



Aplicação de simetria para a visualização dos orbitais moleculares de moléculas pequenas e compostos de coordenação

Roberto B. Faria

faria@iq.ufrj.br

www.iq.ufrj.br/~faria

Universidade Federal do Rio de Janeiro

Aula 4 - Mudança de geometria

H₂O NH₃ CH₄

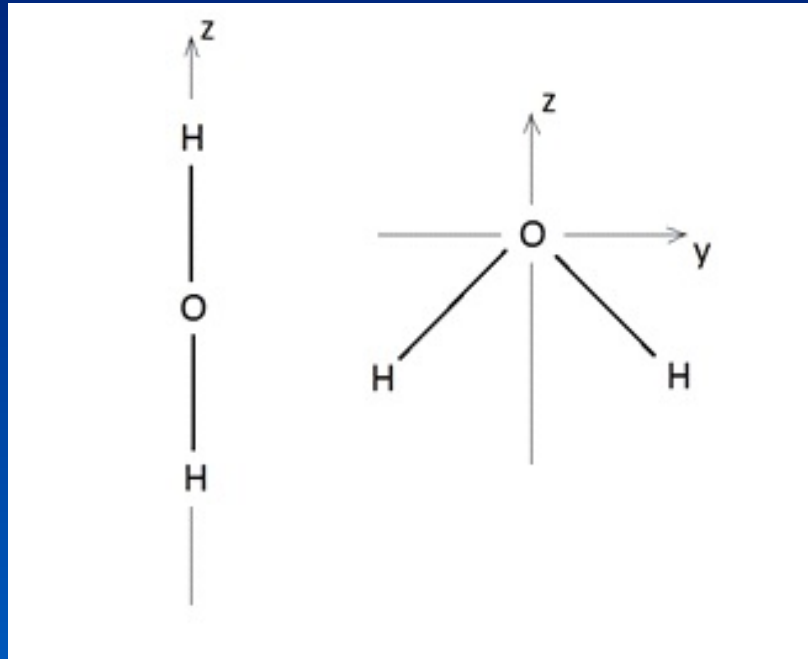
Simetrias D_{∞h} D_{3h} C_{4h}



Sociedade Brasileira de Química

11 a 15 de março de 2024

Água linear ($D_{\infty h}$)
×
Água angular (C_{2v})

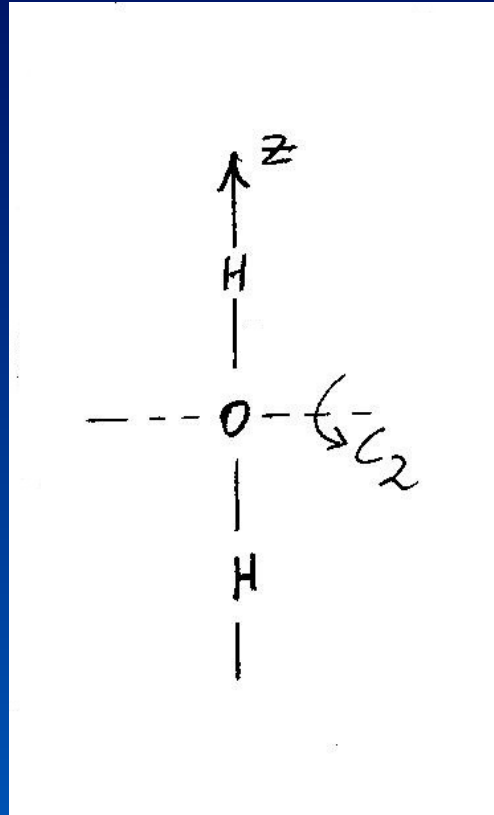


Água (linear) - $D_{\infty h}$

$D_{\infty h}$	E	$2C_{\infty}^{\varphi}$	$\infty\sigma_v$	i	$2S_{\infty}^{\varphi}$	∞C_2
Σ_{g}^{+}	1	1	1	1	1	1
Σ_{g}^{-}	1	1	-1	1	1	-1
Π_{g}	2	$2\cos\varphi$	0	2	$-2\cos\varphi$	0
Δ_{g}	2	$2\cos 2\varphi$	0	2	$2\cos 2\varphi$	0
Σ_{u}^{+}	1	1	1	-1	-1	-1
Σ_{u}^{-}	1	1	-1	-1	-1	1
Π_{u}	2	$2\cos\varphi$	0	-2	$2\cos\varphi$	0
Δ_{u}	2	$2\cos 2\varphi$	0	-2	$-2\cos 2\varphi$	0

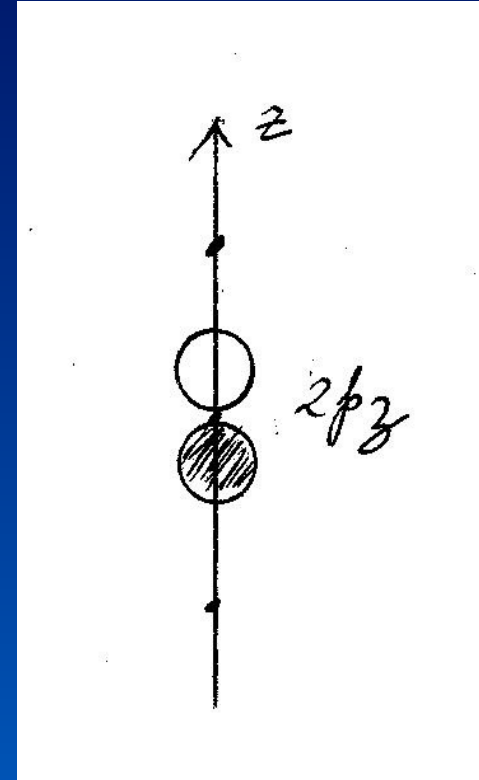
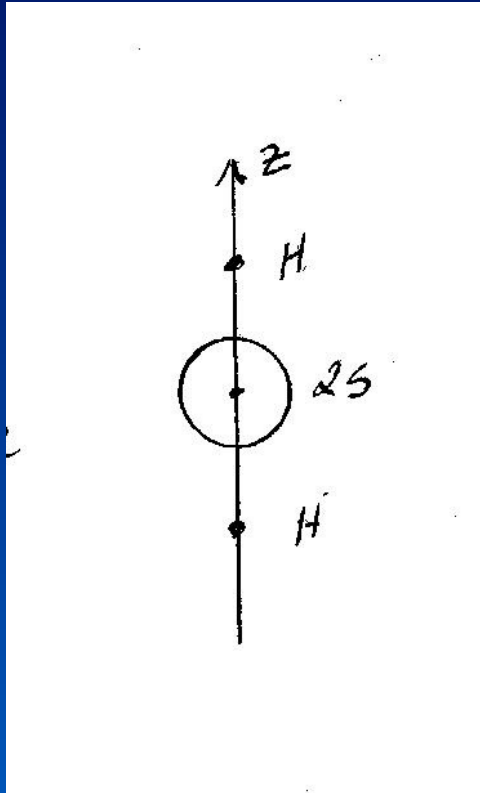
Água (linear) - $D_{\infty h}$

O eixo z, vertical, é o eixo C_{∞}



Água (linear) - $D_{\infty h}$

Orbitais 2s e 2p_z

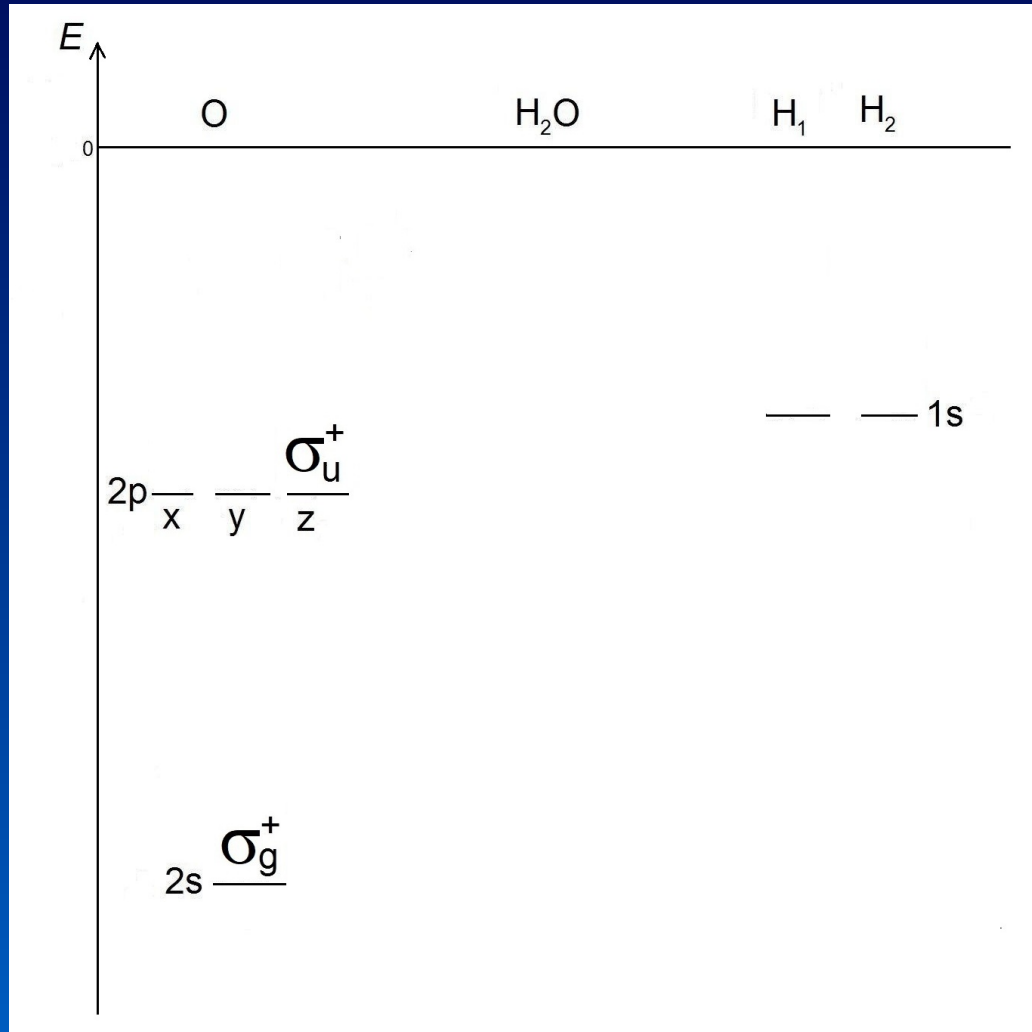


Água (linear) - $D_{\infty h}$

$D_{\infty h}$	E	$2C_{\infty}^{\varphi}$	$\infty\sigma_v$	i	$2S_{\infty}^{\varphi}$	∞C_2	
Σ_{g}^{+}	1	1	1	1	1	1	
Σ_{g}^{-}	1	1	-1	1	1	-1	
Π_{g}	2	$2\cos\varphi$	0	2	$-2\cos\varphi$	0	
Δ_{g}	2	$2\cos 2\varphi$	0	2	$2\cos 2\varphi$	0	
Σ_{u}^{+}	1	1	1	-1	-1	-1	
Σ_{u}^{-}	1	1	-1	-1	-1	1	
Π_{u}	2	$2\cos\varphi$	0	-2	$2\cos\varphi$	0	
Δ_{u}	2	$2\cos 2\varphi$	0	-2	$-2\cos 2\varphi$	0	
<hr/>							
2s	1	1	1	1	1	1	Σ_{g}^{+}
2p _z	1	1	1	-1	-1	-1	Σ_{u}^{+}

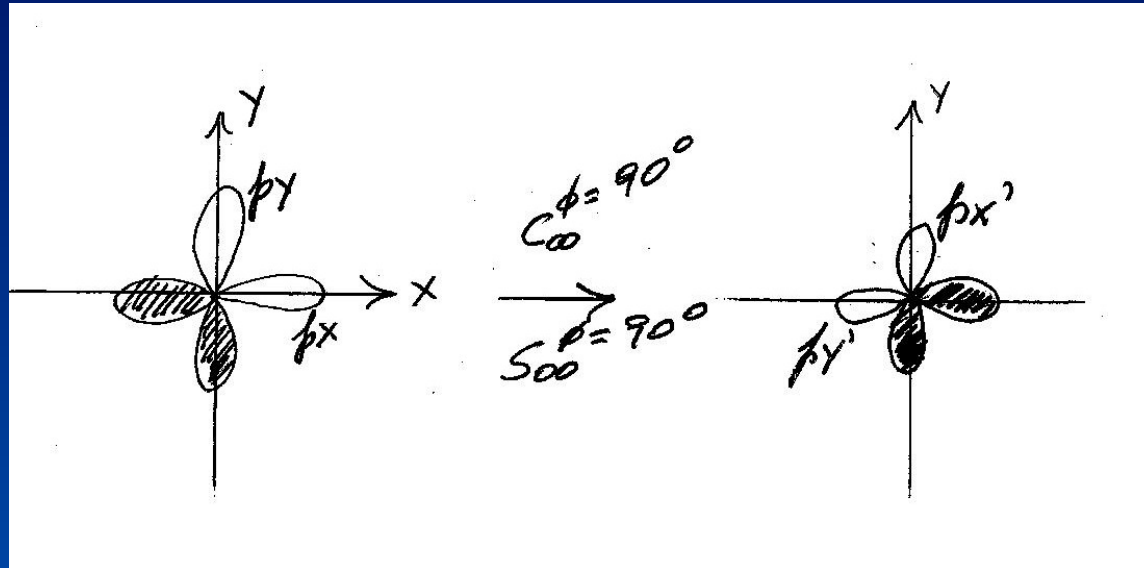
Água (linear) - $D_{\infty h}$

Construindo o diagrama de energia dos orbitais moleculares



Água (linear) - $D_{\infty h}$

Orbitais $2p_x$ e $2p_y$ do Oxigênio - INSEPARÁVEIS



Água (linear) - $D_{\infty h}$

Orbitais $2p_x$ e $2p_y$ do Oxigênio - INSEPARÁVEIS

$$\begin{array}{cc} & \begin{array}{c} 2p_x \\ 2p_y \end{array} \\ \begin{array}{c} 2p_x \\ 2p_y \end{array} & \begin{array}{cc} 1 & 0 \\ 0 & 1 \end{array} \end{array} \xrightarrow[\text{S}_{\infty}^{\varphi=90^\circ}]{\text{C}_{\infty}^{\varphi=90^\circ}} \begin{array}{cc} & \begin{array}{c} 2p_x \\ 2p_y \end{array} \\ \begin{array}{c} 2p_x \\ 2p_y \end{array} & \begin{array}{cc} 0 & 1 \\ -1 & 0 \end{array} \end{array}$$

$\chi = 2$ $\chi = 0$

Água (linear) - $D_{\infty h}$

$D_{\infty h}$	E	$2C_{\infty}^{\varphi}$	$\infty\sigma_v$	i	$2S_{\infty}^{\varphi}$	∞C_2
Σ_{g}^{+}	1	1	1	1	1	1
Σ_{g}^{-}	1	1	-1	1	1	-1
Π_{g}	2	$2\cos\varphi$	0	2	$-2\cos\varphi$	0
Δ_{g}	2	$2\cos 2\varphi$	0	2	$2\cos 2\varphi$	0
Σ_{u}^{+}	1	1	1	-1	-1	-1
Σ_{u}^{-}	1	1	-1	-1	-1	1
Π_{u}	2	$2\cos\varphi$	0	-2	$2\cos\varphi$	0
Δ_{u}	2	$2\cos 2\varphi$	0	-2	$-2\cos 2\varphi$	0
p_x, p_y	2	0			0	

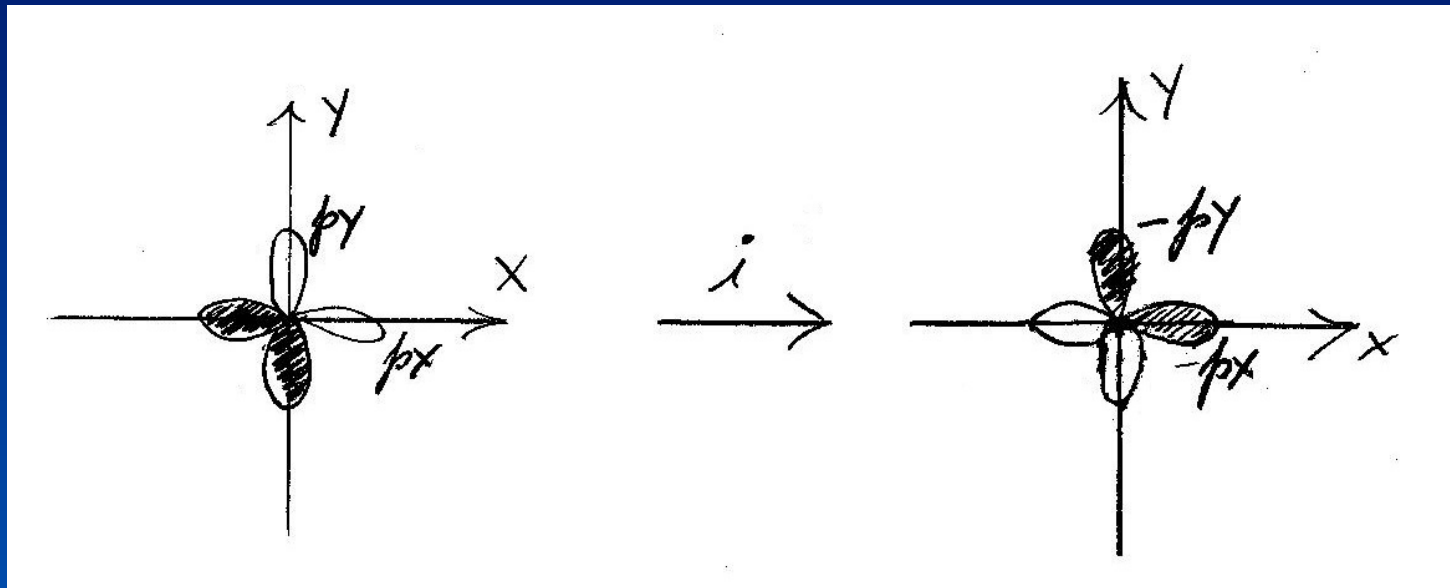
Água (linear) - $D_{\infty h}$

$$\varphi = 90^\circ$$

$D_{\infty h}$	E	$2C_\infty^\varphi$	$\infty\sigma_v$	i	$2S_\infty^\varphi$	∞C_2
Σ_{g^+}	1	1	1	1	1	1
Σ_{g^-}	1	1	-1	1	1	-1
Π_g	2	0	0	2	0	0
Δ_g	2	-2	0	2	-2	0
Σ_{u^+}	1	1	1	-1	-1	-1
Σ_{u^-}	1	1	-1	-1	-1	1
Π_u	2	0	0	-2	0	0
Δ_u	2	-2	0	-2	-2	0
p_x, p_y	2	0			0	

Água (linear) - $D_{\infty h}$

Orbitais $2p_x$ e $2p_y$ do Oxigênio - INSEPARÁVEIS



Água (linear) - $D_{\infty h}$

Orbitais $2p_x$ e $2p_y$ do Oxigênio - INSEPARÁVEIS

$$\begin{array}{cc} & \begin{array}{cc} 2p_x & 2p_y \end{array} \\ \begin{array}{c} 2p_x \\ 2p_y \end{array} & \begin{array}{cc} 1 & 0 \\ 0 & 1 \end{array} \end{array} \quad \begin{array}{c} i \\ \rightarrow \end{array} \quad \begin{array}{cc} & \begin{array}{cc} 2p_x & 2p_y \end{array} \\ \begin{array}{c} 2p_x \\ 2p_y \end{array} & \begin{array}{cc} -1 & 0 \\ 0 & -1 \end{array} \end{array}$$

$$\chi = -2$$

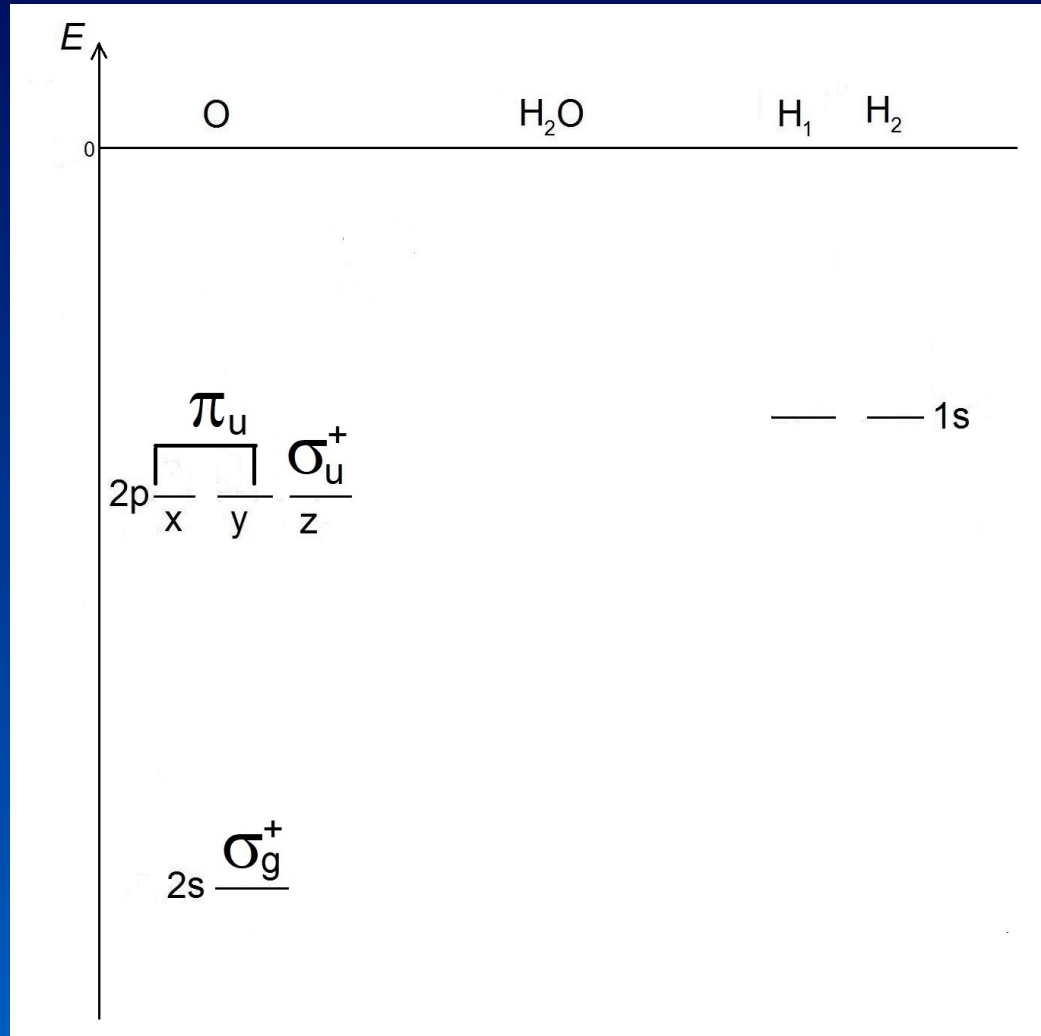
Água (linear) - $D_{\infty h}$

$$\varphi = 90^\circ$$

$D_{\infty h}$	E	$2C_{\infty}^{\varphi}$	$\infty\sigma_v$	i	$2S_{\infty}^{\varphi}$	∞C_2	
Σ_{g}^{+}	1	1	1	1	1	1	
Σ_{g}^{-}	1	1	-1	1	1	-1	
Π_{g}	2	0	0	2	0	0	
Δ_{g}	2	-2	0	2	-2	0	
Σ_{u}^{+}	1	1	1	-1	-1	-1	
Σ_{u}^{-}	1	1	-1	-1	-1	1	
Π_{u}	2	0	0	-2	0	0	
Δ_{u}	2	-2	0	-2	-2	0	
p_x, p_y	2	0		-2	0		Π_u

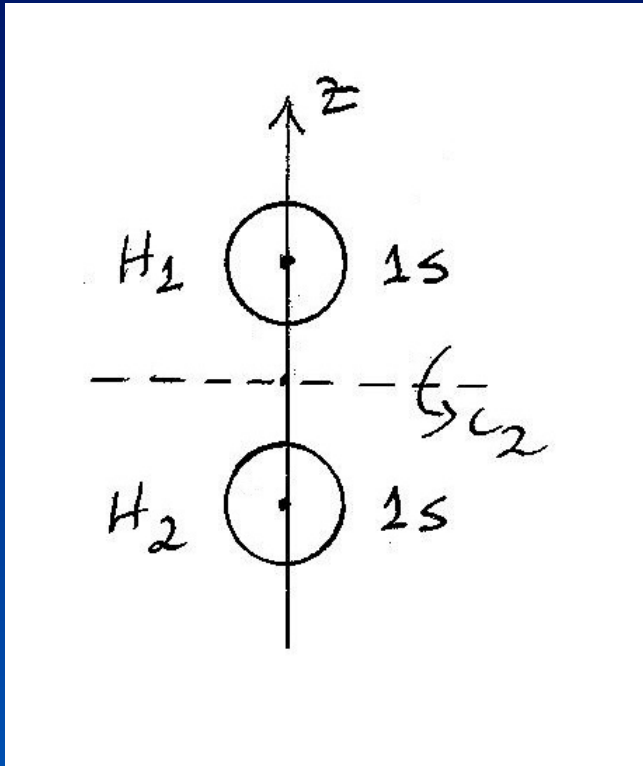
Água (linear) - $D_{\infty h}$

Construindo o diagrama de energia dos orbitais moleculares



Água (linear) - $D_{\infty h}$

Os orbitais 1s dos hidrogênios - INSEPARÁVEIS



$$\begin{array}{cc}
 & \begin{array}{cc} \varphi_1 & \varphi_2 \end{array} \\
 \begin{array}{c} \varphi_1 \\ \varphi_2 \end{array} & \begin{array}{cc} 1 & 0 \\ 0 & 1 \end{array} & \begin{array}{c} C_2 \\ \rightarrow \\ i \\ S_{\infty} \end{array} & \begin{array}{cc} \varphi_1 & \varphi_2 \\ 0 & 1 \\ 1 & 0 \end{array}
 \end{array}$$

$$\chi = 2 \text{ (E, } C_{\infty}, \sigma_v)$$

$$\chi = 0$$

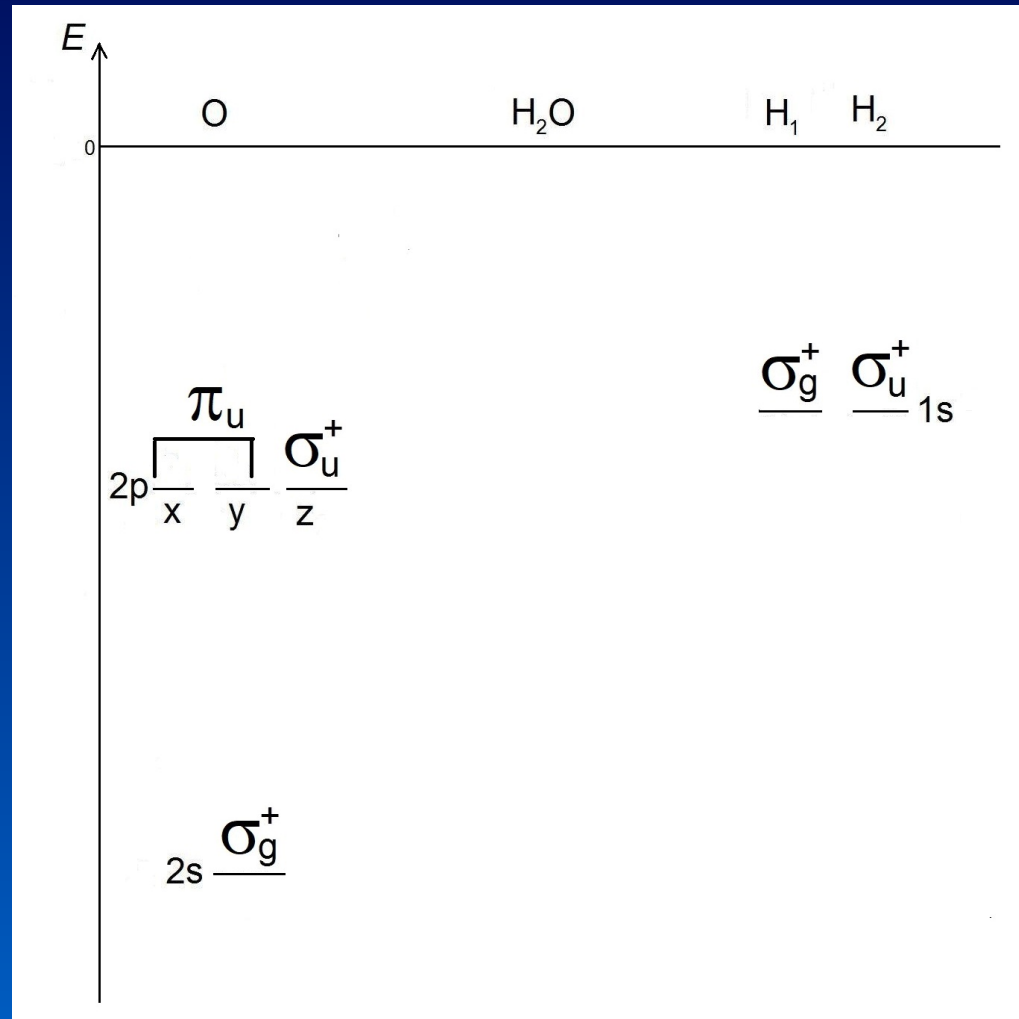
Água (linear) - $D_{\infty h}$

$D_{\infty h}$	E	$2C_{\infty}^{\varphi}$	$\infty\sigma_v$	i	$2S_{\infty}^{\varphi}$	∞C_2
Σ_g^+	1	1	1	1	1	1
Σ_g^-	1	1	-1	1	1	-1
Π_g	2	$2\cos\varphi$	0	2	$-2\cos\varphi$	0
Δ_g	2	$2\cos 2\varphi$	0	2	$2\cos 2\varphi$	0
Σ_u^+	1	1	1	-1	-1	-1
Σ_u^-	1	1	-1	-1	-1	1
Π_u	2	$2\cos\varphi$	0	-2	$2\cos\varphi$	0
Δ_u	2	$2\cos 2\varphi$	0	-2	$-2\cos 2\varphi$	0

φ_1, φ_2 2 2 2 0 0 0 $\Sigma_g^+ + \Sigma_u^+$

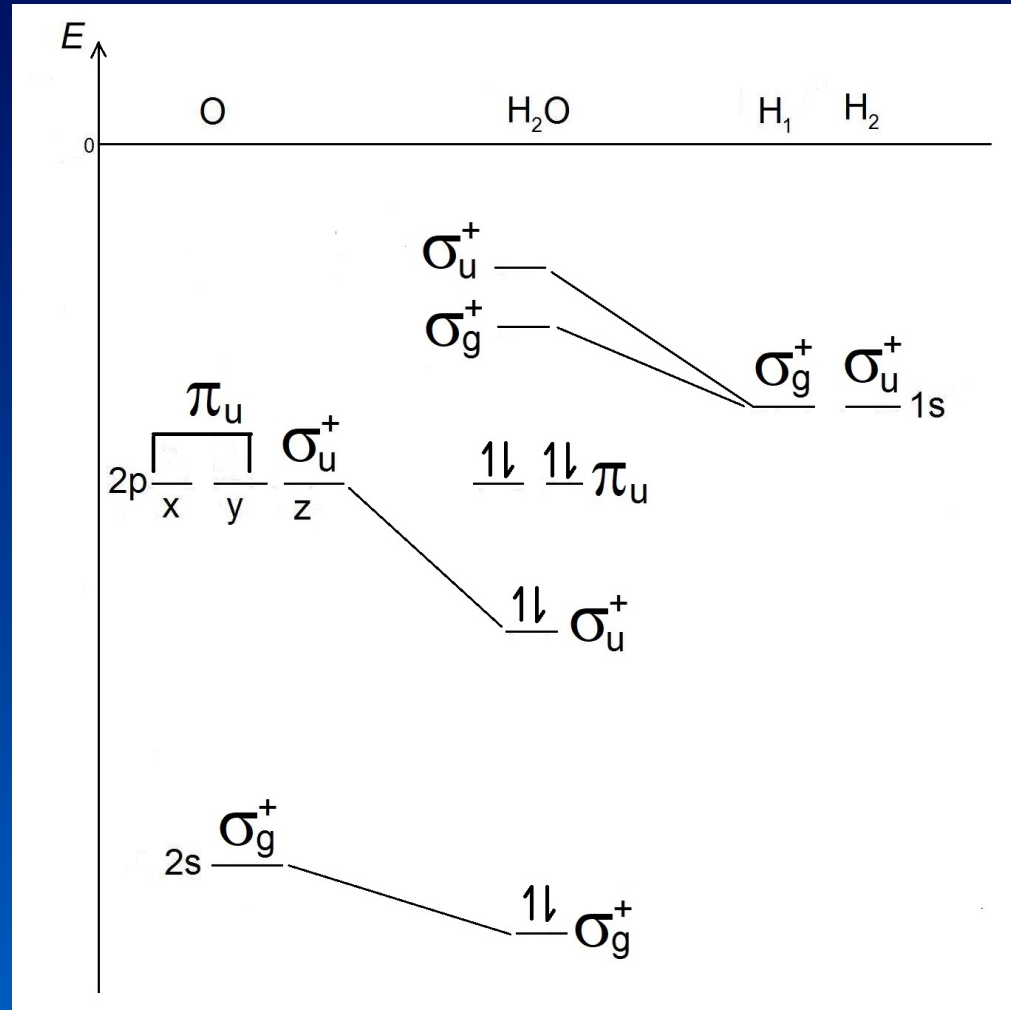
Água (linear) - $D_{\infty h}$

Construindo o diagrama de energia dos orbitais moleculares



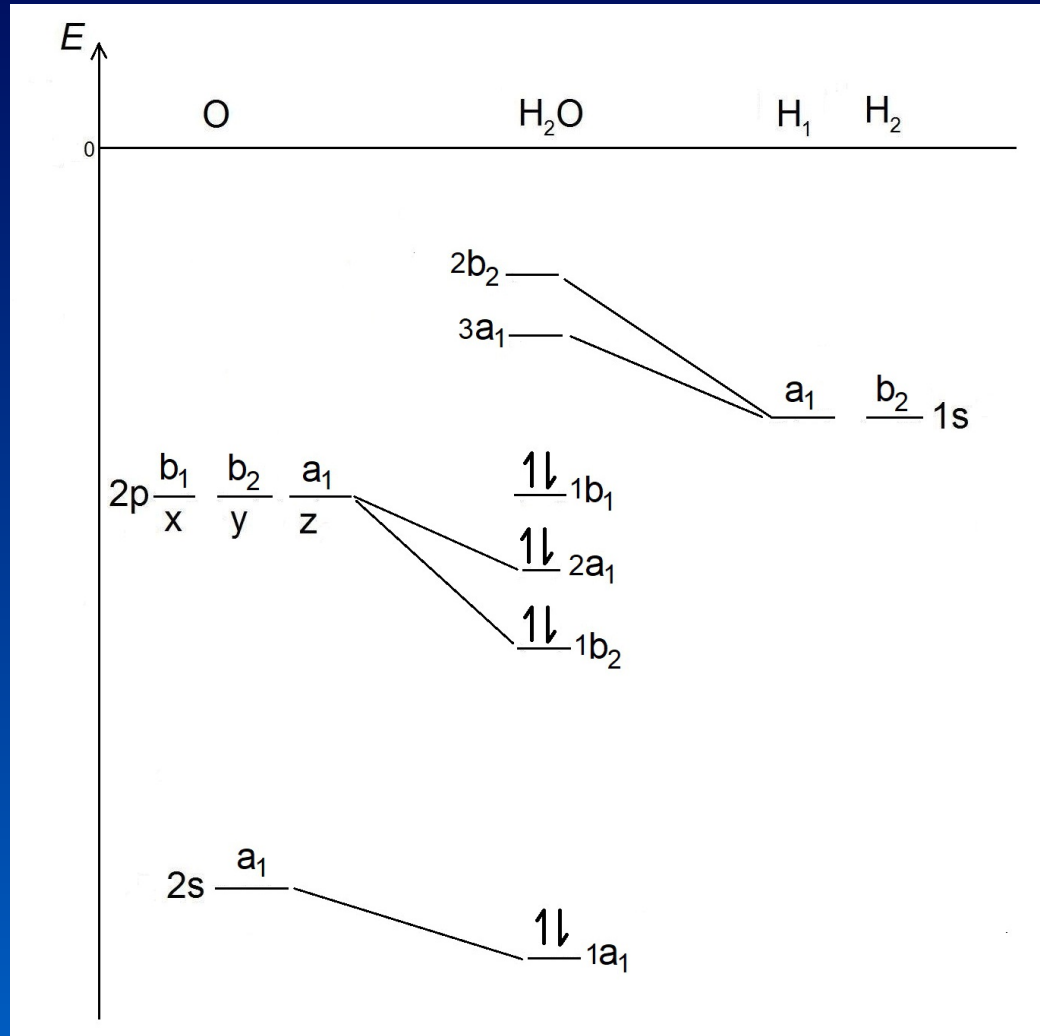
Água (linear) - $D_{\infty h}$

Construindo o diagrama de energia dos orbitais moleculares



Água (angular) - C_{2v}

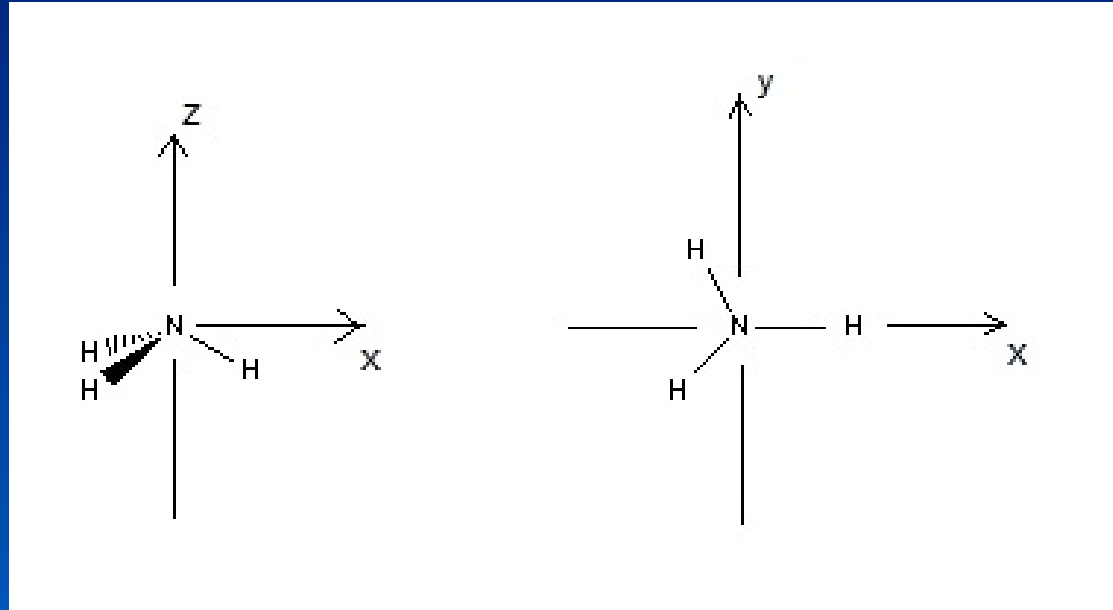
Construindo o diagrama de energia dos orbitais moleculares



Comparação água linear e angular

- Na água linear, dois pares de elétrons ficam na mesma energia dos orbitais 2p do oxigênio. São orbitais não ligantes.
- Na água angular, somente um par de elétrons fica com a mesma energia dos orbitais 2p do oxigênio (orbital não ligante). O outro par de elétrons, reduz de energia pois interage com os orbitais dos hidrogênios.

Amônia plana (D_{3h})
×
Amônia piramidal (C_{3v})

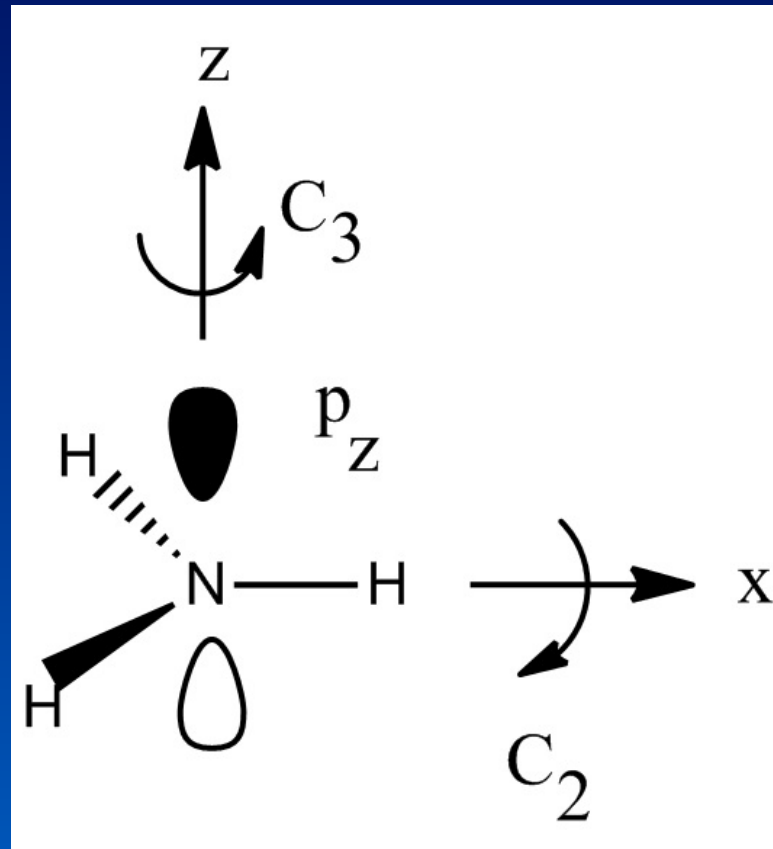


Amônia (plana) - D_{3h}

D_{3h}	E	$2C_3$	$3C_2$	σ_h	$2S_3$	$3\sigma_v$
A_1'	1	1	1	1	1	1
A_2'	1	1	-1	1	1	-1
E'	2	-1	0	2	-1	0
A_1''	1	1	1	-1	-1	-1
A_2''	1	1	-1	-1	-1	1
E''	2	-1	0	-2	1	0

Amônia (plana) - D_{3h}

Orbital $2p_z$

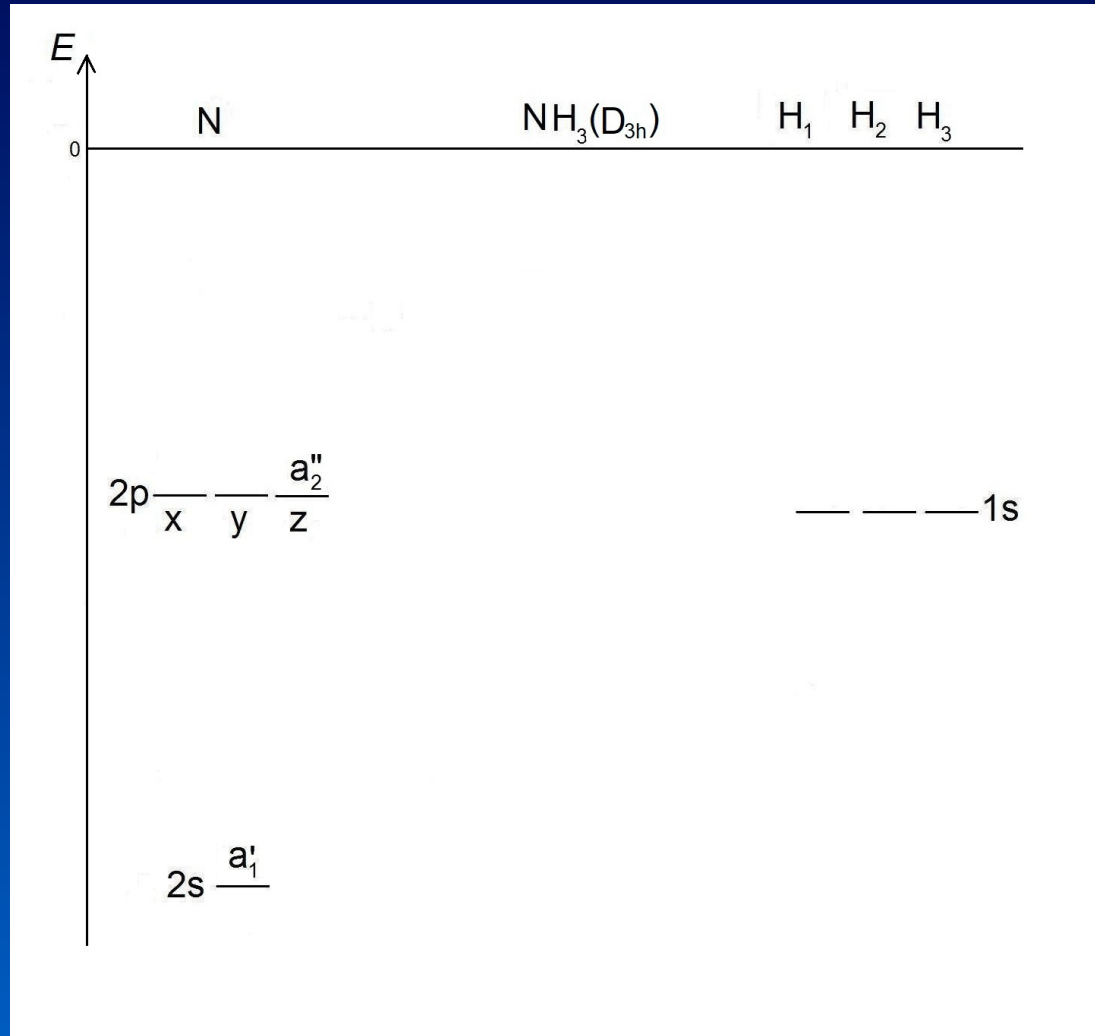


Amônia (plana) - D_{3h}

D_{3h}	E	$2C_3$	$3C_2$	σ_h	$2S_3$	$3\sigma_v$	
A_1'	1	1	1	1	1	1	
A_2'	1	1	-1	1	1	-1	
E'	2	-1	0	2	-1	0	
A_1''	1	1	1	-1	-1	-1	
A_2''	1	1	-1	-1	-1	1	
E''	2	-1	0	-2	1	0	
$2s$	1	1	1	1	1	1	A_1'
$2p_z$	1	1	-1	-1	-1	1	A_2''

Amônia plana - D_{3h}

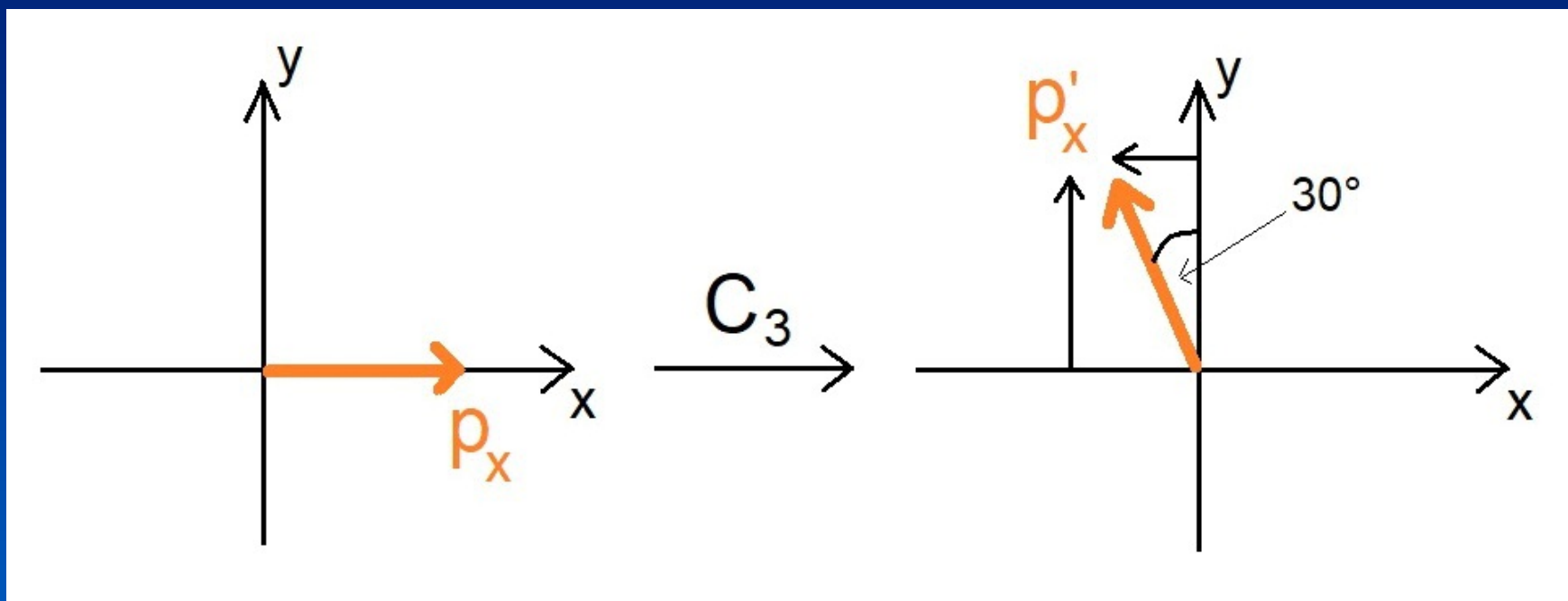
Diagrama de energia dos orbitais moleculares



Amônia plana - D_{3h}

Os orbitais p_x e p_y do N são **INSEPARÁVEIS**

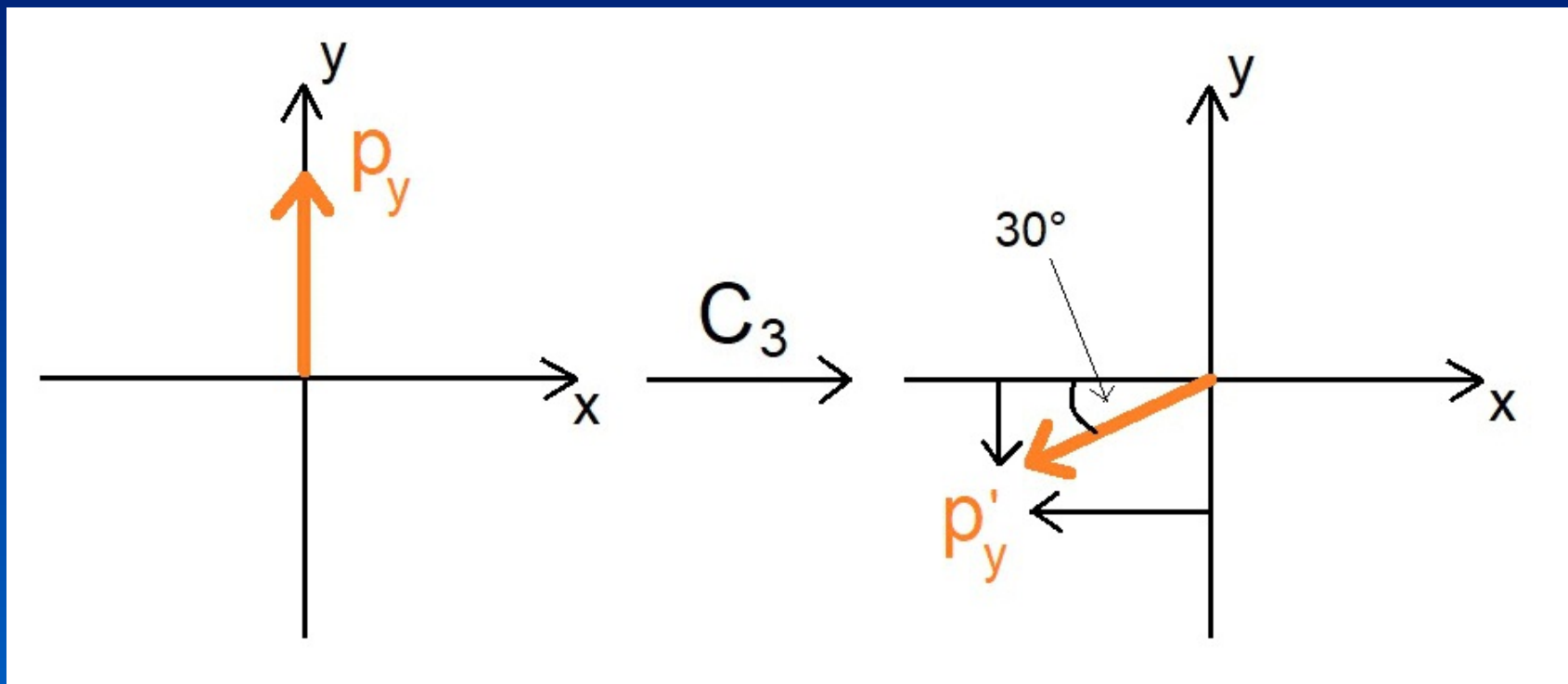
$$p_x' = -p_x \sin 30^\circ + p_y \cos 30^\circ = (-1/2)p_x + (\sqrt{3}/2)p_y$$



Amônia plana - D_{3h}

Os orbitais p_x e p_y do N são **INSEPARÁVEIS**

$$p_y' = -p_x \cos 30^\circ - p_y \sin 30^\circ = (-\sqrt{3}/2)p_x + (-1/2)p_y$$



Amônia plana - D_{3h}

Os orbitais $2p_x$ e $2p_y$ do N são INSEPARÁVEIS

$$\begin{array}{cc} & \begin{array}{c} 2p_x \\ 2p_y \end{array} \\ \begin{array}{c} 2p_x \\ 2p_y \end{array} & \begin{array}{cc} 1 & 0 \\ 0 & 1 \end{array} \end{array} \xrightarrow{C_3} \begin{array}{cc} & \begin{array}{c} 2p_x' \\ 2p_y' \end{array} \\ \begin{array}{c} 2p_x' \\ 2p_y' \end{array} & \begin{array}{cc} -1/2 & \sqrt{3}/2 \\ -\sqrt{3}/2 & -1/2 \end{array} \end{array}$$

$$\chi = -1$$

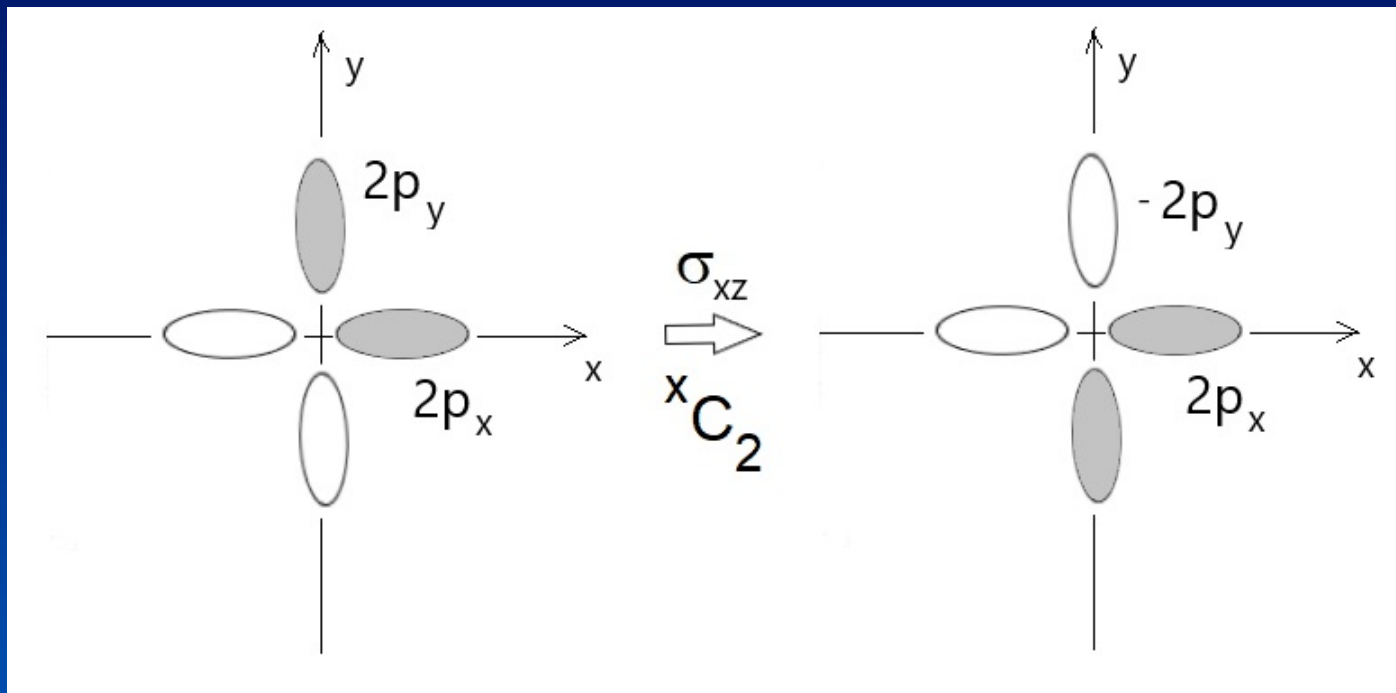
Amônia (plana) - D_{3h}

D_{3h}	E	$2C_3$	$3C_2$	σ_h	$2S_3$	$3\sigma_v$
A_1'	1	1	1	1	1	1
A_2'	1	1	-1	1	1	-1
E'	2	-1	0	2	-1	0
A_1''	1	1	1	-1	-1	-1
A_2''	1	1	-1	-1	-1	1
E''	2	-1	0	-2	1	0

(p_x, p_y) 2 -1

Amônia (plana) - D_{3h}

Orbitais $2p_x$ e $2p_y$



Amônia plana - D_{3h}

Os orbitais $2p_x$ e $2p_y$ do N são INSEPARÁVEIS

	$2p_x$	$2p_y$		$2p_x$	$2p_y$	
$2p_x$	1	0	$C_2^{(x)}$	$2p_x'$	1	0
$2p_y$	0	1	\rightarrow	$2p_y'$	0	-1
			$\sigma^{(xz)}$			

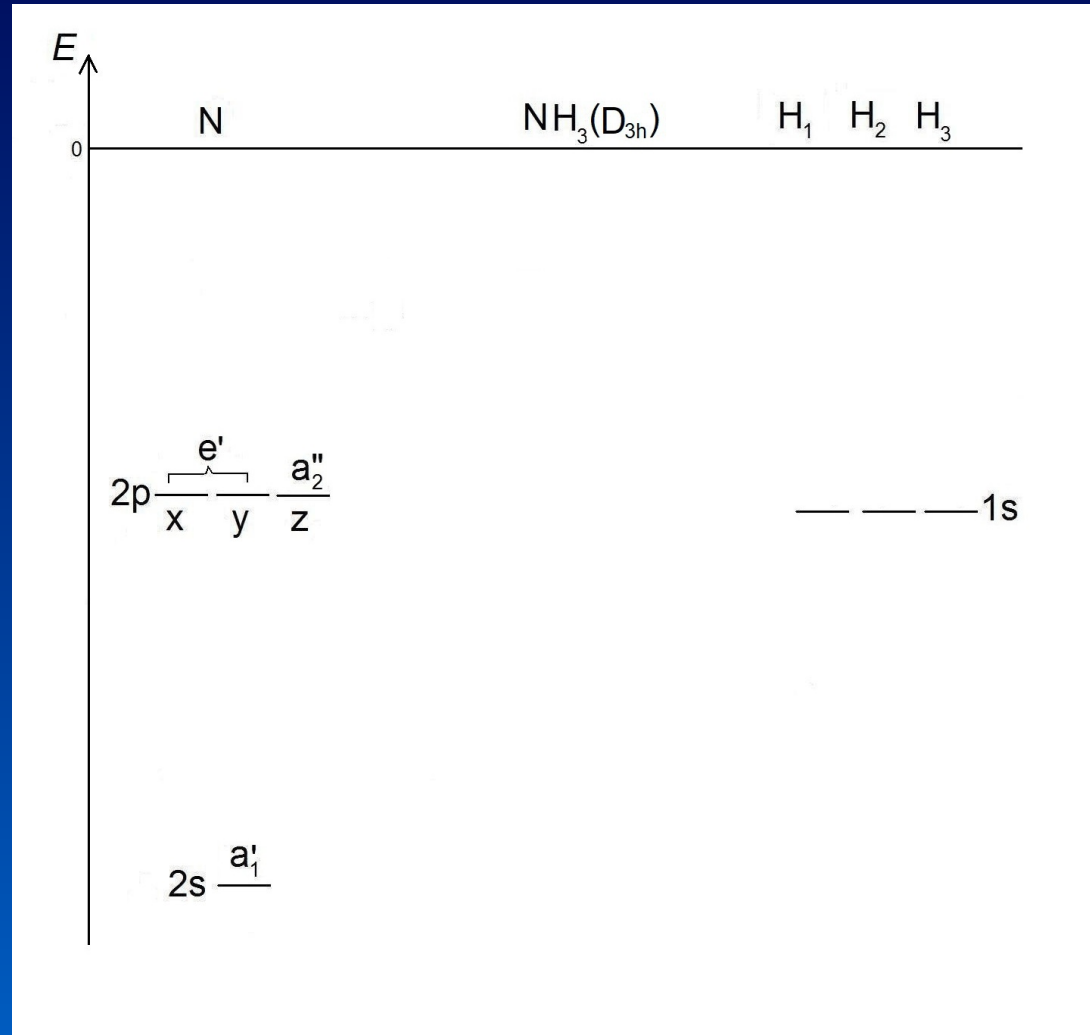
$\chi = 0$

Amônia (plana) - D_{3h}

D_{3h}	E	$2C_3$	$3C_2$	σ_h	$2S_3$	$3\sigma_v$	
A_1'	1	1	1	1	1	1	
A_2'	1	1	-1	1	1	-1	
E'	2	-1	0	2	-1	0	
A_1''	1	1	1	-1	-1	-1	
A_2''	1	1	-1	-1	-1	1	
E''	2	-1	0	-2	1	0	
<hr/>							
(p_x, p_y)	2	-1	0	2	-1	0	E'

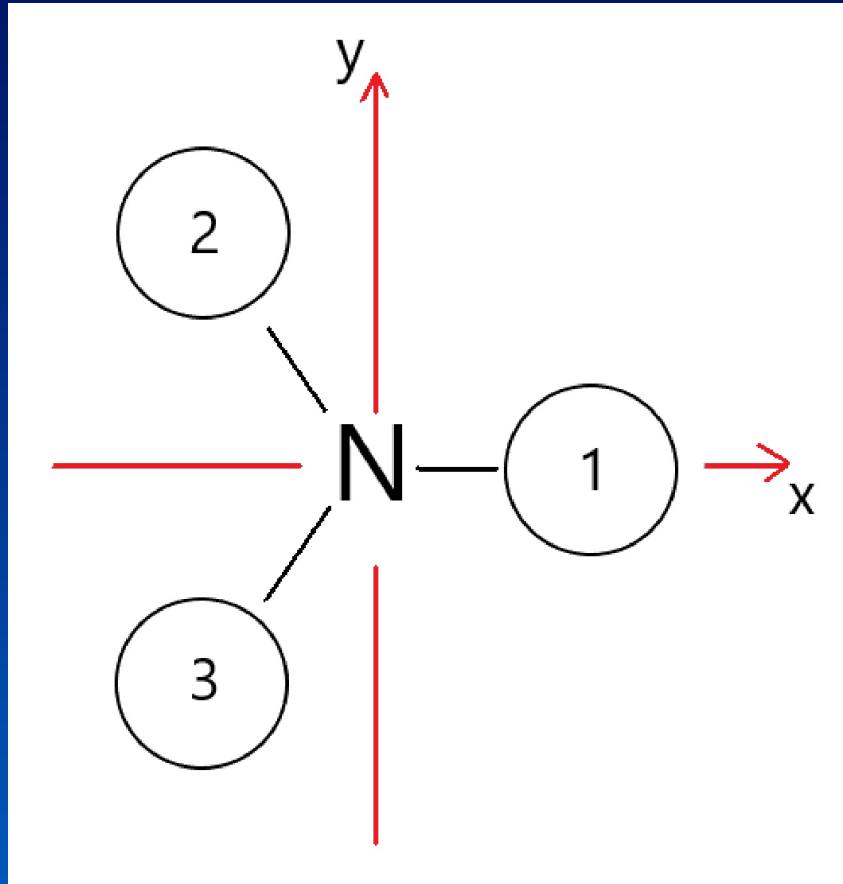
Amônia plana - D_{3h}

Diagrama de energia dos orbitais moleculares



Amônia (plana) - D_{3h}

Orbitais 1s dos H são INSEPARÁVEIS



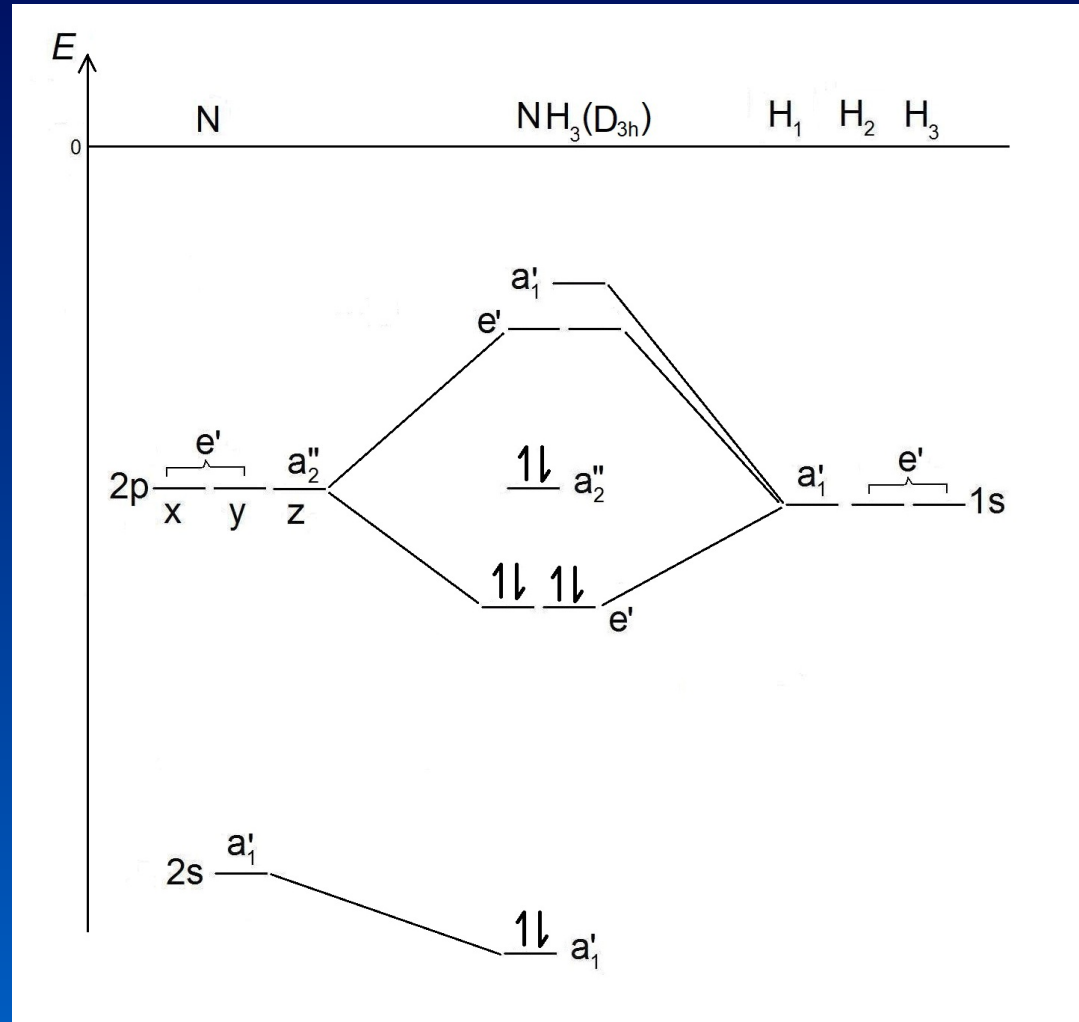
Amônia (plana) - D_{3h}

D_{3h}	E	$2C_3$	$3C_2$	σ_h	$2S_3$	$3\sigma_v$
A_1'	1	1	1	1	1	1
A_2'	1	1	-1	1	1	-1
E'	2	-1	0	2	-1	0
A_1''	1	1	1	-1	-1	-1
A_2''	1	1	-1	-1	-1	1
E''	2	-1	0	-2	1	0

(H_1, H_2, H_3) 3 0 1 3 0 1 $A_1' + E'$

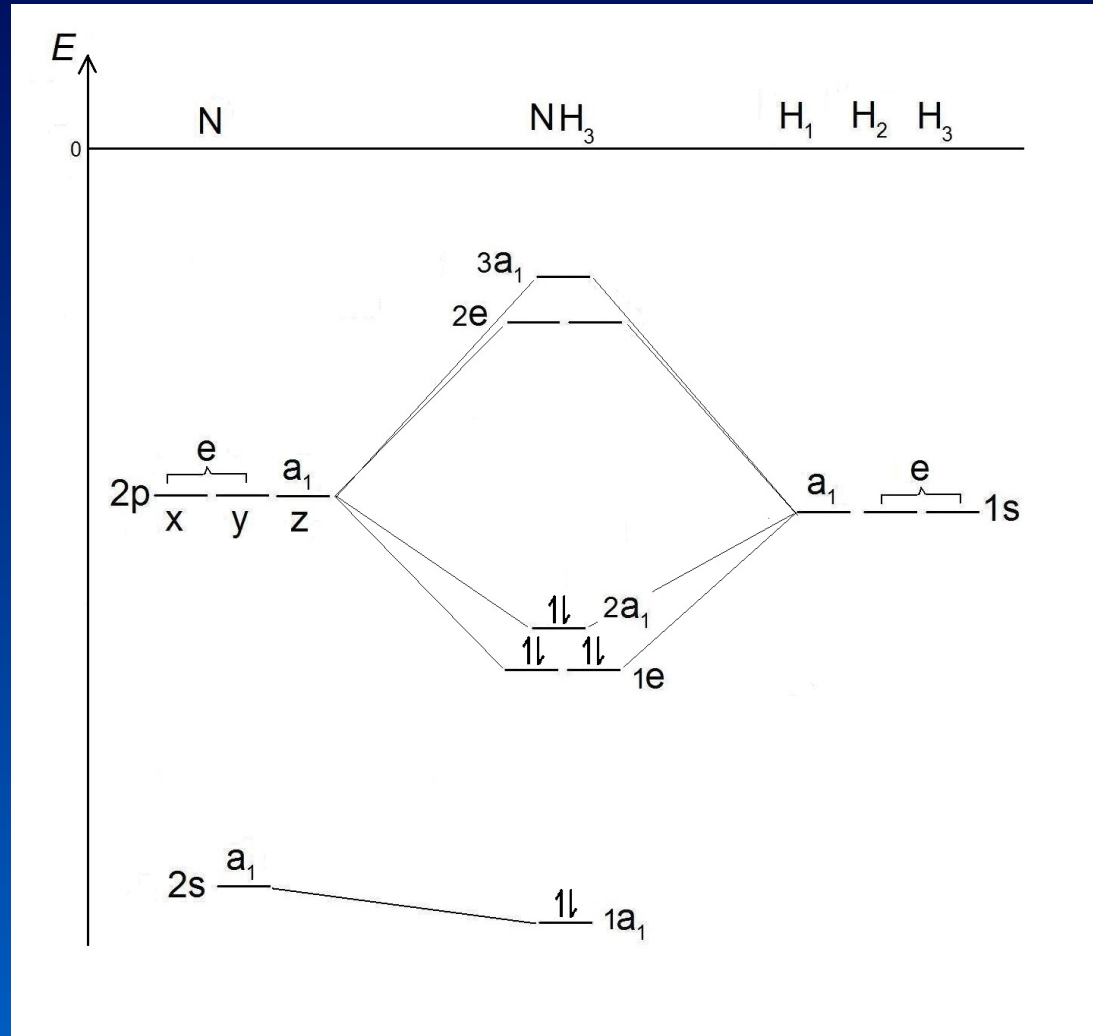
Amônia plana - D_{3h}

Diagrama de energia dos orbitais moleculares



Amônia piramidal - C_{3v}

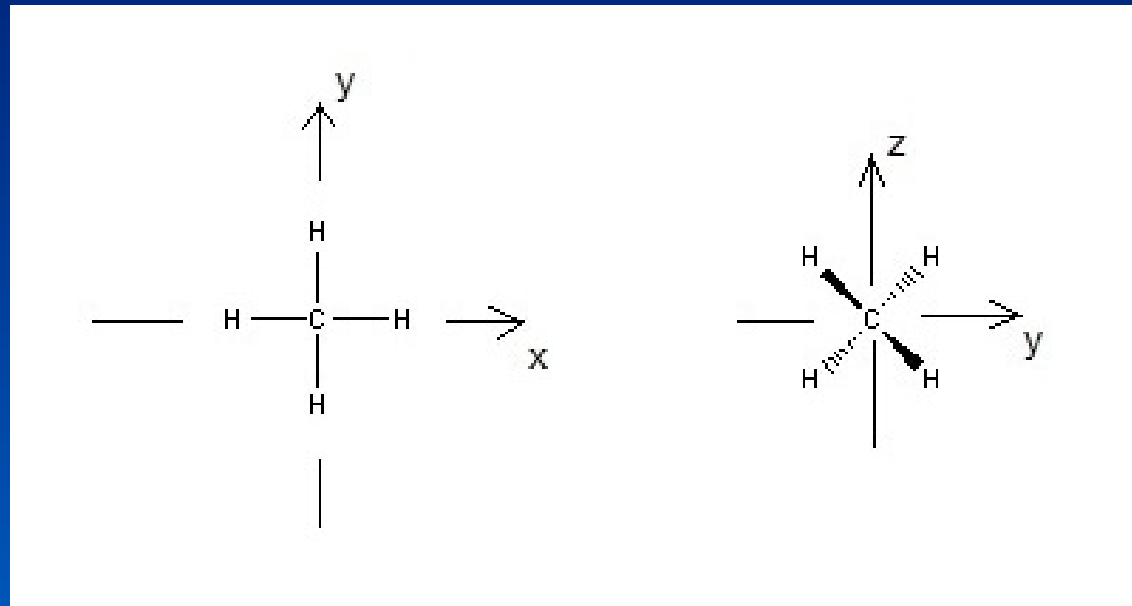
Diagrama de energia dos orbitais moleculares



Comparação amônia plana e piramidal

- Na amônia plana, um par de elétrons fica num orbital não ligante, que tem a mesma energia dos orbitais 2p do nitrogênio.
- Na amônia piramidal, não há pares de elétrons não ligantes, ficando a molécula, portanto, mais estável.

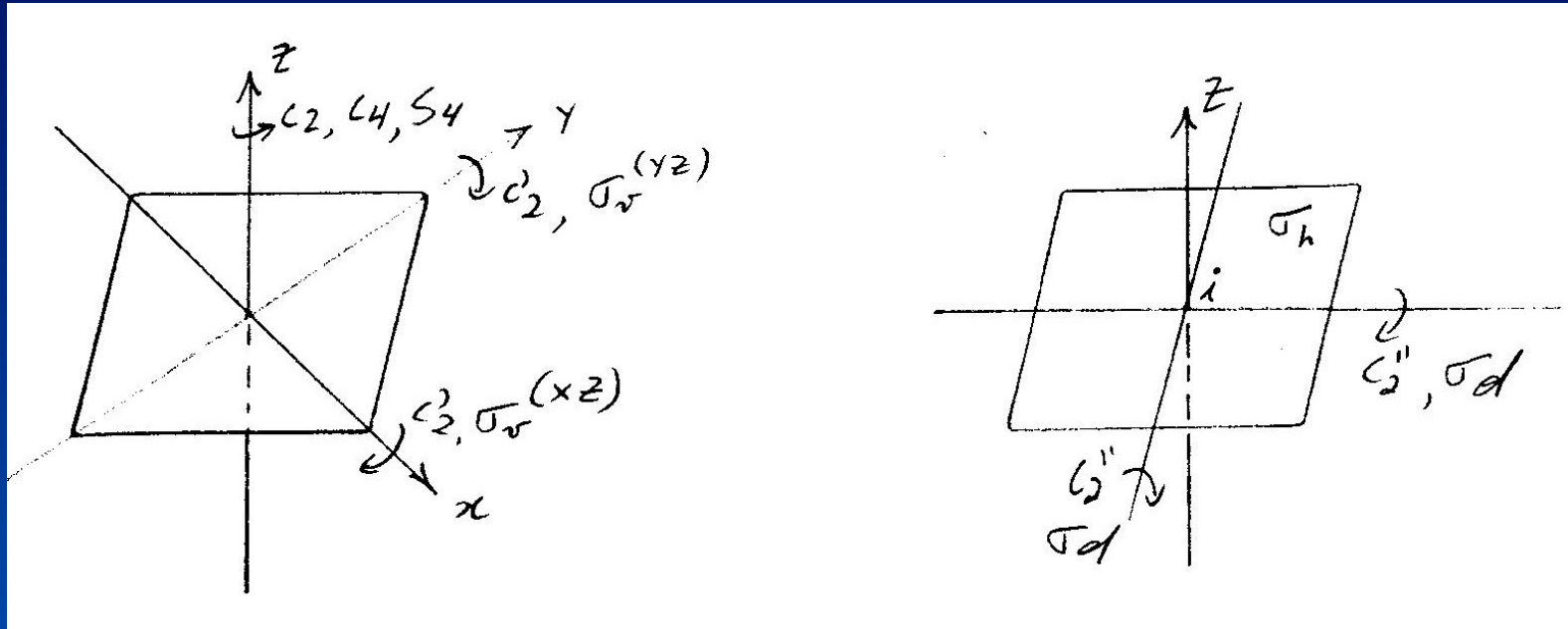
Metano plano (D_{4h})
×
Metano tetraédrico (T_d)



Metano plano - D_{4h}

D_{4h}	E	$2C_4$	C_2	$2C_2'$	$2C_2''$	i	$2S_4$	σ_h	$2\sigma_v$	$2\sigma_d$
A_{1g}	1	1	1	1	1	1	1	1	1	1
A_{2g}	1	1	1	-1	-1	1	1	1	-1	-1
B_{1g}	1	-1	1	1	-1	1	-1	1	1	-1
B_{2g}	1	-1	1	-1	1	1	-1	1	-1	1
E_g	2	0	-2	0	0	2	0	-2	0	0
A_{1u}	1	1	1	1	1	-1	-1	-1	-1	-1
A_{2u}	1	1	1	-1	-1	-1	-1	-1	1	1
B_{1u}	1	-1	1	1	-1	-1	1	-1	-1	1
B_{2u}	1	-1	1	-1	1	-1	1	-1	1	-1
E_u	2	0	-2	0	0	-2	0	2	0	0

Operações de simetria do D_{4h}

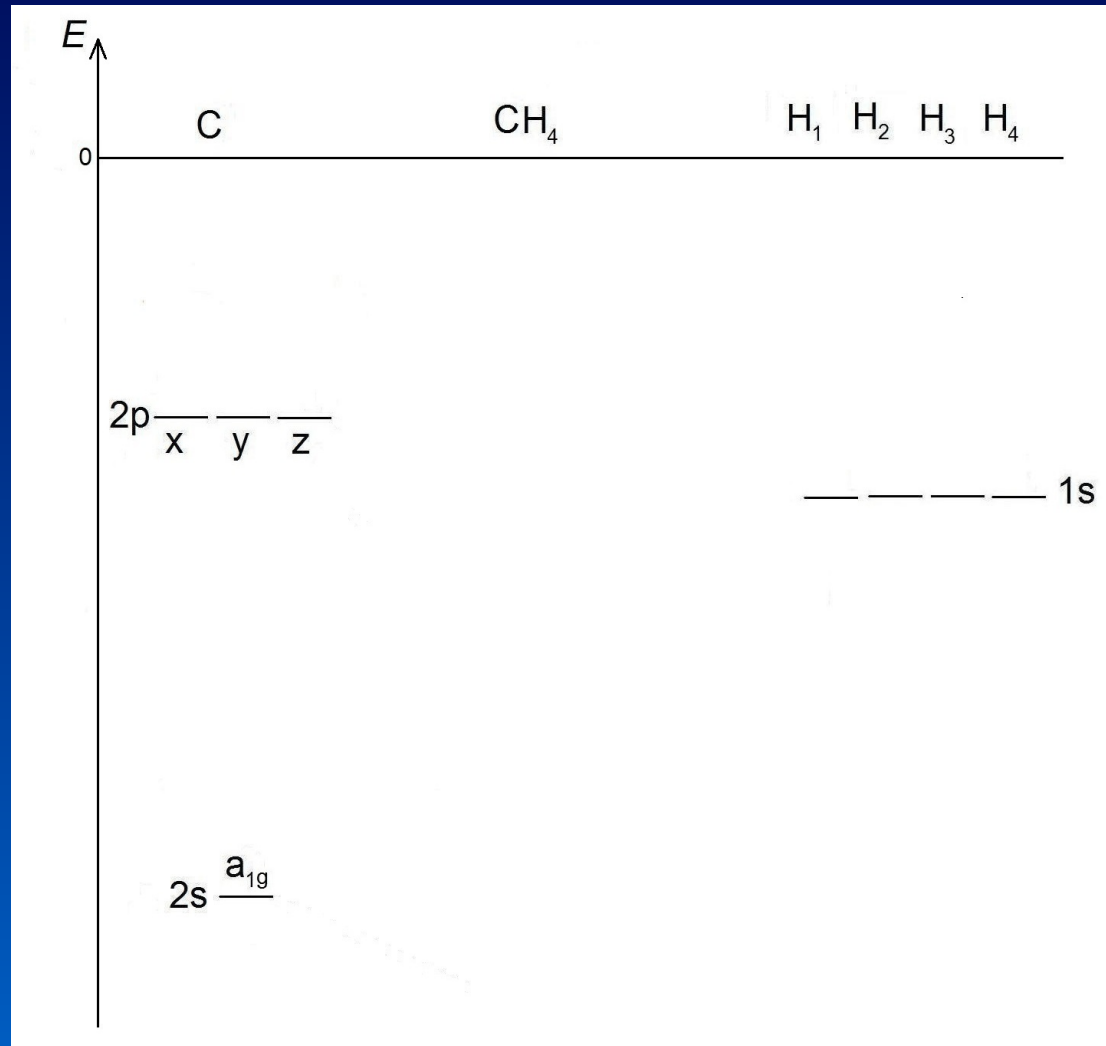


Classificando o orbital 2s do carbono

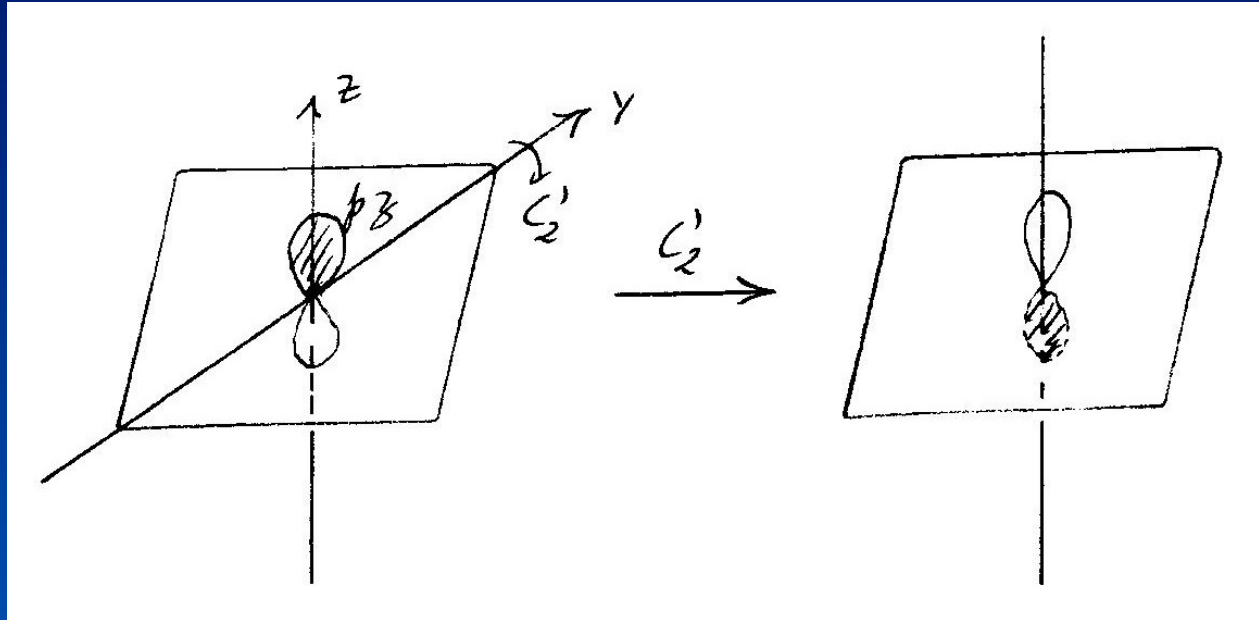
D_{4h}	E	$2C_4$	C_2	$2C_2'$	$2C_2''$	i	$2S_4$	σ_h	$2\sigma_v$	$2\sigma_d$	
A_{1g}	1	1	1	1	1	1	1	1	1	1	
A_{2g}	1	1	1	-1	-1	1	1	1	-1	-1	
B_{1g}	1	-1	1	1	-1	1	-1	1	1	-1	
B_{2g}	1	-1	1	-1	1	1	-1	1	-1	1	
E_g	2	0	-2	0	0	2	0	-2	0	0	
A_{1u}	1	1	1	1	1	-1	-1	-1	-1	-1	
A_{2u}	1	1	1	-1	-1	-1	-1	-1	1	1	
B_{1u}	1	-1	1	1	-1	-1	1	-1	-1	1	
B_{2u}	1	-1	1	-1	1	-1	1	-1	1	-1	
E_u	2	0	-2	0	0	-2	0	2	0	0	
<hr/>											
2s	1	1	1	1	1	1	1	1	1	1	A_{1g}

Metano plano - D_{4h}

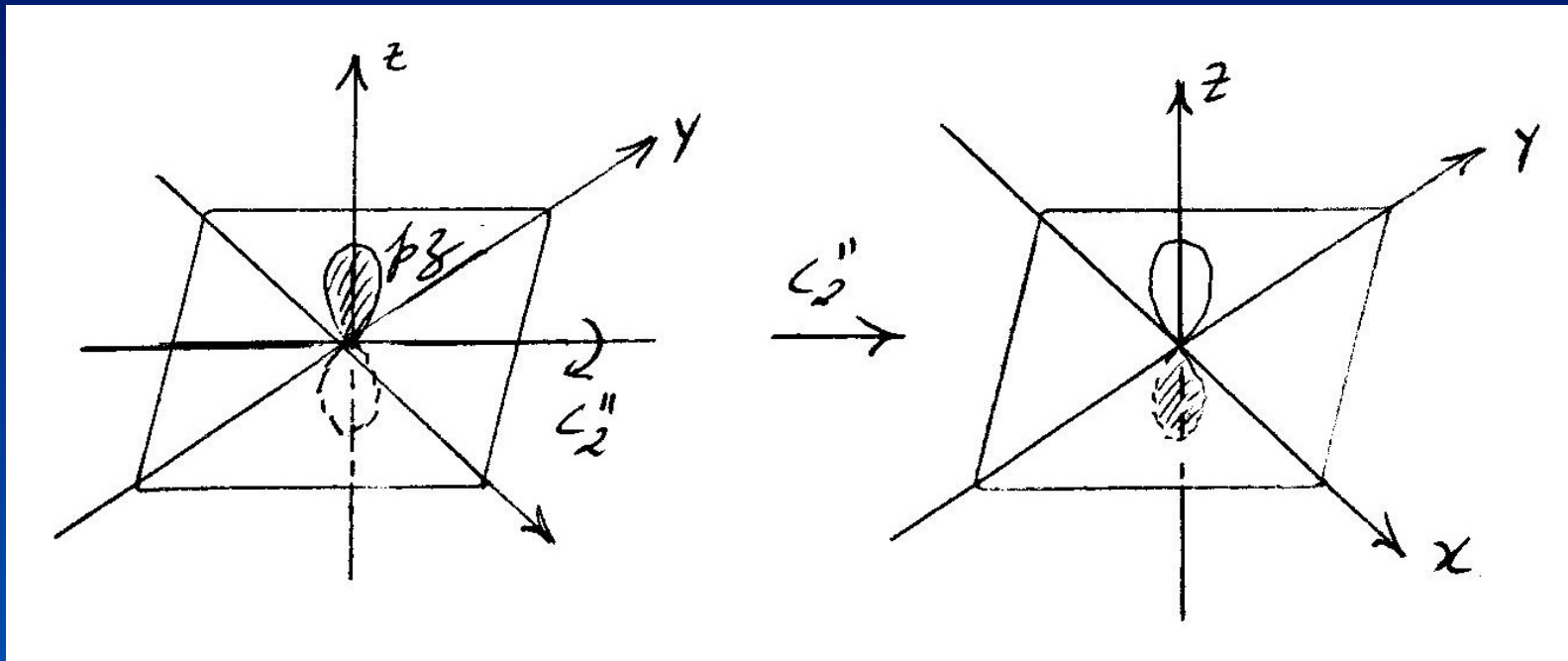
Diagrama de energia dos orbitais moleculares



Classificando o orbital $2p_z$ do carbono



Classificando o orbital $2p_z$ do carbono

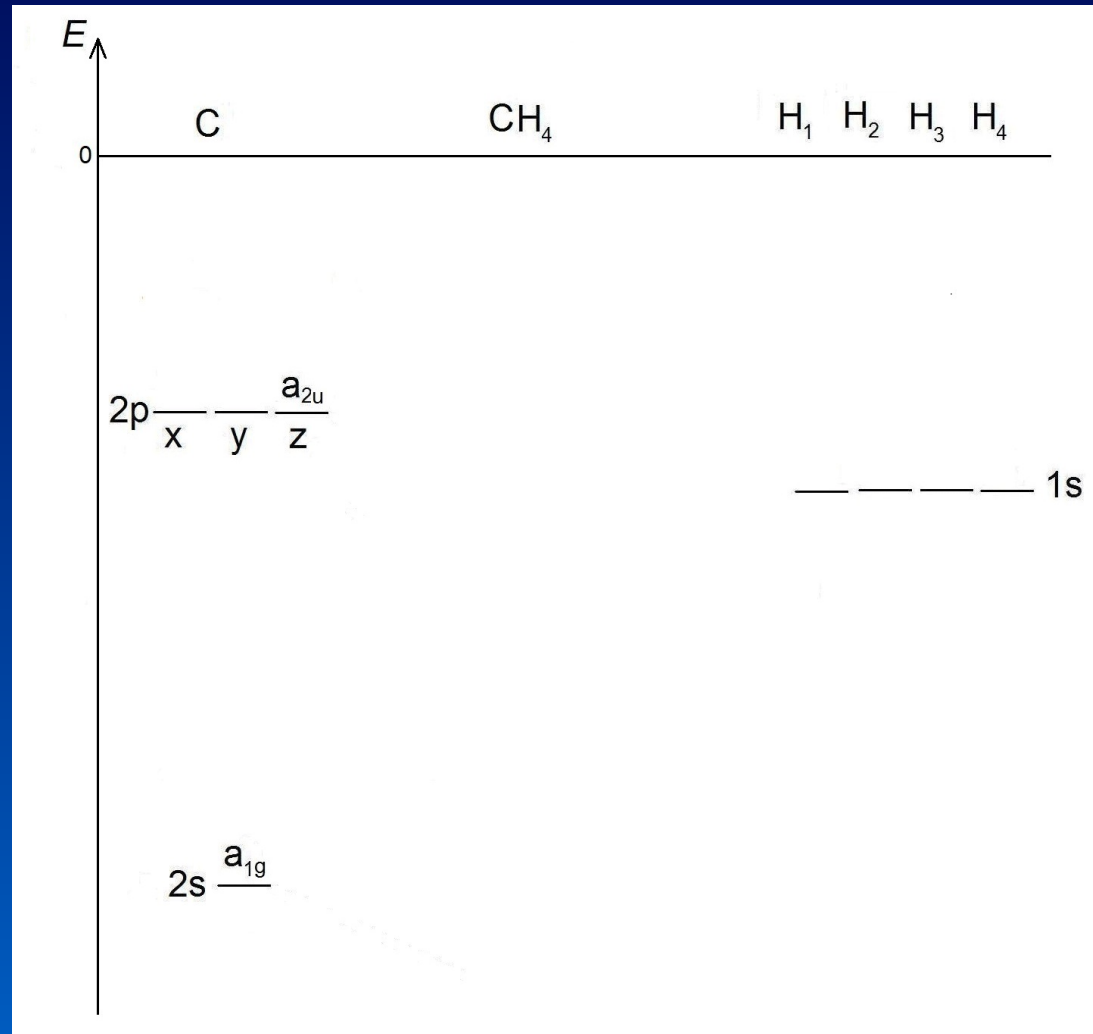


Classificando o orbital $2p_z$ do carbono

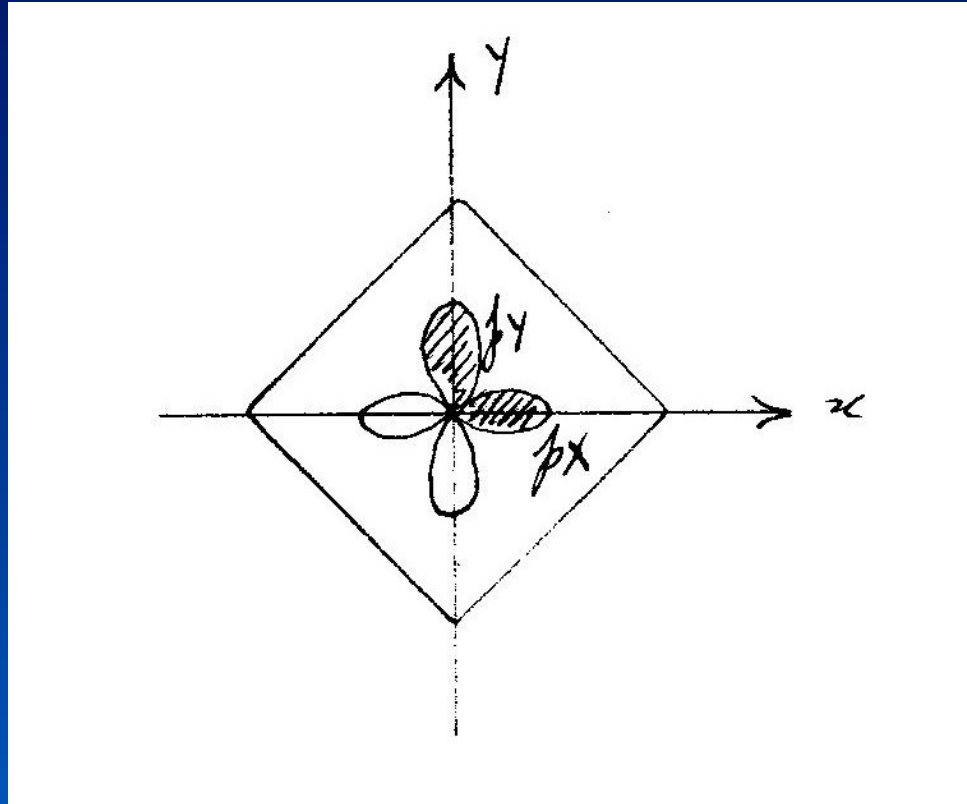
D_{4h}	E	$2C_4$	C_2	$2C_2'$	$2C_2''$	i	$2S_4$	σ_h	$2\sigma_v$	$2\sigma_d$	
A_{1g}	1	1	1	1	1	1	1	1	1	1	
A_{2g}	1	1	1	-1	-1	1	1	1	-1	-1	
B_{1g}	1	-1	1	1	-1	1	-1	1	1	-1	
B_{2g}	1	-1	1	-1	1	1	-1	1	-1	1	
E_g	2	0	-2	0	0	2	0	-2	0	0	
A_{1u}	1	1	1	1	1	-1	-1	-1	-1	-1	
A_{2u}	1	1	1	-1	-1	-1	-1	-1	1	1	
B_{1u}	1	-1	1	1	-1	-1	1	-1	-1	1	
B_{2u}	1	-1	1	-1	1	-1	1	-1	1	-1	
E_u	2	0	-2	0	0	-2	0	2	0	0	
$2p_z$	1	1	1	-1	-1	-1	-1	-1	1	1	A_{2u}

Metano plano - D_{4h}

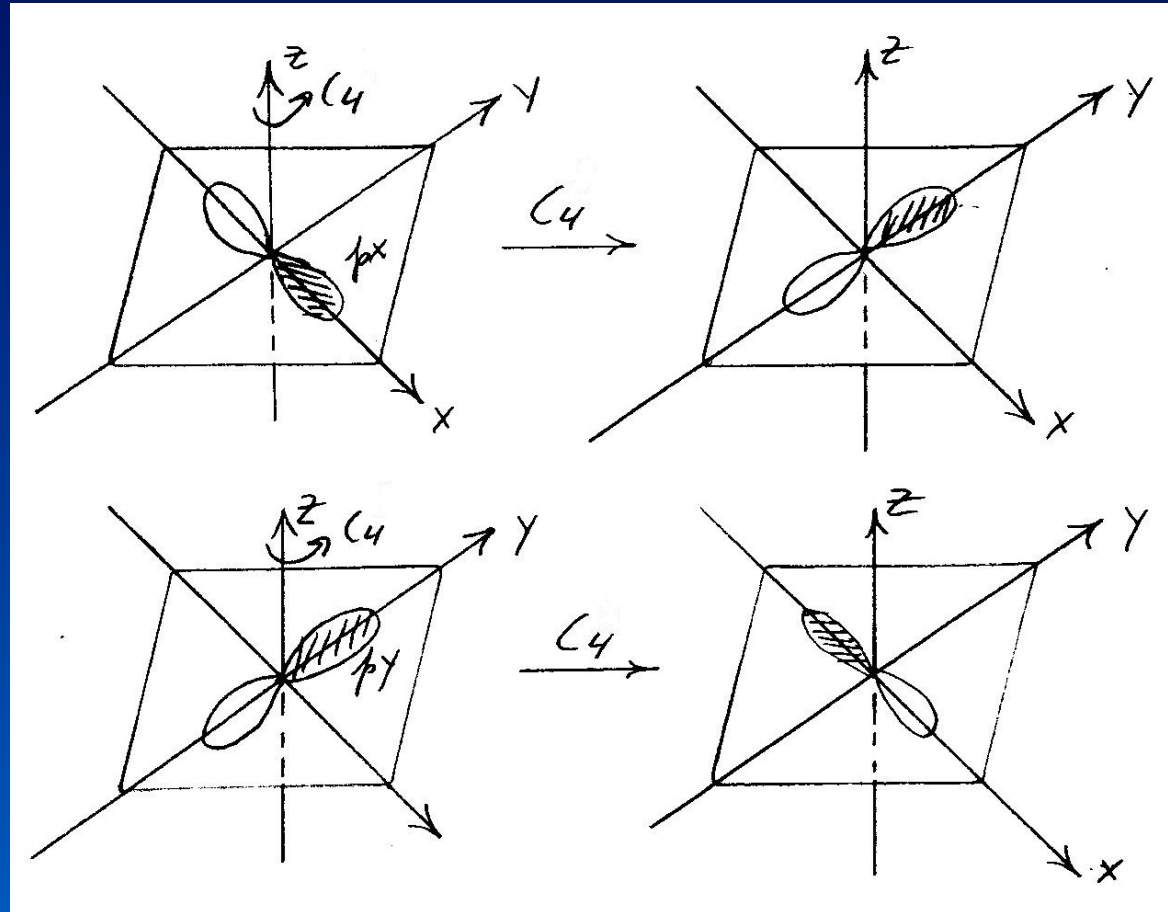
Diagrama de energia dos orbitais moleculares



Classificando os orbitais (inseparáveis) $2p_x$ e $2p_y$ do carbono



Classificando os orbitais (inseparáveis) $2p_x$ e $2p_y$ do carbono



Metano plano - D_{4h}

Os orbitais $2p_x$ e $2p_y$ do C são INSEPARÁVEIS

$$\begin{array}{cc} & \begin{array}{cc} 2p_x & 2p_y \end{array} \\ \begin{array}{c} 2p_x \\ 2p_y \end{array} & \begin{array}{cc} 1 & 0 \\ 0 & 1 \end{array} \end{array} \xrightarrow{C_4} \begin{array}{cc} & \begin{array}{cc} 2p_x' & 2p_y' \end{array} \\ \begin{array}{c} 2p_x' \\ 2p_y' \end{array} & \begin{array}{cc} 0 & 1 \\ -1 & 0 \end{array} \end{array}$$

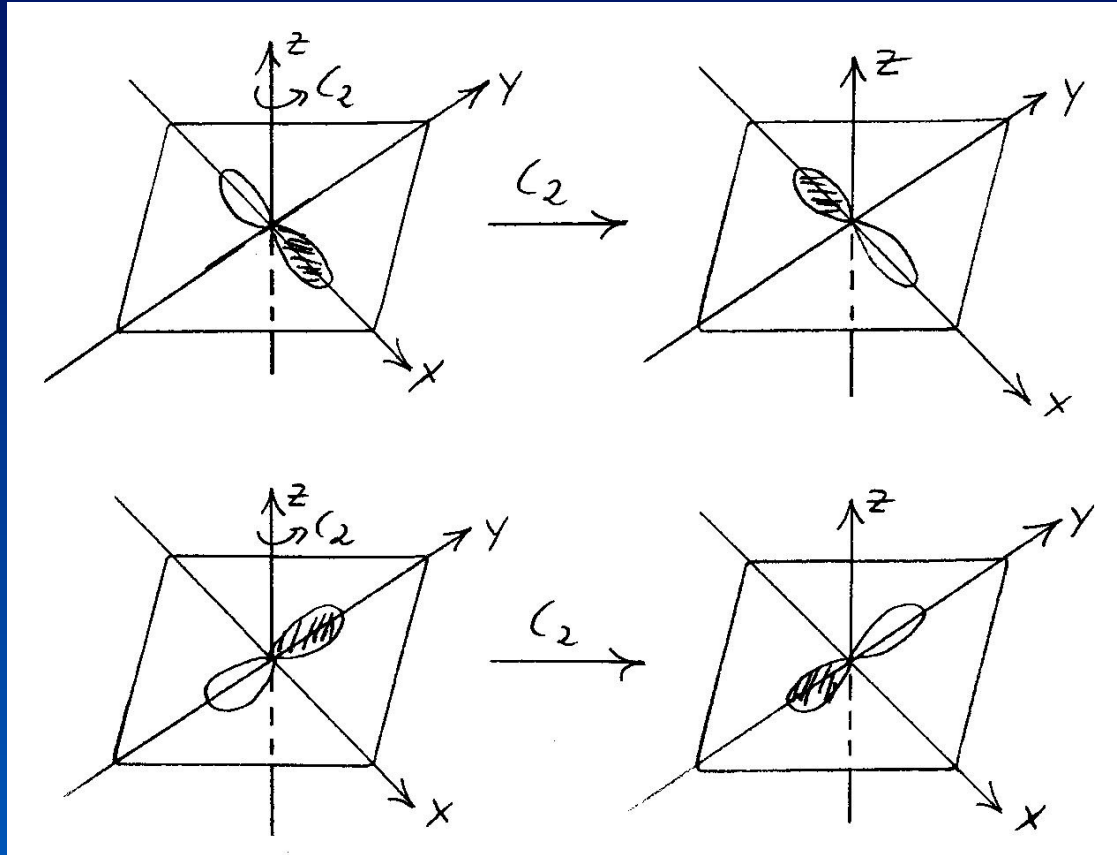
$$\chi = 0$$

Classificando os orbitais $2p_x$ e $2p_y$ do carbono

D_{4h}	E	$2C_4$	C_2	$2C_2'$	$2C_2''$	i	$2S_4$	σ_h	$2\sigma_v$	$2\sigma_d$
A_{1g}	1	1	1	1	1	1	1	1	1	1
A_{2g}	1	1	1	-1	-1	1	1	1	-1	-1
B_{1g}	1	-1	1	1	-1	1	-1	1	1	-1
B_{2g}	1	-1	1	-1	1	1	-1	1	-1	1
E_g	2	0	-2	0	0	2	0	-2	0	0
A_{1u}	1	1	1	1	1	-1	-1	-1	-1	-1
A_{2u}	1	1	1	-1	-1	-1	-1	-1	1	1
B_{1u}	1	-1	1	1	-1	-1	1	-1	-1	1
B_{2u}	1	-1	1	-1	1	-1	1	-1	1	-1
E_u	2	0	-2	0	0	-2	0	2	0	0

p_x, p_y 2 0

Classificando os orbitais (inseparáveis) $2p_x$ e $2p_y$ do carbono



Metano plano - D_{4h}

Os orbitais $2p_x$ e $2p_y$ do C são INSEPARÁVEIS

$$\begin{array}{cc} & \begin{array}{cc} 2p_x & 2p_y \end{array} \\ \begin{array}{c} 2p_x \\ 2p_y \end{array} & \begin{array}{cc} 1 & 0 \\ 0 & 1 \end{array} \end{array} \xrightarrow{C_2} \begin{array}{cc} & \begin{array}{cc} 2p_x' & 2p_y' \end{array} \\ \begin{array}{c} 2p_x' \\ 2p_y' \end{array} & \begin{array}{cc} -1 & 0 \\ 0 & -1 \end{array} \end{array}$$

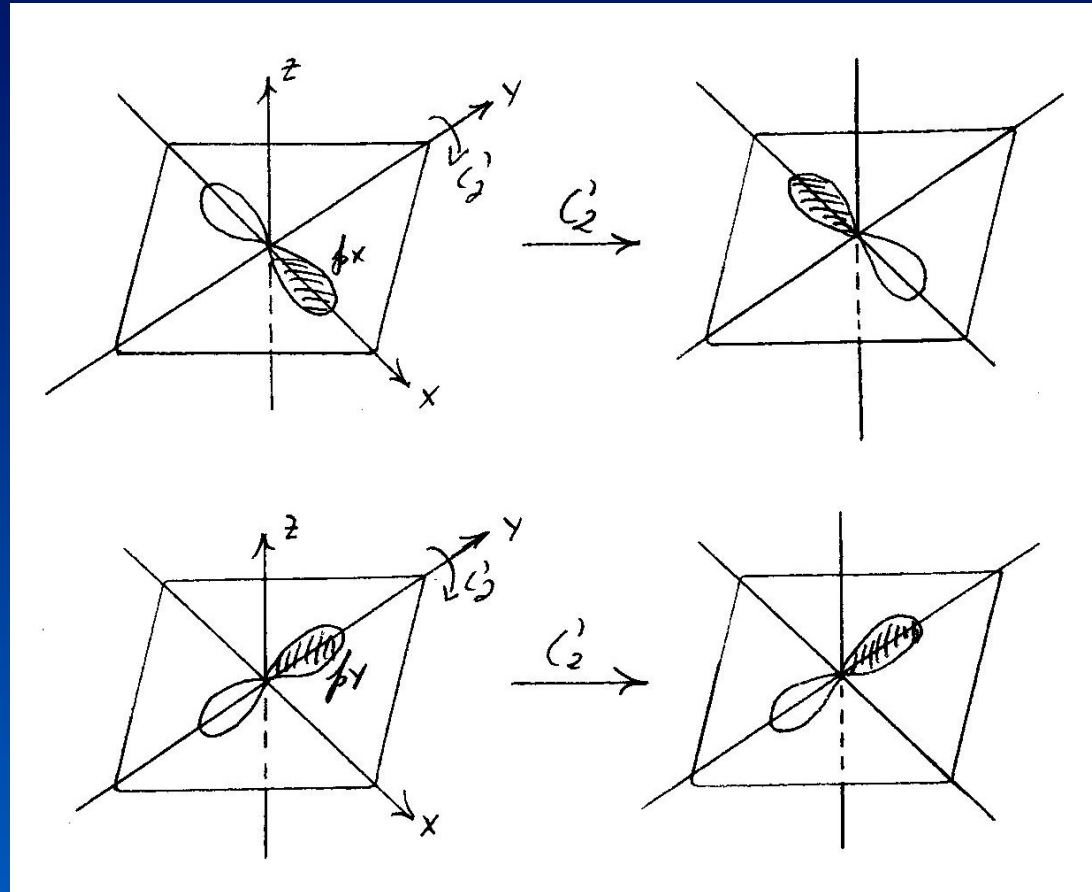
$$\chi = -2$$

Classificando os orbitais $2p_x$ e $2p_y$ do carbono

D_{4h}	E	$2C_4$	C_2	$2C_2'$	$2C_2''$	i	$2S_4$	σ_h	$2\sigma_v$	$2\sigma_d$
A_{1g}	1	1	1	1	1	1	1	1	1	1
A_{2g}	1	1	1	-1	-1	1	1	1	-1	-1
B_{1g}	1	-1	1	1	-1	1	-1	1	1	-1
B_{2g}	1	-1	1	-1	1	1	-1	1	-1	1
E_g	2	0	-2	0	0	2	0	-2	0	0
A_{1u}	1	1	1	1	1	-1	-1	-1	-1	-1
A_{2u}	1	1	1	-1	-1	-1	-1	-1	1	1
B_{1u}	1	-1	1	1	-1	-1	1	-1	-1	1
B_{2u}	1	-1	1	-1	1	-1	1	-1	1	-1
E_u	2	0	-2	0	0	-2	0	2	0	0

p_x, p_y 2 0 -2

Classificando os orbitais (inseparáveis) $2p_x$ e $2p_y$ do carbono



Metano plano - D_{4h}

Os orbitais $2p_x$ e $2p_y$ do C são INSEPARÁVEIS

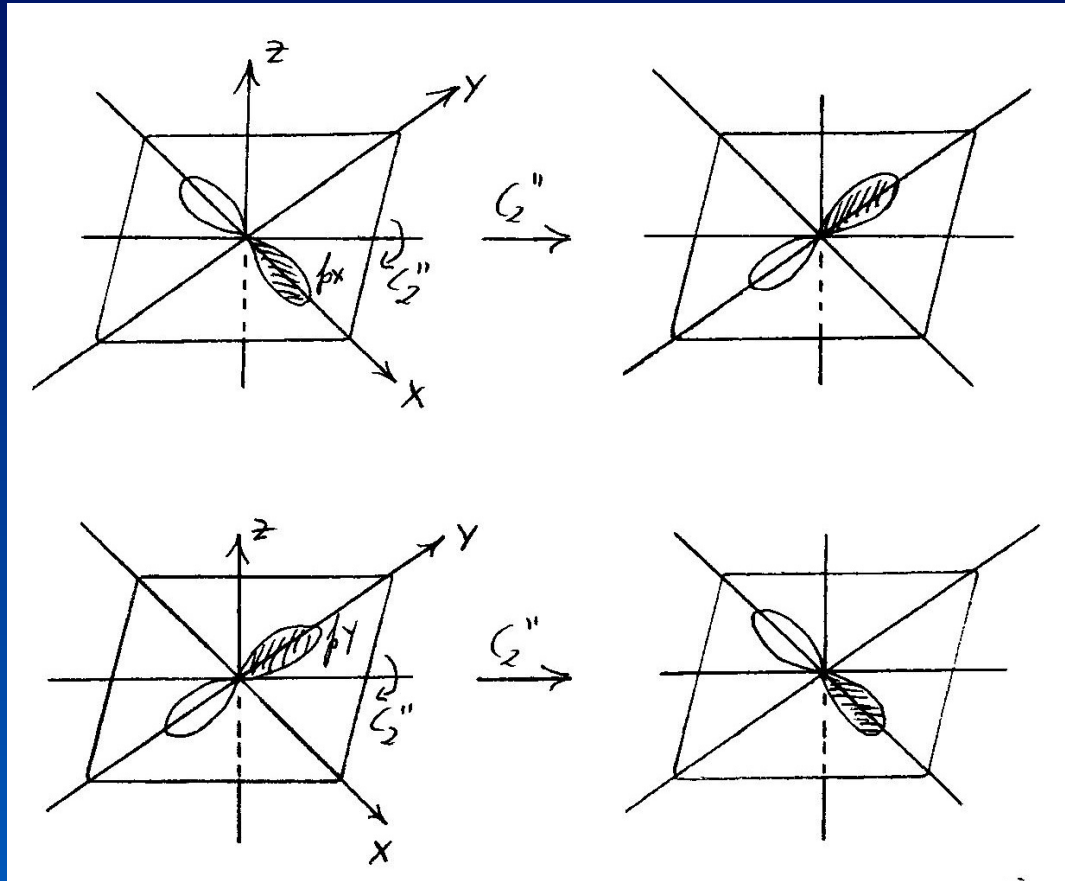
$$\begin{array}{cc} & \begin{array}{c} 2p_x \\ 2p_y \end{array} \\ \begin{array}{c} 2p_x \\ 2p_y \end{array} & \begin{array}{cc} 1 & 0 \\ 0 & 1 \end{array} \end{array} \xrightarrow{C_2'(y)} \begin{array}{cc} & \begin{array}{c} 2p_x' \\ 2p_y' \end{array} \\ \begin{array}{c} 2p_x' \\ 2p_y' \end{array} & \begin{array}{cc} -1 & 0 \\ 0 & 1 \end{array} \end{array}$$

$$\chi = 0$$

Classificando os orbitais $2p_x$ e $2p_y$ do carbono

D_{4h}	E	$2C_4$	C_2	$2C_2'$	$2C_2''$	i	$2S_4$	σ_h	$2\sigma_v$	$2\sigma_d$
A_{1g}	1	1	1	1	1	1	1	1	1	1
A_{2g}	1	1	1	-1	-1	1	1	1	-1	-1
B_{1g}	1	-1	1	1	-1	1	-1	1	1	-1
B_{2g}	1	-1	1	-1	1	1	-1	1	-1	1
E_g	2	0	-2	0	0	2	0	-2	0	0
A_{1u}	1	1	1	1	1	-1	-1	-1	-1	-1
A_{2u}	1	1	1	-1	-1	-1	-1	-1	1	1
B_{1u}	1	-1	1	1	-1	-1	1	-1	-1	1
B_{2u}	1	-1	1	-1	1	-1	1	-1	1	-1
E_u	2	0	-2	0	0	-2	0	2	0	0
p_x, p_y	2	0	-2	0						

Classificando os orbitais (inseparáveis) $2p_x$ e $2p_y$ do carbono



Metano plano - D_{4h}

Os orbitais $2p_x$ e $2p_y$ do C são INSEPARÁVEIS

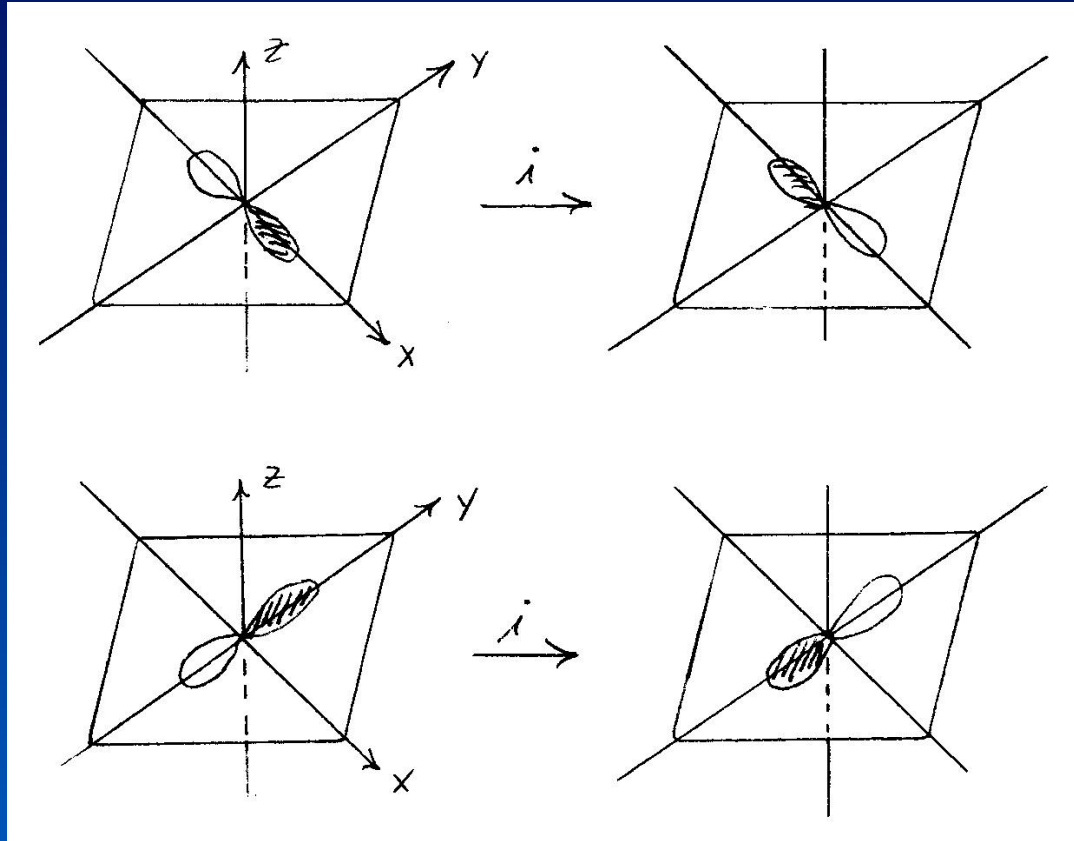
$$\begin{array}{cc} & \begin{array}{cc} 2p_x & 2p_y \end{array} \\ \begin{array}{c} 2p_x \\ 2p_y \end{array} & \begin{array}{cc} 1 & 0 \\ 0 & 1 \end{array} \end{array} \xrightarrow{C_2''} \begin{array}{cc} & \begin{array}{cc} 2p_x' & 2p_y' \end{array} \\ \begin{array}{c} 2p_x' \\ 2p_y' \end{array} & \begin{array}{cc} 0 & 1 \\ 1 & 0 \end{array} \end{array}$$

$$\chi = 0$$

Classificando os orbitais $2p_x$ e $2p_y$ do carbono

D_{4h}	E	$2C_4$	C_2	$2C_2'$	$2C_2''$	i	$2S_4$	σ_h	$2\sigma_v$	$2\sigma_d$
A_{1g}	1	1	1	1	1	1	1	1	1	1
A_{2g}	1	1	1	-1	-1	1	1	1	-1	-1
B_{1g}	1	-1	1	1	-1	1	-1	1	1	-1
B_{2g}	1	-1	1	-1	1	1	-1	1	-1	1
E_g	2	0	-2	0	0	2	0	-2	0	0
A_{1u}	1	1	1	1	1	-1	-1	-1	-1	-1
A_{2u}	1	1	1	-1	-1	-1	-1	-1	1	1
B_{1u}	1	-1	1	1	-1	-1	1	-1	-1	1
B_{2u}	1	-1	1	-1	1	-1	1	-1	1	-1
E_u	2	0	-2	0	0	-2	0	2	0	0
p_x, p_y	2	0	-2	0	0					

Classificando os orbitais (inseparáveis) $2p_x$ e $2p_y$ do carbono



Metano plano - D_{4h}

Os orbitais $2p_x$ e $2p_y$ do C são INSEPARÁVEIS

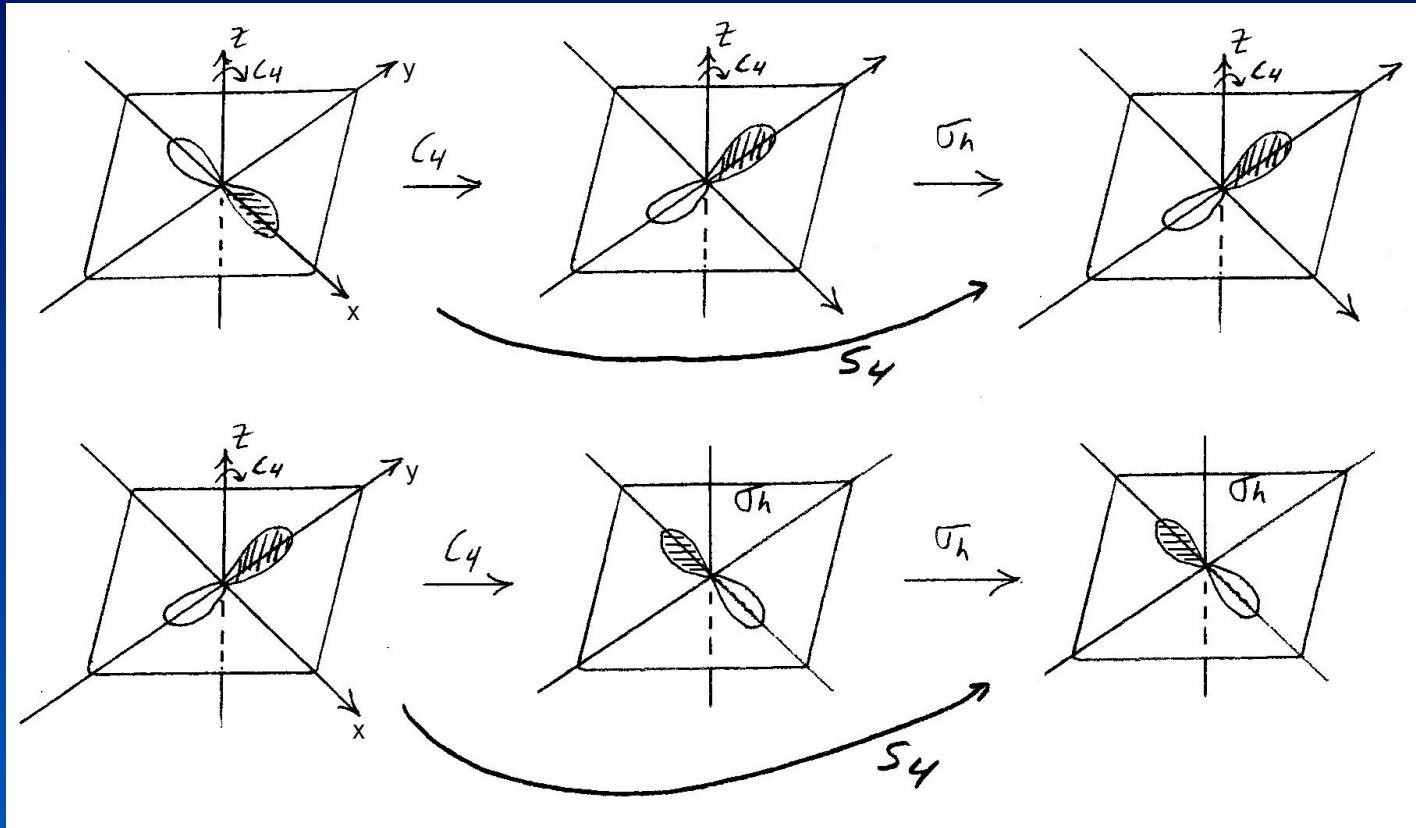
$$\begin{array}{cc} & \begin{array}{cc} 2p_x & 2p_y \end{array} \\ \begin{array}{c} 2p_x \\ 2p_y \end{array} & \begin{array}{cc} 1 & 0 \\ 0 & 1 \end{array} \end{array} \xrightarrow{i} \begin{array}{cc} & \begin{array}{cc} 2p_x' & 2p_y' \end{array} \\ \begin{array}{c} 2p_x' \\ 2p_y' \end{array} & \begin{array}{cc} -1 & 0 \\ 0 & -1 \end{array} \end{array}$$

$$\chi = -2$$

Classificando os orbitais $2p_x$ e $2p_y$ do carbono

D_{4h}	E	$2C_4$	C_2	$2C_2'$	$2C_2''$	i	$2S_4$	σ_h	$2\sigma_v$	$2\sigma_d$
A_{1g}	1	1	1	1	1	1	1	1	1	1
A_{2g}	1	1	1	-1	-1	1	1	1	-1	-1
B_{1g}	1	-1	1	1	-1	1	-1	1	1	-1
B_{2g}	1	-1	1	-1	1	1	-1	1	-1	1
E_g	2	0	-2	0	0	2	0	-2	0	0
A_{1u}	1	1	1	1	1	-1	-1	-1	-1	-1
A_{2u}	1	1	1	-1	-1	-1	-1	-1	1	1
B_{1u}	1	-1	1	1	-1	-1	1	-1	-1	1
B_{2u}	1	-1	1	-1	1	-1	1	-1	1	-1
E_u	2	0	-2	0	0	-2	0	2	0	0
p_x, p_y	2	0	-2	0	0	-2				

Classificando os orbitais (inseparáveis) $2p_x$ e $2p_y$ do carbono



Metano plano - D_{4h}

Os orbitais $2p_x$ e $2p_y$ do C são INSEPARÁVEIS

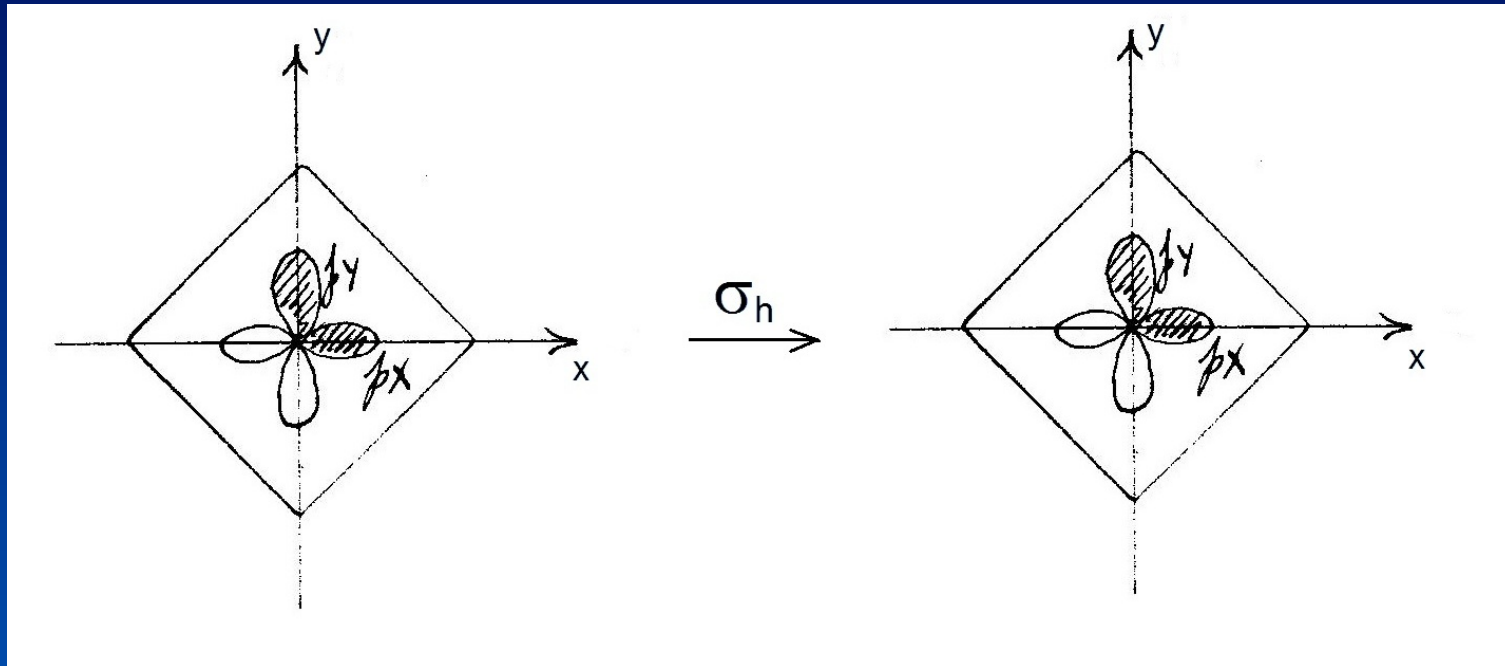
$$\begin{array}{cc} & \begin{array}{cc} 2p_x & 2p_y \end{array} \\ \begin{array}{c} 2p_x \\ 2p_y \end{array} & \begin{array}{cc} 1 & 0 \\ 0 & 1 \end{array} \end{array} \xrightarrow{S_4} \begin{array}{cc} & \begin{array}{cc} 2p_x' & 2p_y' \end{array} \\ \begin{array}{c} 2p_x' \\ 2p_y' \end{array} & \begin{array}{cc} 0 & 1 \\ -1 & 0 \end{array} \end{array}$$

$$\chi = 0$$

Classificando os orbitais $2p_x$ e $2p_y$ do carbono

D_{4h}	E	$2C_4$	C_2	$2C_2'$	$2C_2''$	i	$2S_4$	σ_h	$2\sigma_v$	$2\sigma_d$
A_{1g}	1	1	1	1	1	1	1	1	1	1
A_{2g}	1	1	1	-1	-1	1	1	1	-1	-1
B_{1g}	1	-1	1	1	-1	1	-1	1	1	-1
B_{2g}	1	-1	1	-1	1	1	-1	1	-1	1
E_g	2	0	-2	0	0	2	0	-2	0	0
A_{1u}	1	1	1	1	1	-1	-1	-1	-1	-1
A_{2u}	1	1	1	-1	-1	-1	-1	-1	1	1
B_{1u}	1	-1	1	1	-1	-1	1	-1	-1	1
B_{2u}	1	-1	1	-1	1	-1	1	-1	1	-1
E_u	2	0	-2	0	0	-2	0	2	0	0
p_x, p_y	2	0	-2	0	0	-2	0			

Classificando os orbitais (inseparáveis) $2p_x$ e $2p_y$ do carbono



Metano plano - D_{4h}

Os orbitais $2p_x$ e $2p_y$ do C são INSEPARÁVEIS

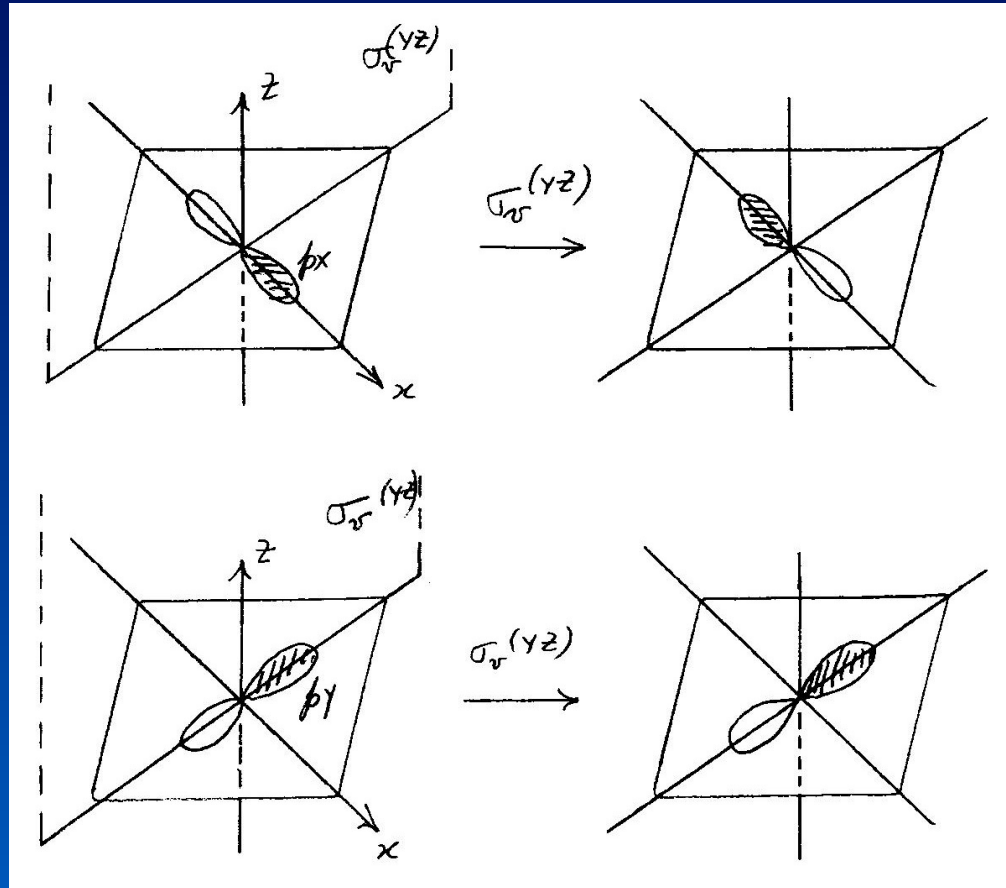
$$\begin{array}{cc} & \begin{array}{cc} 2p_x & 2p_y \end{array} \\ \begin{array}{c} 2p_x \\ 2p_y \end{array} & \begin{array}{cc} 1 & 0 \\ 0 & 1 \end{array} \end{array} \xrightarrow{\sigma_h} \begin{array}{cc} & \begin{array}{cc} 2p_x' & 2p_y' \end{array} \\ \begin{array}{c} 2p_x' \\ 2p_y' \end{array} & \begin{array}{cc} 1 & 0 \\ 0 & 1 \end{array} \end{array}$$

$$\chi = 2$$

Classificando os orbitais $2p_x$ e $2p_y$ do carbono

D_{4h}	E	$2C_4$	C_2	$2C_2'$	$2C_2''$	i	$2S_4$	σ_h	$2\sigma_v$	$2\sigma_d$
A_{1g}	1	1	1	1	1	1	1	1	1	1
A_{2g}	1	1	1	-1	-1	1	1	1	-1	-1
B_{1g}	1	-1	1	1	-1	1	-1	1	1	-1
B_{2g}	1	-1	1	-1	1	1	-1	1	-1	1
E_g	2	0	-2	0	0	2	0	-2	0	0
A_{1u}	1	1	1	1	1	-1	-1	-1	-1	-1
A_{2u}	1	1	1	-1	-1	-1	-1	-1	1	1
B_{1u}	1	-1	1	1	-1	-1	1	-1	-1	1
B_{2u}	1	-1	1	-1	1	-1	1	-1	1	-1
E_u	2	0	-2	0	0	-2	0	2	0	0
p_x, p_y	2	0	-2	0	0	-2	0	2		

Classificando os orbitais (inseparáveis) $2p_x$ e $2p_y$ do carbono



Metano plano - D_{4h}

Os orbitais $2p_x$ e $2p_y$ do C são INSEPARÁVEIS

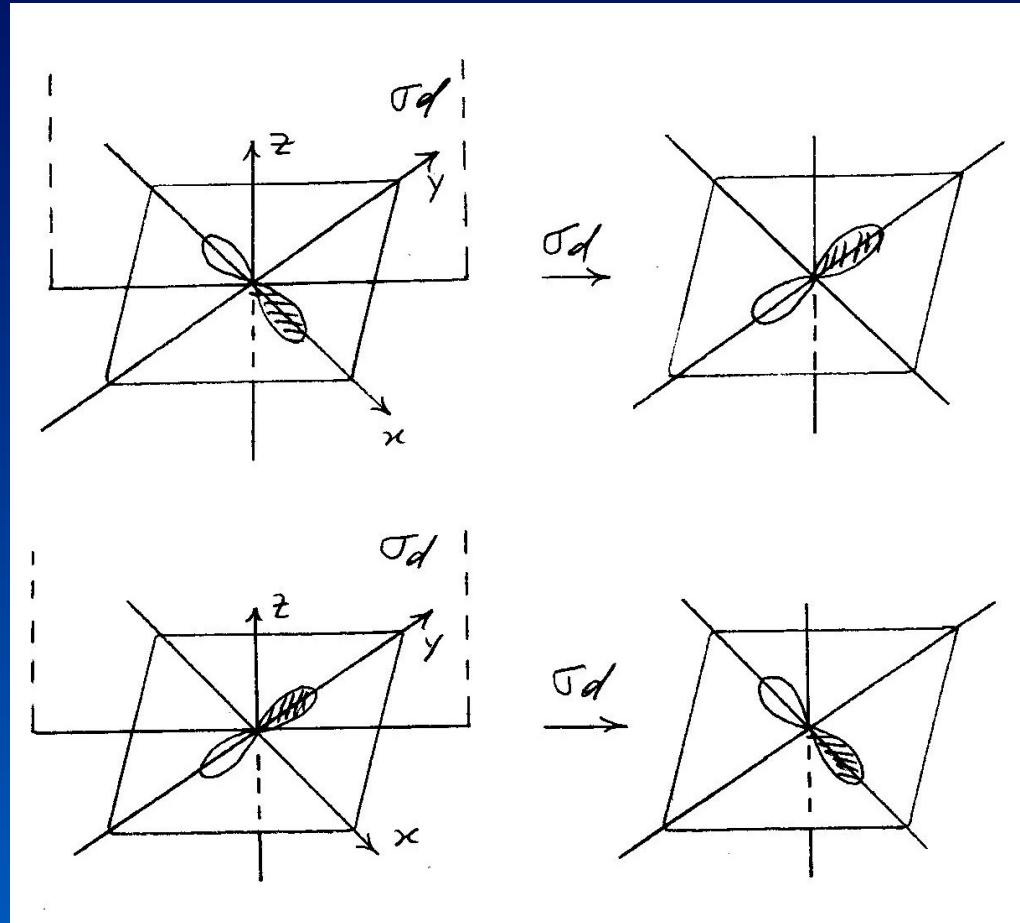
$$\begin{array}{cc} & \begin{array}{cc} 2p_x & 2p_y \end{array} \\ \begin{array}{c} 2p_x \\ 2p_y \end{array} & \begin{array}{cc} 1 & 0 \\ 0 & 1 \end{array} \end{array} \xrightarrow{\sigma_v^{(yz)}} \begin{array}{cc} & \begin{array}{cc} 2p_x & 2p_y \end{array} \\ \begin{array}{c} 2p_x' \\ 2p_y' \end{array} & \begin{array}{cc} -1 & 0 \\ 0 & 1 \end{array} \end{array}$$

$$\chi = 0$$

Classificando os orbitais $2p_x$ e $2p_y$ do carbono

D_{4h}	E	$2C_4$	C_2	$2C_2'$	$2C_2''$	i	$2S_4$	σ_h	$2\sigma_v$	$2\sigma_d$
A_{1g}	1	1	1	1	1	1	1	1	1	1
A_{2g}	1	1	1	-1	-1	1	1	1	-1	-1
B_{1g}	1	-1	1	1	-1	1	-1	1	1	-1
B_{2g}	1	-1	1	-1	1	1	-1	1	-1	1
E_g	2	0	-2	0	0	2	0	-2	0	0
A_{1u}	1	1	1	1	1	-1	-1	-1	-1	-1
A_{2u}	1	1	1	-1	-1	-1	-1	-1	1	1
B_{1u}	1	-1	1	1	-1	-1	1	-1	-1	1
B_{2u}	1	-1	1	-1	1	-1	1	-1	1	-1
E_u	2	0	-2	0	0	-2	0	2	0	0
p_x, p_y	2	0	-2	0	0	-2	0	2	0	

Classificando os orbitais (inseparáveis) $2p_x$ e $2p_y$ do carbono



Metano plano - D_{4h}

Os orbitais $2p_x$ e $2p_y$ do C são INSEPARÁVEIS

$$\begin{array}{cc} & \begin{array}{cc} 2p_x & 2p_y \end{array} \\ \begin{array}{c} 2p_x \\ 2p_y \end{array} & \begin{array}{cc} 1 & 0 \\ 0 & 1 \end{array} \end{array} \xrightarrow{\sigma_d} \begin{array}{cc} & \begin{array}{cc} 2p_x' & 2p_y' \end{array} \\ \begin{array}{c} 2p_x' \\ 2p_y' \end{array} & \begin{array}{cc} 0 & 1 \\ 1 & 0 \end{array} \end{array}$$

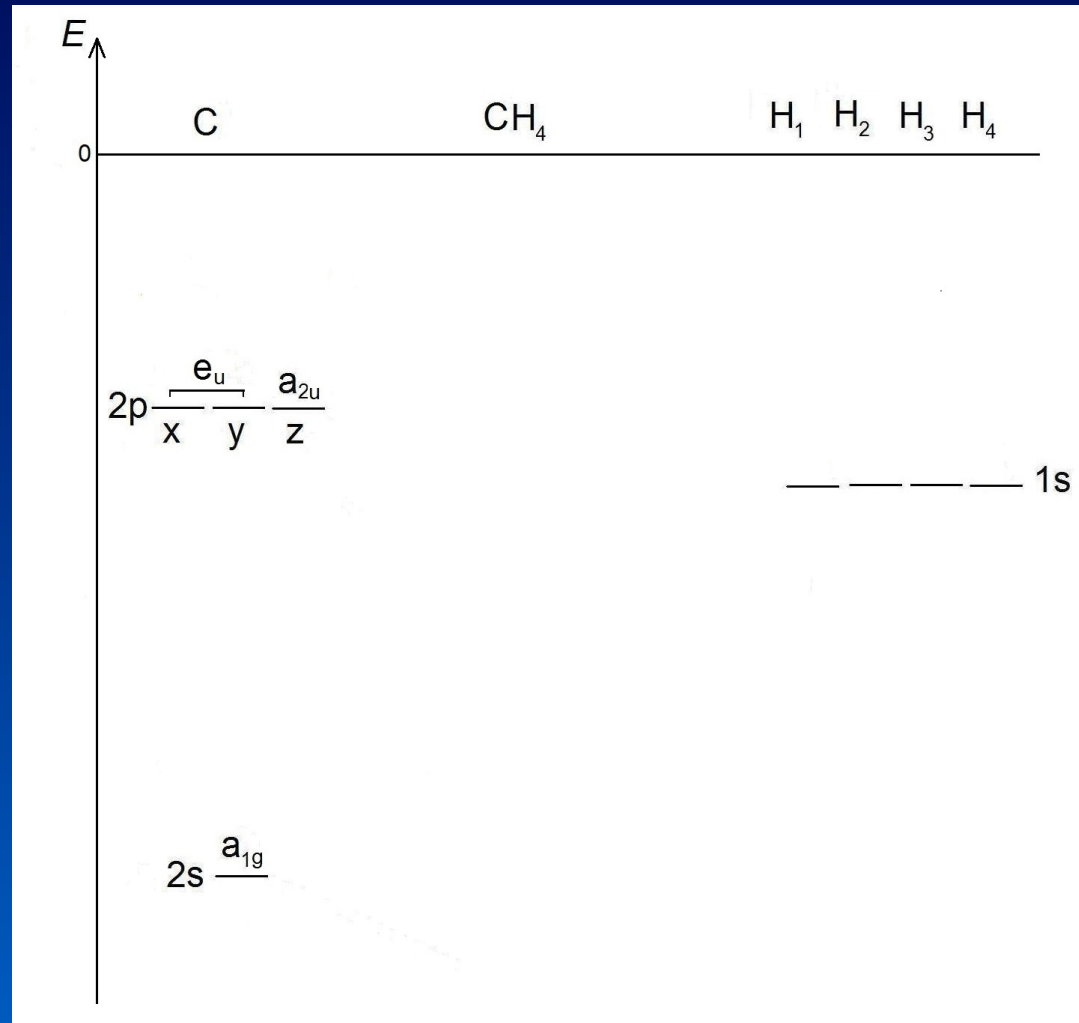
$$\chi = 0$$

Classificando os orbitais $2p_x$ e $2p_y$ do carbono

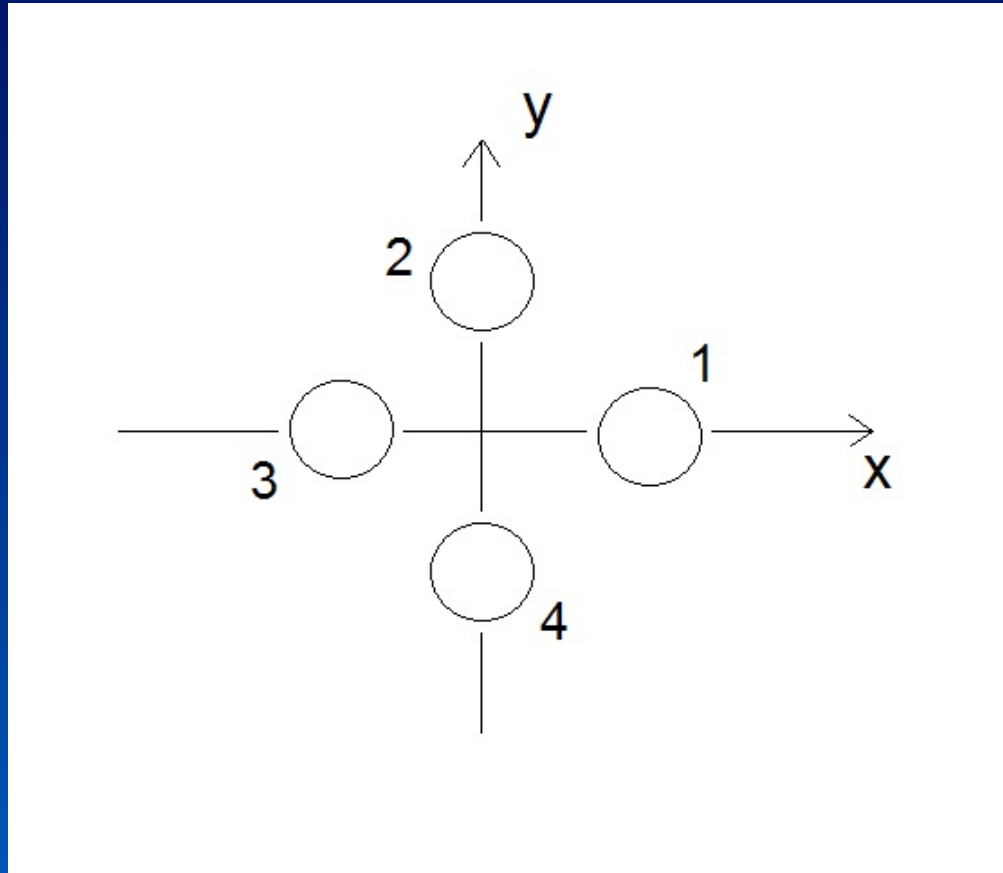
D_{4h}	E	$2C_4$	C_2	$2C_2'$	$2C_2''$	i	$2S_4$	σ_h	$2\sigma_v$	$2\sigma_d$	
A_{1g}	1	1	1	1	1	1	1	1	1	1	
A_{2g}	1	1	1	-1	-1	1	1	1	-1	-1	
B_{1g}	1	-1	1	1	-1	1	-1	1	1	-1	
B_{2g}	1	-1	1	-1	1	1	-1	1	-1	1	
E_g	2	0	-2	0	0	2	0	-2	0	0	
A_{1u}	1	1	1	1	1	-1	-1	-1	-1	-1	
A_{2u}	1	1	1	-1	-1	-1	-1	-1	1	1	
B_{1u}	1	-1	1	1	-1	-1	1	-1	-1	1	
B_{2u}	1	-1	1	-1	1	-1	1	-1	1	-1	
E_u	2	0	-2	0	0	-2	0	2	0	0	
p_x, p_y	2	0	-2	0	0	-2	0	2	0	0	E_u

Metano plano - D_{4h}

Diagrama de energia dos orbitais moleculares



Classificando os orbitais 1s (inseparáveis) dos H

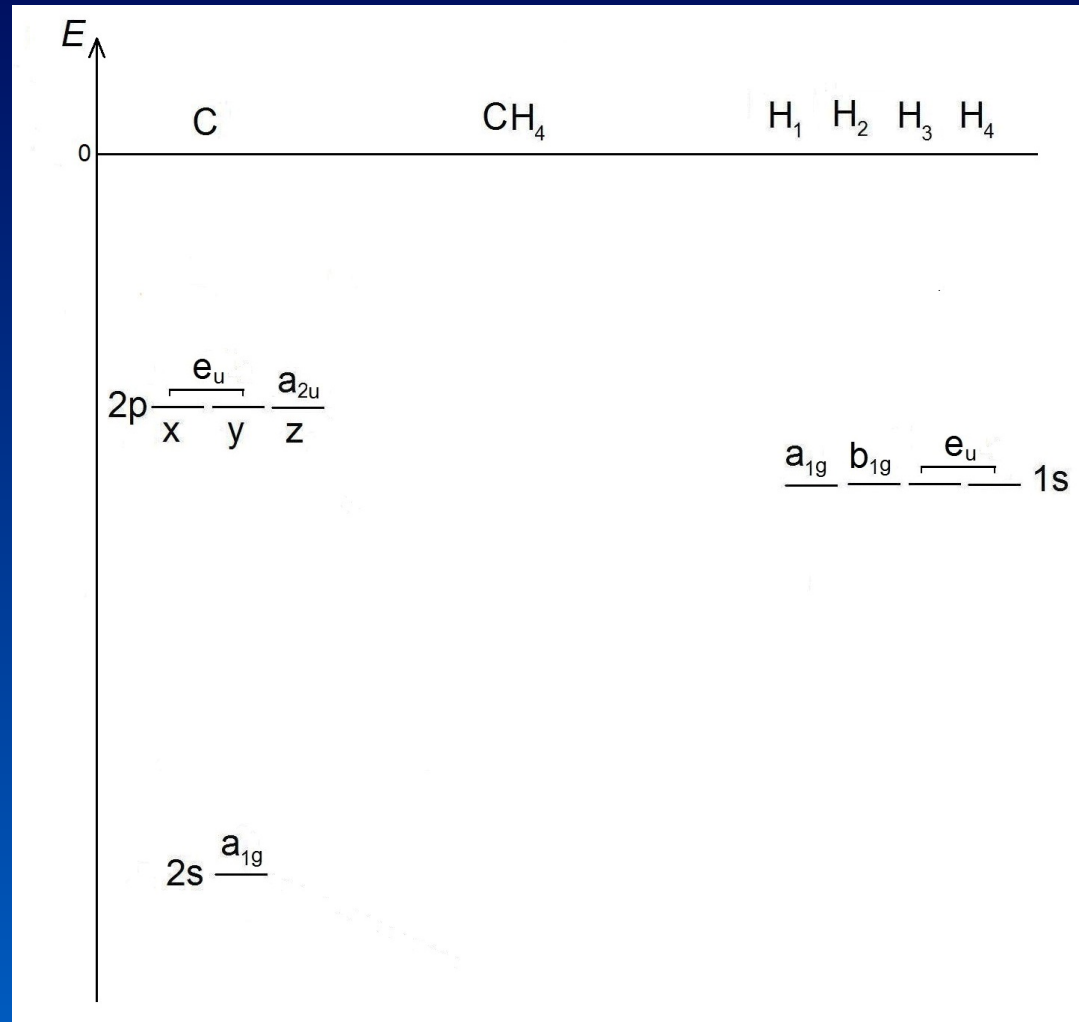


Classificando os orbitais 1s dos hidrogênios

D_{4h}	E	$2C_4$	C_2	$2C_2'$	$2C_2''$	i	$2S_4$	σ_h	$2\sigma_v$	$2\sigma_d$
A_{1g}	1	1	1	1	1	1	1	1	1	1
A_{2g}	1	1	1	-1	-1	1	1	1	-1	-1
B_{1g}	1	-1	1	1	-1	1	-1	1	1	-1
B_{2g}	1	-1	1	-1	1	1	-1	1	-1	1
E_g	2	0	-2	0	0	2	0	-2	0	0
A_{1u}	1	1	1	1	1	-1	-1	-1	-1	-1
A_{2u}	1	1	1	-1	-1	-1	-1	-1	1	1
B_{1u}	1	-1	1	1	-1	-1	1	-1	-1	1
B_{2u}	1	-1	1	-1	1	-1	1	-1	1	-1
E_u	2	0	-2	0	0	-2	0	2	0	0
<hr/>										
$4(1s)$	4	0	0	2	0	0	0	4	2	0 $A_{1g}+B_{1g}+E_u$

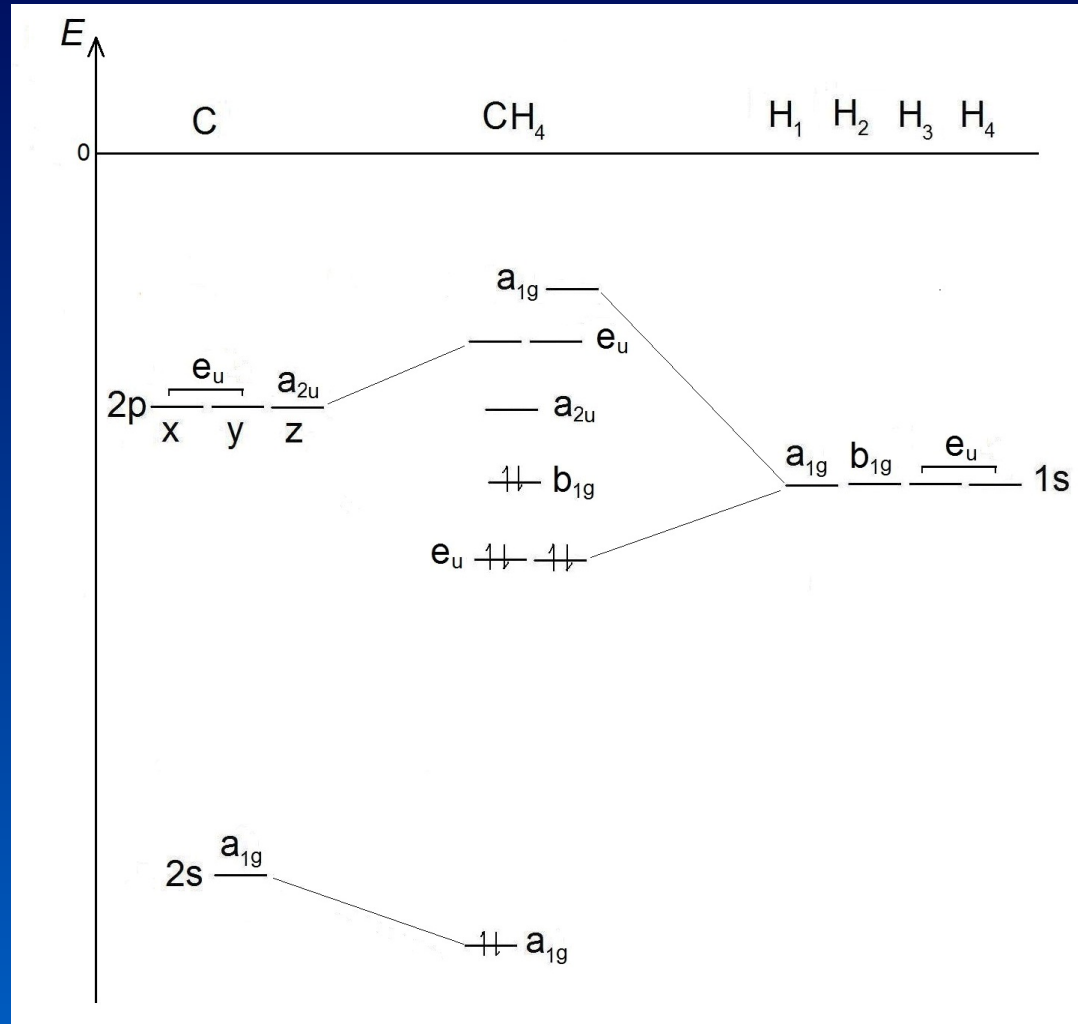
Metano plano - D_{4h}

Diagrama de energia dos orbitais moleculares



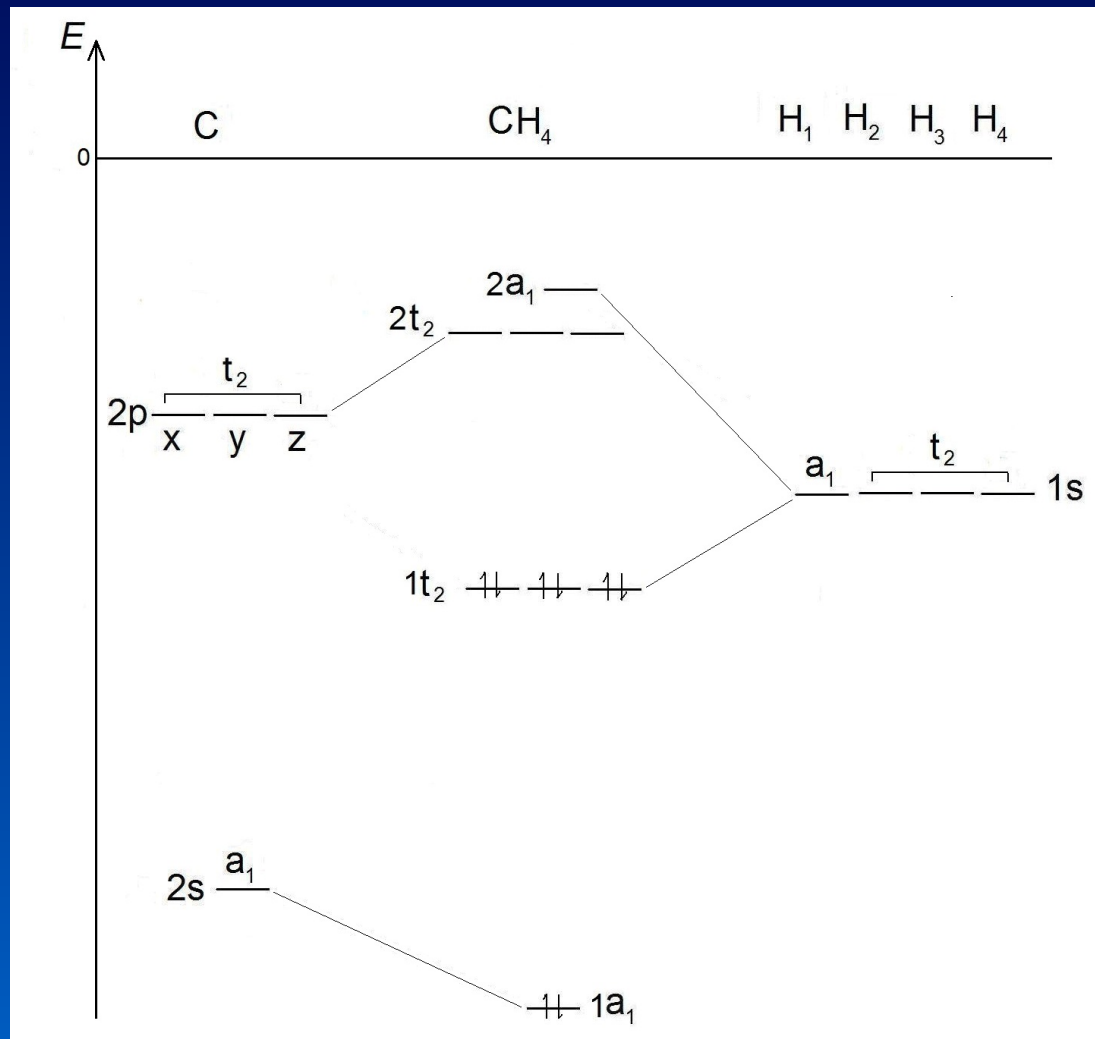
Metano plano - D_{4h}

Diagrama de energia dos orbitais moleculares



Metano tetraédrico - T_d

Diagrama de energia dos orbitais moleculares



Comparação metano plano e tetraédrico

- No metano plano, um par de elétrons fica num orbital não ligante, que tem a mesma energia dos orbitais 2p do carbono.
- No metano tetraédrico, não há pares de elétrons não ligantes, ficando a molécula, portanto, mais estável.

CO₂ linear (D_{∞h})

×

CO₂ angular (C_{2v})

Moléculas AB₂

Diagrama de energia dos orbitais moleculares

Moléculas/íons lineares (16 elétrons):



Moléculas/íons angulares:

17 elétrons: NO_2^\cdot

18 elétrons: O_3 NO_2^- SO_2

19 elétrons: ClO_2^\cdot

20 elétrons: ClO_2^-

AB₂ (linear) - D_{∞h}

$$\varphi = 90^\circ$$

D _{∞h}	E	2C _∞ ^φ	∞σ _v	i	2S _∞ ^φ	∞C ₂
Σ _g ⁺	1	1	1	1	1	1
Σ _g ⁻	1	1	-1	1	1	-1
Π _g	2	0	0	2	0	0
Δ _g	2	-2	0	2	-2	0
Σ _u ⁺	1	1	1	-1	-1	-1
Σ _u ⁻	1	1	-1	-1	-1	1
Π _u	2	0	0	-2	0	0
Δ _u	2	-2	0	-2	-2	0
<hr/>						
A(p _x ,p _y)	2	0		-2	0	Π _u

AB₂ (linear) - D_{∞h}

Classificando os 4 orbitais 2p_x e 2p_y INSEPARÁVEIS, dos átomos B

	2p _x ^{B1}	2p _y ^{B1}	2p _x ^{B2}	2p _y ^{B2}		2p _x ^{B1}	2p _y ^{B1}	2p _x ^{B2}	2p _y ^{B2}	
2p _x ^{B1}	1	0	0	0	C _∞ ^{φ = 90°}	2p _x ^{B1}	0	1	0	0
2p _y ^{B1}	0	1	0	0		2p _x ^{B1}	-1	0	0	0
2p _x ^{B2}	0	0	1	0		2p _x ^{B2}	0	0	0	1
2p _y ^{B2}	0	0	0	1		2p _x ^{B2}	0	0	-1	0

$$\chi = 4$$

$$\chi = 0$$

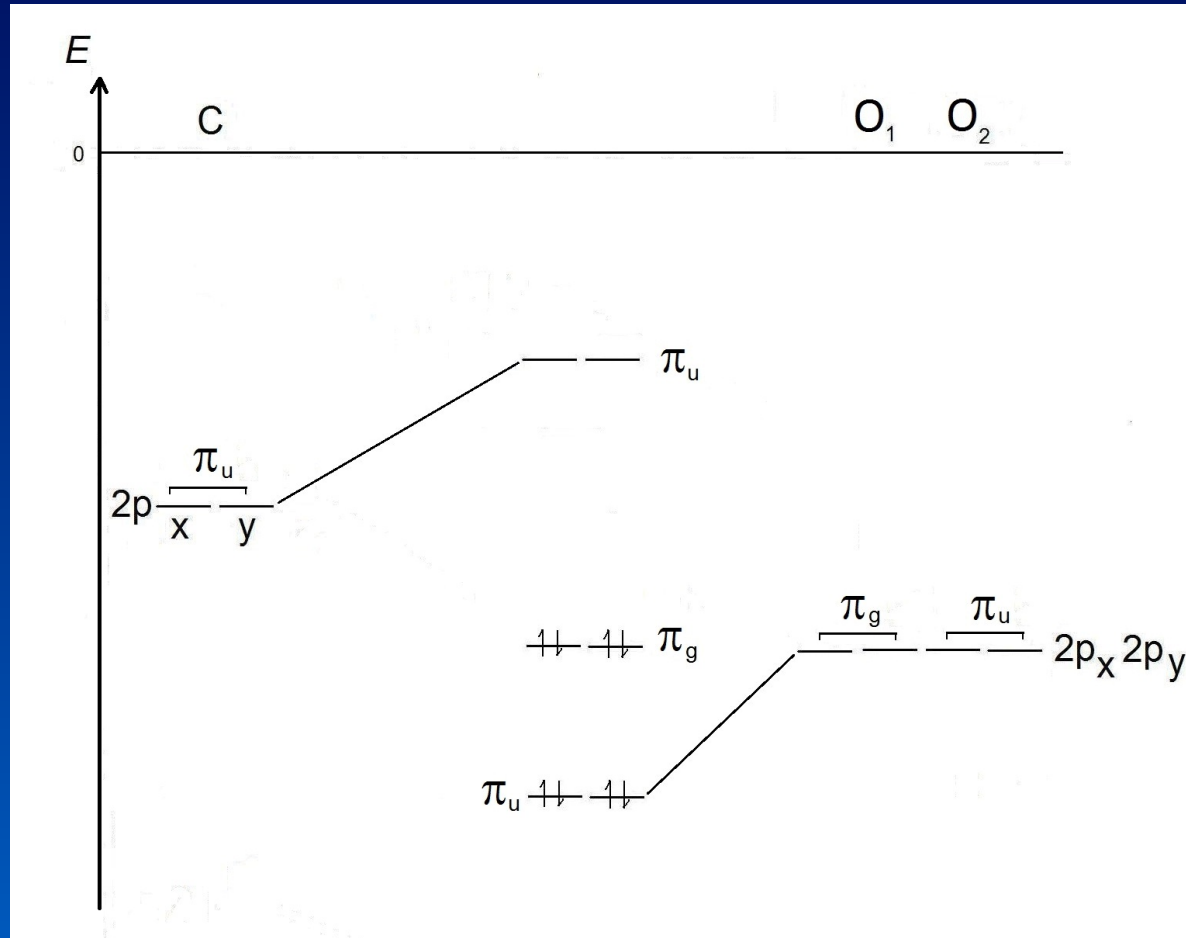
AB₂ (linear) - D_{∞h}

$$\varphi = 90^\circ$$

D _{∞h}	E	2C _∞ ^φ	∞σ _v	i	2S _∞ ^φ	∞C ₂
Σ _g ⁺	1	1	1	1	1	1
Σ _g ⁻	1	1	-1	1	1	-1
Π _g	2	0	0	2	0	0
Δ _g	2	-2	0	2	-2	0
Σ _u ⁺	1	1	1	-1	-1	-1
Σ _u ⁻	1	1	-1	-1	-1	1
Π _u	2	0	0	-2	0	0
Δ _u	2	-2	0	-2	-2	0
BB(p _x ,p _y)	4	0	0	0	0	0 Π _u + Π _g

CO₂ linear - D_{∞h}

Diagrama de energia dos orbitais moleculares



Comparação simplificada de moléculas e íons lineares e angulares

- No CO_2 linear existem dois pares de elétrons em orbitais π_g não ligantes.
- No caso das moléculas ou íons com 17 elétrons, um elétron ficaria em um dos orbitais π_u , resultando em um estado eletrônico degenerado.

Comparação simplificada de moléculas e íons lineares e angulares

- Segundo o Teorema de Jahn-Teller, toda molécula ou íon em um estado eletrônico degenerado, sofrerá uma distorção na sua geometria que irá remover essa degenerescência e reduzir a energia da molécula ou íon.
- Isso explica a geometria angular do NO_2^\cdot (com 17 elétrons) bem como o fato do CO_2 no estado excitado ser angular.

Comparação simplificada de moléculas e íons lineares e angulares

- Para as moléculas ou íons com 19 elétrons, também forma-se um estado eletrônico degenerado, com 3 elétrons nos orbitais π_u , o que explica o fato do $\text{ClO}_2\cdot$ (19 elétrons) ser angular.
- Para as outras moléculas ou íons com 18 ou 20 elétrons, o fato dos orbitais π_u , antiligantes, de maior energia, estarem ocupados, torna a geometria linear desses íons e moléculas desfavorável.

Machado, S.P.; Roberto B. Faria, R.B.; Explaining the geometry of simple molecules using molecular orbital energy-level diagrams built by using symmetry principles. *Quim. Nova* 41(5):587-593 (2018).
DOI: <http://dx.doi.org/10.21577/0100-4042.20170198>

FIM DA AULA 4
