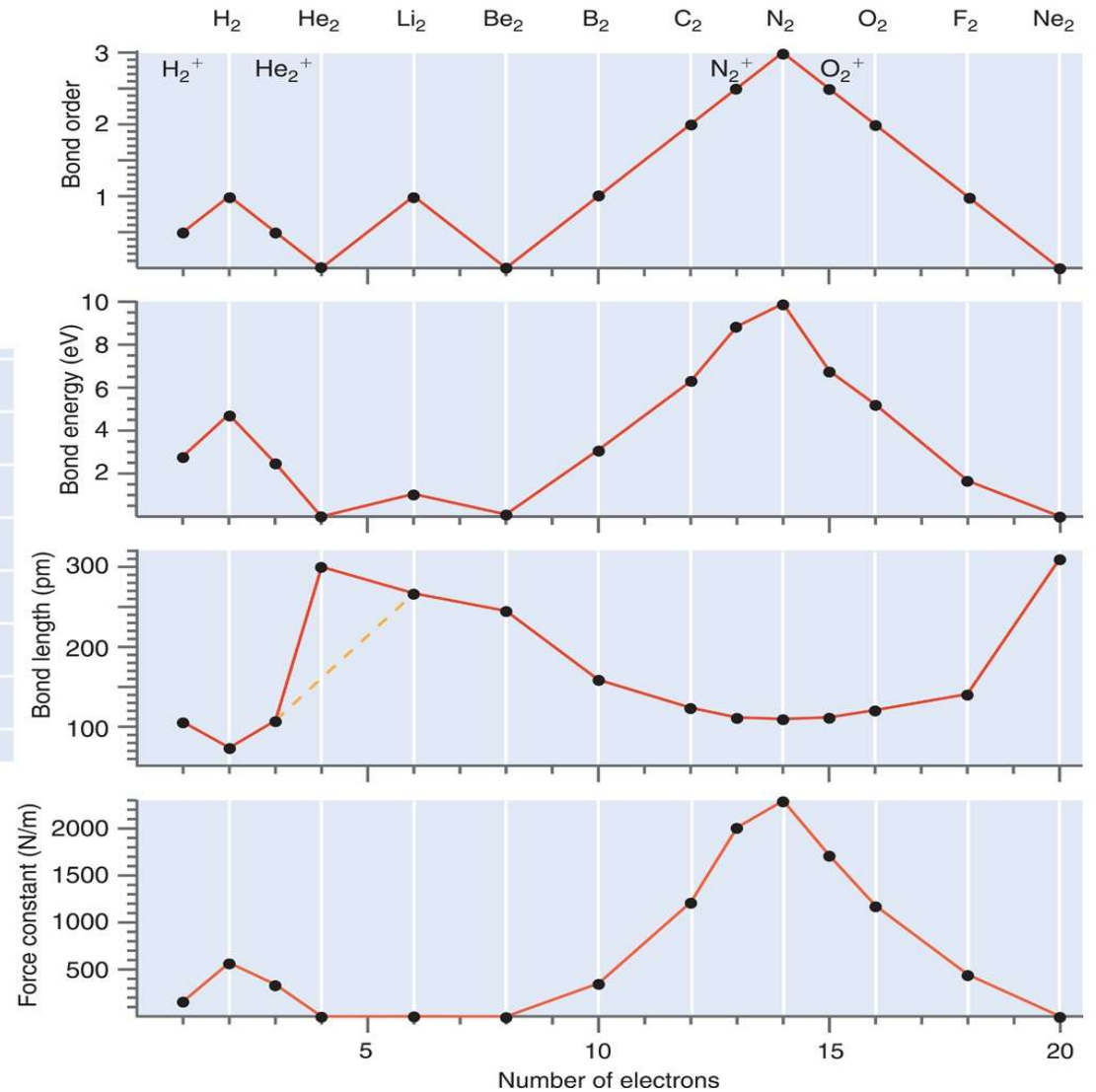
$$\psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_n) = \phi_1(\mathbf{r}_1)\phi_2(\mathbf{r}_2)\dots\phi_n(\mathbf{r}_n)$$

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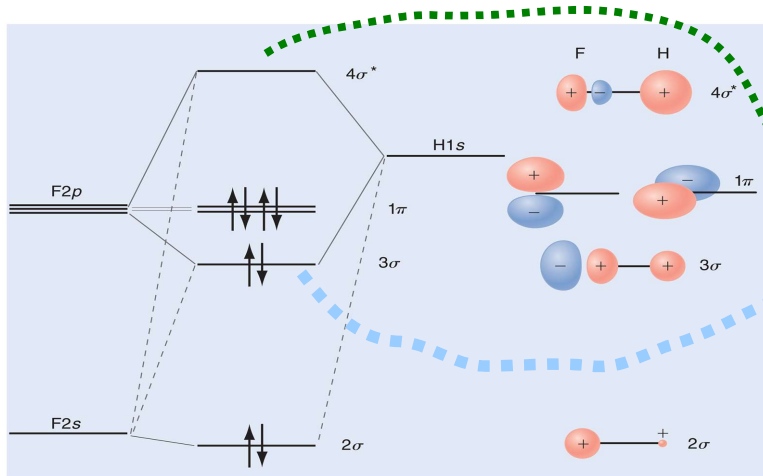
$$\text{Orden de enlace} = \frac{1}{2} (n^{\circ} e^{-}_{\text{enlazantes}} - n^{\circ} e^{-}_{\text{antienlazantes}})$$



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# Moléculas Bioatómicas Heteronucleares

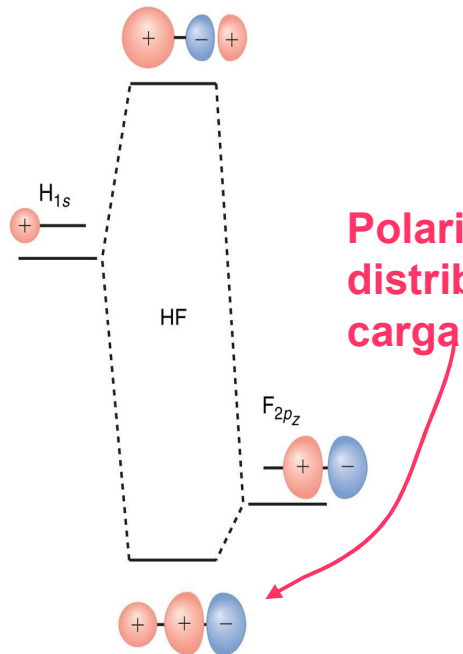


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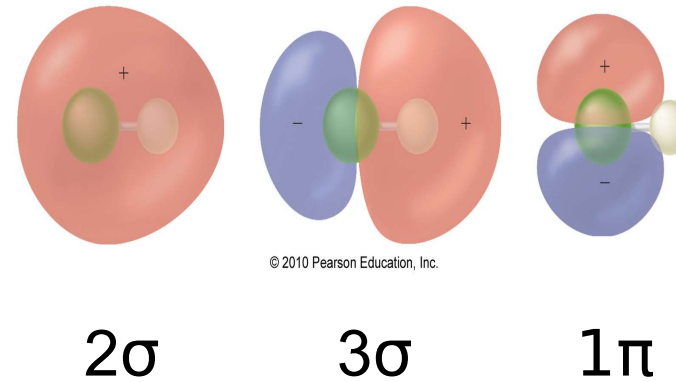
$$\begin{aligned} \epsilon_b &= -19.6 \text{ eV} & \psi_b &= 0.34\phi_{H1s} + 0.84\phi_{F2p_z} \\ \epsilon_a &= -10.3 \text{ eV} & \psi_a &= 0.99\phi_{H1s} - 0.63\phi_{F2p_z} \end{aligned}$$

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## Esquema CLOA-OM para FH



Polarización de la distribución de carga



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OM (CLOA) :

$$\psi_j(1) = \sum_{i=1}^N c_{ij} \phi_i(1)$$

obtenidos mediante método HF

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