Simetria e Orbitais Moleculares

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Mudança de geometria

H_2O NH_3 CH_4

Simetrias $D_{\infty h}$ D_{3h} C_{4h}

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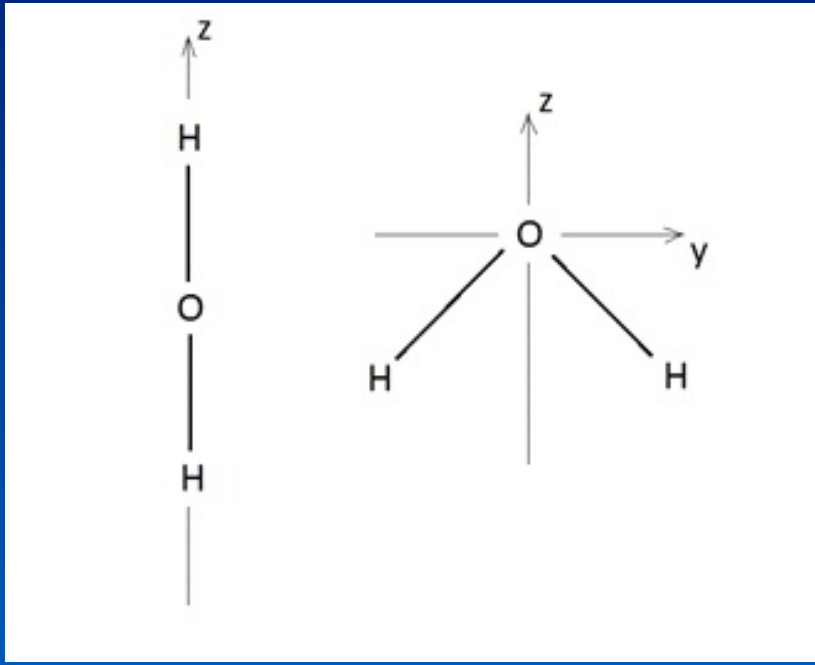
Água linear ($D_{\infty h}$)
×
Água angular (C_{2v})

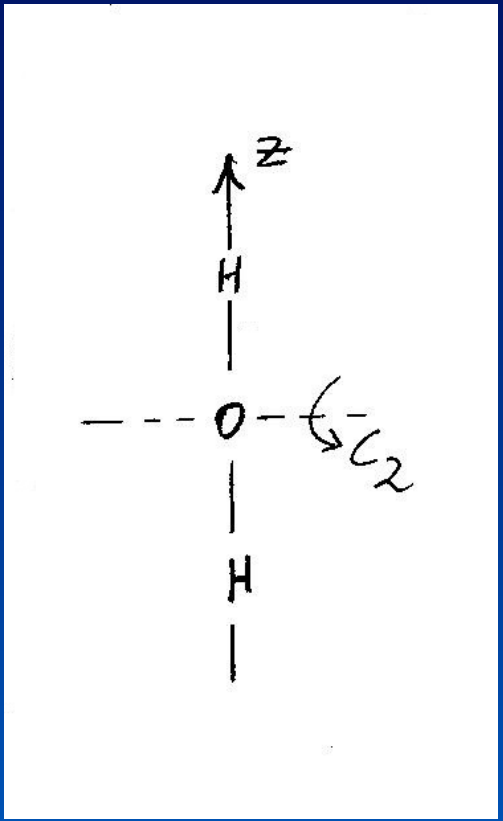


Água (linear) - $D_{\infty h}$

$D_{\infty h}$	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

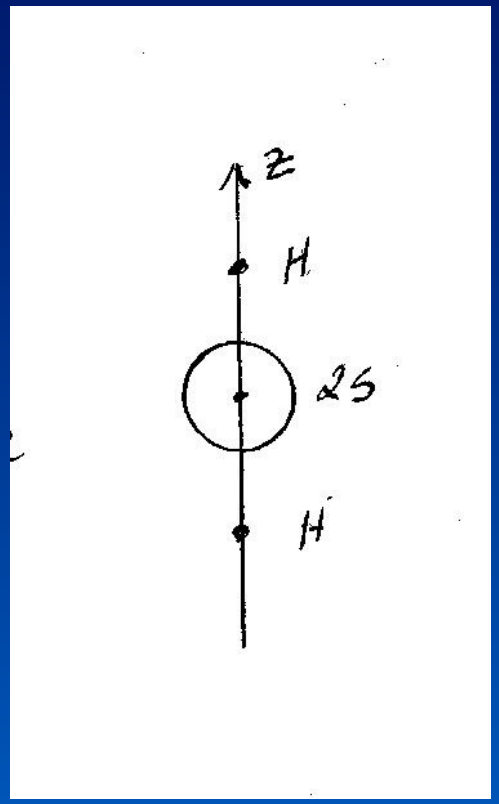
Água (linear) - $D_{\infty h}$

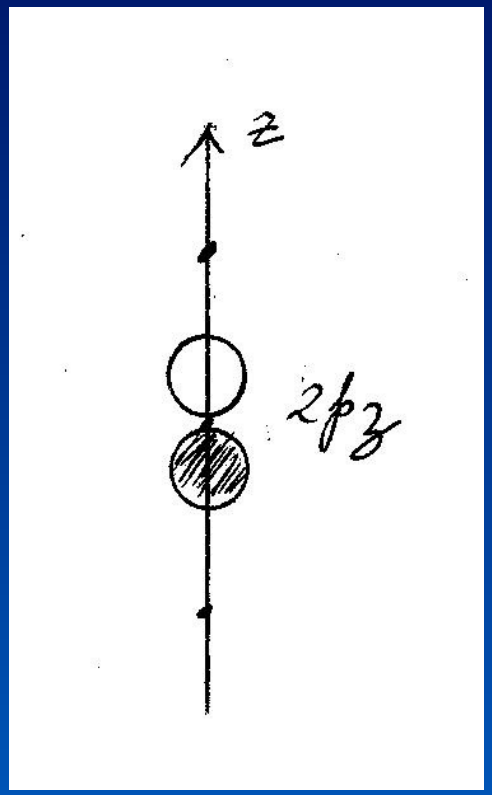
O eixo z, vertical, é o eixo C_∞



Água (linear) - $D_{\infty h}$

Orbitais 2s e $2p_z$



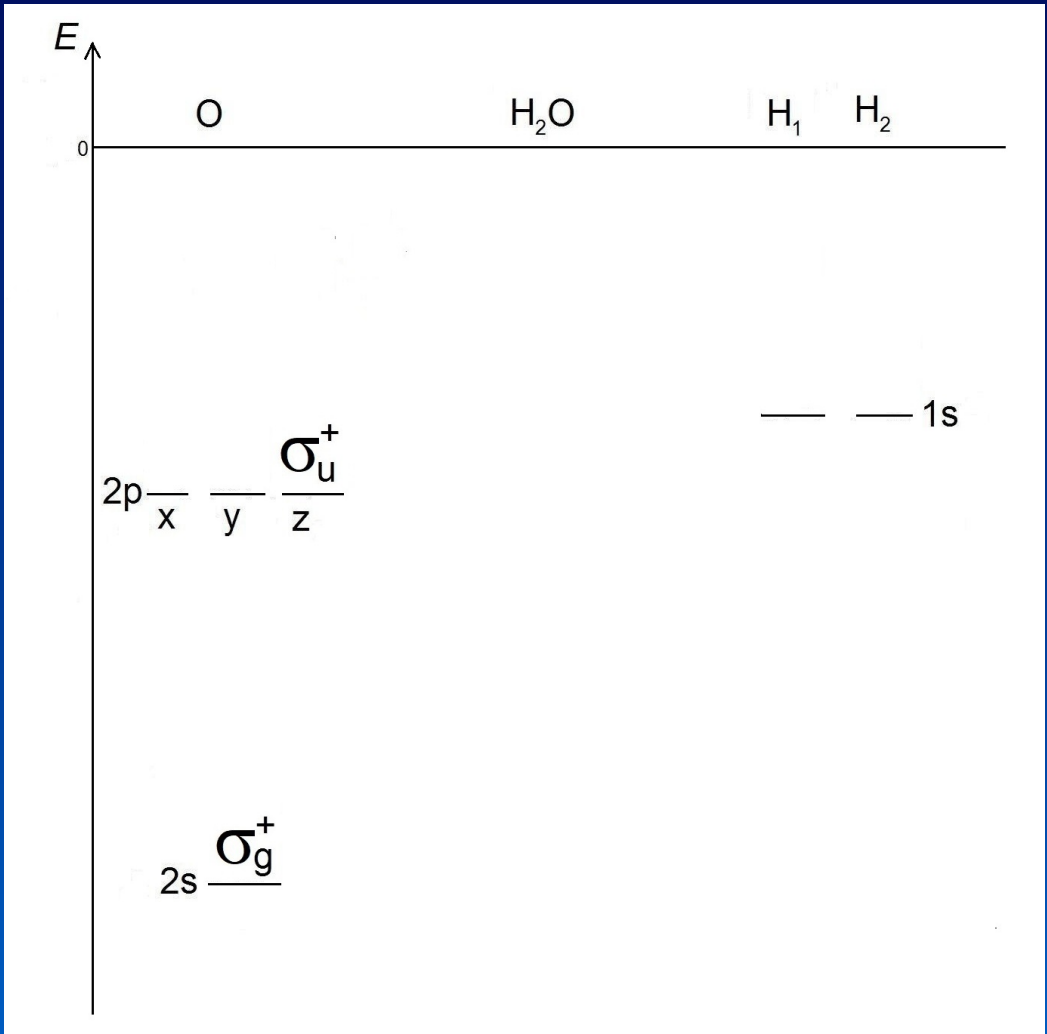


Água (linear) - $D_{\infty h}$

$D_{\infty h}$	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	$2\cos2\varphi$	0	2	$2\cos2\varphi$	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	$2\cos2\varphi$	0	-2	$-2\cos2\varphi$	0	
2s	1	1	1	1	1	1	Σ_g^+
$2p_z$	1	1	1	-1	-1	-1	Σ_u^+

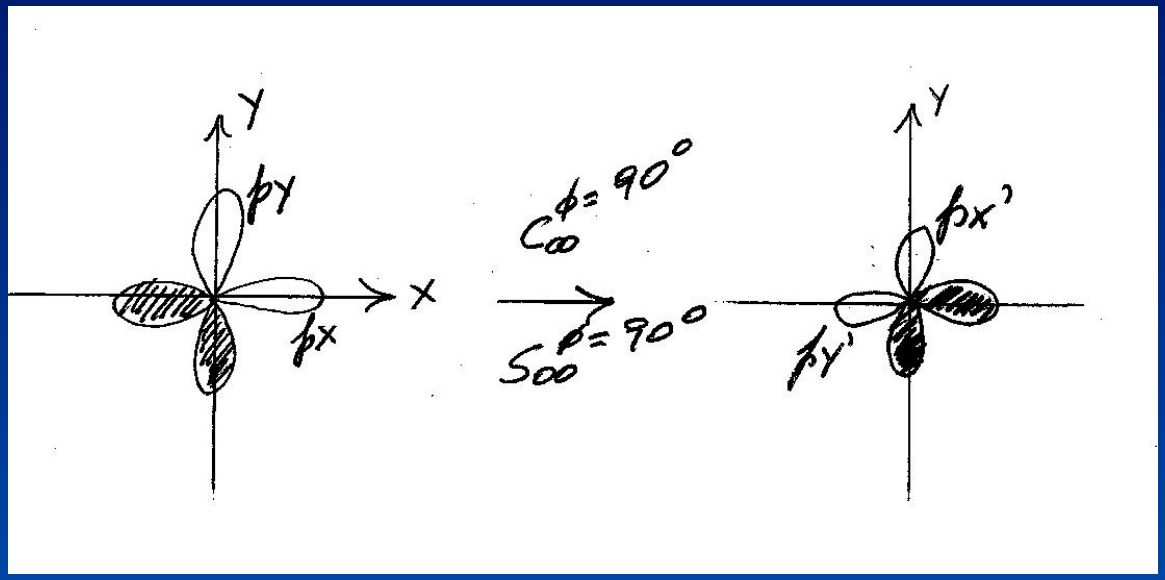
Água (linear) - $D_{\infty h}$

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

	$2p_X$	$2p_y$
$2p_X$	1	0
$2p_y$	0	1

$\chi = 2$

$C_\infty^{\varphi = 90°}$

$\rightarrow$

$S_\infty^{\varphi = 90°}$

	$2p_X$	$2p_y$
$2p_X$	0	1
$2p_y$	-1	0

$\chi = 0$

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	

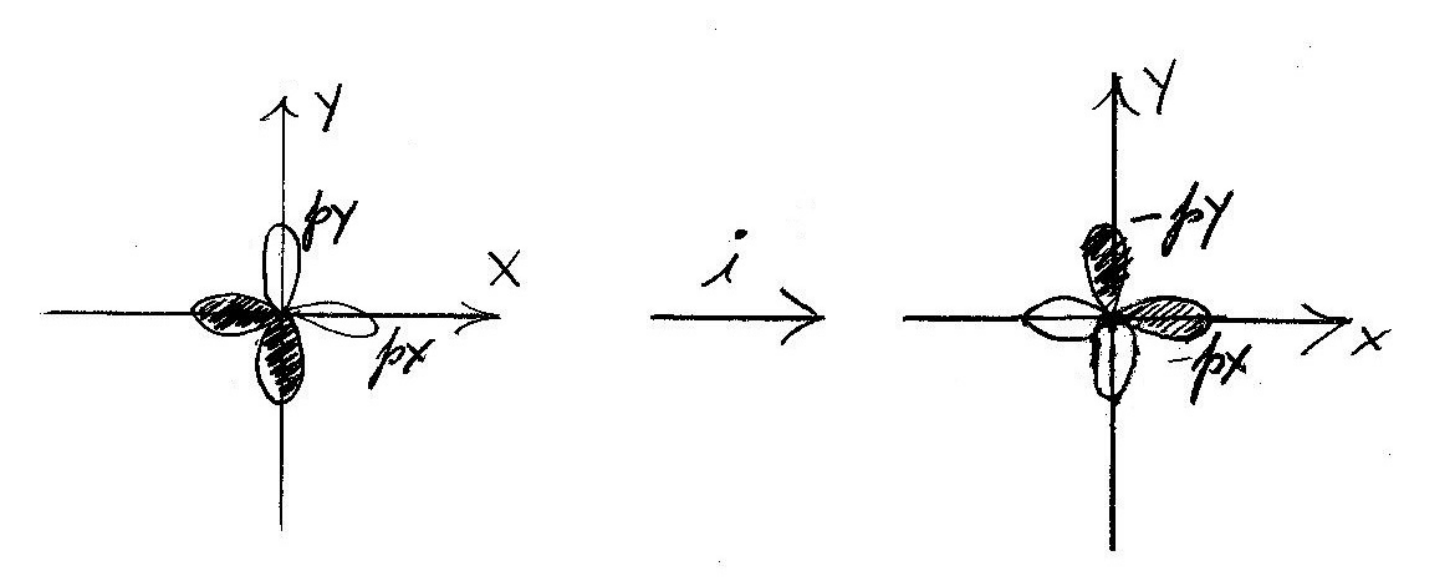
Água (linear) - $D_{\infty h}$

$\varphi = 90°$

$D_{\infty h}$	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

	$2p_X$	$2p_y$
$2p_X$	1	0
$2p_y$	0	1

$\xrightarrow{i}$

	$2p_X$	$2p_y$
$2p_X$	-1	0
$2p_y$	0	-1

$\chi = -2$

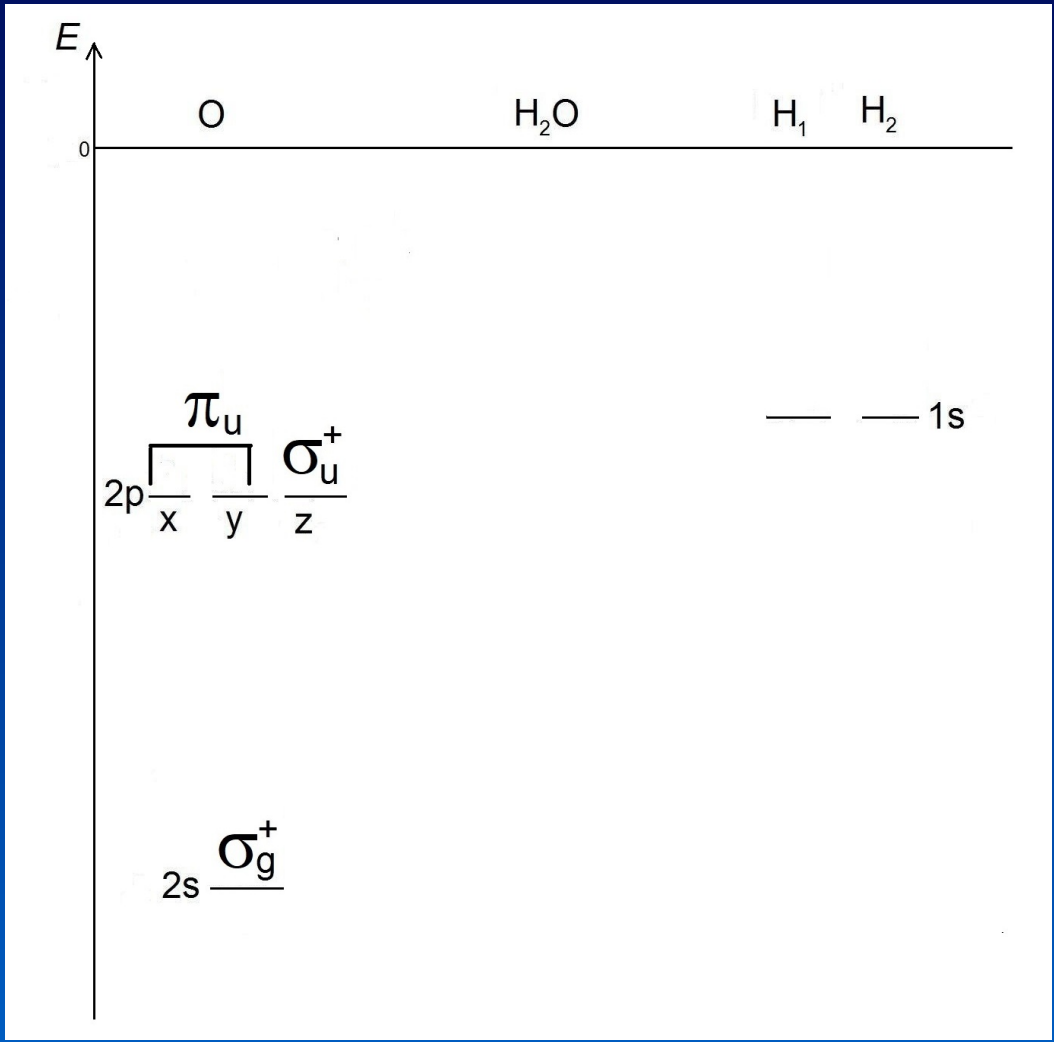
Água (linear) - $D_{\infty h}$

$\varphi = 90°$

$D_{\infty h}$	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

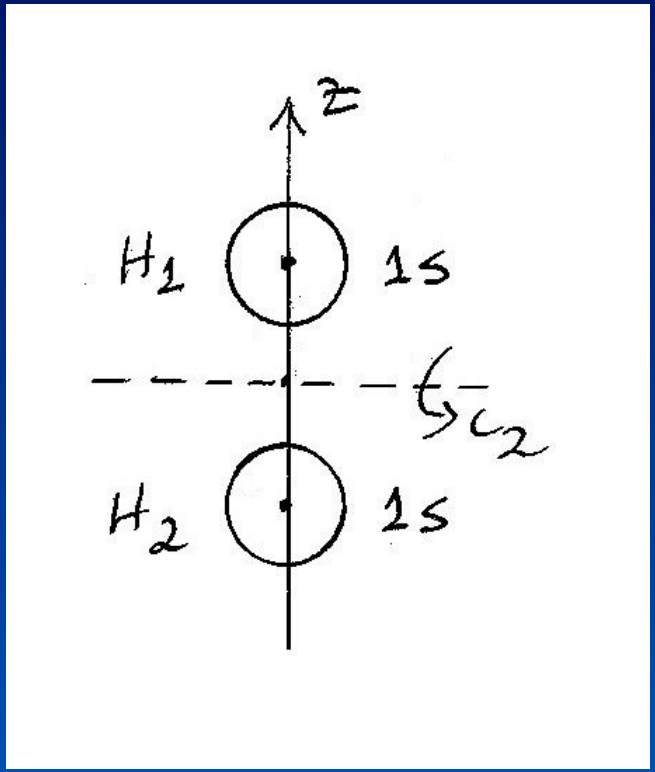
Água (linear) - $D_{\infty h}$

Construindo o diagrama de energia dos orbitais moleculares



Água (linear) - $D_{\infty h}$

Os orbitais 1s dos hidrogênios - INSEPARÁVEIS



$$\begin{array}{c|cc} & \varphi_1 & \varphi_2 \\ \hline \varphi_1 & 1 & 0 \\ \varphi_2 & 0 & 1 \end{array} \xrightarrow[i\ S_\infty]{C_2} \begin{array}{c|cc} & \varphi_1 & \varphi_2 \\ \hline \varphi_1 & 0 & 1 \\ \varphi_2 & 1 & 0 \end{array}$$

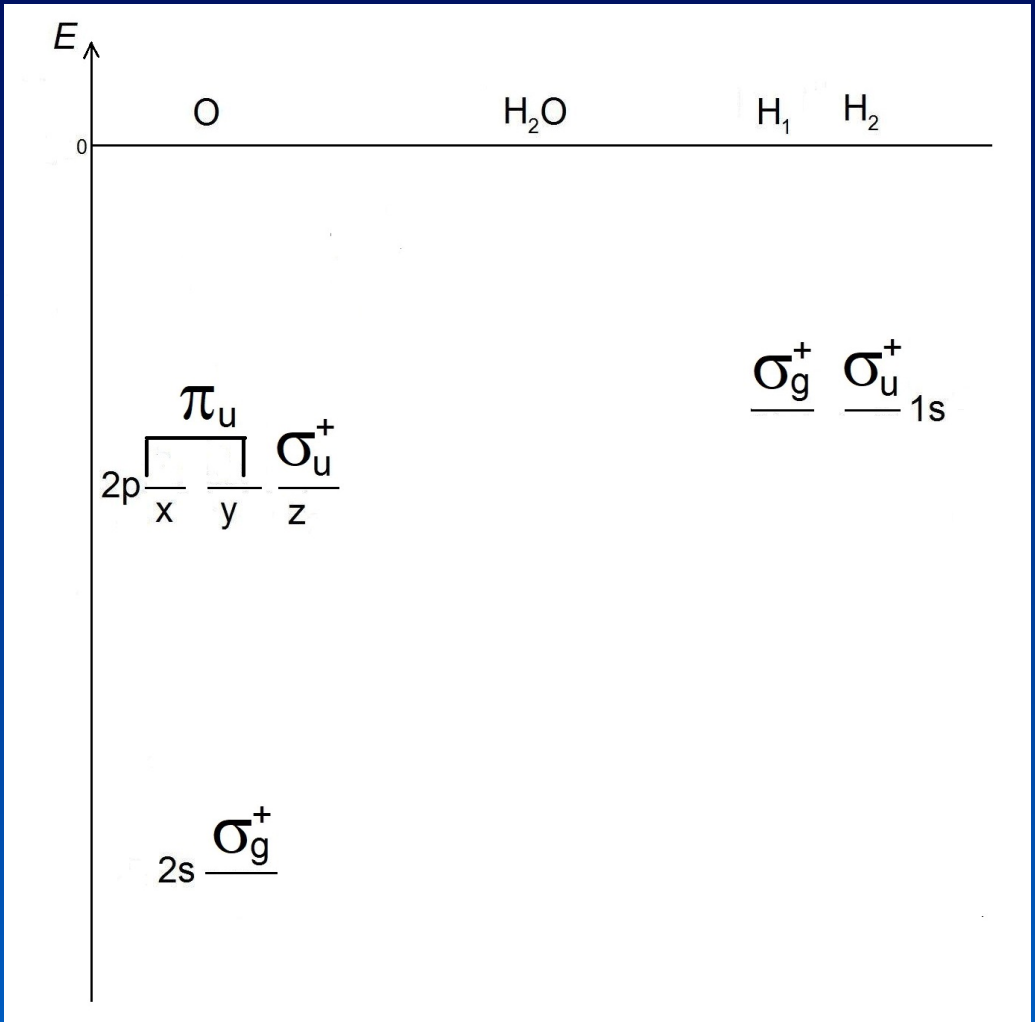
$\chi = 2\ (E, C_\infty, \sigma_v)$ $\qquad$ $\chi = 0$

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	$\Sigma_g^+ + \Sigma_u^+$

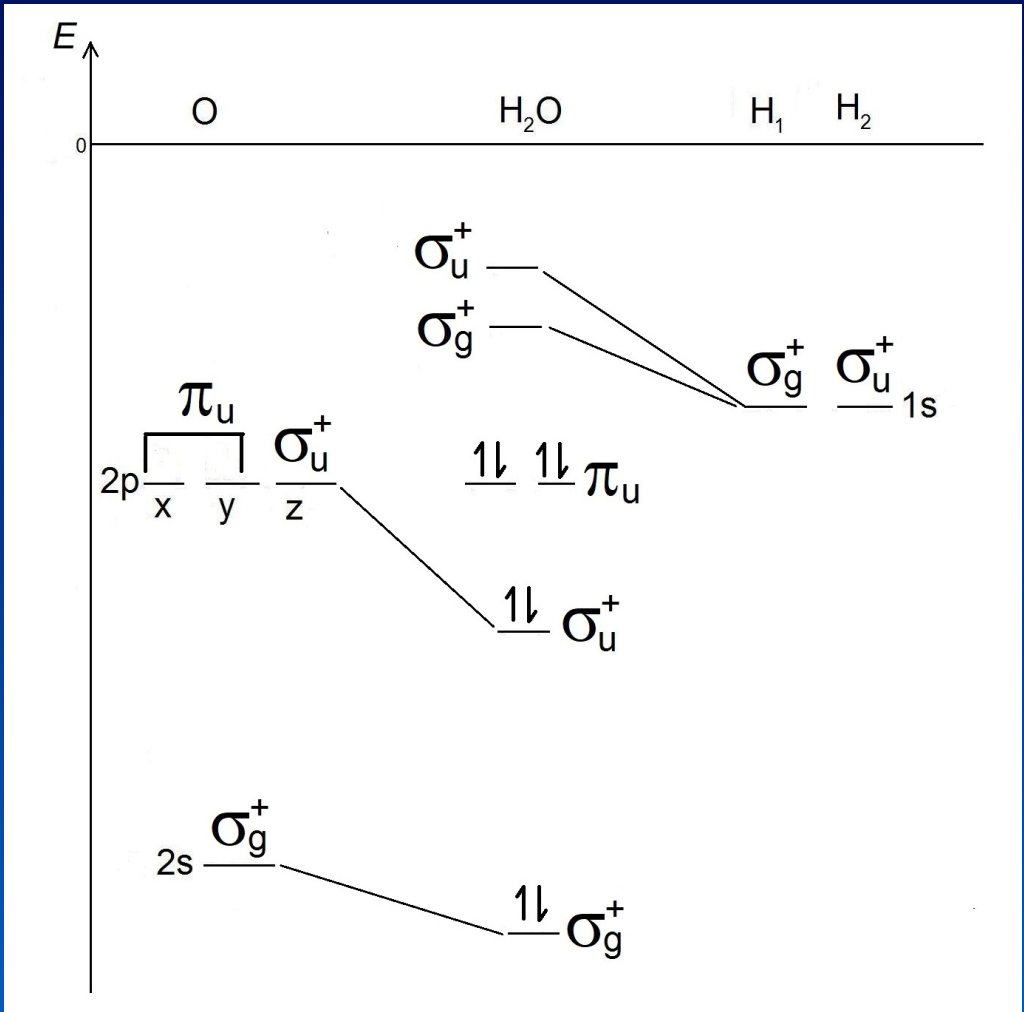
Água (linear) - $D_{\infty h}$

Construindo o diagrama de energia dos orbitais moleculares



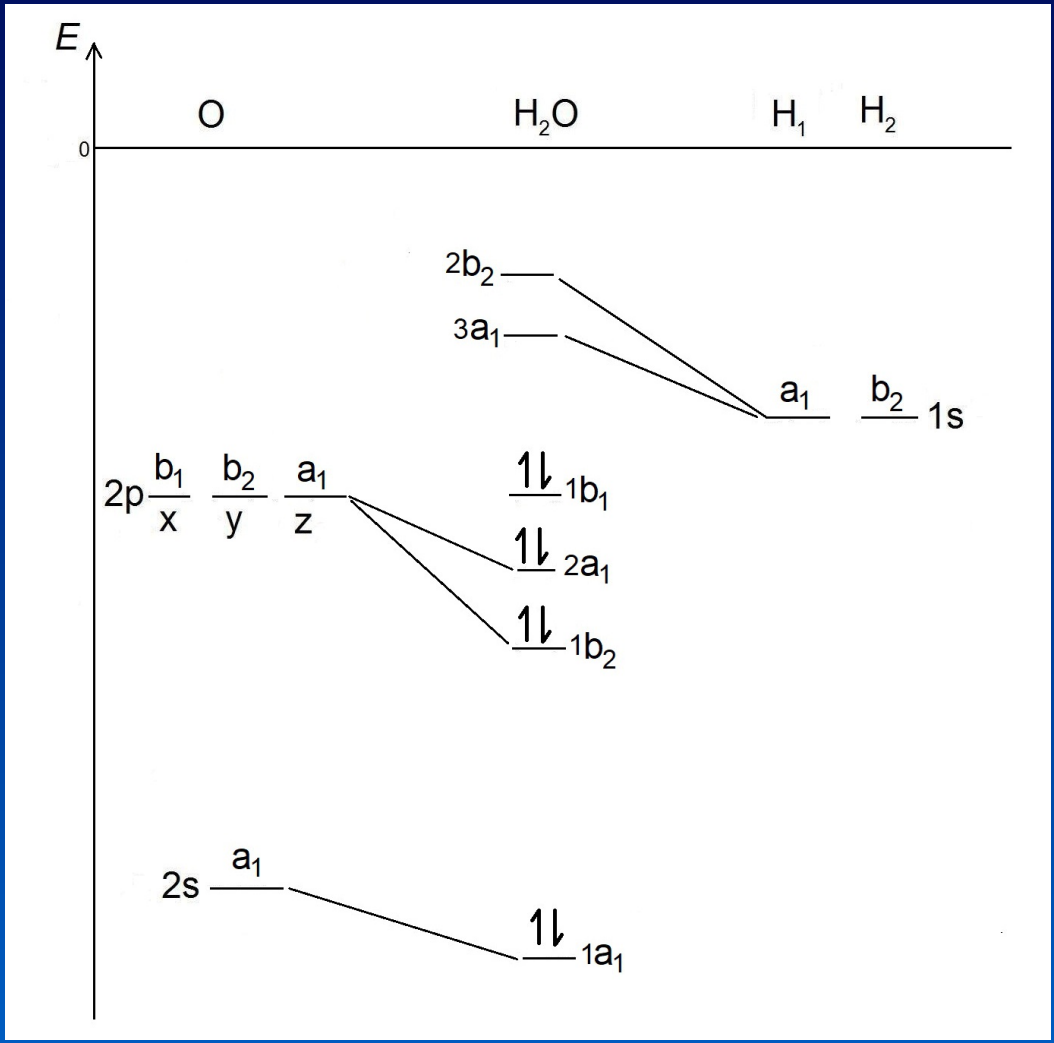
Água (linear) - $D_{\infty h}$

Construindo o diagrama de energia dos orbitais moleculares



Água (angular) - C_{2v}

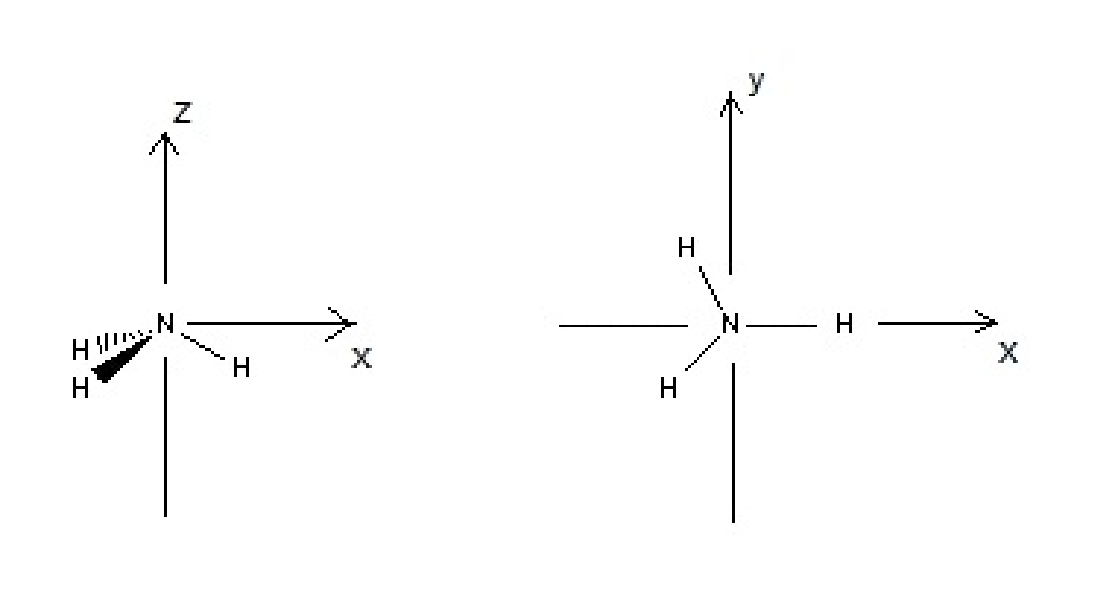
Construindo o diagrama de energia dos orbitais moleculares



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})

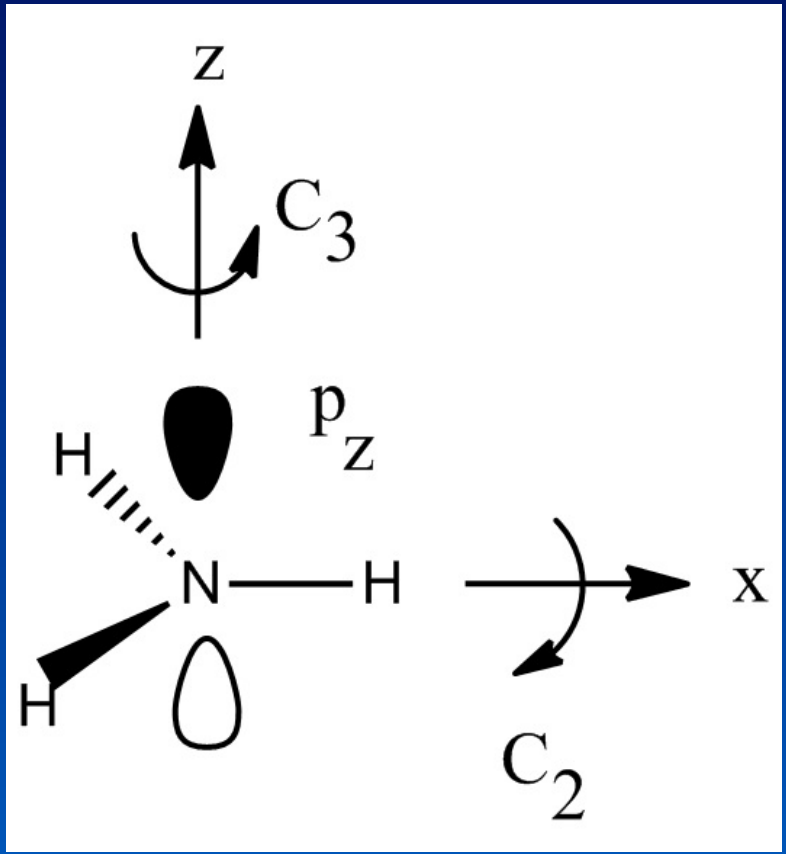


Amônia (plana) - D_{3h}

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 $2p_z$

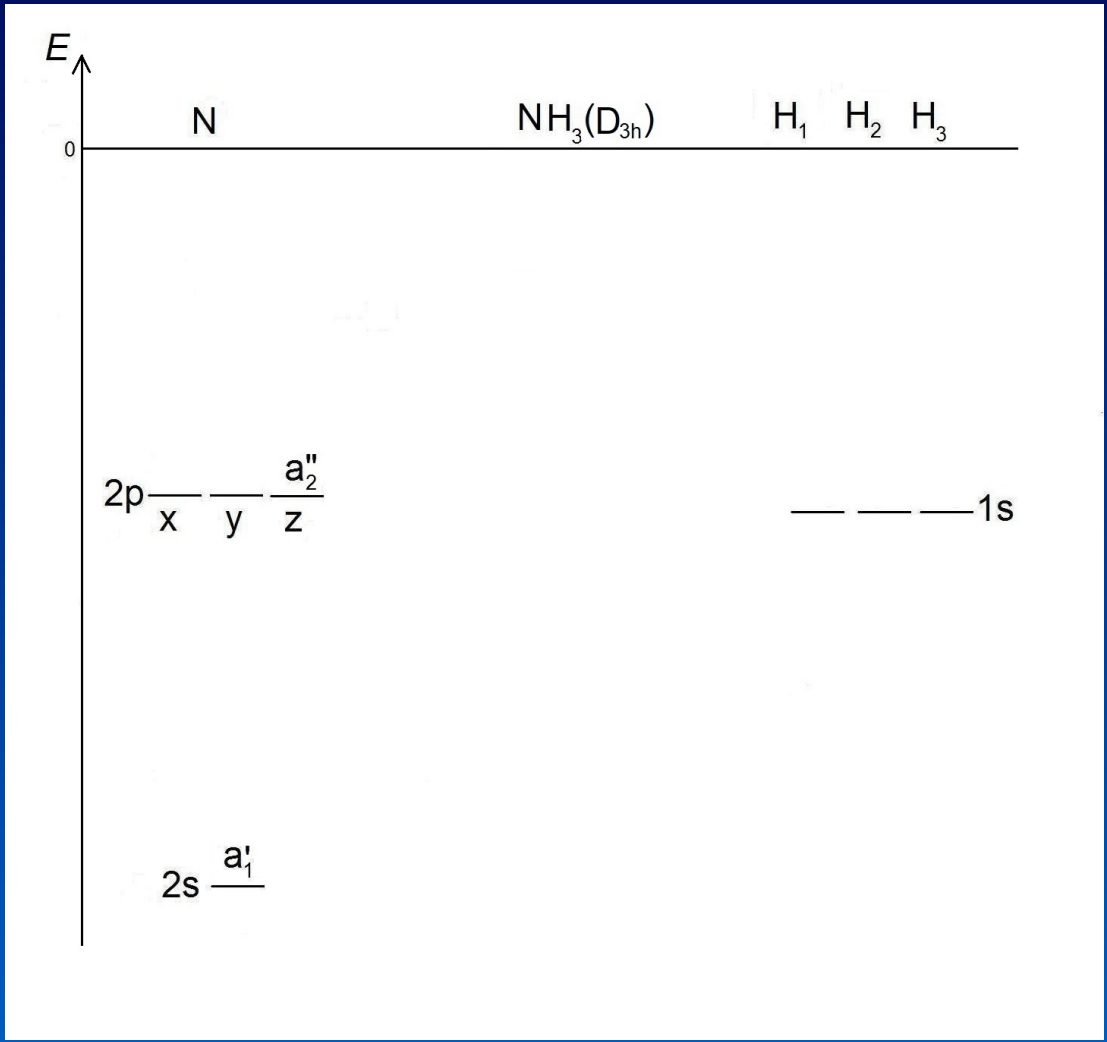


Amônia (plana) - D_{3h}

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}

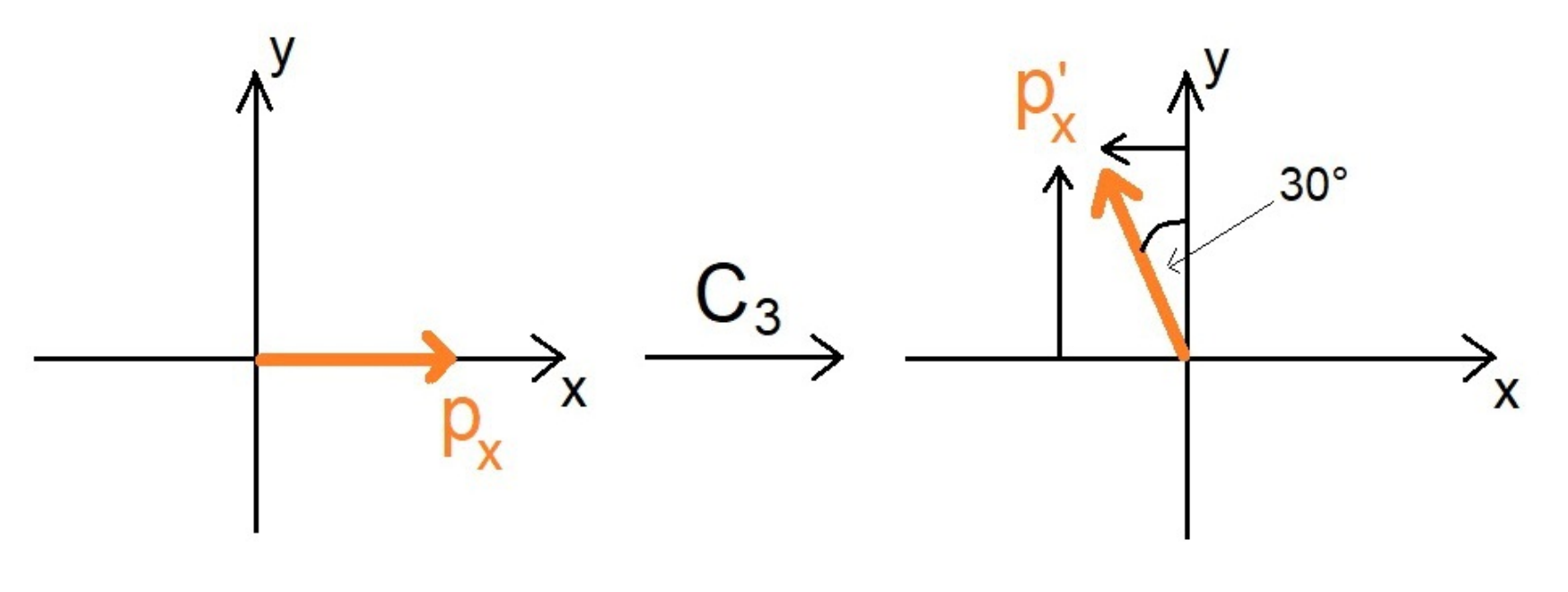
Diagrama de energia dos orbitais moleculares



Amônia plana - D_{3h}

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

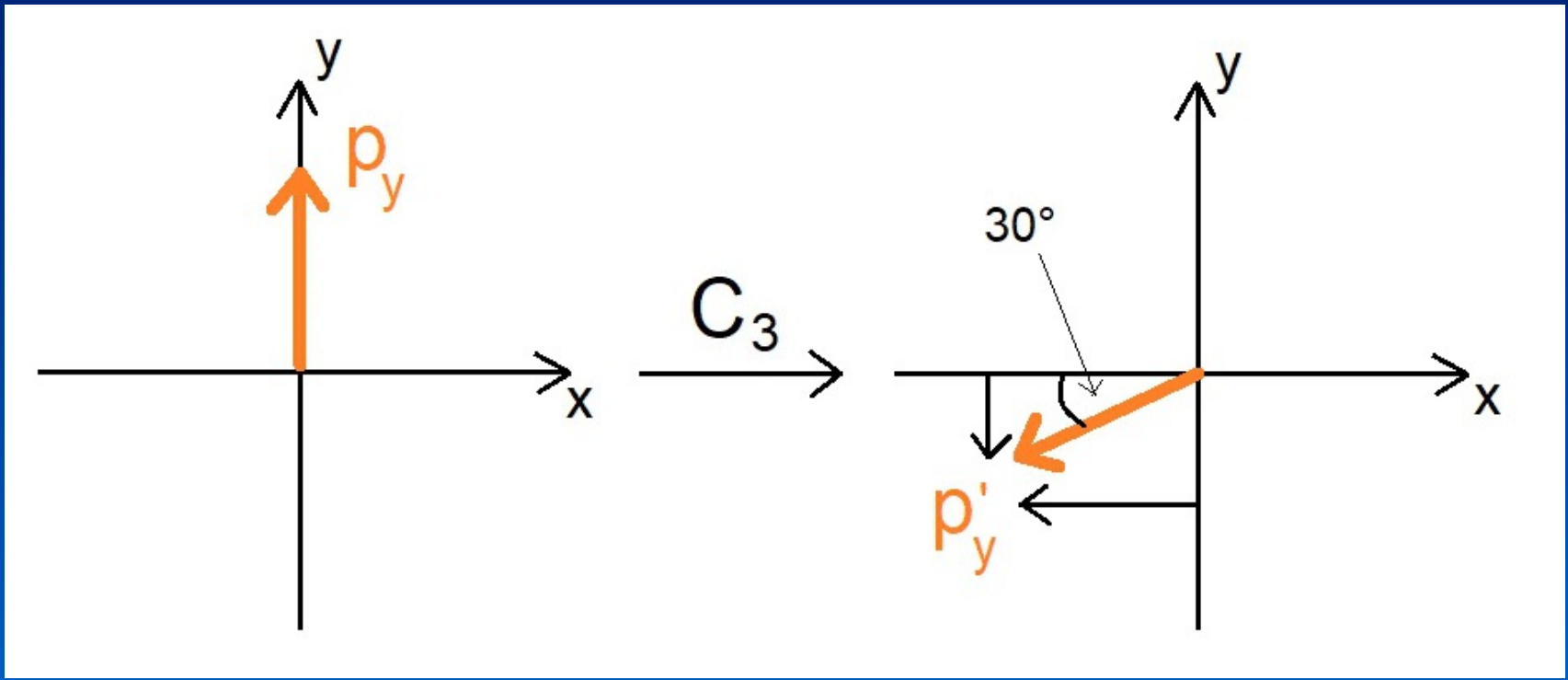
$$p_x' = -p_x \text{ sen } 30° + p_y \cos 30° = (-1/2)p_x + (\sqrt{3}/2)p_y$$



Amônia plana - D_{3h}

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

$$p_y' = -p_x \cos 30° - p_y \operatorname{sen} 30° = (-\sqrt{3}/2)p_x + (-1/2)p_y$$



Amônia plana - D_{3h}

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

	$2p_x$	$2p_y$
$2p_x$	1	0
$2p_y$	0	1

C_3 $\rightarrow$

	$2p_x$	$2p_y$
$2p_x'$	$-1/2$	$\sqrt{3}/2$
$2p_y'$	$-\sqrt{3}/2$	$-1/2$

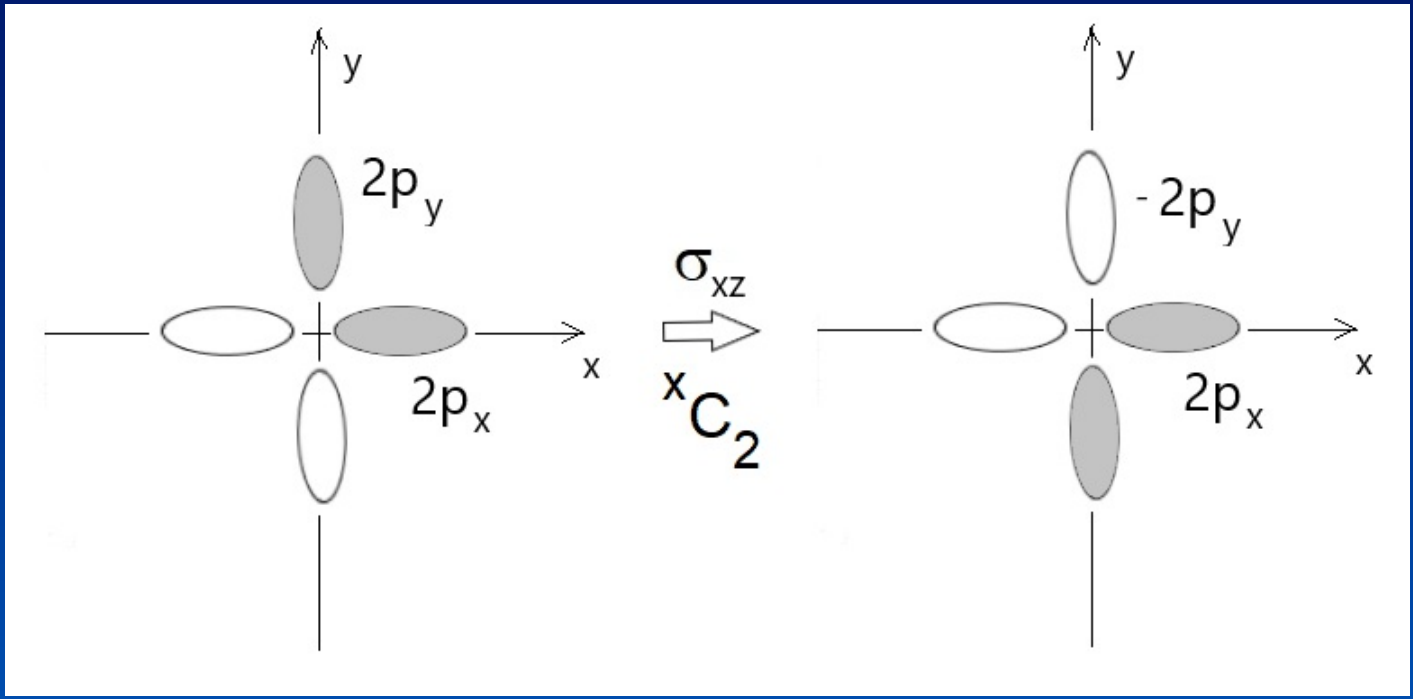
$$\chi = -1$$

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

	$2p_x$	$2p_y$
$2p_x$	1	0
$2p_y$	0	1

$$\xrightarrow[\sigma^{(xz)}]{C_2^{(x)}}$$

	$2p_x$	$2p_y$
$2p_x'$	1	0
$2p_y'$	0	-1

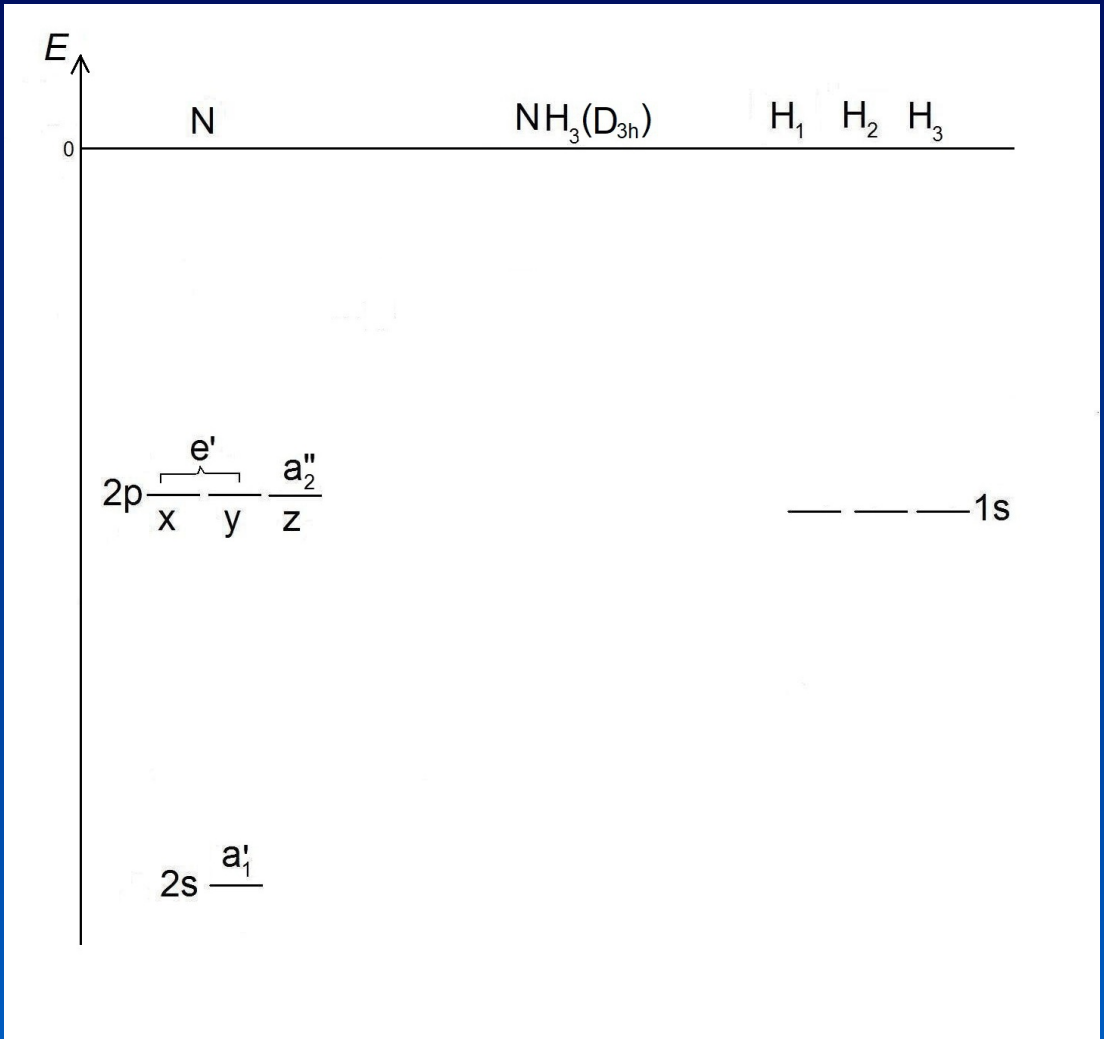
$$\chi = 0$$

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	
(p_x,p_y)	2	-1	0	2	-1	0	E'

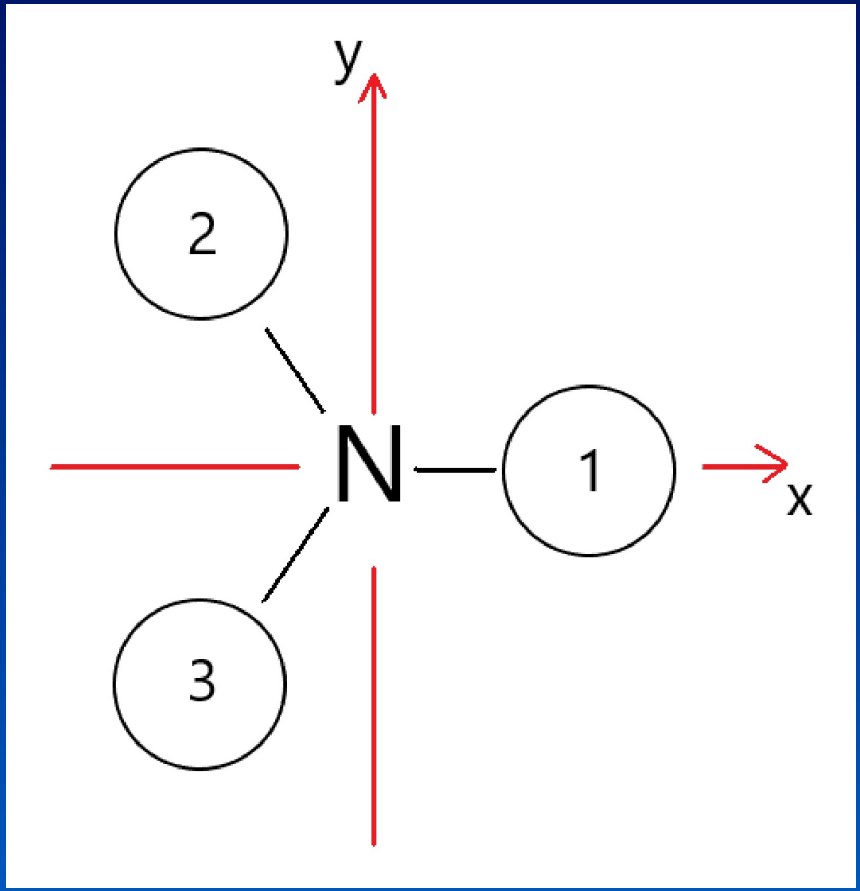
Amônia plana - D_{3h}

Diagrama de energia dos orbitais moleculares



Amônia (plana) - D_{3h}

Orbitais 1s dos H são INSEPARÁVEIS

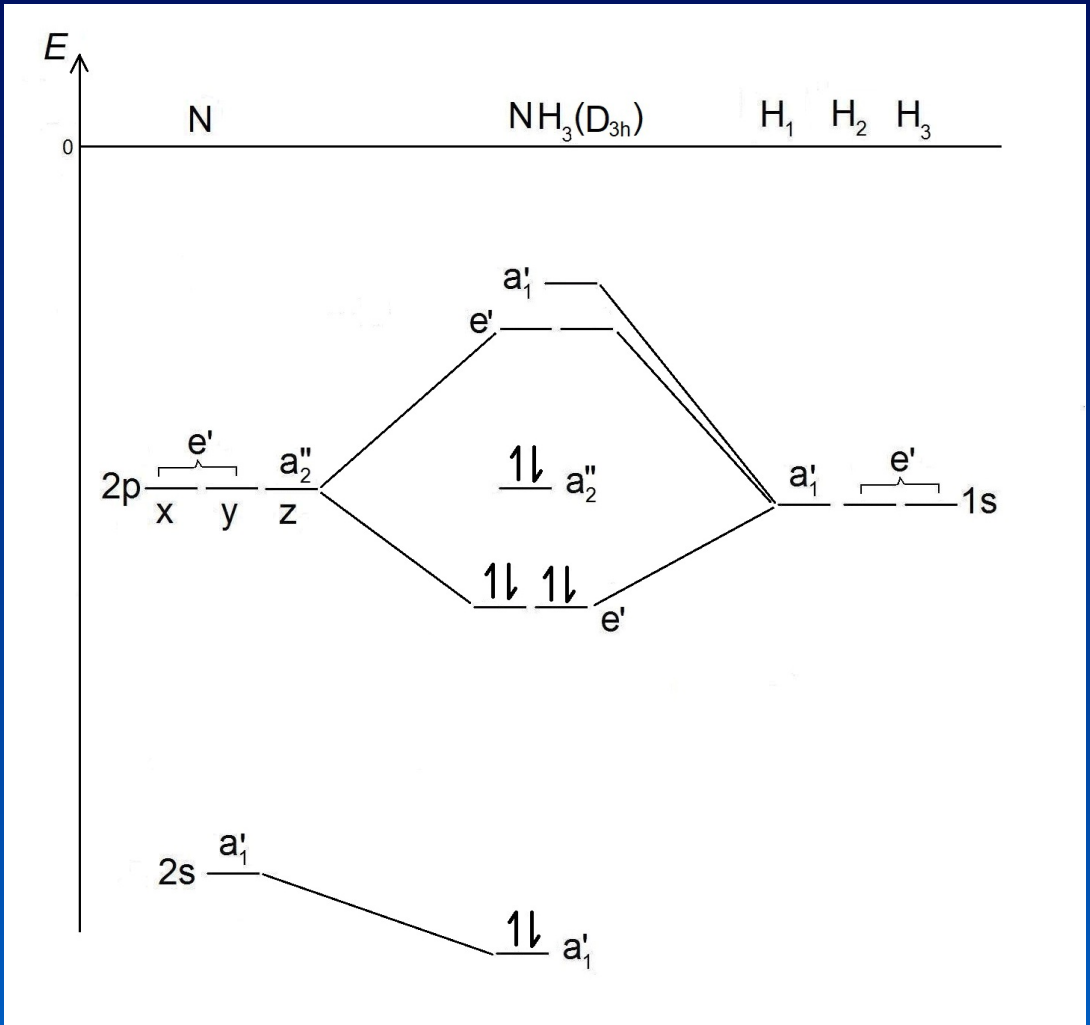


Amônia (plana) - D_{3h}

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	$A_1' + E'$

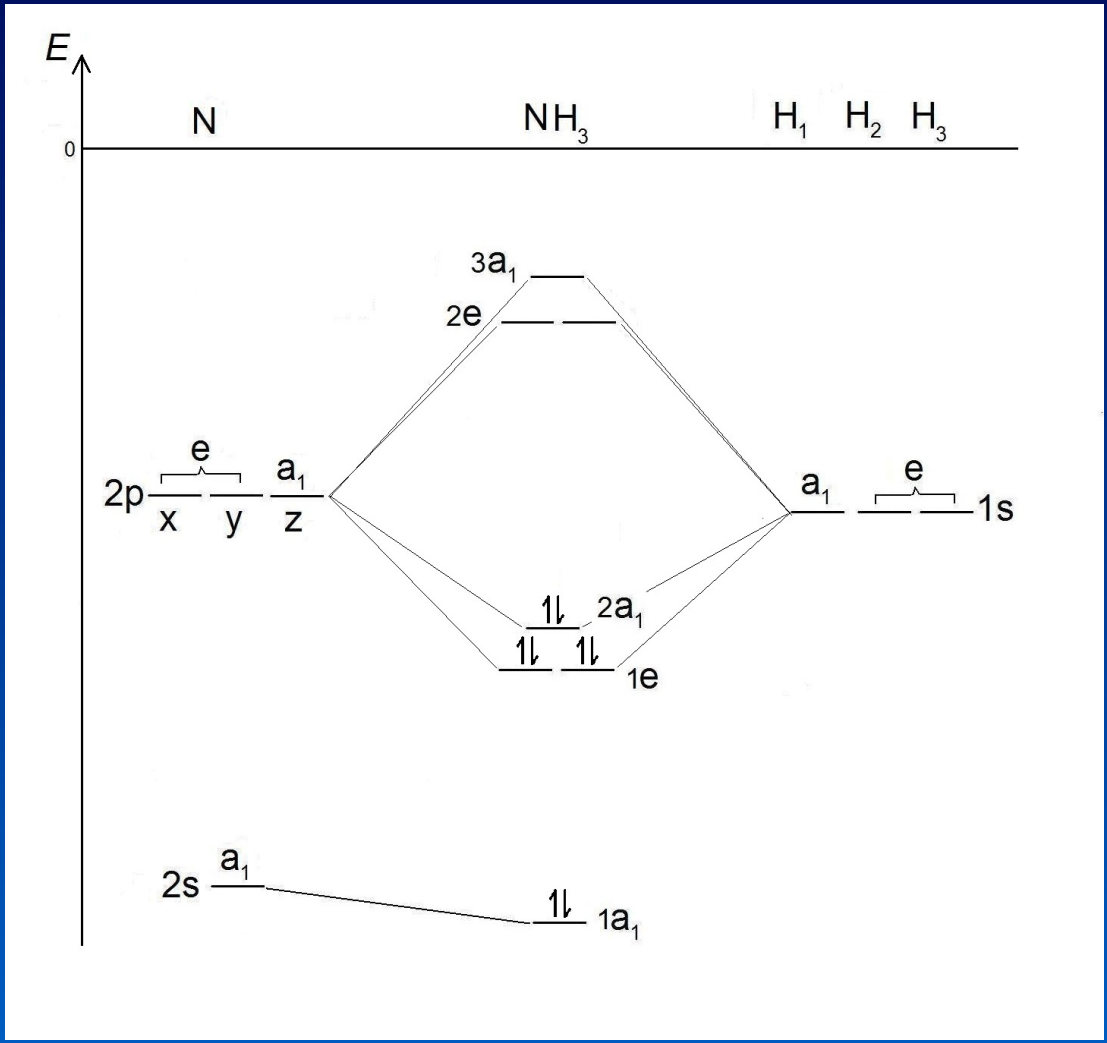
Amônia plana - D_{3h}

Diagrama de energia dos orbitais moleculares



Amônia piramidal - C_{3v}

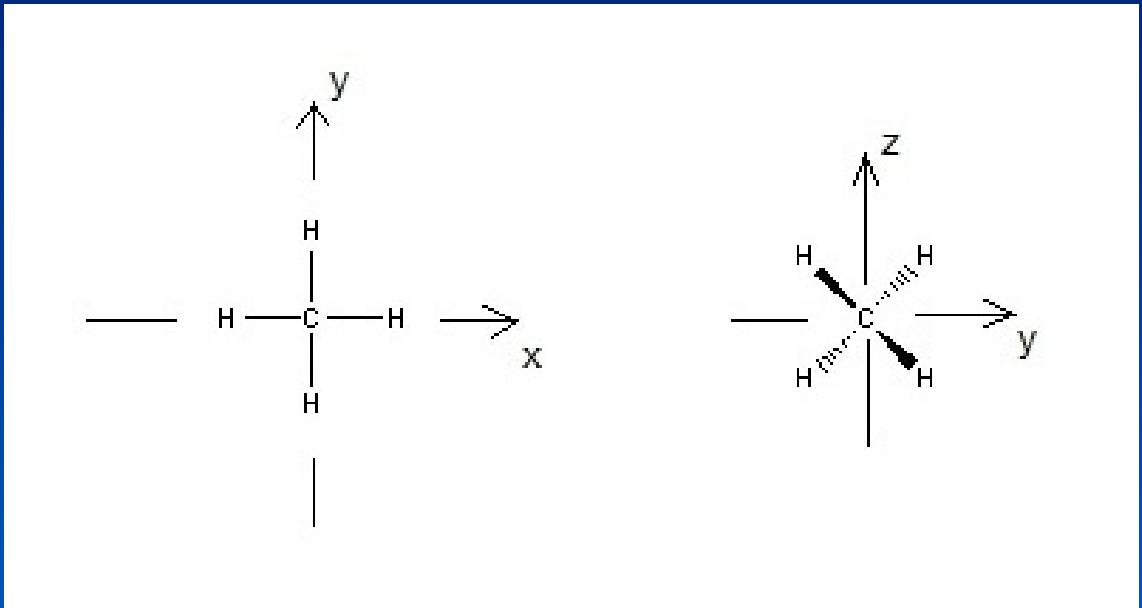
Diagrama de energia dos orbitais moleculares



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.

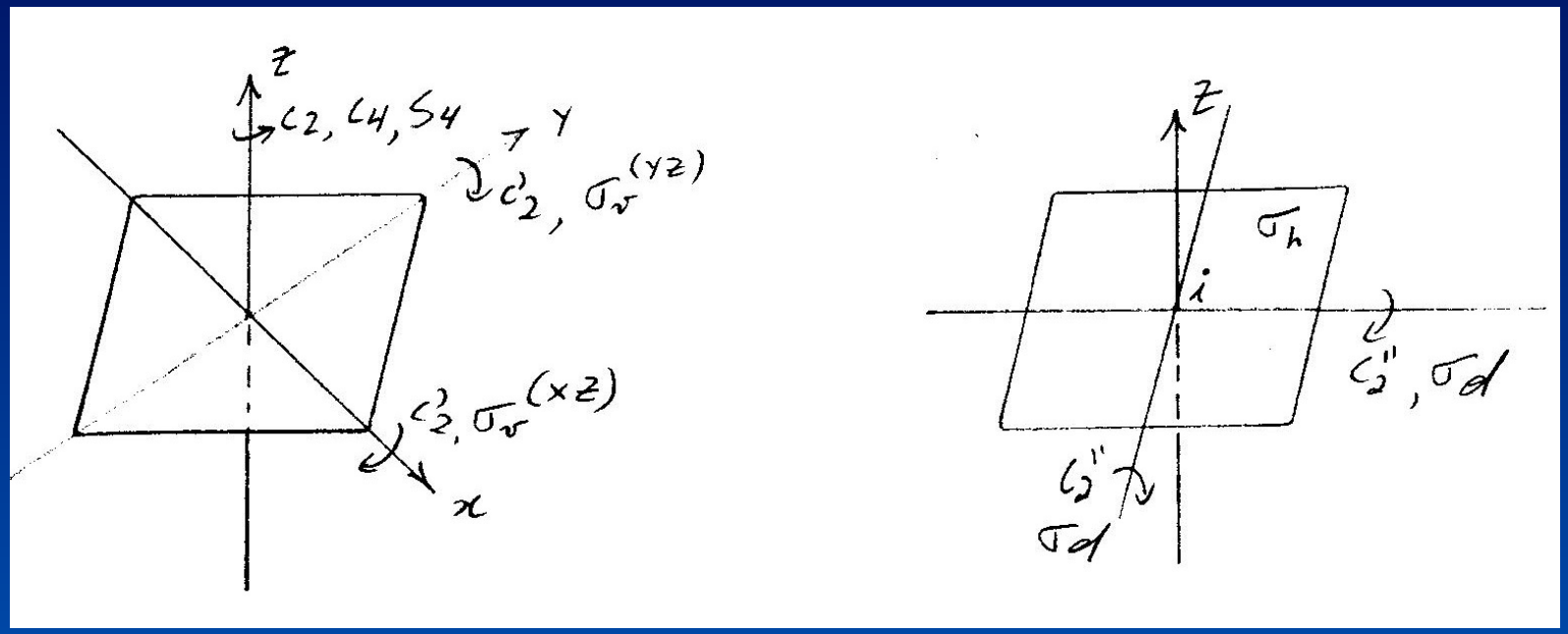
Metano plano (D_{4h})
×
Metano tetraédrico (T_d)



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}

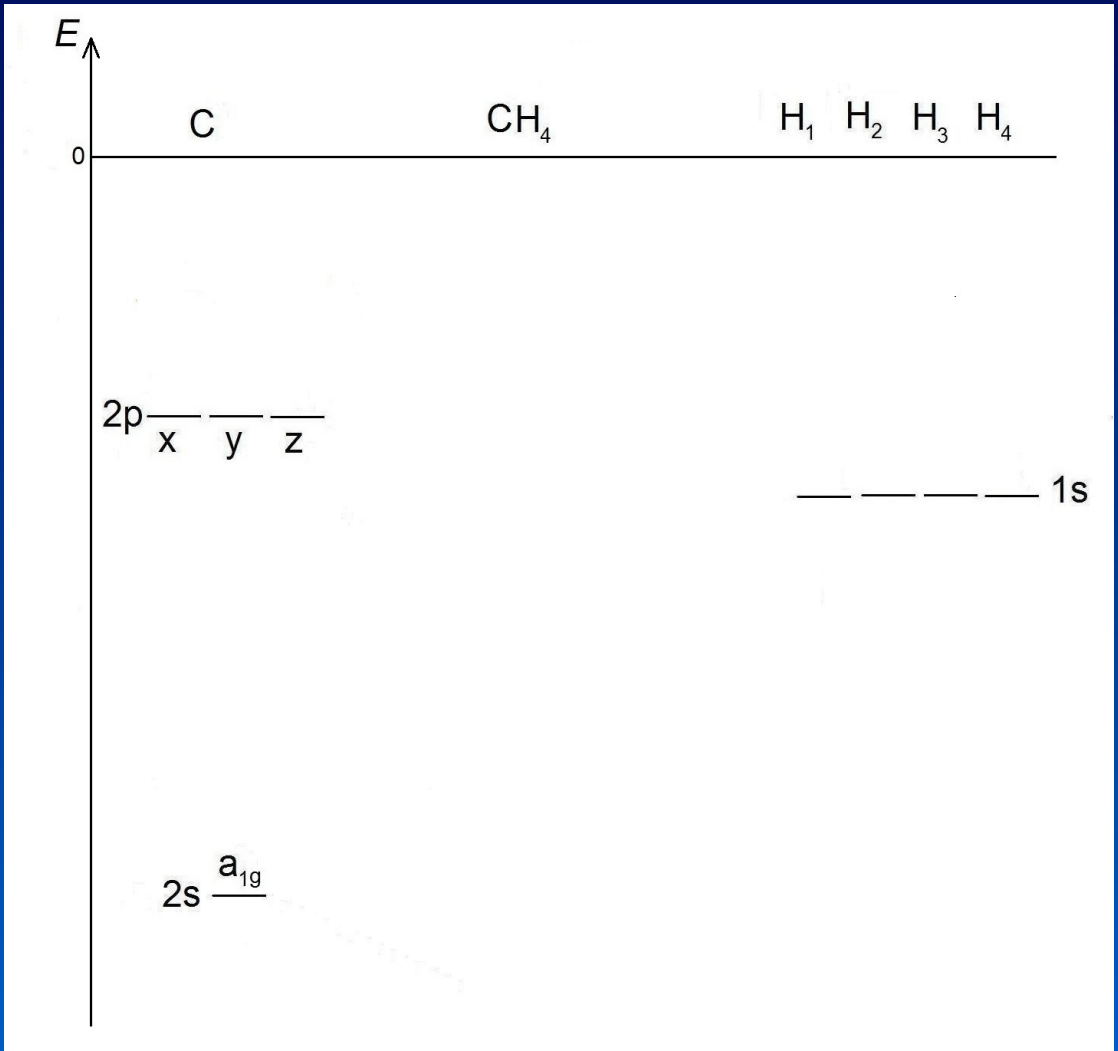


Classificando o orbital 2s do carbono

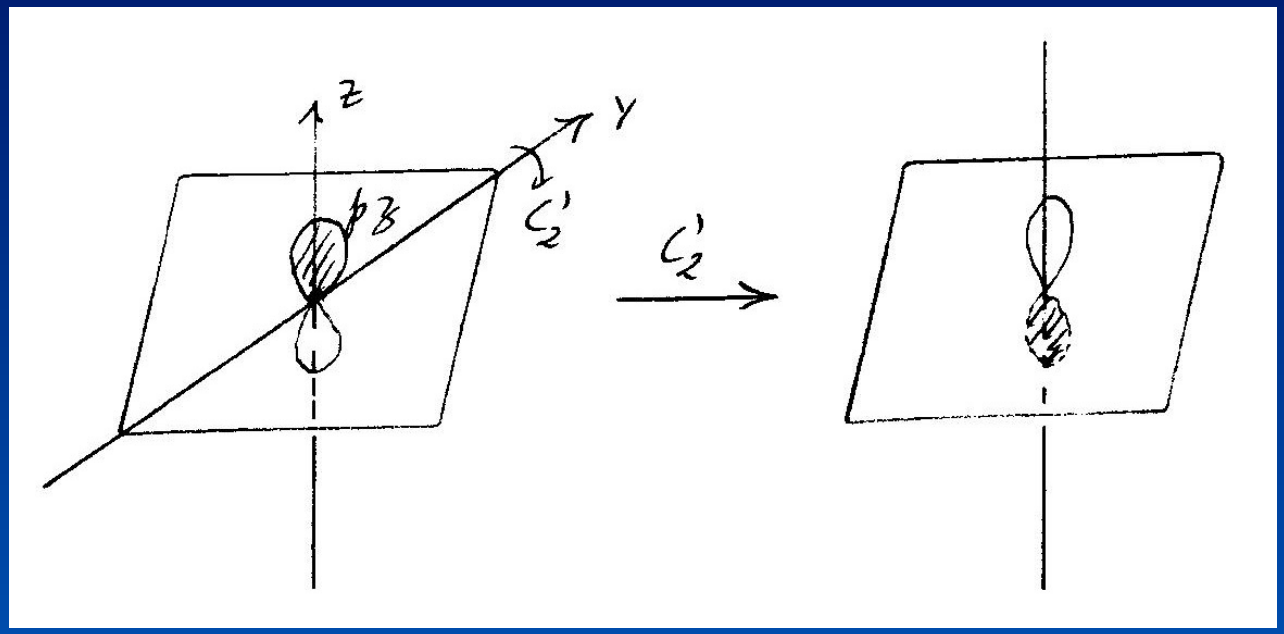
D_{4h}	E	$2C_4$	C_2	$2C_2'$	$2C_2''$	i	$2S_4$	σ_h	$2\sigma_v$	$2\sigma_d$	
A_{1g}	1	1	1	1	1	1	1	1	1	1	
A_{2g}	1	1	1	-1	-1	1	1	1	-1	-1	
B_{1g}	1	-1	1	1	-1	1	-1	1	1	-1	
B_{2g}	1	-1	1	-1	1	1	-1	1	-1	1	
E_g	2	0	-2	0	0	2	0	-2	0	0	
A_{1u}	1	1	1	1	1	-1	-1	-1	-1	-1	
A_{2u}	1	1	1	-1	-1	-1	-1	-1	1	1	
B_{1u}	1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

Metano plano - D_{4h}

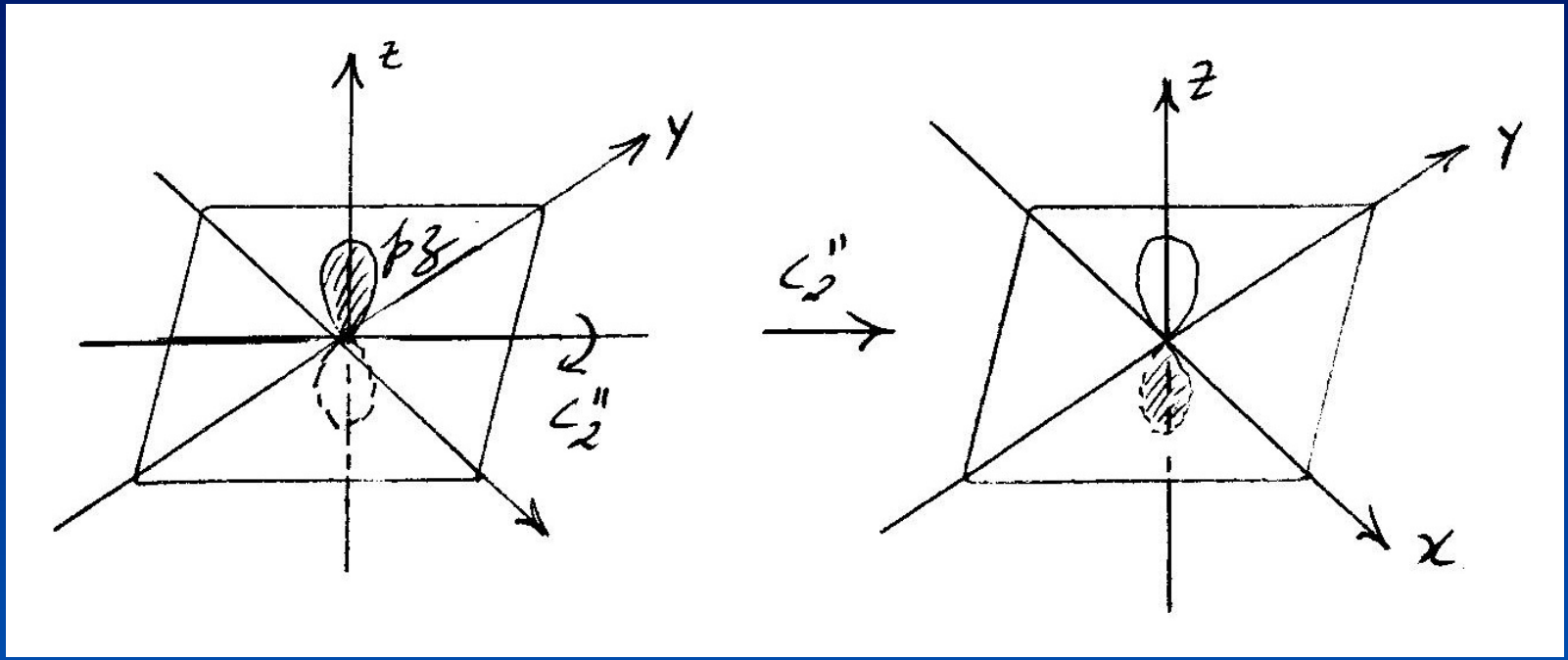
Diagrama de energia dos orbitais moleculares



Classificando o orbital $2p_z$ do carbono



Classificando o orbital $2p_z$ do carbono

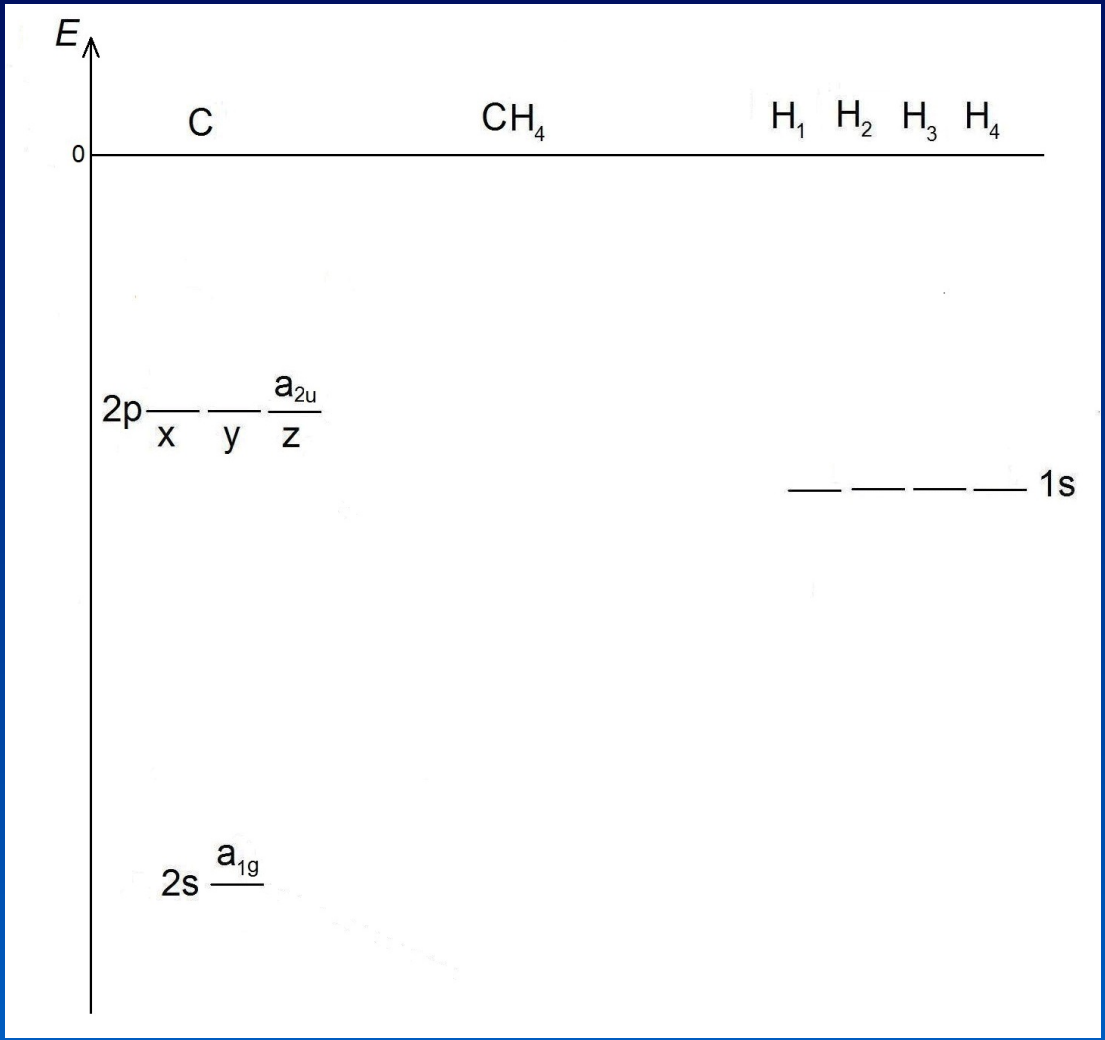


Classificando o orbital $2p_z$ do carbono

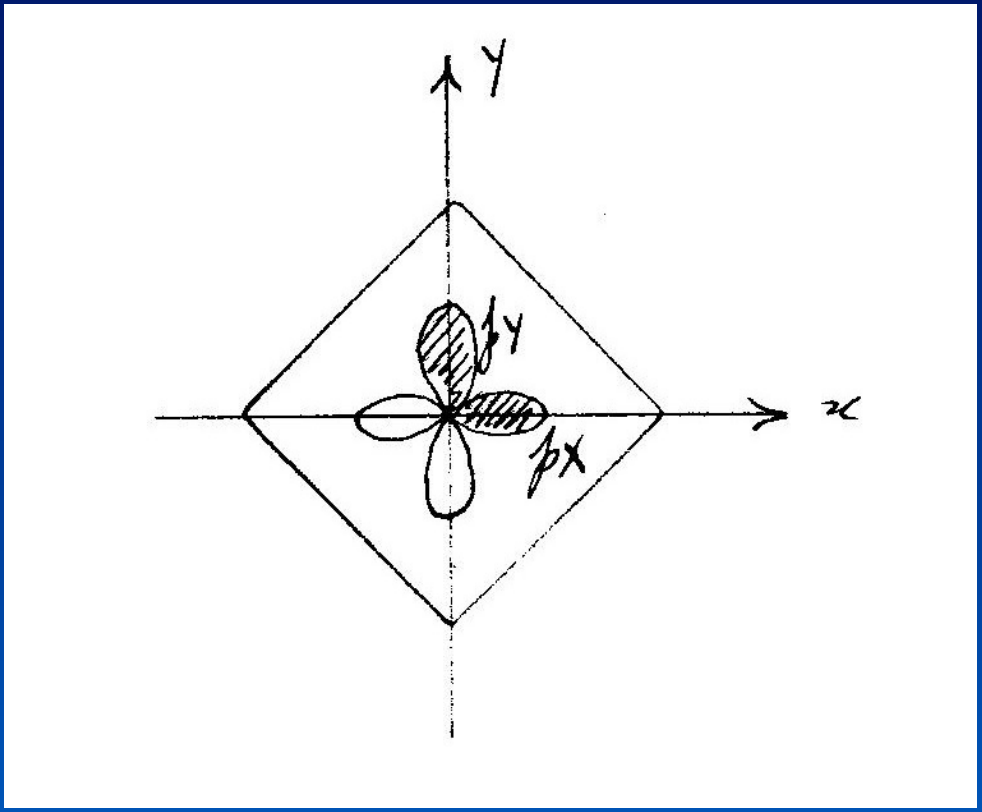
D_{4h}	E	$2C_4$	C_2	$2C_2'$	$2C_2''$	i	$2S_4$	σ_h	$2\sigma_v$	$2\sigma_d$	
A_{1g}	1	1	1	1	1	1	1	1	1	1	
A_{2g}	1	1	1	-1	-1	1	1	1	-1	-1	
B_{1g}	1	-1	1	1	-1	1	-1	1	1	-1	
B_{2g}	1	-1	1	-1	1	1	-1	1	-1	1	
E_g	2	0	-2	0	0	2	0	-2	0	0	
A_{1u}	1	1	1	1	1	-1	-1	-1	-1	-1	
A_{2u}	1	1	1	-1	-1	-1	-1	-1	1	1	
B_{1u}	1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

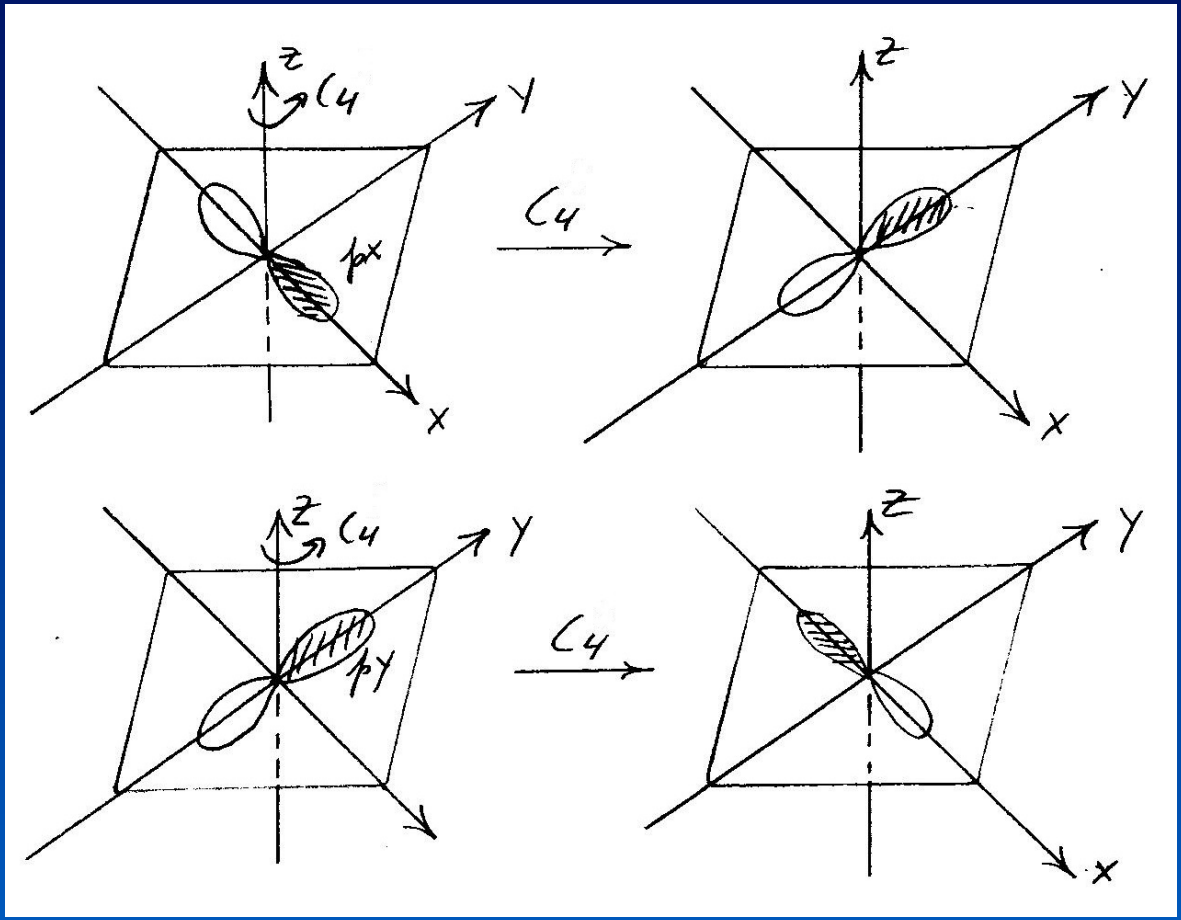
Diagrama de energia dos orbitais moleculares



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

	$2p_x$	$2p_y$
$2p_x$	1	0
$2p_y$	0	1

$$\xrightarrow{C_4}$$

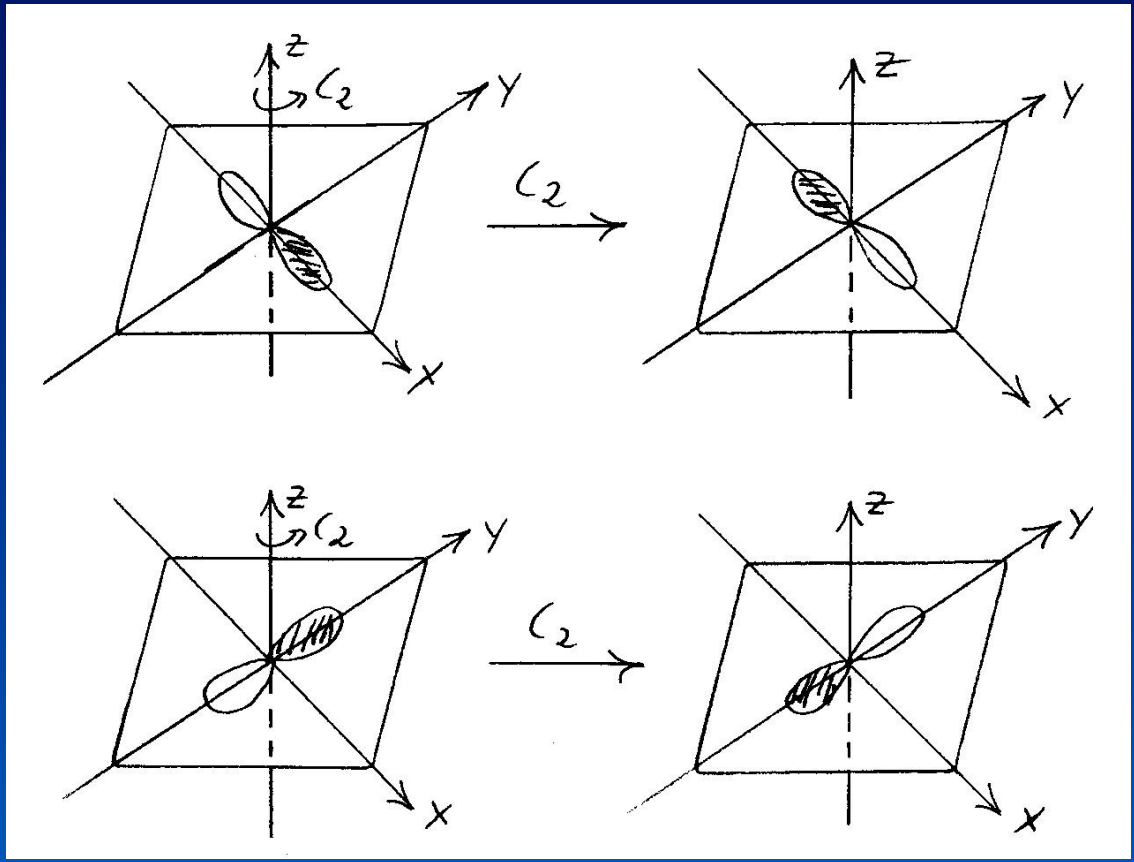
	$2p_x$	$2p_y$
$2p_x'$	0	1
$2p_y'$	-1	0

$$\chi = 0$$

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

	$2p_x$	$2p_y$
$2p_x$	1	0
$2p_y$	0	1

C_2 $\rightarrow$

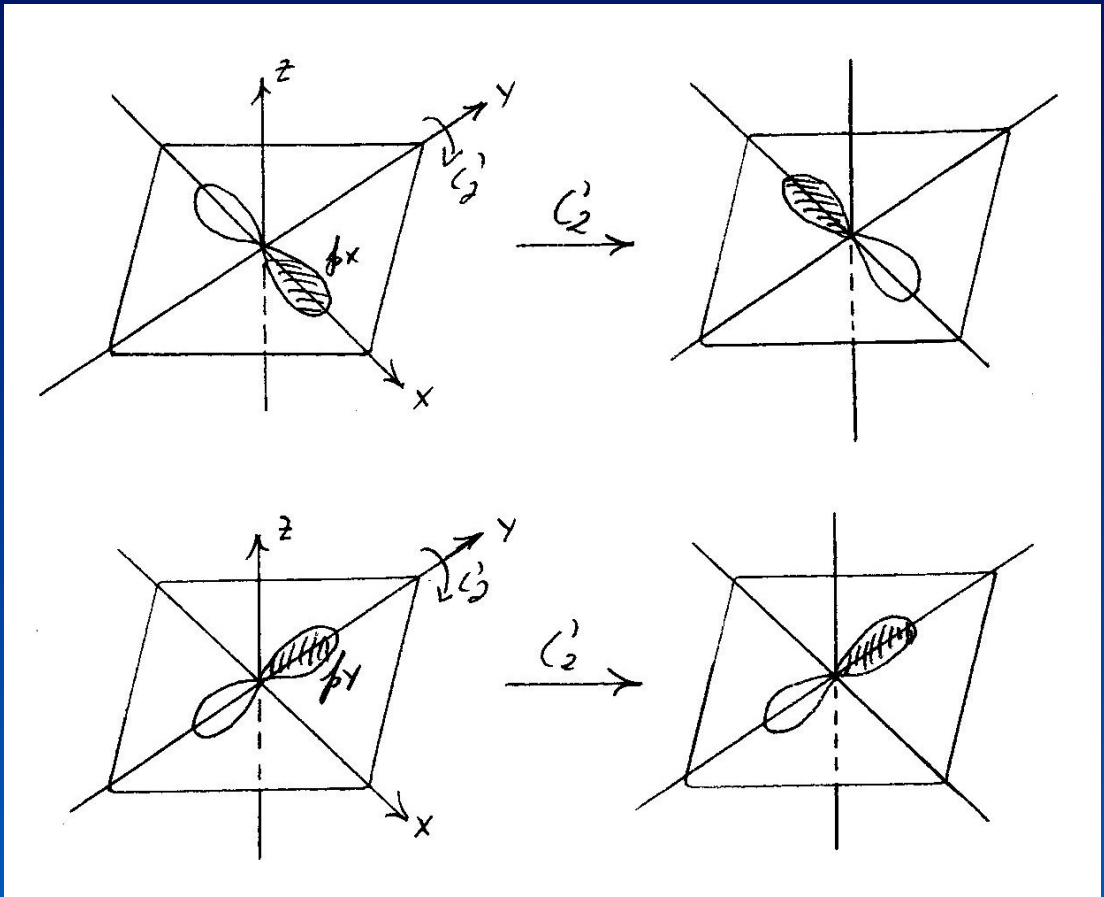
	$2p_x$	$2p_y$
$2p_x'$	-1	0
$2p_y'$	0	-1

$\chi = -2$

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

	$2p_x$	$2p_y$
$2p_x$	1	0
$2p_y$	0	1

$$\xrightarrow{C_2'^{(y)}}$$

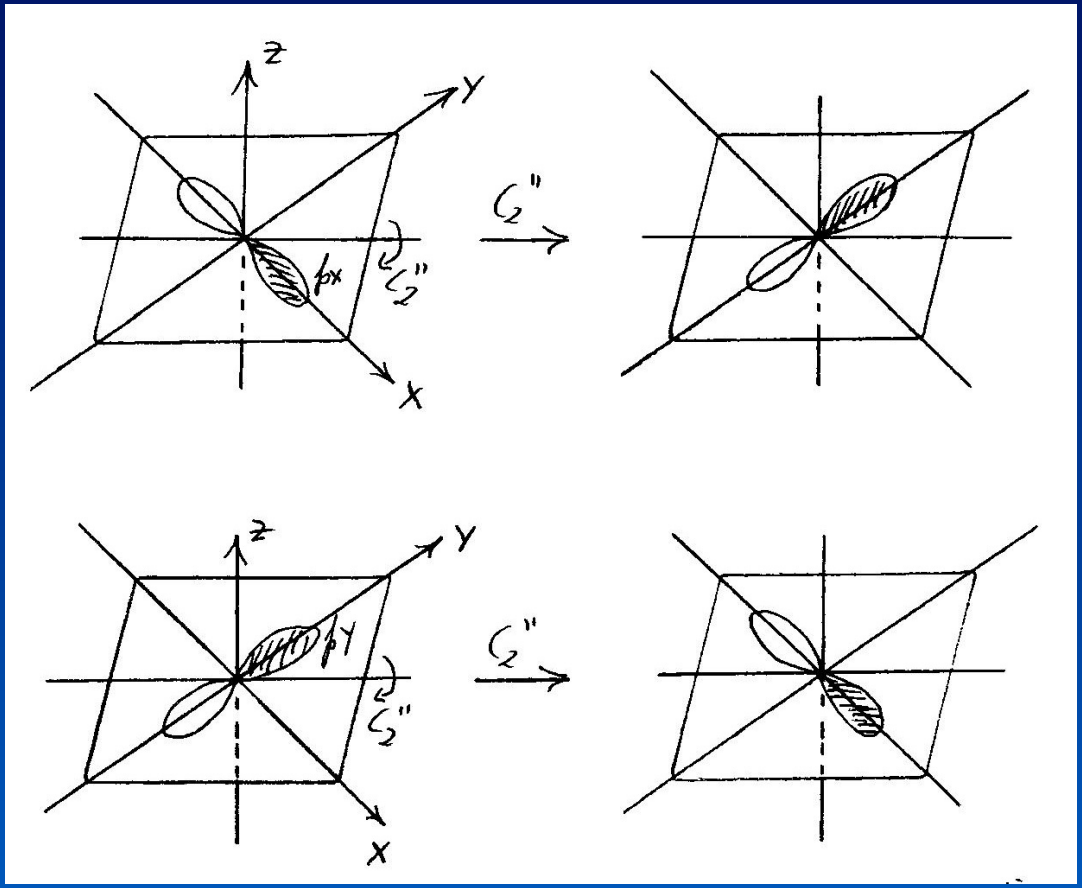
	$2p_x$	$2p_y$
$2p_x'$	-1	0
$2p_y'$	0	1

$$\chi = 0$$

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

	$2p_x$	$2p_y$
$2p_x$	1	0
$2p_y$	0	1

$$\xrightarrow{C_2''}$$

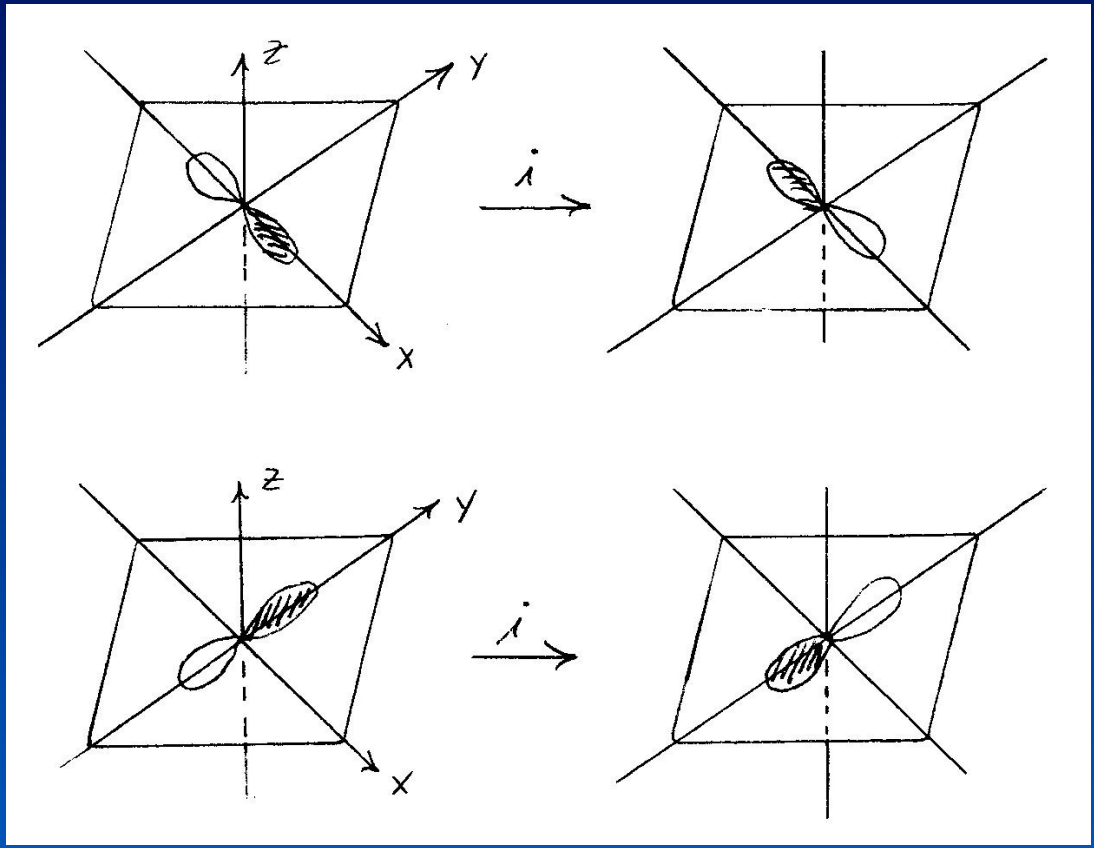
	$2p_x$	$2p_y$
$2p_x'$	0	1
$2p_y'$	1	0

$$\chi = 0$$

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

	$2p_x$	$2p_y$
$2p_x$	1	0
$2p_y$	0	1

$\xrightarrow{i}$

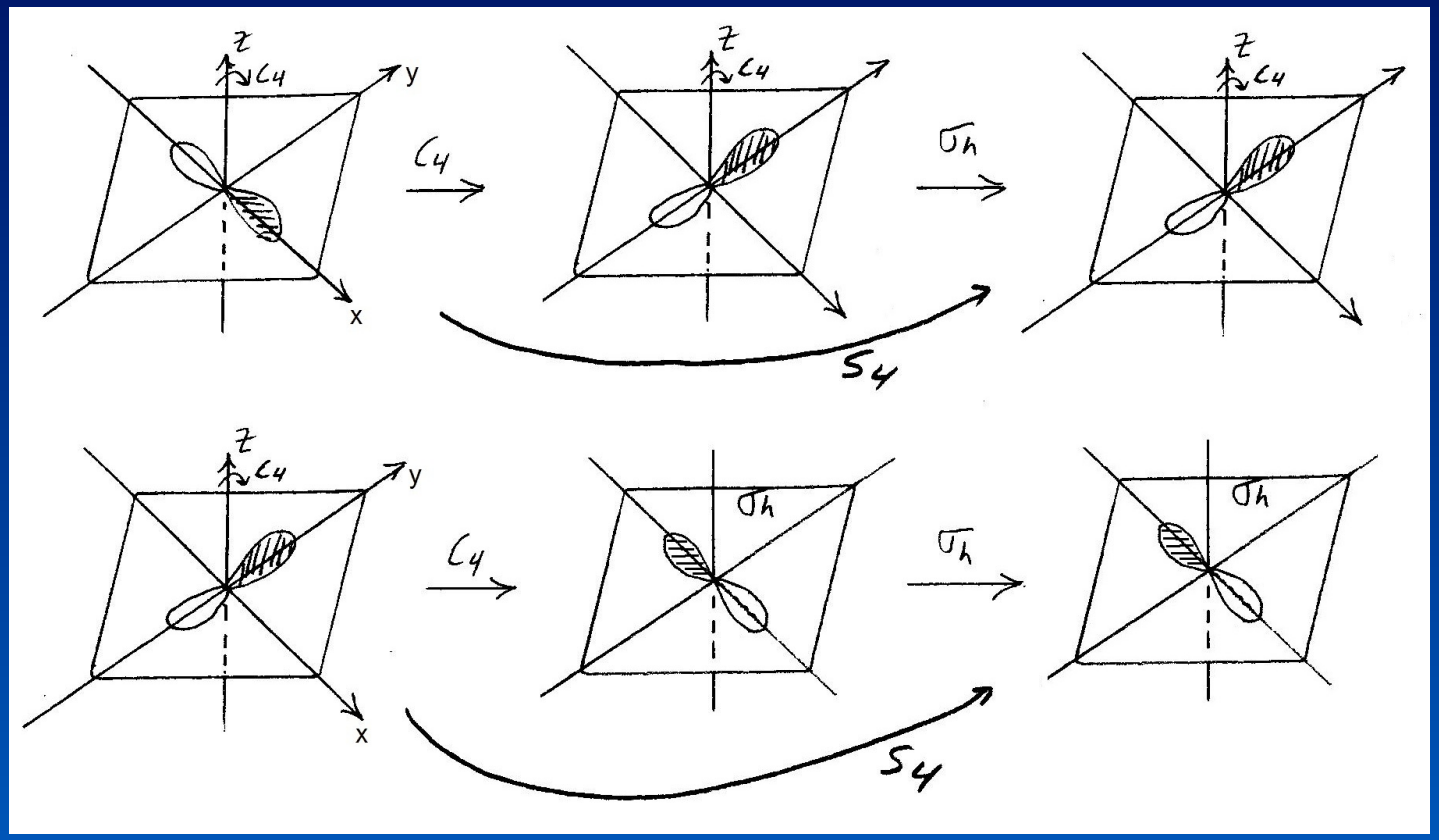
	$2p_x$	$2p_y$
$2p_x'$	-1	0
$2p_y'$	0	-1

$\chi = -2$

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

	$2p_x$	$2p_y$
$2p_x$	1	0
$2p_y$	0	1

$\xrightarrow{S_4}$

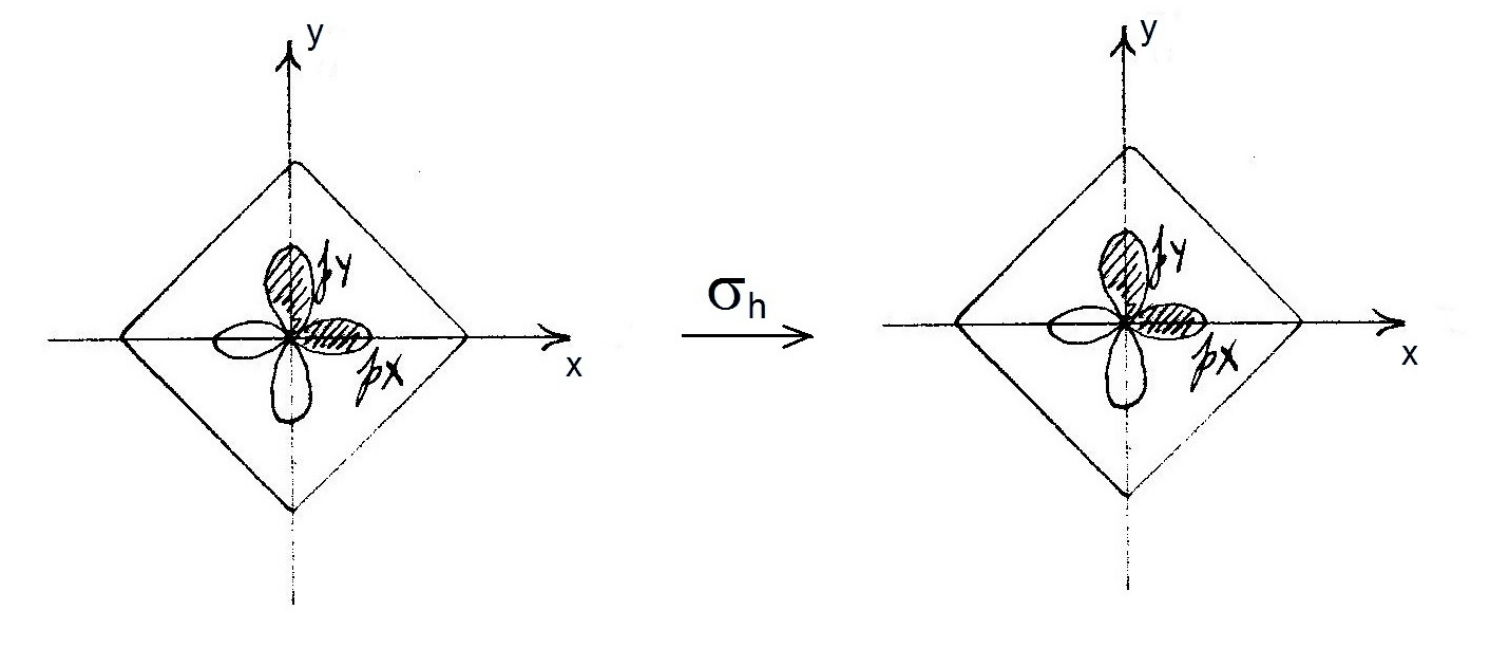
	$2p_x$	$2p_y$
$2p_x'$	0	1
$2p_y'$	-1	0

$$\chi = 0$$

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

	$2p_x$	$2p_y$
$2p_x$	1	0
$2p_y$	0	1

$\xrightarrow{\sigma_h}$

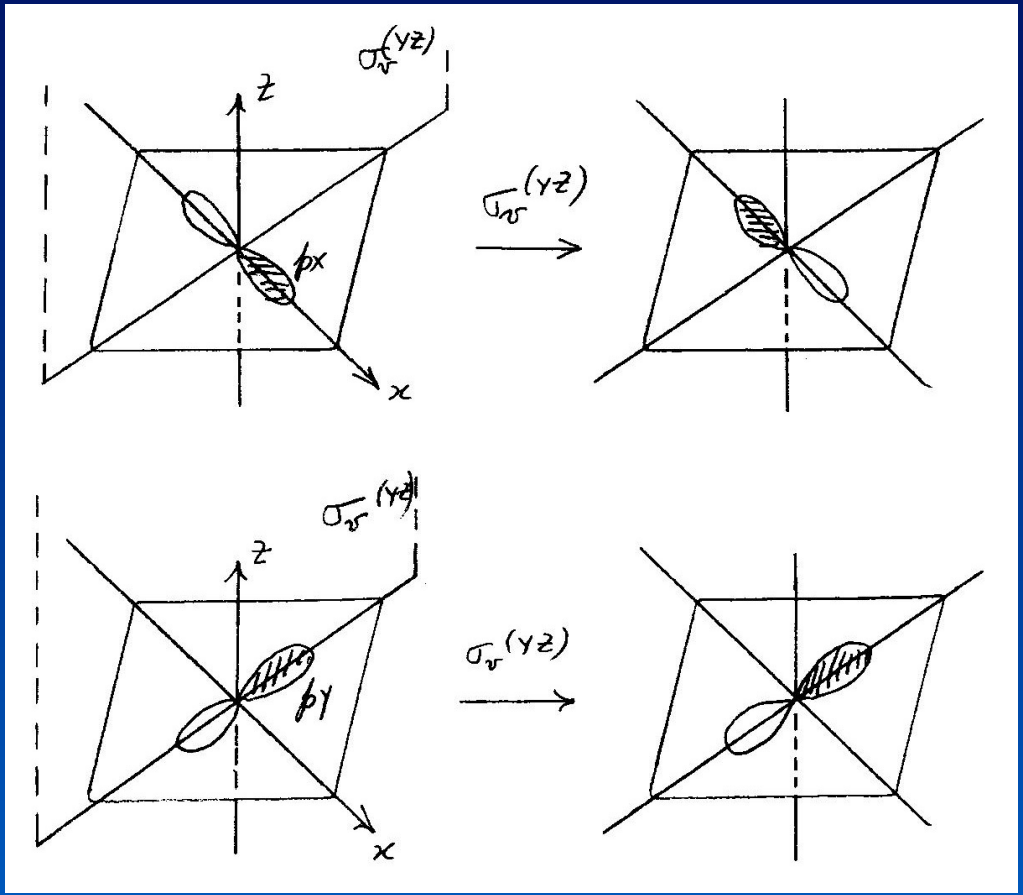
	$2p_x$	$2p_y$
$2p_x'$	1	0
$2p_y'$	0	1

$\chi = 2$

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

	$2p_x$	$2p_y$
$2p_x$	1	0
$2p_y$	0	1

$\sigma_v^{(yz)}$ $\rightarrow$

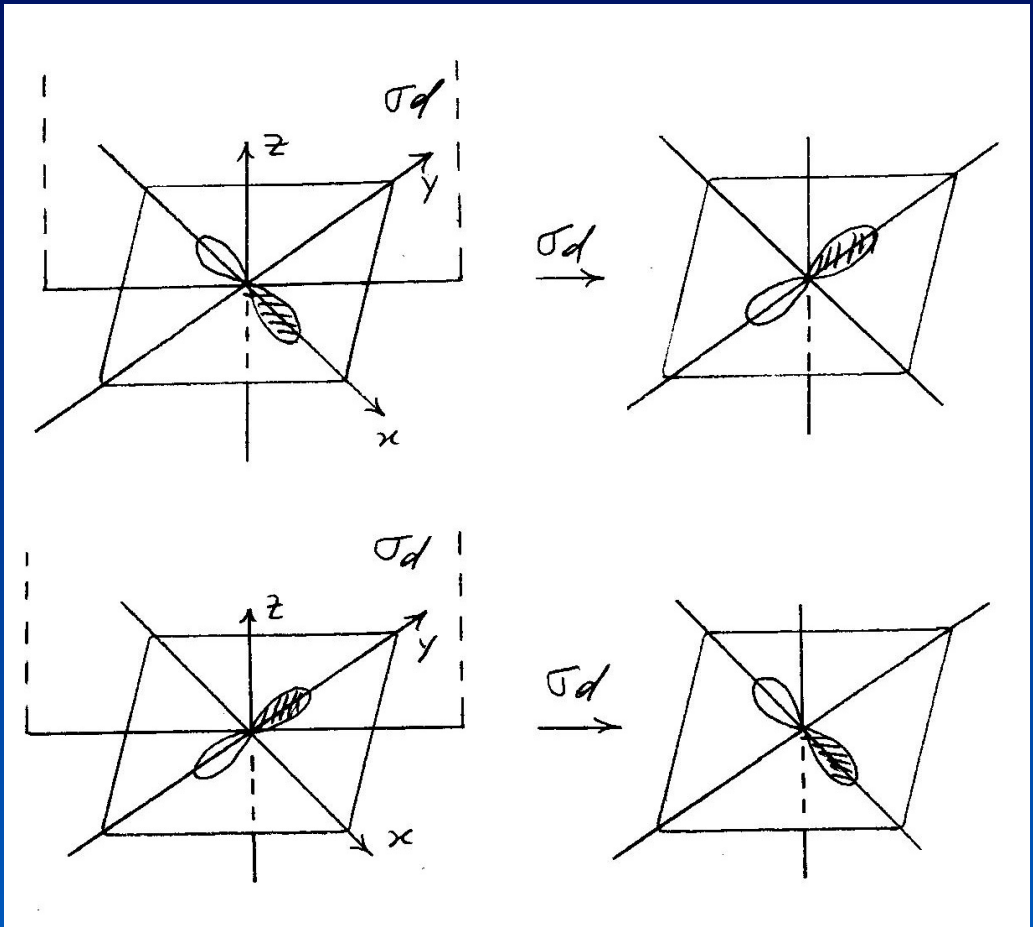
	$2p_x$	$2p_y$
$2p_x'$	-1	0
$2p_y'$	0	1

$\chi = 0$

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

	$2p_x$	$2p_y$
$2p_x$	1	0
$2p_y$	0	1

$\xrightarrow{\sigma_d}$

	$2p_x$	$2p_y$
$2p_x'$	0	1
$2p_y'$	1	0

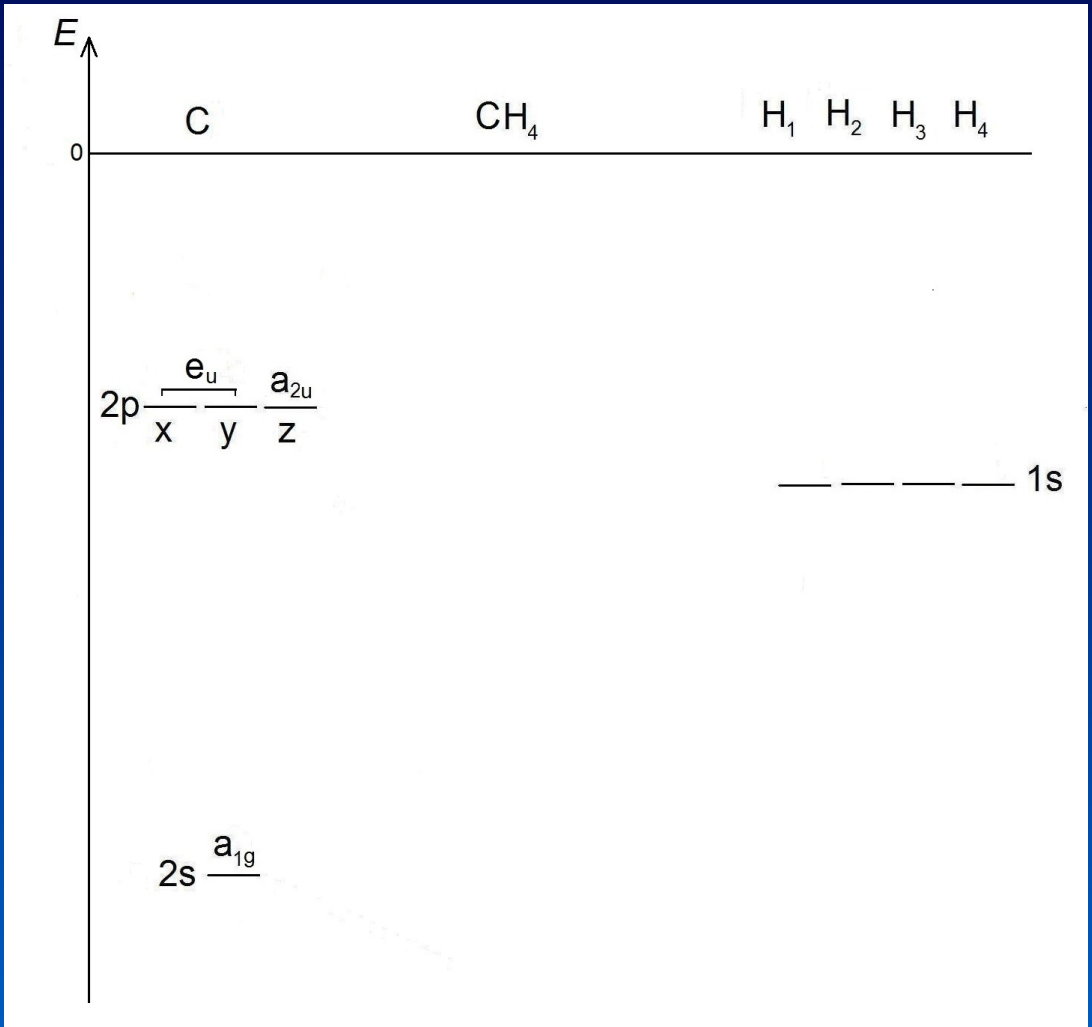
$$\chi = 0$$

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

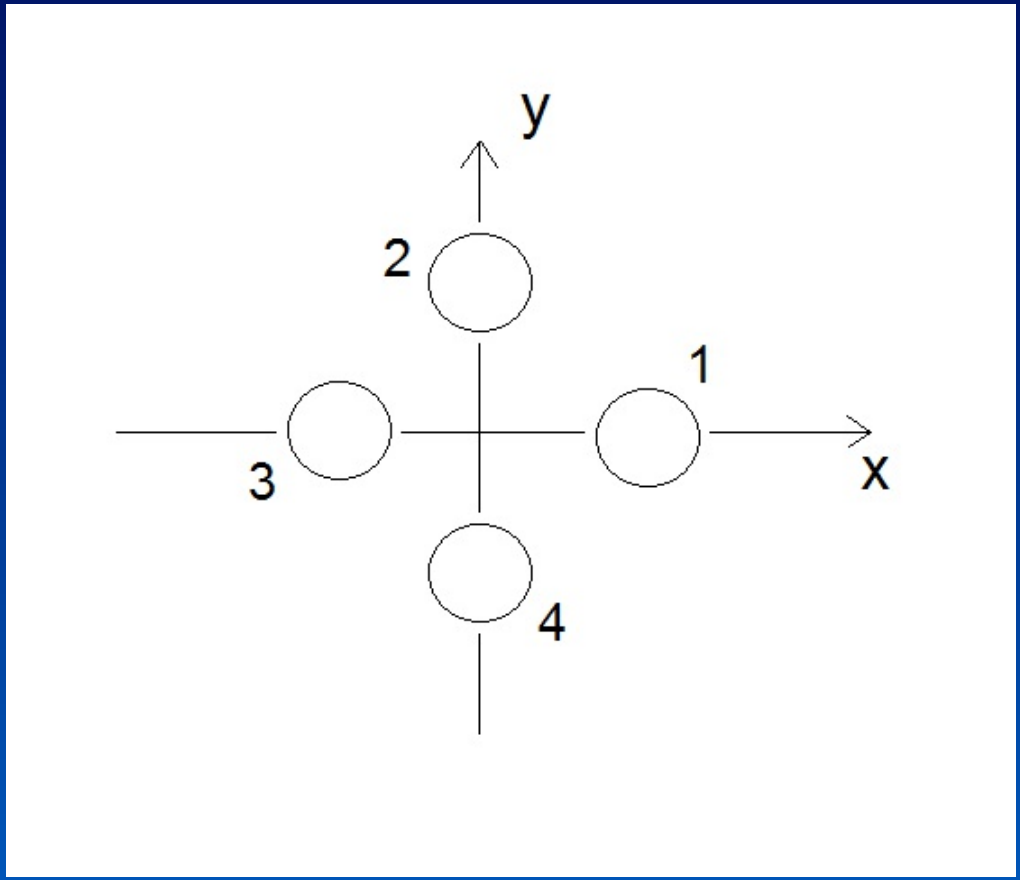
D_{4h}	E	$2C_4$	C_2	$2C_2'$	$2C_2''$	i	$2S_4$	σ_h	$2\sigma_v$	$2\sigma_d$	
A_{1g}	1	1	1	1	1	1	1	1	1	1	
A_{2g}	1	1	1	-1	-1	1	1	1	-1	-1	
B_{1g}	1	-1	1	1	-1	1	-1	1	1	-1	
B_{2g}	1	-1	1	-1	1	1	-1	1	-1	1	
E_g	2	0	-2	0	0	2	0	-2	0	0	
A_{1u}	1	1	1	1	1	-1	-1	-1	-1	-1	
A_{2u}	1	1	1	-1	-1	-1	-1	-1	1	1	
B_{1u}	1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

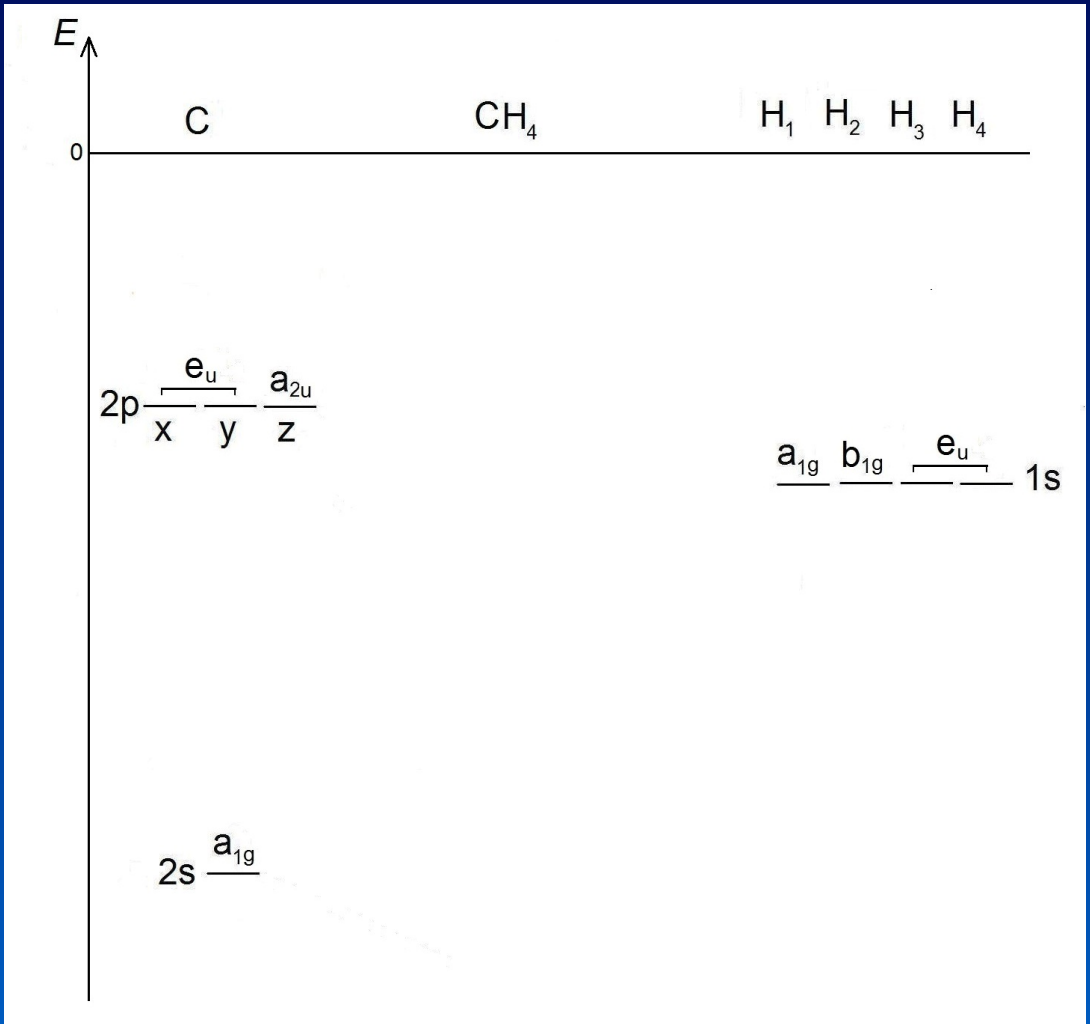


Classificando os orbitais 1s dos hidrogênios

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	
4(1s)	4	0	0	2	0	0	0	4	2	0	$A_{1g}+B_{1g}+E_u$

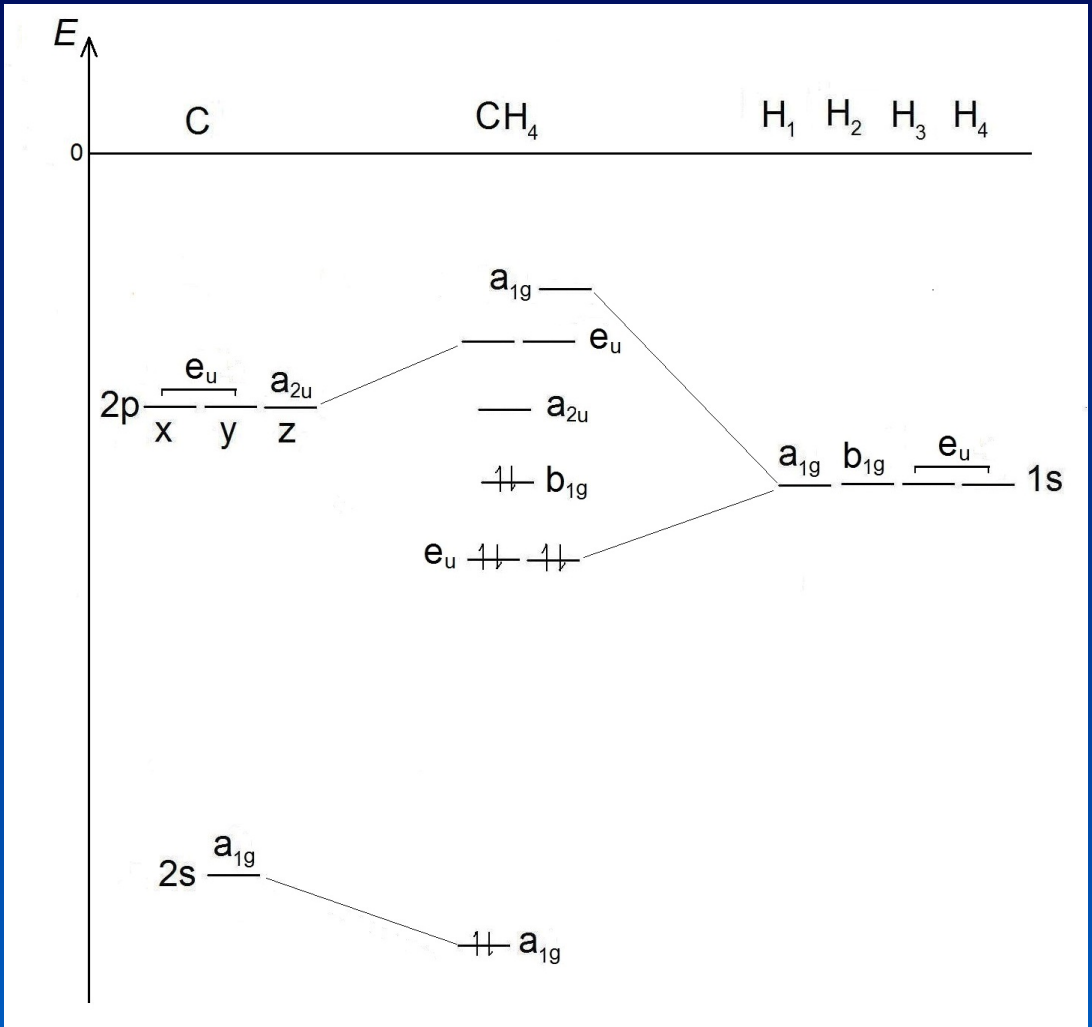
Metano plano - D_{4h}

Diagrama de energia dos orbitais moleculares



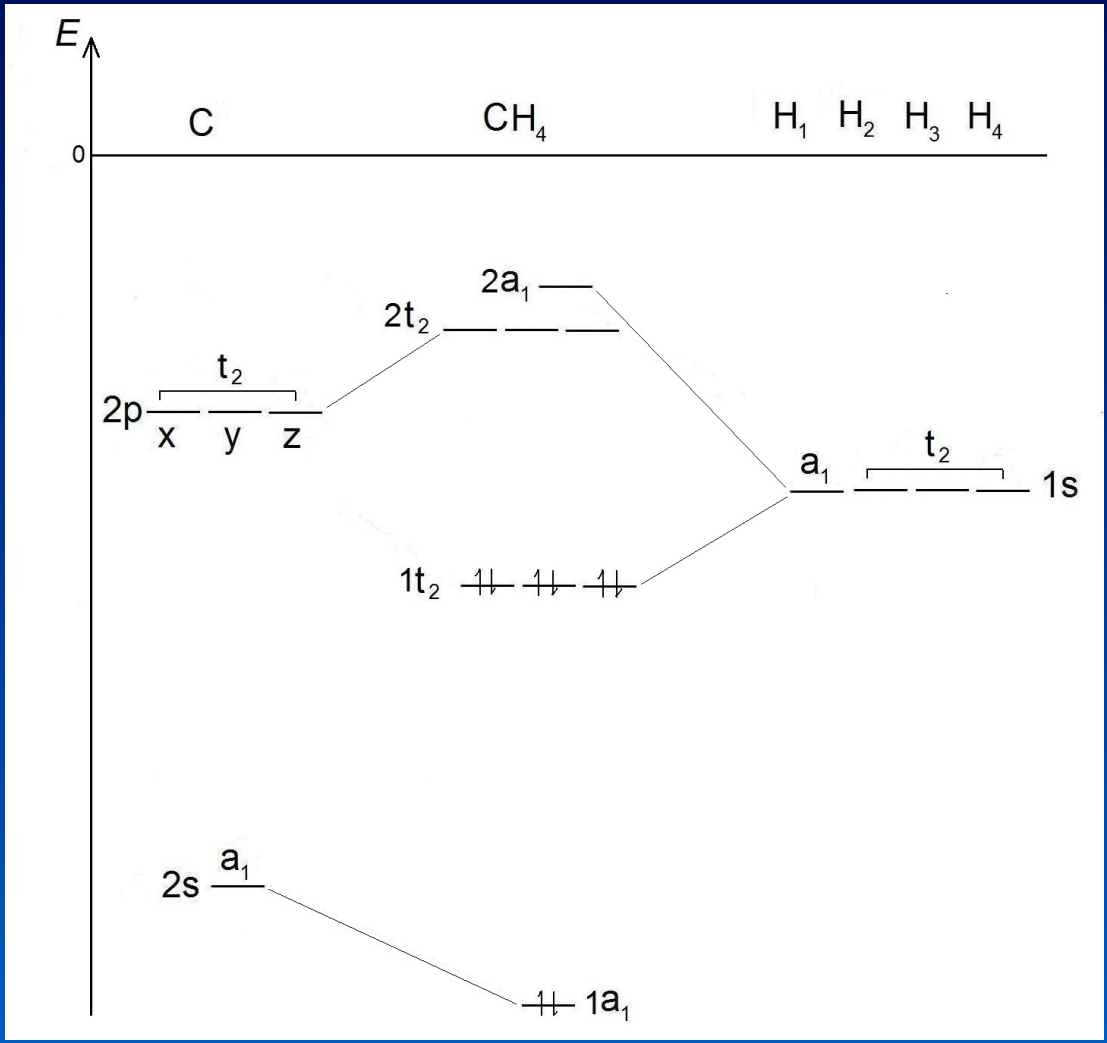
Metano plano - D_{4h}

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.

CO_2 linear ($D_{\infty h}$)

$\times$

CO_2 angular (C_{2v})

Moléculas AB_2

Diagrama de energia dos orbitais moleculares

Moléculas/íons lineares (16 elétrons):

CO_2 N_3^- NO_2^+ N_2O

Moléculas/íons angulares:

17 elétrons: $NO_2^\bullet$

18 elétrons: O_3 NO_2^- SO_2

19 elétrons: $ClO_2^\bullet$

20 elétrons: ClO_2^-

AB_2 (linear) - $D_{\infty h}$

$\varphi = 90°$

$D_{\infty h}$	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	
$A(p_x,p_y)$	2	0		-2	0		Π_u

AB_2 (linear) - $D_{\infty h}$

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

	$2p_x^{B1}$	$2p_y^{B1}$	$2p_x^{B2}$	$2p_y^{B2}$
$2p_x^{B1}$	1	0	0	0
$2p_y^{B1}$	0	1	0	0
$2p_x^{B2}$	0	0	1	0
$2p_y^{B2}$	0	0	0	1

$\xrightarrow{C_\infty^{\varphi = 90°}}$

	$2p_x^{B1}$	$2p_y^{B1}$	$2p_x^{B2}$	$2p_y^{B2}$
$2p_x^{B1}$	0	1	0	0
$2p_x^{B1}$	-1	0	0	0
$2p_x^{B2}$	0	0	0	1
$2p_x^{B2}$	0	0	-1	0

$\chi = 4$

$\chi = 0$

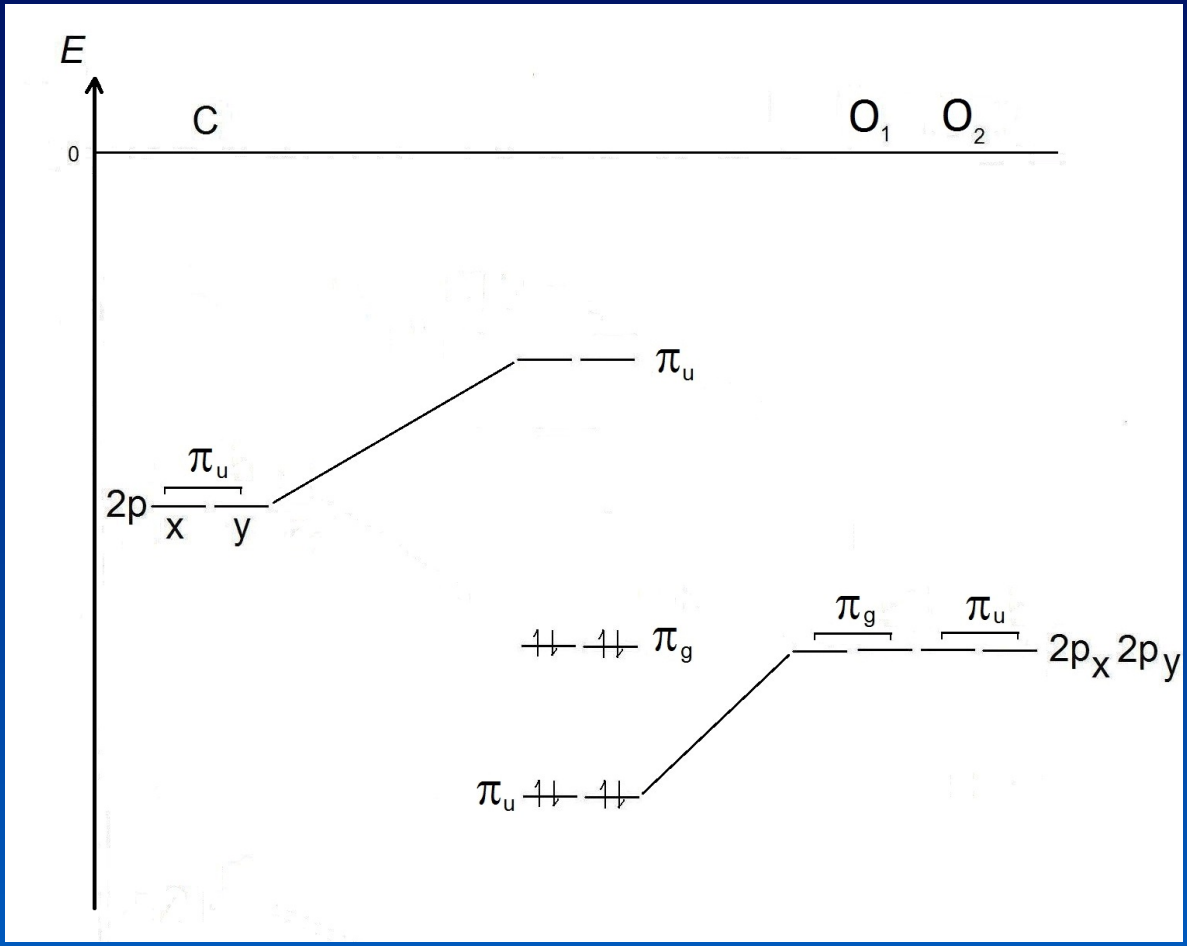
AB_2 (linear) - $D_{\infty h}$

$\varphi = 90°$

$D_{\infty h}$	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
$BB(p_x,p_y)$	4	0	0	0	0	0 $\Pi_u + \Pi_g$

CO_2 linear - $D_{\infty h}$

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 $NO_2^{\bullet}$ (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 $ClO_2^{\bullet}$ (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.