Química Inorgânica Avançada
IQU-708

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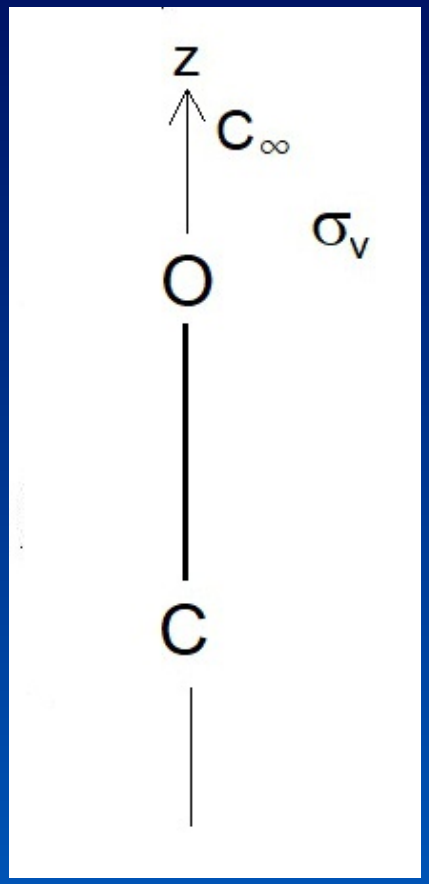
Simetria - Aula 3 - Moléculas lineares
Diatômicas heteronucleares - $C_{\infty v}$
Diatômicas homonucleares - $D_{\infty h}$
Termos espectroscópicos para moléculas

09/08/2024

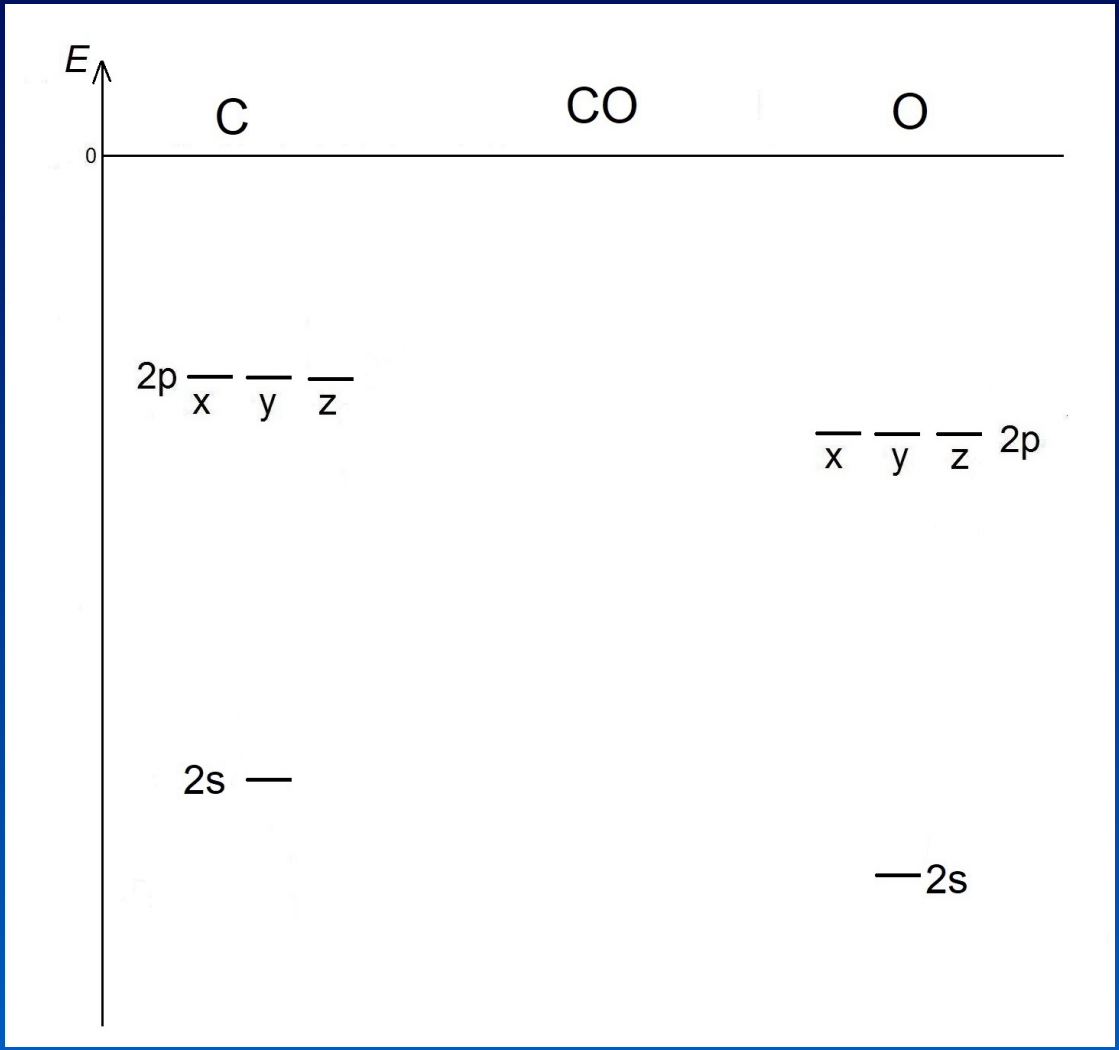
Diatômicas heteronucleares - $C_{\infty v}$

CO - $C_{\infty v}$



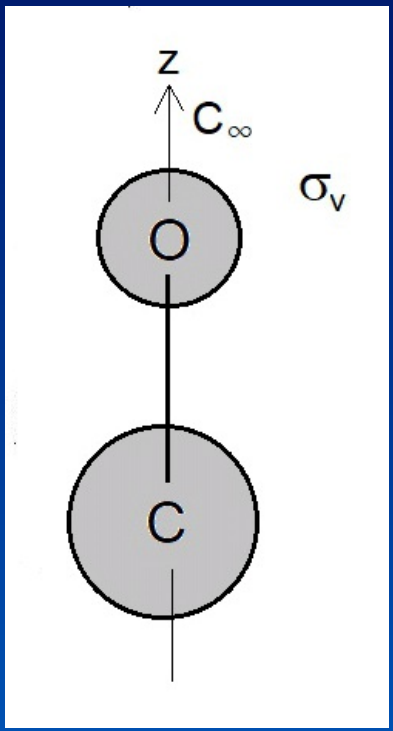
$C_{\infty v}$	E	$2C_{\infty}^{\varphi}$	$\infty\sigma_v$
Σ^+	1	1	1
Σ^-	1	1	-1
Π	2	$2\cos\varphi$	0
Δ	2	$2\cos2\varphi$	0
Φ	2	$2\cos3\varphi$	0

CO - $C_{\infty v}$



CO - $C_{\infty v}$

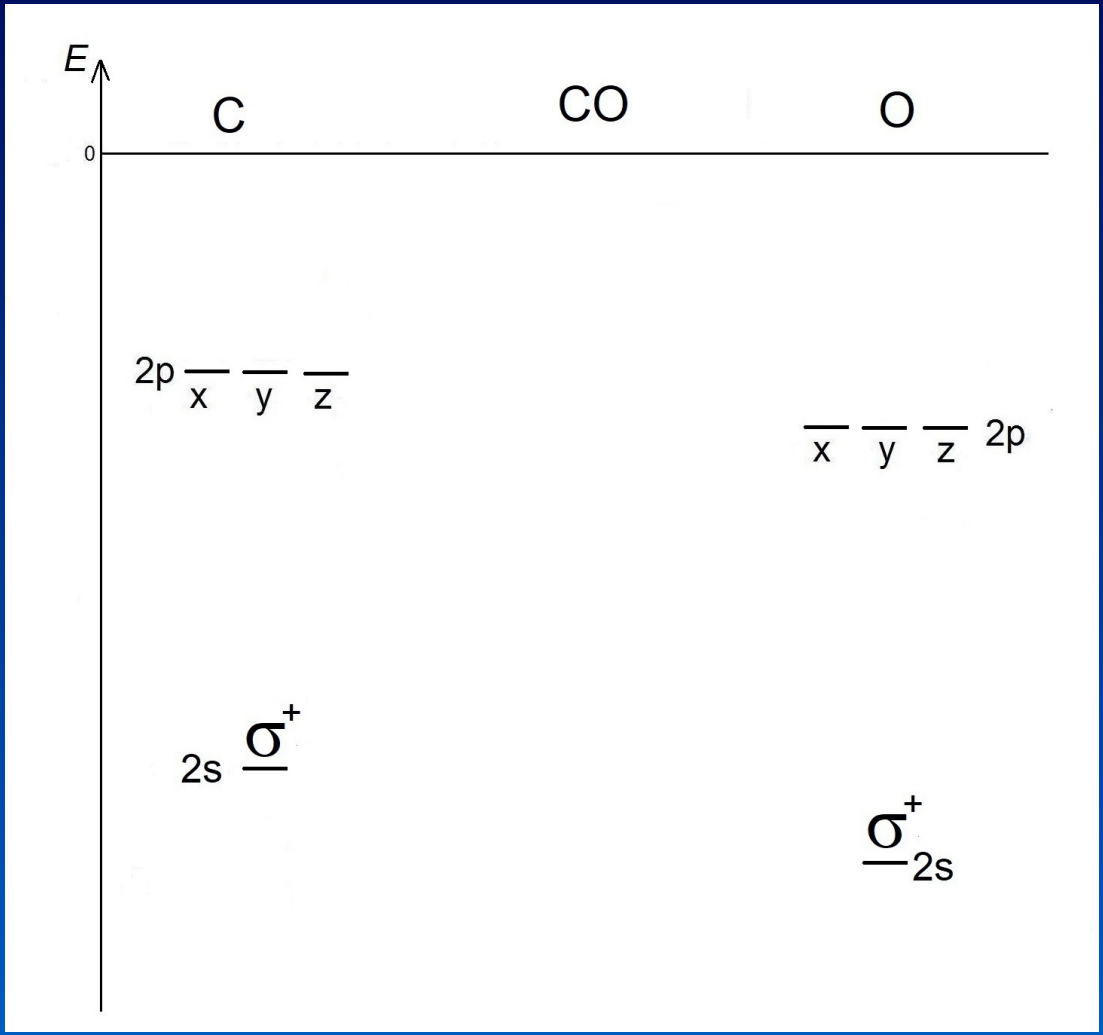
Orbitais 2s -independentes



$C_{\infty v}$	E	$2C_\infty^{\varphi}$	$\infty\sigma_v$
Σ^+	1	1	1
Σ^-	1	1	-1
Π	2	$2\cos\varphi$	0
Δ	2	$2\cos 2\varphi$	0
Φ	2	$2\cos 3\varphi$	0

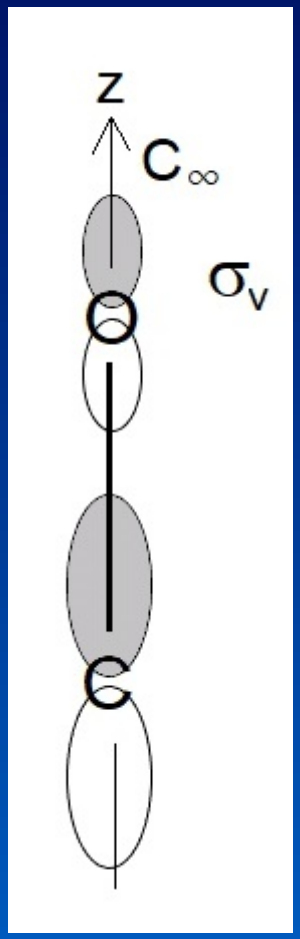
2s(C)	1	1	1	Σ^+
2s(O)	1	1	1	Σ^+

CO - $C_{\infty v}$



CO - $C_{\infty v}$

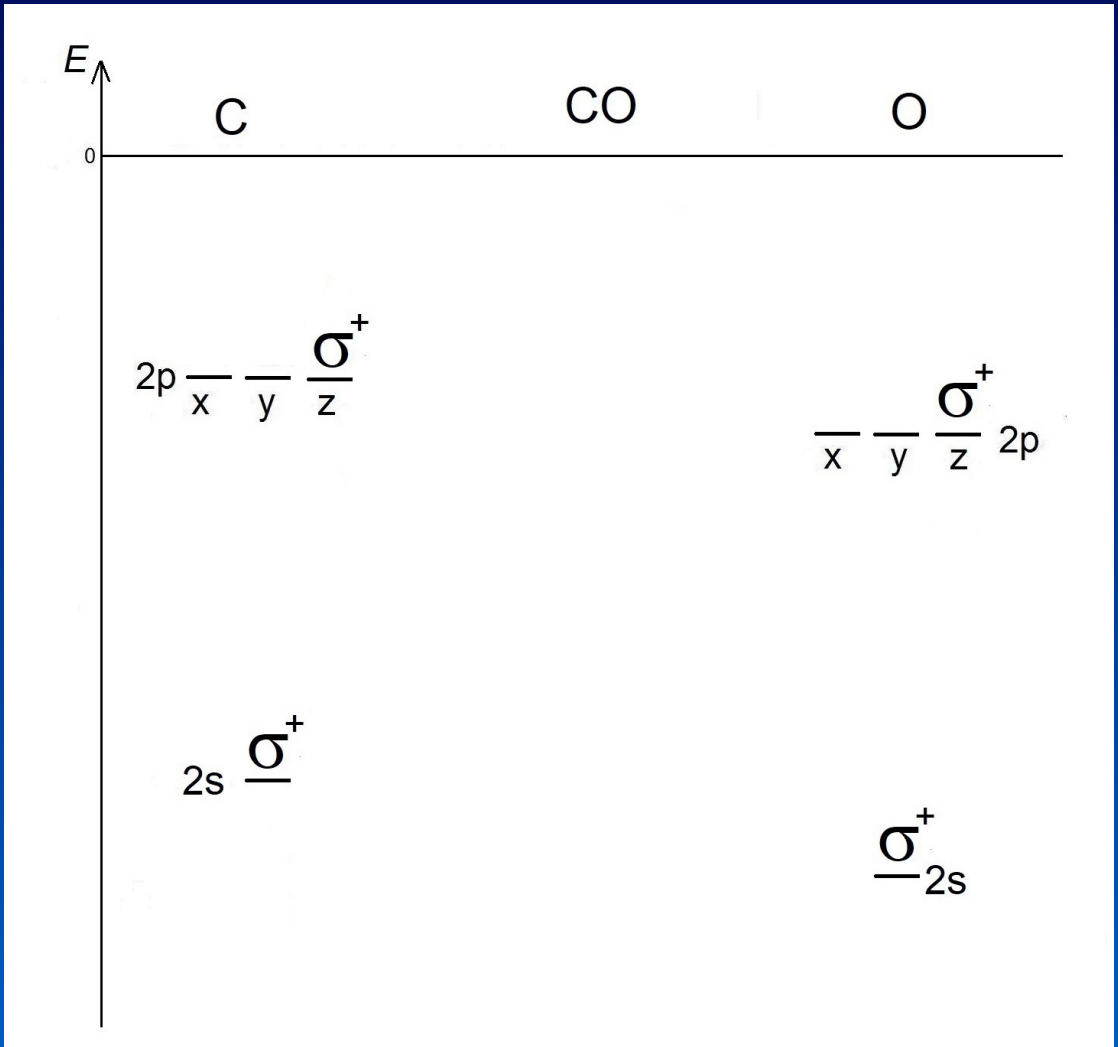
Orbitais $2p_z$ - independentes



$C_{\infty v}$	E	$2C_{\infty}^{\varphi}$	$\infty\sigma_v$
Σ^+	1	1	1
Σ^-	1	1	-1
Π	2	$2\cos\varphi$	0
Δ	2	$2\cos 2\varphi$	0
Φ	2	$2\cos 3\varphi$	0

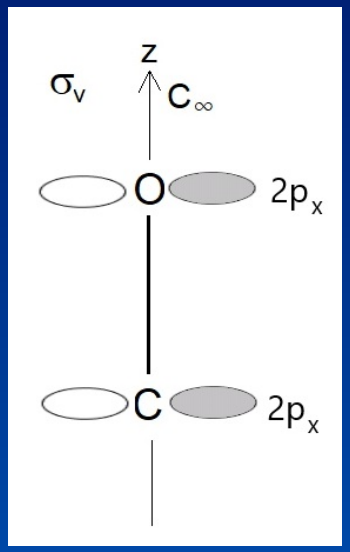
$2p_z(C)$	1	1	1	Σ^+
$2p_z(O)$	1	1	1	Σ^+

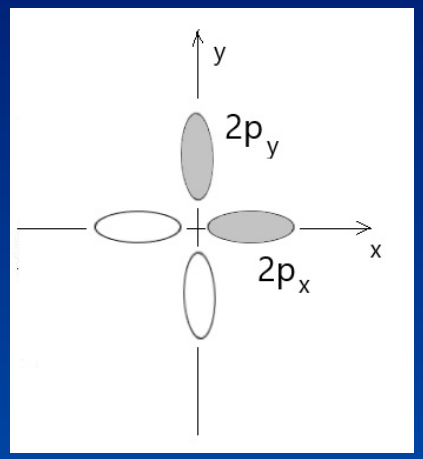
CO - $C_{\infty v}$



CO - $C_{\infty v}$

Orbitais do carbono ou do oxigênio
$2p_x$ e $2p_y$ - inseparáveis





Escolhendo $\varphi = 90°$

$C_\infty^{\varphi} = C_4$

$p_x \rightarrow p_y$

$p_y \rightarrow -p_x$

CO - $C_{\infty v}$

Orbitais do carbono $2p_x$ e $2p_y$ -inseparáveis

$C_{\infty v}$	E	$2C_{\infty}^{\varphi}$	$\infty\sigma_v$
Σ^+	1	1	1
Σ^-	1	1	-1
Π	2	$2\cos\varphi$	0
Δ	2	$2\cos2\varphi$	0
Φ	2	$2\cos3\varphi$	0

φ	$2\cos\varphi$	$2\cos2\varphi$	$2\cos3\varphi$
90°	0	-2	0
180°	-2	2	-2
45°	$\sqrt{2}$	0	$-\sqrt{2}$

CO - $C_{\infty v}$

Orbitais do carbono $2p_x$ e $2p_y$ -inseparáveis

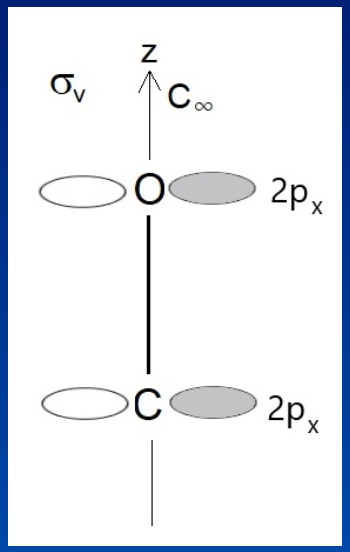
Escolhendo $\varphi = 45°$

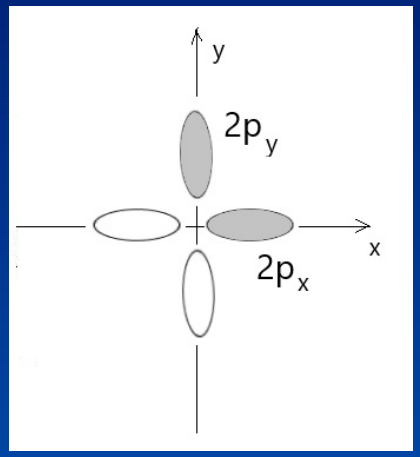
$C_{\infty v}$	E	$2C_{\infty}^{\varphi}$	$\infty\sigma_v$
Σ^+	1	1	1
Σ^-	1	1	-1
Π	2	$\sqrt{2}$	0
Δ	2	0	0
Φ	2	$-\sqrt{2}$	0

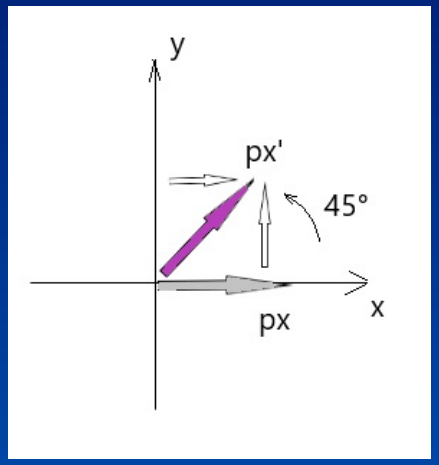
φ	$2\cos\varphi$	$2\cos2\varphi$	$2\cos3\varphi$
90°	0	-2	0
180°	-2	2	-2
45°	$\sqrt{2}$	0	$-\sqrt{2}$

CO - $C_{\infty v}$

Orbitais do carbono ou do oxigênio
$2p_x$ e $2p_y$ - inseparáveis
Escolhendo $\varphi = 45°$



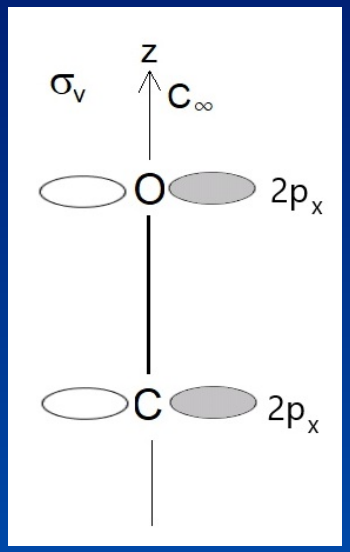


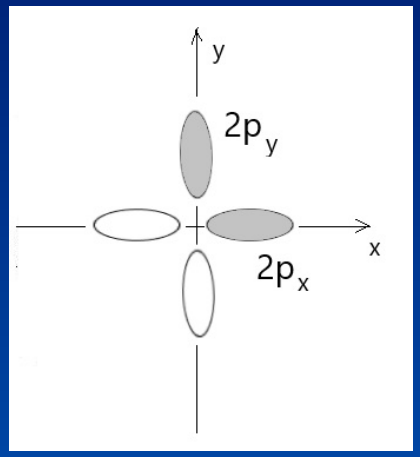


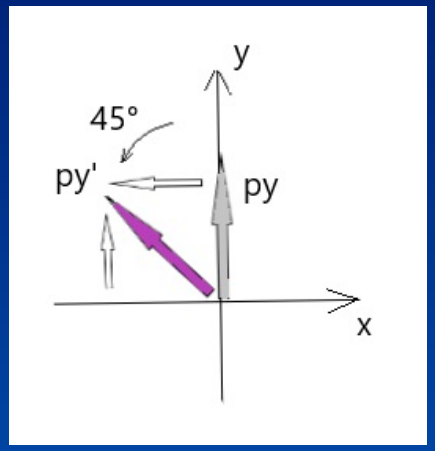
$$(C_8)p_x \rightarrow p_x' = \cos(45°)p_x + \text{sen}(45°)p_y$$
$$= (\sqrt{2}/2)p_x + (\sqrt{2}/2)p_y$$

CO - $C_{\infty v}$

Orbitais do carbono ou do oxigênio
$2p_x$ e $2p_y$ - inseparáveis
Escolhendo $\varphi = 45°$







$$(C_8)p_y \rightarrow p_y' = -\text{sen}(45°)p_x + \cos(45°)p_y$$
$$= -(\sqrt{2}/2)p_x + (\sqrt{2}/2)p_y$$

CO - $C_{\infty v}$

Orbitais do carbono ou do oxigênio
$2p_x$ e $2p_y$ - inseparáveis
Escolhendo $\varphi = 45°$

$$(C_8)p_x \rightarrow p_x' = (\sqrt{2}/2)p_x + (\sqrt{2}/2)p_y$$
$$(C_8)p_y \rightarrow p_y' = -(\sqrt{2}/2)p_x + (\sqrt{2}/2)p_y$$

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

$$\xrightarrow{C_8}$$

	$2p_x$	$2p_y$
$2p_x$	$\sqrt{2}/2$	$\sqrt{2}/2$
$2p_y$	$-\sqrt{2}/2$	$\sqrt{2}/2$

$$\chi = \sqrt{2}$$

CO - $C_{\infty v}$

Orbitais do carbono $2p_x$ e $2p_y$ -inseparáveis
Orbitais do carbono ou do oxigênio
$2p_x$ e $2p_y$ - inseparáveis ($\varphi = 45°$)

$C_{\infty v}$	E	$2C_{\infty}^{\varphi}$	$\infty\sigma_v$
Σ^+	1	1	1
Σ^-	1	1	-1
Π	2	$\sqrt{2}$	0
Δ	2	0	0
Φ	2	$-\sqrt{2}$	0
$(p_x,p_y)_C$	2	$\sqrt{2}$	
$(p_x,p_y)_O$	2	$\sqrt{2}$	

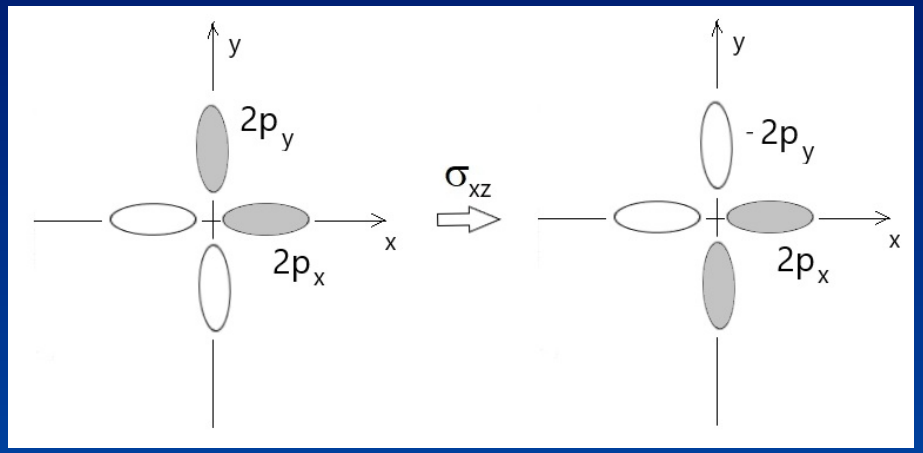
φ	$2\cos\varphi$	$2\cos2\varphi$	$2\cos3\varphi$
90°	0	-2	0
180°	-2	2	-2
45°	$\sqrt{2}$	0	$-\sqrt{2}$

CO - $C_{\infty v}$

Orbitais do carbono ou do oxigênio

$2p_x$ e $2p_y$ - inseparáveis

Escolhendo $\varphi = 45°$



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

σ_{xz} $\rightarrow$

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

$\chi = 0$

CO - $C_{\infty v}$

Orbitais do carbono $2p_x$ e $2p_y$ -inseparáveis
Orbitais do carbono ou do oxigênio
$2p_x$ e $2p_y$ - inseparáveis ($\varphi = 45°$)

$C_{\infty v}$	E	$2C_{\infty}^{\varphi}$	$\infty\sigma_v$
Σ^+	1	1	1
Σ^-	1	1	-1
Π	2	$\sqrt{2}$	0
Δ	2	0	0
Φ	2	$-\sqrt{2}$	0
$(p_x,p_y)_C$	2	$\sqrt{2}$	0
$(p_x,p_y)_O$	2	$\sqrt{2}$	0

φ	$2\cos\varphi$	$2\cos2\varphi$	$2\cos3\varphi$
90°	0	-2	0
180°	-2	2	-2
45°	$\sqrt{2}$	0	$-\sqrt{2}$

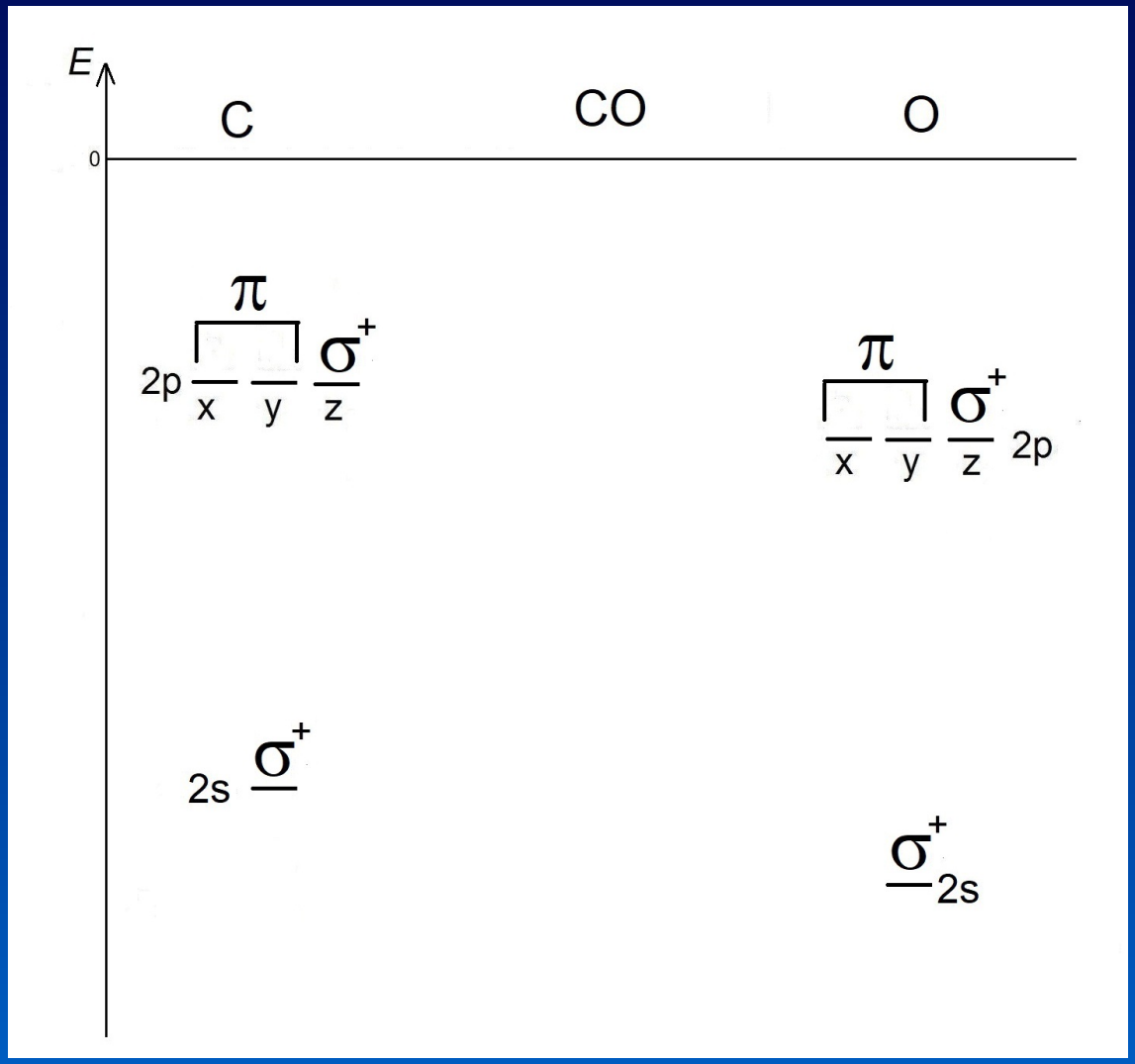
CO - $C_{\infty v}$

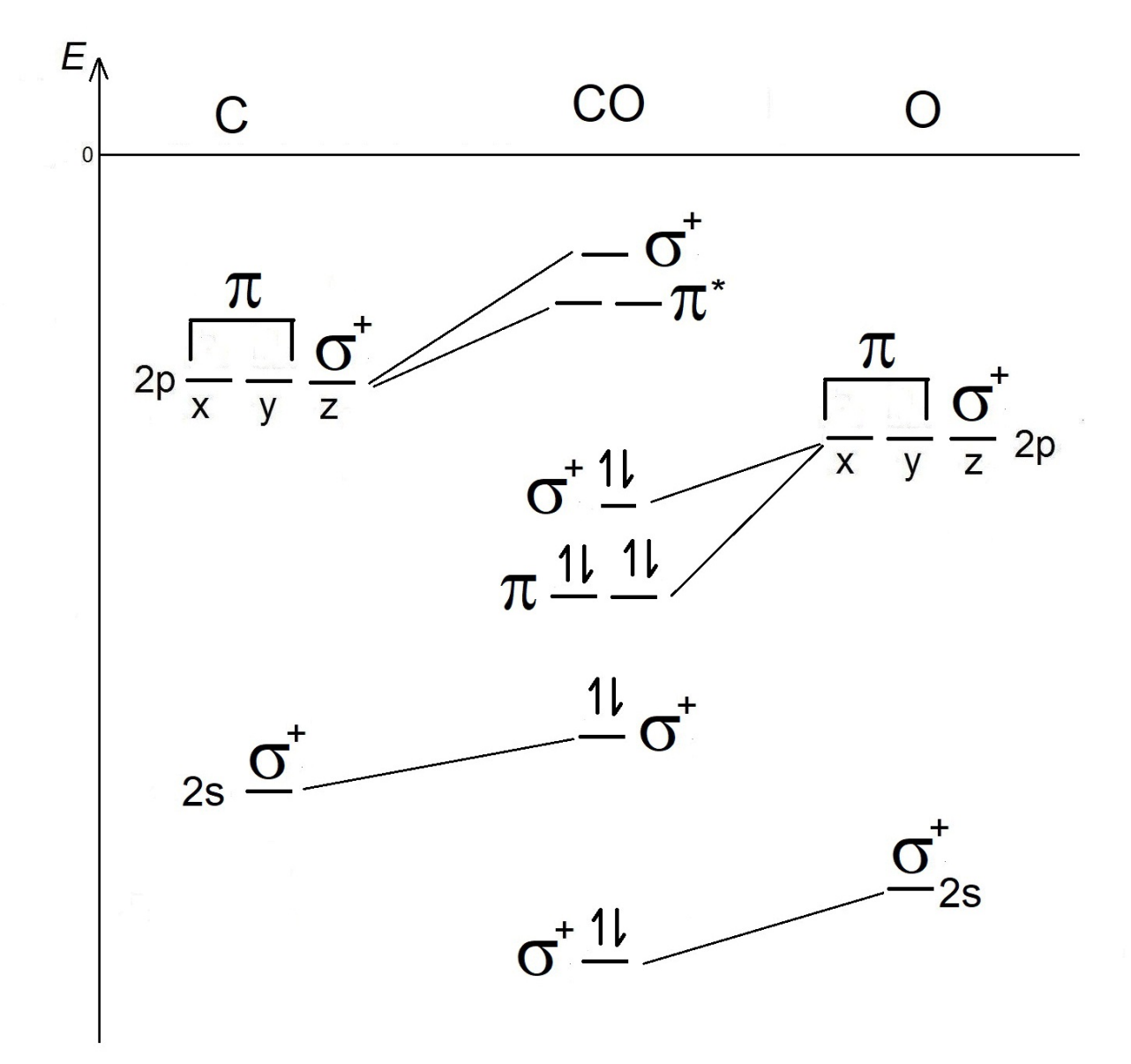
Orbitais do carbono $2p_x$ e $2p_y$ -inseparáveis
Orbitais do carbono ou do oxigênio
$2p_x$ e $2p_y$ - inseparáveis ($\varphi = 45°$)

$C_{\infty v}$	E	$2C_{\infty}^{\varphi}$	$\infty\sigma_v$	
Σ^+	1	1	1	
Σ^-	1	1	-1	
Π	2	$\sqrt{2}$	0	
Δ	2	0	0	
Φ	2	$-\sqrt{2}$	0	
$(p_x,p_y)_C$	2	$\sqrt{2}$	0	Π
$(p_x,p_y)_O$	2	$\sqrt{2}$	0	Π

φ	$2\cos\varphi$	$2\cos2\varphi$	$2\cos3\varphi$
90°	0	-2	0
180°	-2	2	-2
45°	$\sqrt{2}$	0	$-\sqrt{2}$

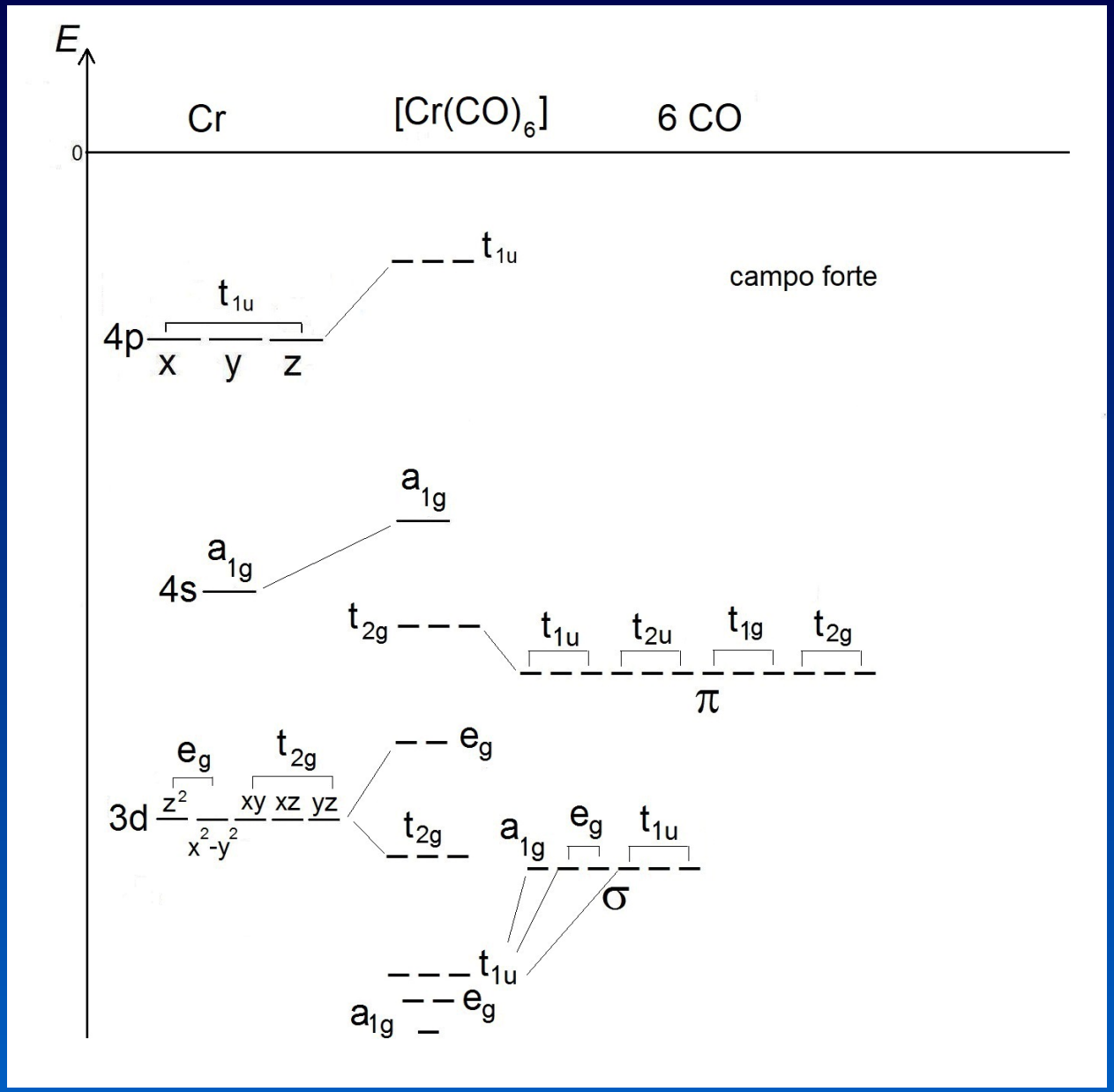
CO - $C_{\infty v}$



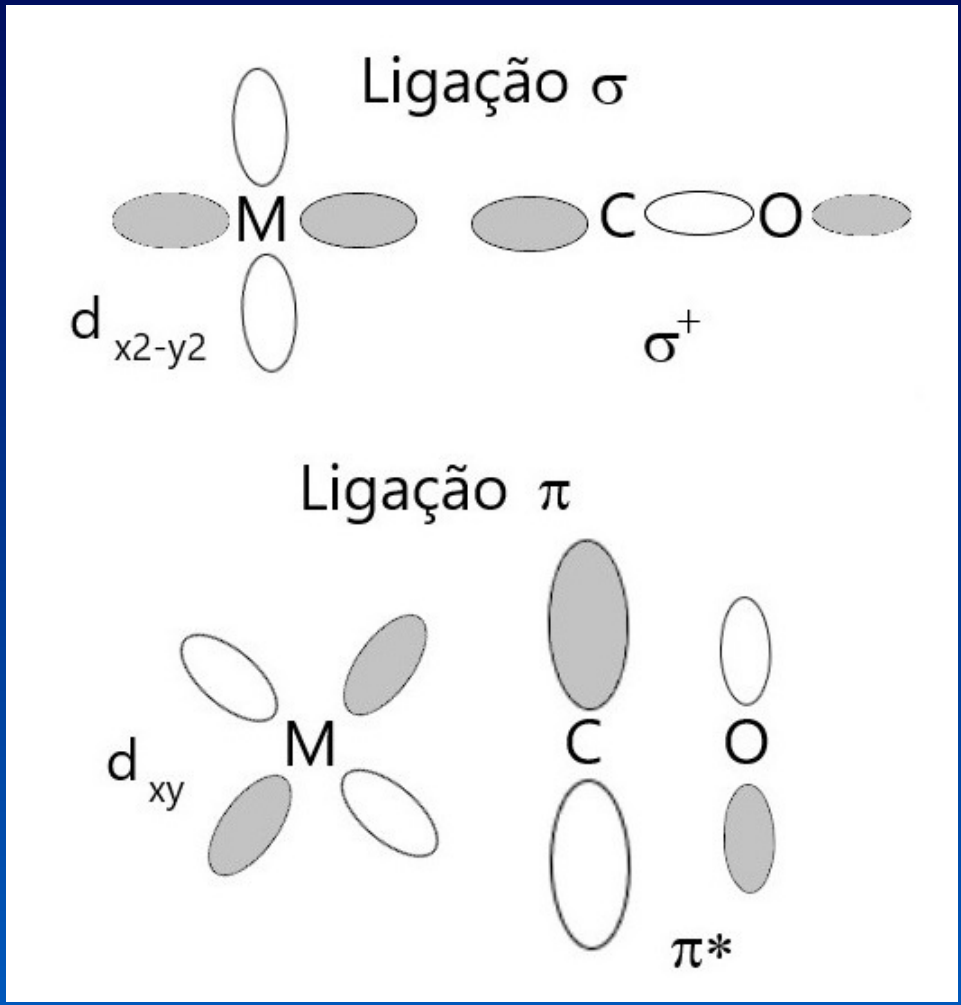

E
0
C
CO
O
π
2p
x
y
z
σ+
σ+
π*
π
σ+
x
y
z
2p
σ+
1↓
π
1↓
1↓
1↓
σ+
2s
σ+
σ+
1↓
σ+
2s

Espectros de fotoelétron - CO

Weller, M.; Overton, T.; Rourke, J.; Armstrong, F. Inorganic Chemistry, 6a ed., Oxford University Press, 2014. pg. 63.


E
0
Cr
[Cr(CO)6]
6 CO
campo forte
t1u
4p
x
y
z
t1u
a1g
4s
a1g
t2g
t1u
t2u
t1g
t2g
π
eg
t2g
3d
z2
x2-y2
xy
xz
yz
eg
t2g
a1g
eg
t1u
σ
t1u
eg
a1g

$[Co(CO)_6]^{3-}$ - O_h



Diatômicas homonucleares - $D_{\infty h}$

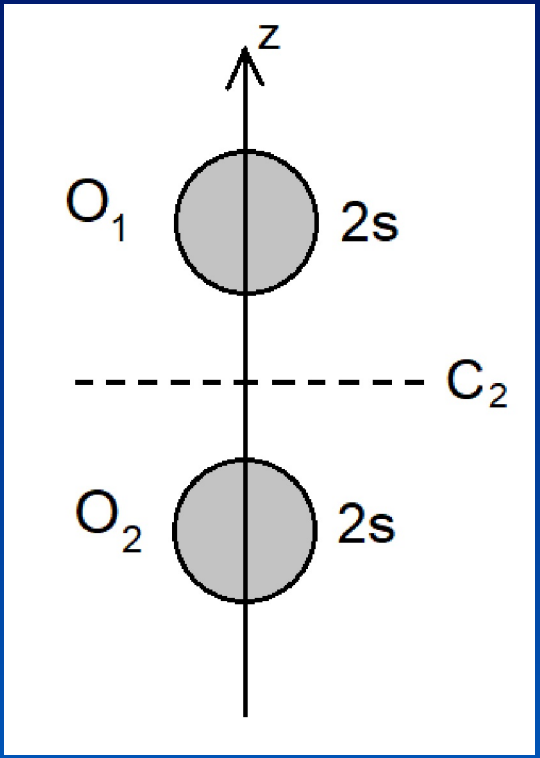
$D_{\infty h}$

$D_{\infty h}$	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

Dioxigênio - O_2

O_2 - $D_{\infty h}$

Orbitais 2s - inseparáveis



O_2 - $D_{\infty h}$

Orbitais 2s - inseparáveis

	$2s(O_1)$	$2s(O_2)$
$2s(O_1)$	1	0
$2s(O_2)$	0	1

$$\xrightarrow[\sigma_v]{E,\ C_\infty}$$

	$2s(O_1)$	$2s(O_2)$
$2s(O_1)$	1	0
$2s(O_2)$	0	1

$\chi = 2$

Dioxigênio - O_2 - $D_{\infty h}$

$D_{\infty h}$	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
$2s(O_1,O_2)$	2	2	2			

O_2 - $D_{\infty h}$

Orbitais 2s - inseparáveis

	$2s(O_1)$	$2s(O_2)$
$2s(O_1)$	1	0
$2s(O_2)$	0	1

$\chi = 2$

$\xrightarrow[S_\infty]{i,\ C_2}$

	$2s(O_1)$	$2s(O_2)$
$2s(O_1)$	0	1
$2s(O_2)$	1	0

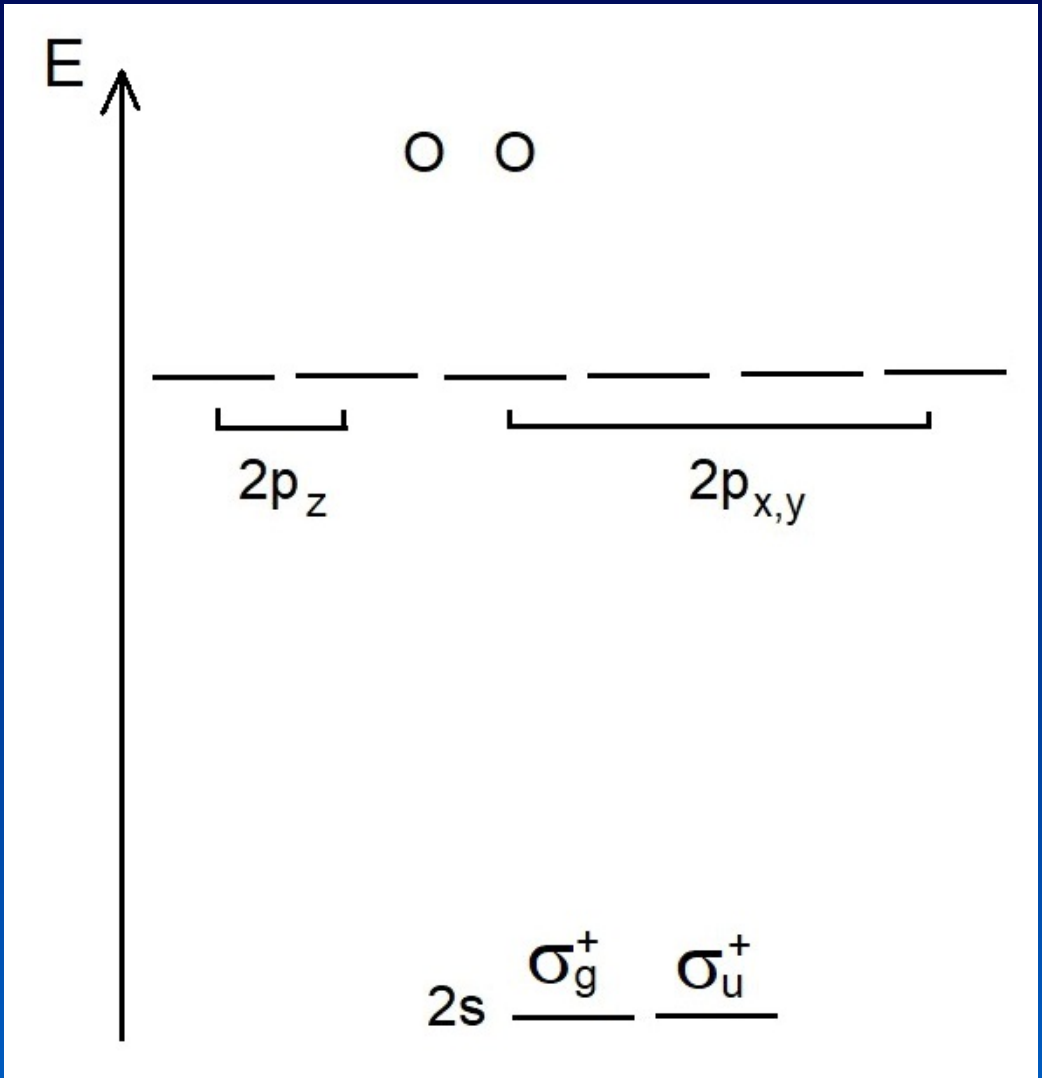
$\chi = 0$

Dioxigênio - O_2 - $D_{\infty h}$

$D_{\infty h}$	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
$2s(O_1,O_2)$	2	2	2	0	0	0

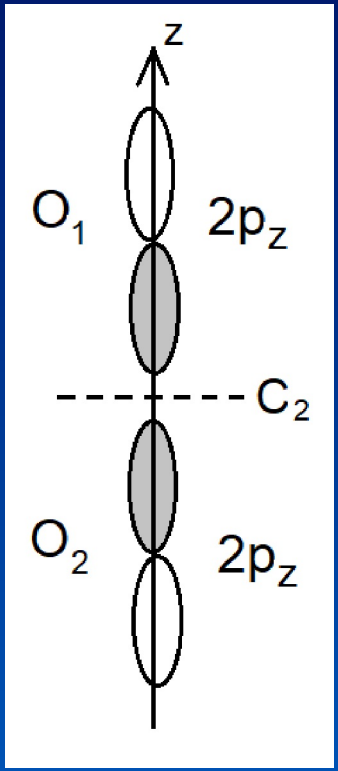
$$\Sigma_g^+ \oplus \Sigma_u^+$$

O_2 - $D_{\infty h}$



O_2 - $D_{\infty h}$

Orbitais $2p_z$ - inseparáveis



O_2 - $D_{\infty h}$

Orbitais $2p_z$ - INSEPARÁVEIS

	$2p_z(O_1)$	$2p_z(O_2)$
$2p_z(O_1)$	1	0
$2p_z(O_2)$	0	1

$$\xrightarrow[\sigma_v]{E,\ C_\infty}$$

	$2p_z(O_1)$	$2p_z(O_2)$
$2p_z(O_1)$	1	0
$2p_z(O_2)$	0	1

$\chi = 2$

Dioxigênio - O_2 - $D_{\infty h}$

$D_{\infty h}$	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
$2p_z(O_1,O_2)$	2	2	2			

O_2 - $D_{\infty h}$

Orbitais $2p_z$ - INSEPARÁVEIS

	$2p_z(O_1)$	$2p_z(O_2)$
$2p_z(O_1)$	1	0
$2p_z(O_2)$	0	1

$\chi = 2$

$\xrightarrow[S_\infty]{i,\ C_2}$

	$2p_z(O_1)$	$2p_z(O_2)$
$2p_z(O_1)$	0	1
$2p_z(O_2)$	1	0

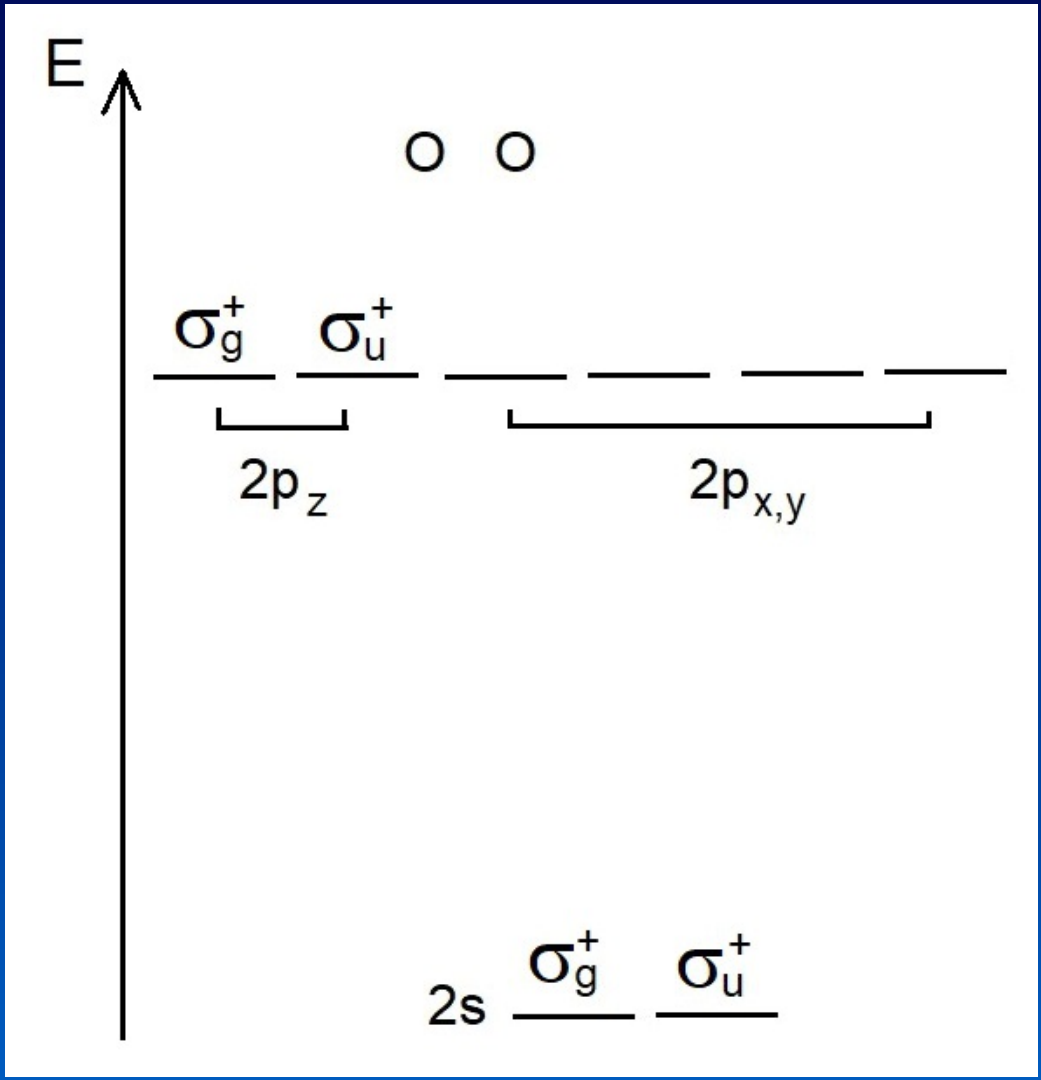
$\chi = 0$

Dioxigênio - O_2 - $D_{\infty h}$

$D_{\infty h}$	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
$2p_z(O_1,O_2)$	2	2	2	0	0	0

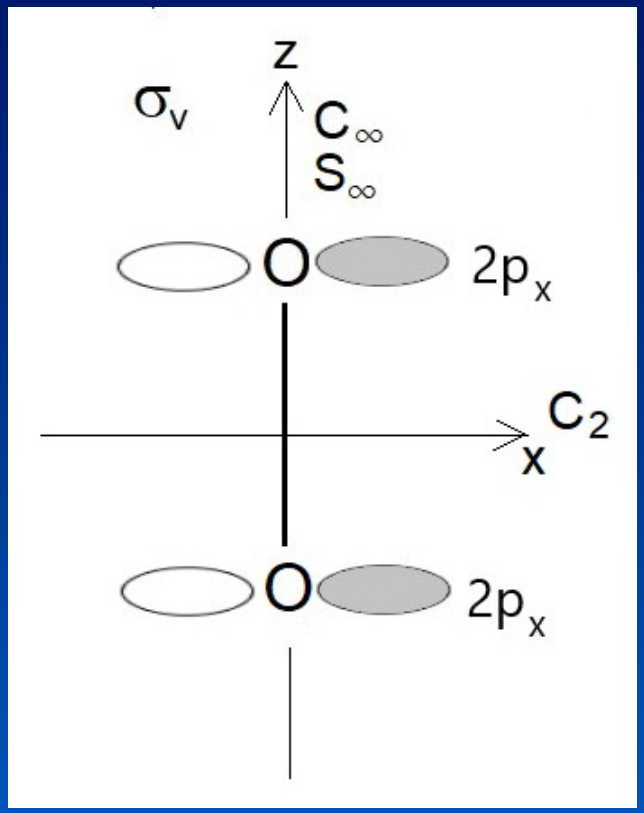
$\Sigma_g^+ \oplus \Sigma_u^+$

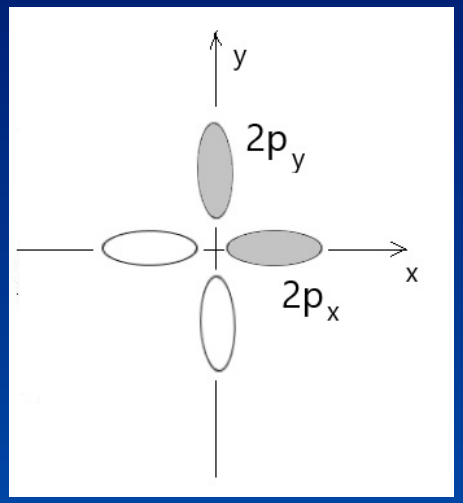
O_2 - $D_{\infty h}$



O_2 - $D_{\infty h}$

Orbitais $2p_x$ e $2p_y$ dos dois oxigênios -inseparáveis





Escolhendo $\varphi = 90°$

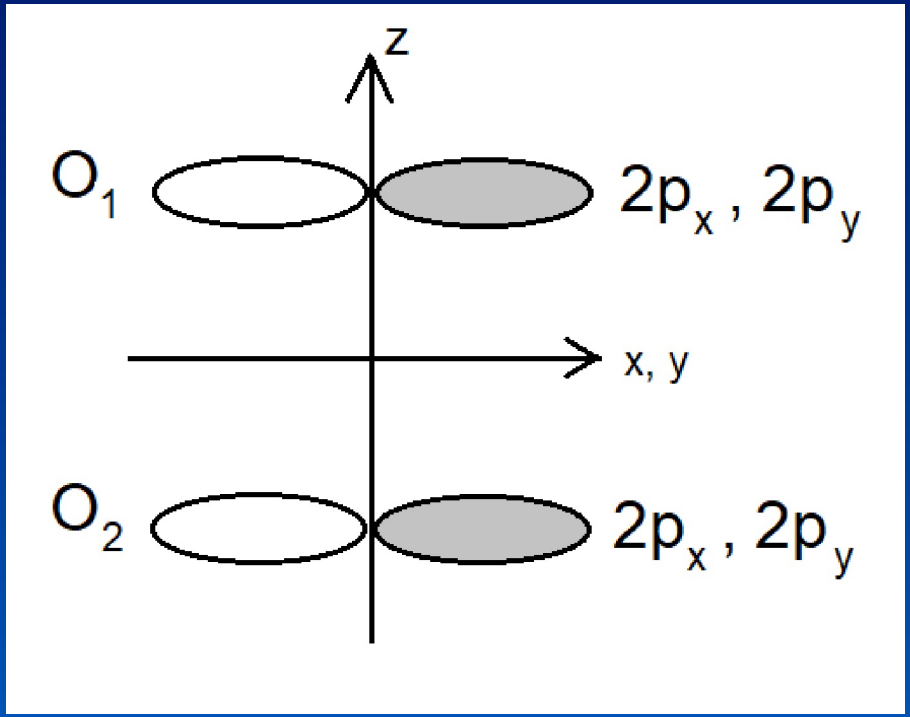
$C_\infty^{\varphi} = C_4$

$p_x \rightarrow p_y$

$p_y \rightarrow -p_x$

O_2 - $D_{\infty h}$

Orbitais $2p_x$ e $2p_y$ dos dois oxigênios, inseparáveis



$D_{\infty h}$

$D_{\infty h}$	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

Escolhendo $\varphi = 90°$ $\cos\varphi = 0$ $\cos 2\varphi = -1$

$D_{\infty h}$

$D_{\infty h}$	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	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

Escolhendo $\varphi = 90°$ $\cos\varphi = 0$ $\cos 2\varphi = -1$

O_2 - $D_{\infty h}$

Orbitais $2p_x$ e $2p_y$ dos dois oxigênios - INSEPARÁVEIS

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

$\chi = 4$

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

	$2p_x^1$	$2p_y^1$	$2p_x^2$	$2p_y^2$
$2p_x^1$	0	1	0	0
$2p_y^1$	-1	0	0	0
$2p_x^2$	0	0	0	1
$2p_y^2$	0	0	-1	0

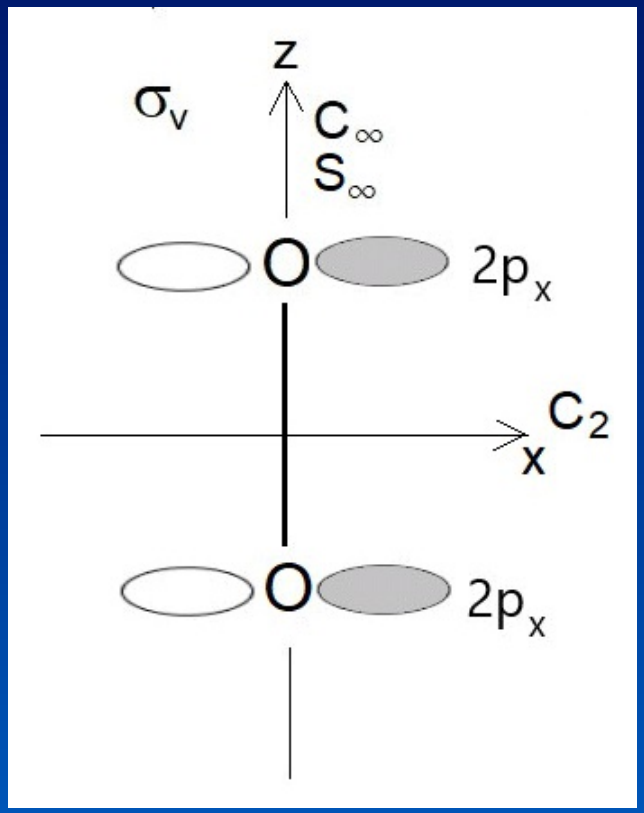
$\chi = 0$

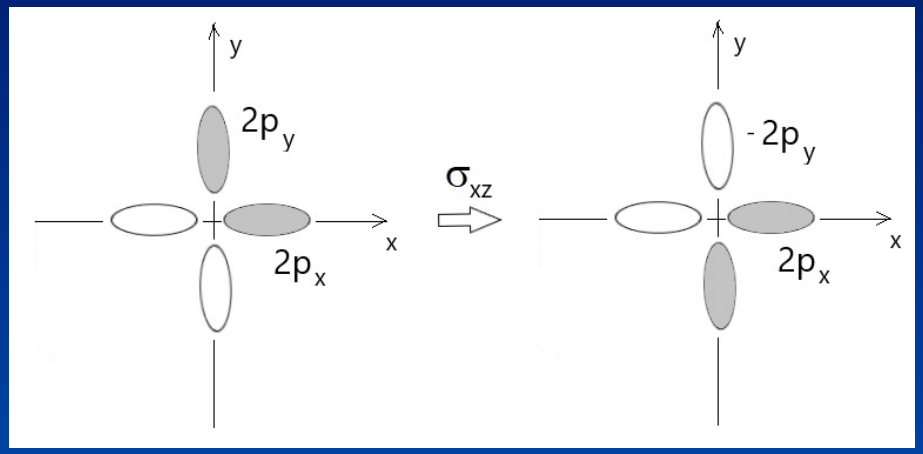
Dioxigênio - O_2 - $D_{\infty h}$

$D_{\infty h}$	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	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
$2p_{x,y}(O_1,O_2)$	4	0				

O_2 - $D_{\infty h}$

Orbitais $2p_x$ e $2p_y$ dos dois oxigênios -inseparáveis





O_2 - $D_{\infty h}$

Orbitais $2p_x$ e $2p_y$ dos dois oxigênios - INSEPARÁVEIS

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

$\chi = 4$

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

	$2p_x^1$	$2p_y^1$	$2p_x^2$	$2p_y^2$
$2p_x^1$	1	0	0	0
$2p_y^1$	0	-1	0	0
$2p_x^2$	0	0	1	0
$2p_y^2$	0	0	0	-1

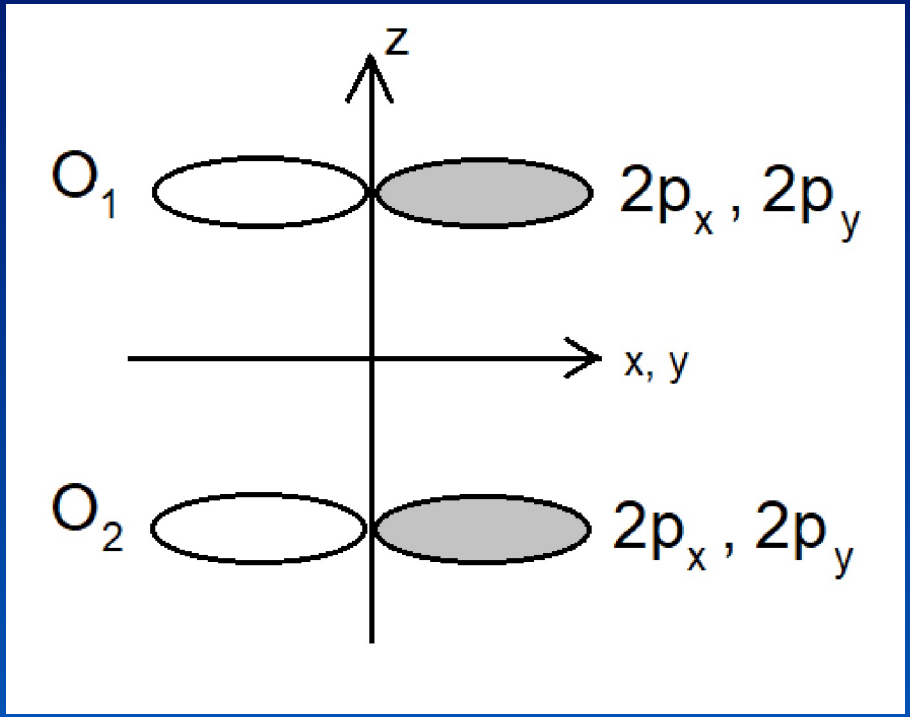
$\chi = 0$

Dioxigênio - O_2 - $D_{\infty h}$

$D_{\infty h}$	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	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
$2p_{x,y}(O_1,O_2)$	4	0	0			

O_2 - $D_{\infty h}$

Orbitais $2p_x$ e $2p_y$ dos dois oxigênios, inseparáveis



Orbitais $2p_x$ e $2p_y$ dos d

O_2 - $D_{\infty h}$

Orbitais $2p_x$ e $2p_y$ dos dois oxigênios - INSEPARÁVEIS

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

$\chi = 4$

$\xrightarrow{i}$

	$2p_x^1$	$2p_y^1$	$2p_x^2$	$2p_y^2$
$2p_x^1$	0	0	-1	0
$2p_y^1$	0	0	0	-1
$2p_x^2$	-1	0	0	0
$2p_y^2$	0	-1	0	0

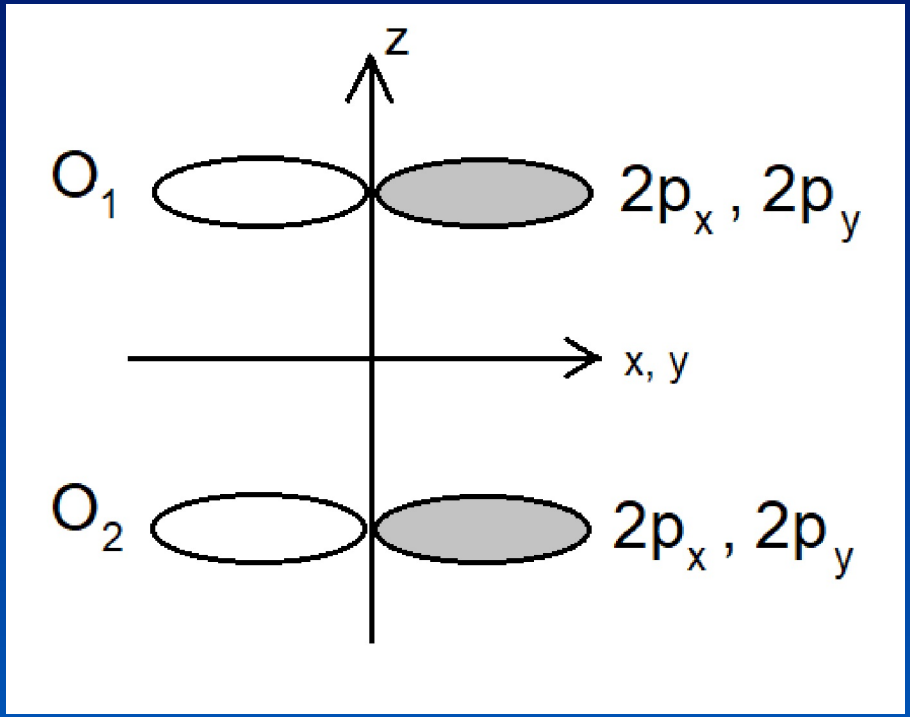
$\chi = 0$

Dioxigênio - O_2 - $D_{\infty h}$

$D_{\infty h}$	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	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
$2p_{x,y}(O_1,O_2)$	4	0	0	0		

O_2 - $D_{\infty h}$

Orbitais $2p_x$ e $2p_y$ dos dois oxigênios, inseparáveis



O_2 - $D_{\infty h}$

Orbitais $2p_x$ e $2p_y$ dos dois oxigênios - INSEPARÁVEIS

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

$\chi = 4$

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

	$2p_x^1$	$2p_y^1$	$2p_x^2$	$2p_y^2$
$2p_x^1$	0	0	0	1
$2p_y^1$	0	0	-1	0
$2p_x^2$	0	1	0	0
$2p_y^2$	-1	0	0	0

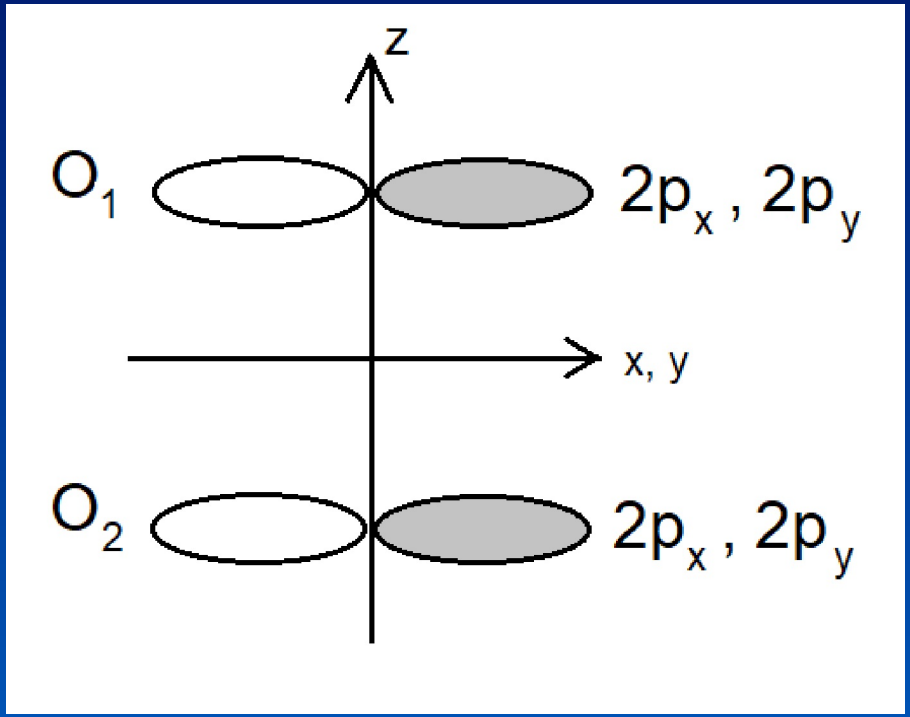
$\chi = 0$

Dioxigênio - O_2 - $D_{\infty h}$

$D_{\infty h}$	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	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
$2p_{x,y}(O_1,O_2)$	4	0	0	0	0	

O_2 - $D_{\infty h}$

Orbitais $2p_x$ e $2p_y$ dos dois oxigênios, inseparáveis



O_2 - $D_{\infty h}$

Orbitais $2p_x$ e $2p_y$ dos dois oxigênios - INSEPARÁVEIS

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

$\chi = 4$

C_2^x $\rightarrow$

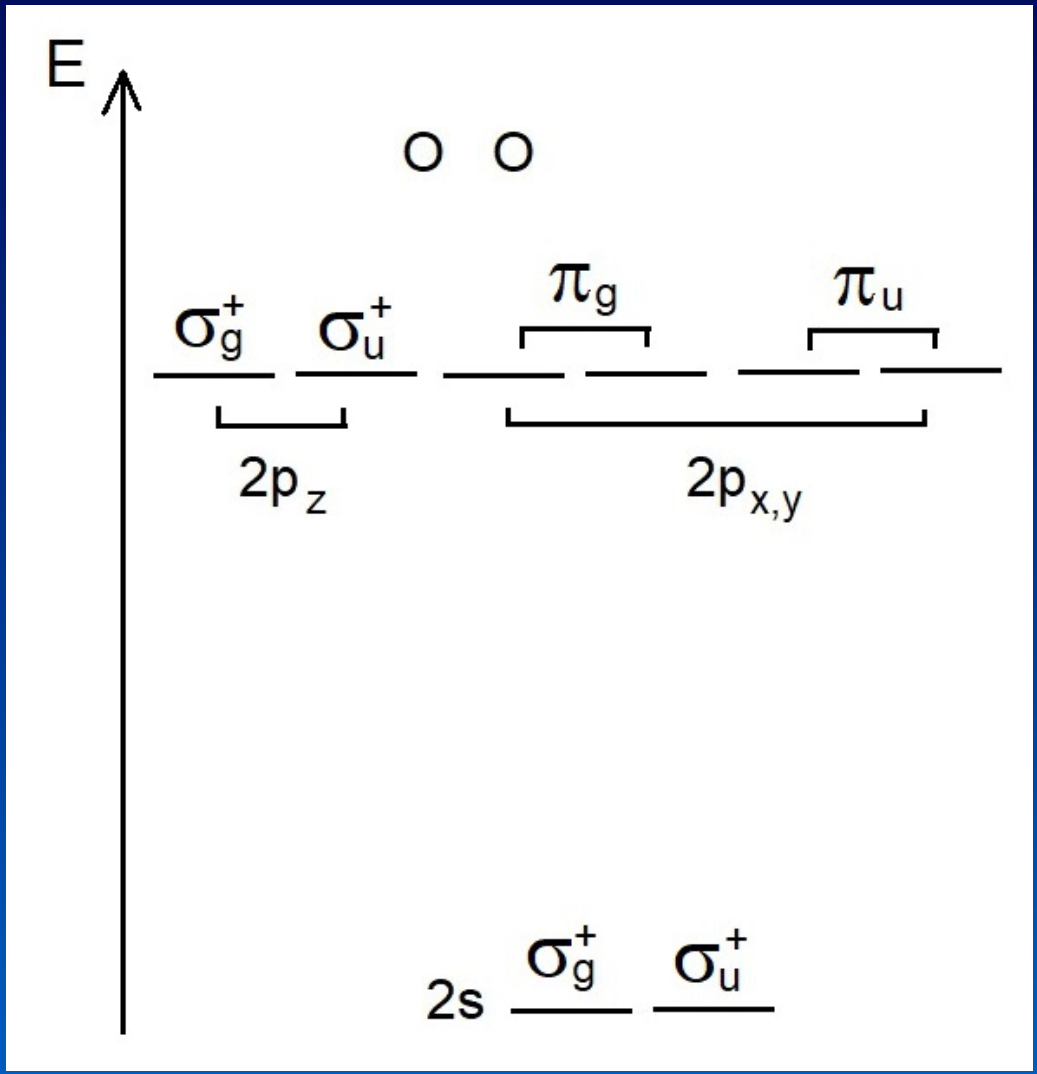
	$2p_x^1$	$2p_y^1$	$2p_x^2$	$2p_y^2$
$2p_x^1$	0	0	1	0
$2p_y^1$	0	0	0	-1
$2p_x^2$	1	0	0	0
$2p_y^2$	0	-1	0	0

$\chi = 0$

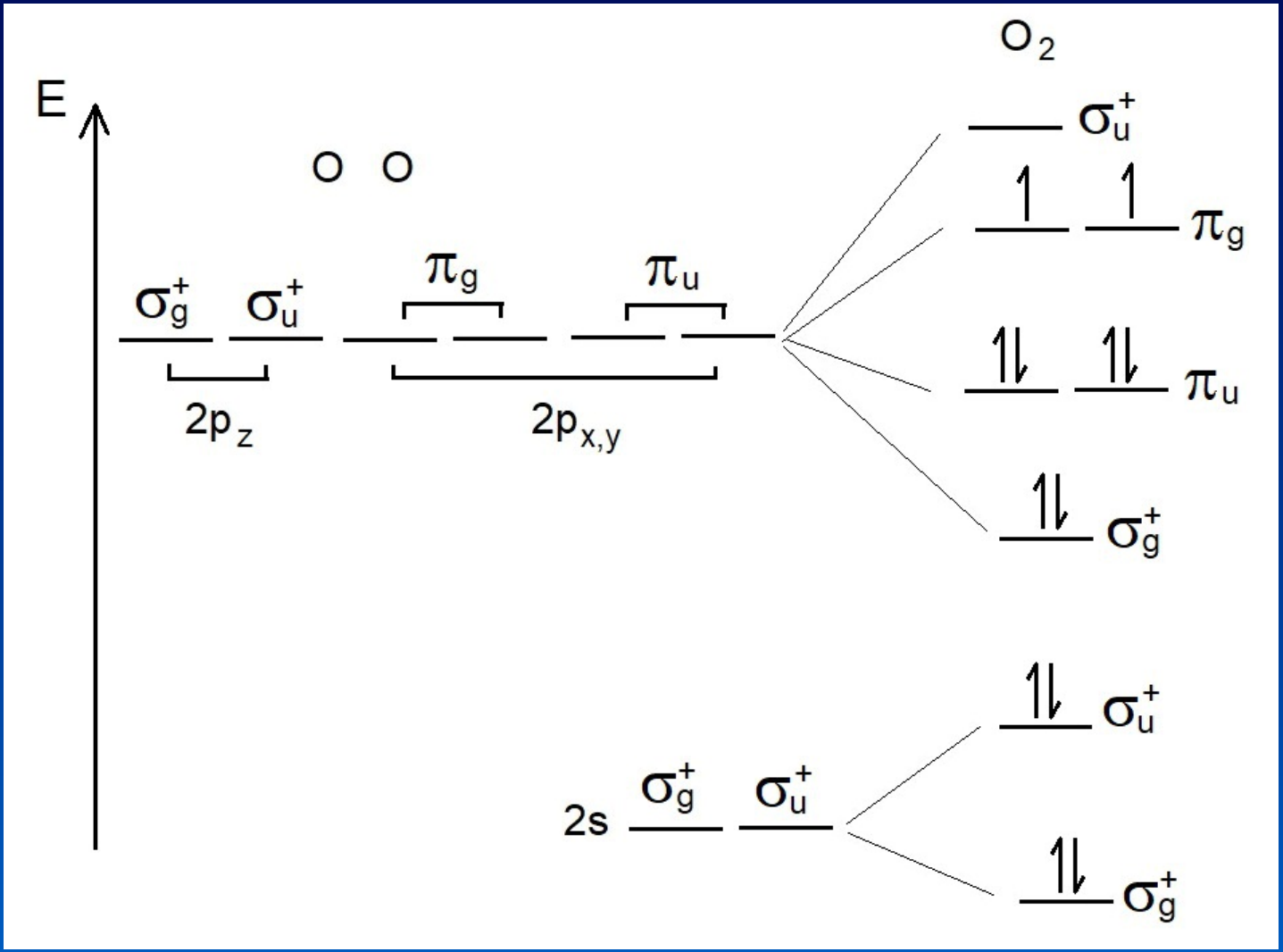
Dioxigênio - O_2 - $D_{\infty h}$

$D_{\infty h}$	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	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
$2p_{x,y}(O_1,O_2)$	4	0	0	0	0	0
						$\Pi_g \oplus \Pi_u$

O_2 - $D_{\infty h}$



O_2 - $D_{\infty h}$



Espectros de fotoelétron - O_2

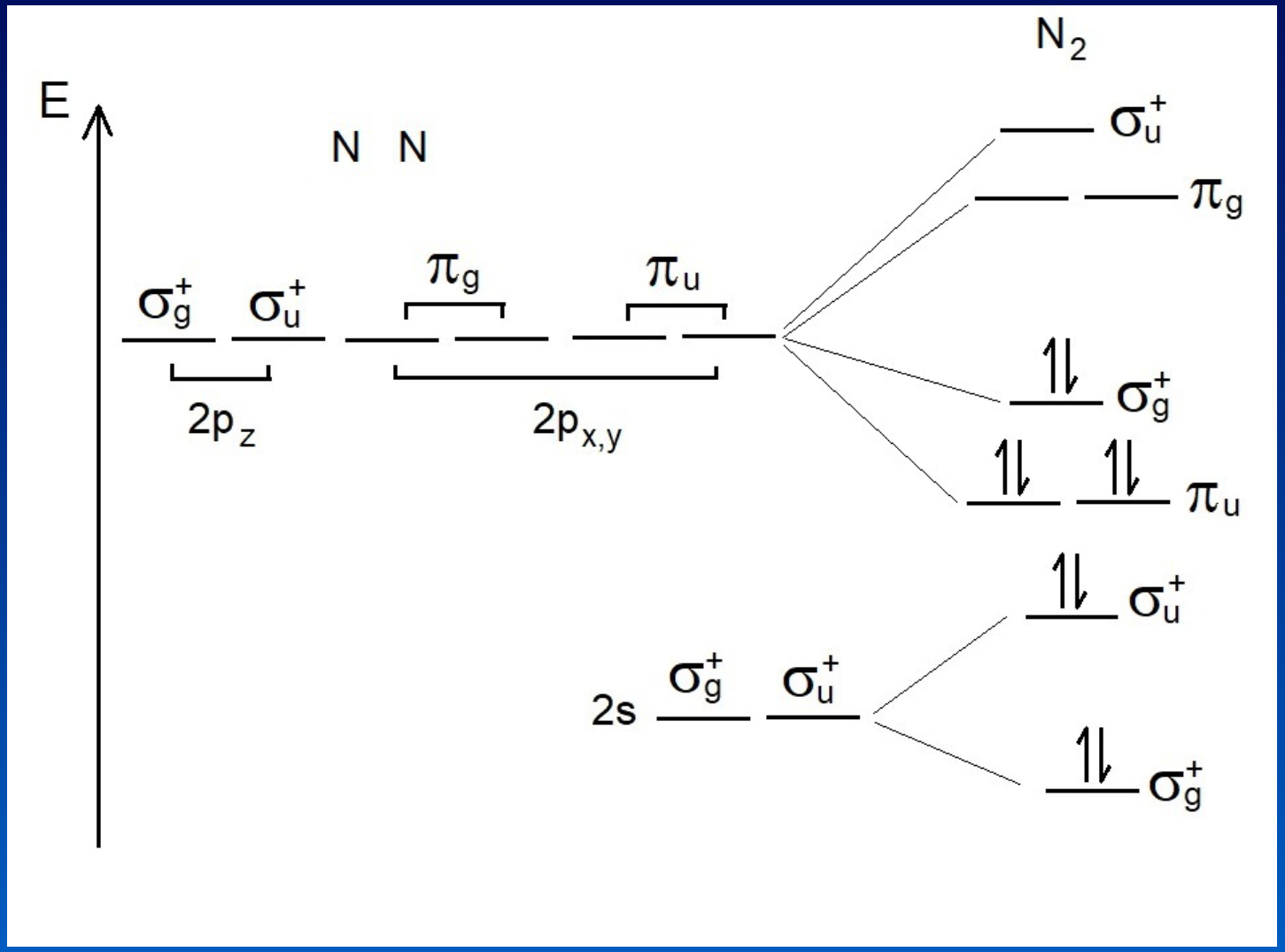
- Weller, M.; Overton, T.; Rourke, J.; Armstrong, F. *Inorganic Chemistry*, 6ª ed., Oxford University Press, 2014. pg. 256.

- Miessler, G. L.; Tarr, D. A. *Inorganic Chemistry*, Prentice-Hall, 1991. pg. 134 (reproduzindo espectro de Eland, J. H. *Photoelectron Spectroscopy*, Butterworths, 1974. pg. 11)

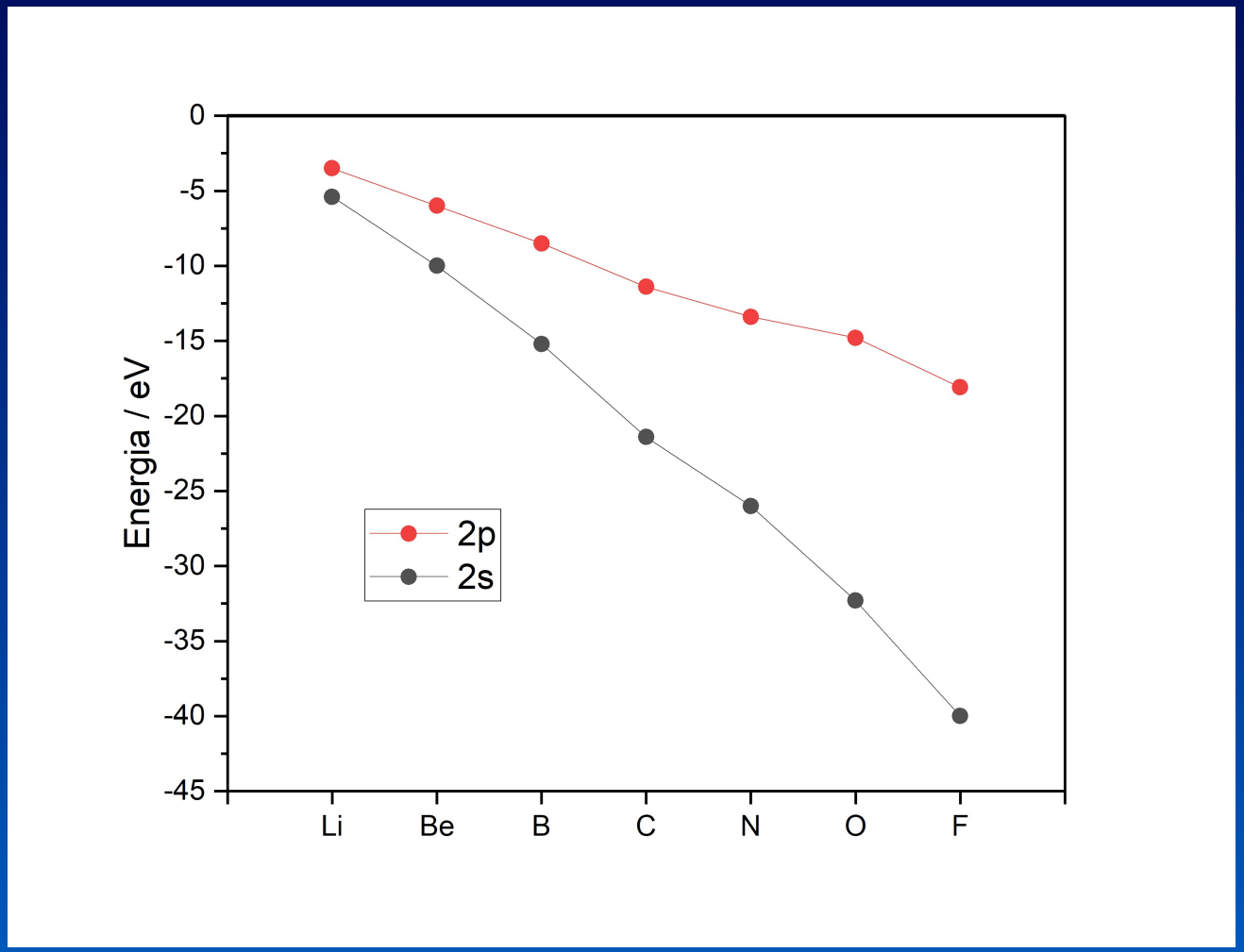
Espectro de fotoelétron - N_2

- Miessler, G. L.; Tarr, D. A. *Inorganic Chemistry*, Prentice-Hall, 1991. pg. 133 (reproduzindo espectro de Gardner, J. L.; Samson, J. A. R. *PJ. Chem. Phys.* *62*:1447 (1975)).

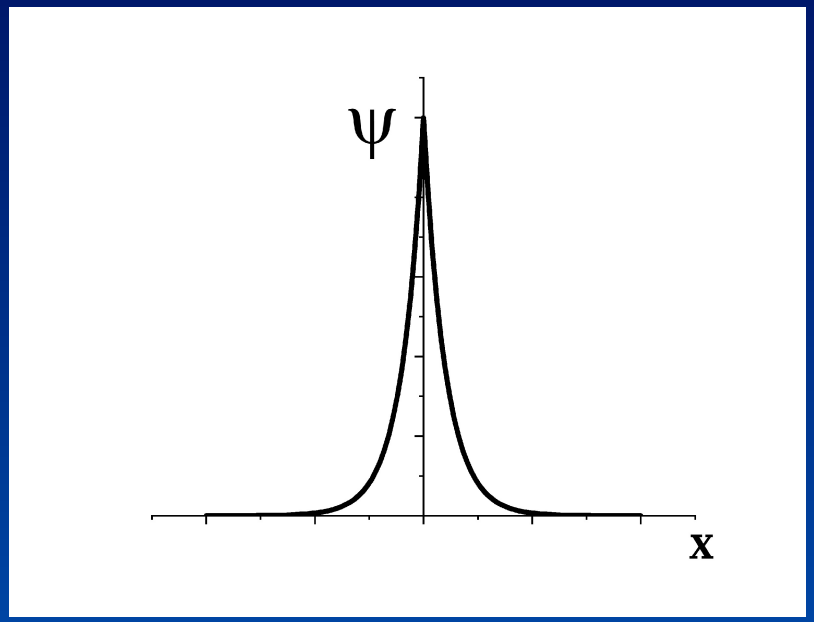
N_2 - $D_{\infty h}$



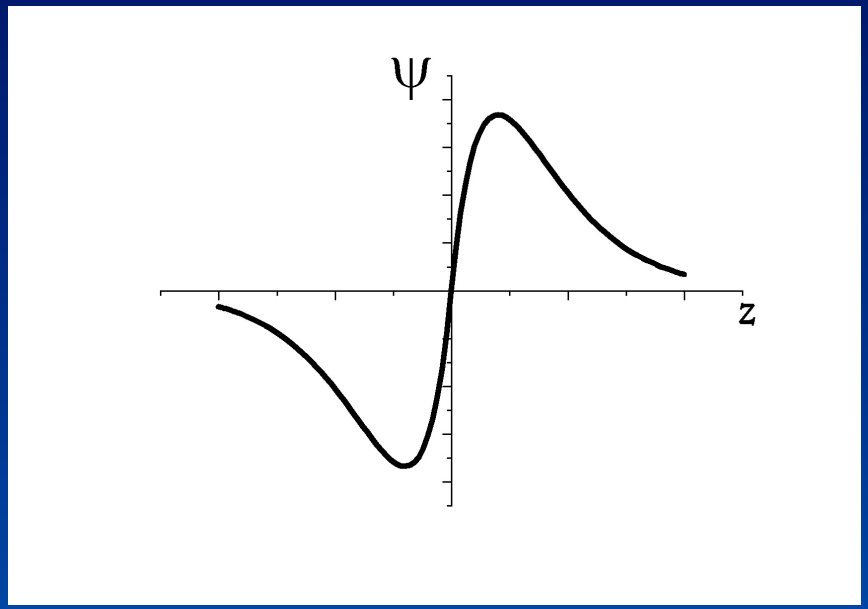
Energias dos orbitais atômicos



Funções de onda dos orbitais atômicos

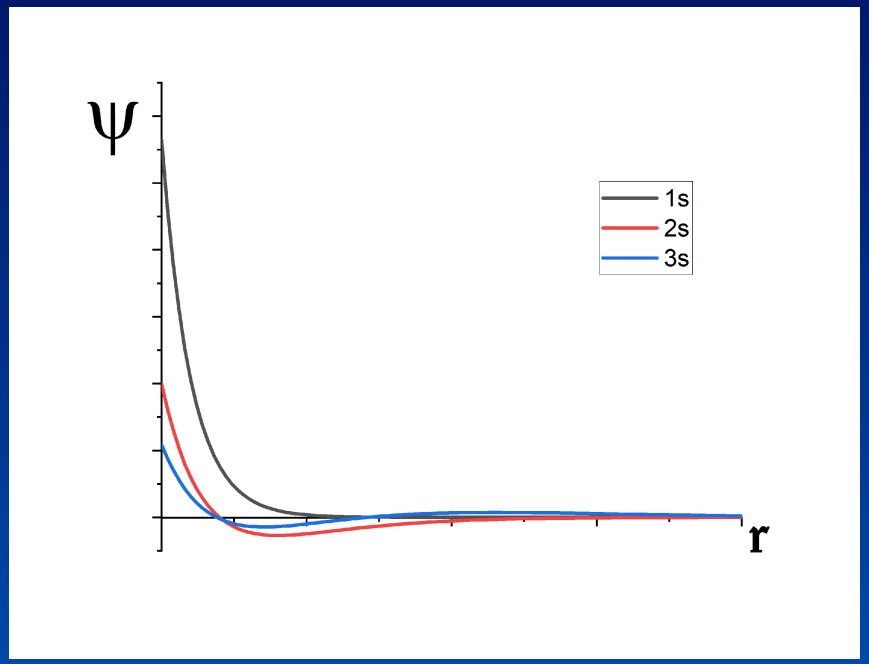


1s

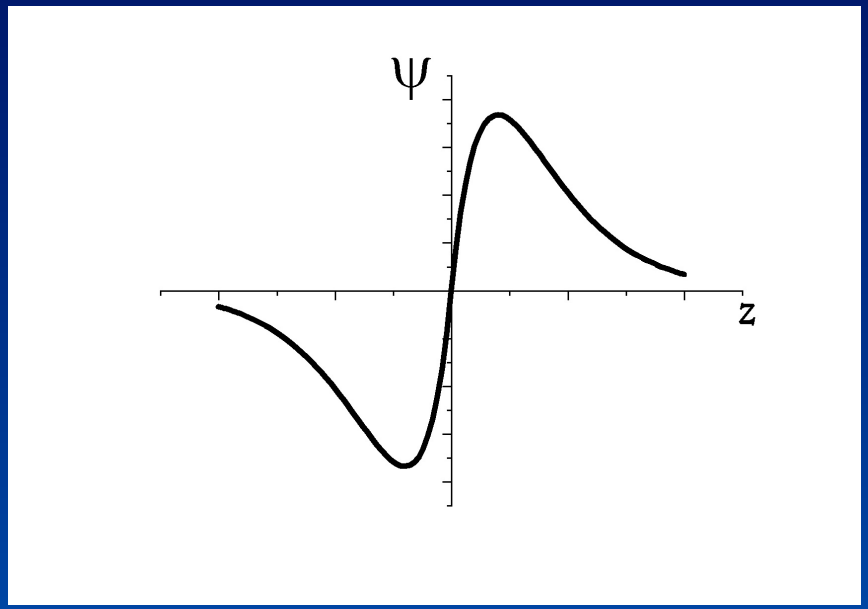


2p

Funções de onda dos orbitais atômicos



1s, 2s, 3s



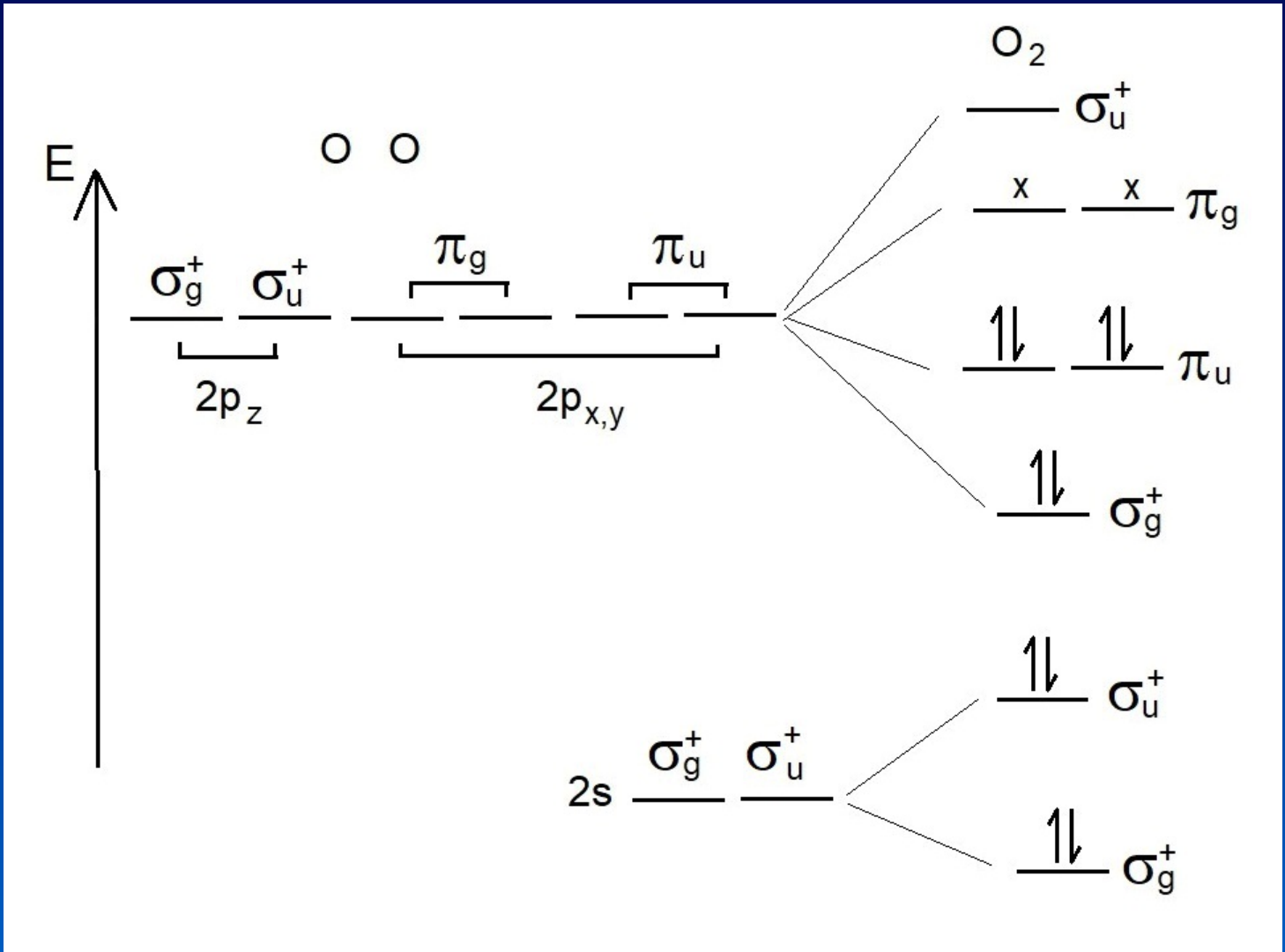
2p

Termos espectroscópicos para moléculas

Termos espectroscópicos para moléculas

dioxigênio - O_2

O_2 - $D_{\infty h}$



$D_{\infty h}$

$D_{\infty h}$	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	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

Escolhendo $\varphi = 90°$ $\cos\varphi = 0$ $\cos 2\varphi = -1$

$D_{\infty h}$

$D_{\infty h}$	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	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
$\Pi_g \otimes \Pi_g$	4	0	0	4	0	0
					$\Sigma_g^+ \oplus \Sigma_g^- \oplus \Delta_g$	

O_2 - $D_{\infty h}$

Determinando os singletos e tripletos

- Uma vez que os elétrons estão em orbitais degenerados, temos as possibilidades:

Π_g		Σ_{ms}
x	x	1, 0, 0, -1
xx		0
	xx	0

tripleto = 1, 0, -1
singleto = 0

6 microestados

$\Pi_g \otimes \Pi_g = {}^a\Sigma_g^+ + {}^b\Sigma_g^- + {}^c\Delta_g$

$a + b + 2c = 6$

(a, b, c) só podem ser 1 ou 3

Soluções possíveis:

$(3, 1, 1) = {}^3\Sigma_g^+ + {}^1\Sigma_g^- + {}^1\Delta_g$

ou

$(1, 3, 1) = {}^1\Sigma_g^+ + {}^3\Sigma_g^- + {}^1\Delta_g$

O_2 - $D_{\infty h}$

Determinando os singletos e tripletos

Para decidir entre as duas soluções possíveis

$$^3\Sigma_g^+ + {}^1\Sigma_g^- + {}^1\Delta_g \quad \text{ou} \quad {}^1\Sigma_g^+ + {}^3\Sigma_g^- + {}^1\Delta_g$$

precisamos saber quais desses termos são simétricos ou antissimétricos

O_2 - $D_{\infty h}$

Determinando os singletos e tripletos

Para o caso do produto direto entre duas representações irredutíveis iguais, as componentes das representações simétricas (χ^+) e antissimétricas (χ^-) são dadas por:

$$\text{caracteres } \chi^+ = (½)\ \{[\chi(R)]^2 + \chi(R^2)\}$$

$$\text{caracteres } \chi^- = (½)\ \{[\chi(R)]^2 - \chi(R^2)\}$$

R^2 é o resultado da aplicação de uma mesma operação de simetria duas vezes. Assim, no $D_{\infty h}$ teremos:

R	E	$2C_\infty^\varphi$	$\infty\sigma_v$	i	$2S_\infty^\varphi$	∞C_2
R^2	E	–	E	E	–	E

O_2 - $D_{\infty h}$

Determinando os singletos e tripletos

$$\text{caracteres } \chi^{+} = (½)\ \{[\chi(R)]^2 + \chi(R^2)\}$$
$$\text{caracteres } \chi^{-} = (½)\ \{[\chi(R)]^2 - \chi(R^2)\}$$

$\chi(R^2)$ é o caracter da operação de simetria resultante. Assim, como para a operação E no Π_g temos $\chi(E) = \chi(R^2) = 2$

R	E	$2C_\infty^\varphi$	$\infty\sigma_v$	i	$2S_\infty^\varphi$	∞C_2
R^2	E	–	E	E	–	E
$\chi(R^2)$	2	–	2	2	–	2

O_2 - $D_{\infty h}$

Determinando os singletos e tripletos

$$\text{caracteres } \chi^{+} = (½)\ \{[\chi(R)]^2 + \chi(R^2)\}$$
$$\text{caracteres } \chi^{-} = (½)\ \{[\chi(R)]^2 - \chi(R^2)\}$$

$[\chi(R)]^2$ é o quadrado do caracter de cada operação de simetria. Assim, para o Π_g no $D_{\infty h}$ teremos:

	E	$2C_\infty^\varphi$	$\infty\sigma_v$	i	$2S_\infty^\varphi$	∞C_2
Π_g	2	$2\cos\varphi$	0	2	$-2\cos\varphi$	0
$[\chi(R)]^2$	4	–	0	4	–	0

O_2 - $D_{\infty h}$

Determinando os singletos e tripletos

$$\text{caracteres } \chi^{+} = (½)\ \{[\chi(R)]^2 + \chi(R^2)\}$$
$$\text{caracteres } \chi^{-} = (½)\ \{[\chi(R)]^2 - \chi(R^2)\}$$

Dessa forma, para o Π_g no $D_{\infty h}$ teremos:

	E	$2C_\infty^\varphi$	$\infty\sigma_v$	i	$2S_\infty^\varphi$	∞C_2
$[\chi(R)]^2$	4	–	0	4	–	0
$\chi(R^2)$	2	–	2	2	–	2
$\chi^{+} =$	3	–	1	3	–	1
$\chi^{-} =$	1	–	-1	1	–	-1

O_2 - $D_{\infty h}$

Determinando os singletos e tripletos

$D_{\infty h}$	E	$2C_{\infty}^{\varphi}$	$\infty\sigma_v$	i	$2S_{\infty}^{\varphi}$	∞C_2
Σ_g^+	1	1	1	1	1	1
Δ_g	2	$2\cos 2\varphi$	0	2	$2\cos 2\varphi$	0
$\chi^+ =$	3	–	1	3	–	1
Σ_g^-	1	1	-1	1	1	-1
$\chi^- =$	1	–	-1	1	–	-1

Representações simétricas
Representações antissimétricas

Harris, D. C.; Bertolucci, M. D.; *Symmetry and Spectroscopy*, Dover: Nova Iorque, 1978. pg 327

O_2 - $D_{\infty h}$

Determinando os singletos e tripletos

- Como os elétrons possuem spin fracionário eles são férmions.

- Para os férmions, $\psi_{orbital}\psi_{spin}$ tem que ser uma função antissimétrica com relação à permutação dos elétrons.

Σ_g^+ (simétrica) $\times$ ψ_{spin} (antissimétrica)
Σ_g^- (antissimétrica) $\times$ ψ_{spin} (simétrica)
Δ_g (simétrica) $\times$ ψ_{spin} (antissimétrica)

O_2 - $D_{\infty h}$

Determinando os singletos e tripletos

- Como os elétrons possuem spin fracionários eles são férmions.

- Para os férmions, $\psi_{orbital}\psi_{spin}$ tem que ser uma função antissimétrica com relação à permutação dos elétrons.

Σ_g^+ (simétrica) $\times$ [$\alpha(1)\beta(2) - \alpha(2)\beta(1)$]
Σ_g^- (antissimétrica) $\times$ ψ_{spin} (simétrica)
Δ_g (simétrica) $\times$ [$\alpha(1)\beta(2) - \alpha(2)\beta(1)$]

O_2 - $D_{\infty h}$

Determinando os singletos e tripletos

- Como a função de spin antissimétrica

$$[\alpha(1)\beta(2) - \alpha(2)\beta(1)]$$

corresponde a uma única possibilidade, trata-se de um singleto.

Σ_g^+ (simétrica) $\times$ singleto
Σ_g^- (antissimétrica) $\times$ ψ_{spin} (simétrica)
Δ_g (simétrica) $\times$ singleto

O_2 - $D_{\infty h}$

Determinando os singletos e tripletos

$$\psi_{spin}\ (\text{simétrica}) = [\alpha(1)\alpha(2)] + [\beta(1)\beta(2)] + [\alpha(1)\beta(2) + \alpha(2)\beta(1)]$$

TRIPLETO

O_2 - $D_{\infty h}$

Determinando os singletos e tripletos

Σ_g^+ (simétrica) $\times$ singleto $= {}^1\Sigma_g^+$

Σ_g^- (antissimétrica) $\times$ tripleto $= {}^3\Sigma_g^-$

Δ_g (simétrica) $\times$ singleto $= {}^1\Delta_g$

O_2 - $D_{\infty h}$

Determinando os singletos e tripletos

Assim, entre as duas soluções possíveis

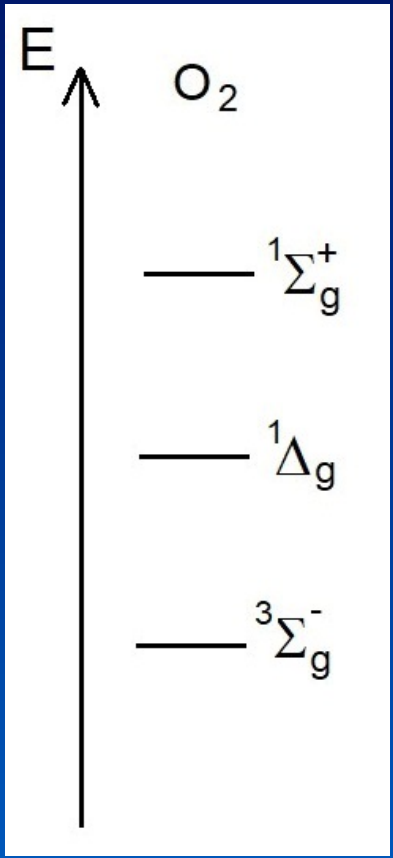
$$^3\Sigma_g^+ + {}^1\Sigma_g^- + {}^1\Delta_g \quad \text{ou} \quad {}^1\Sigma_g^+ + {}^3\Sigma_g^- + {}^1\Delta_g$$

a solução correta é

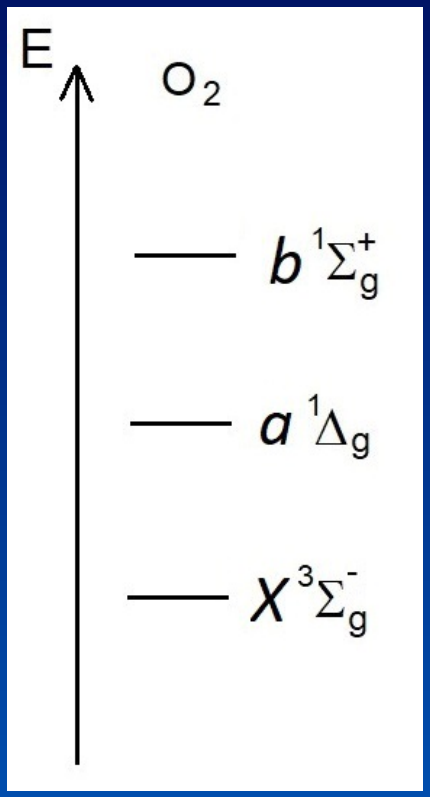
$$^1\Sigma_g^+ \qquad {}^3\Sigma_g^- \qquad {}^1\Delta_g$$

O_2 - $D_{\infty h}$

Níveis de energia da molécula



O_2 - $D_{\infty h}$



Níveis de energia da molécula

Energia da transição 0-0

cm^{-1}	nm	
13120	762	$b\,^1\Sigma_g^+$
7882	1268	$a\,^1\Delta_g$
0	0	$X\,^3\Sigma_g^-$

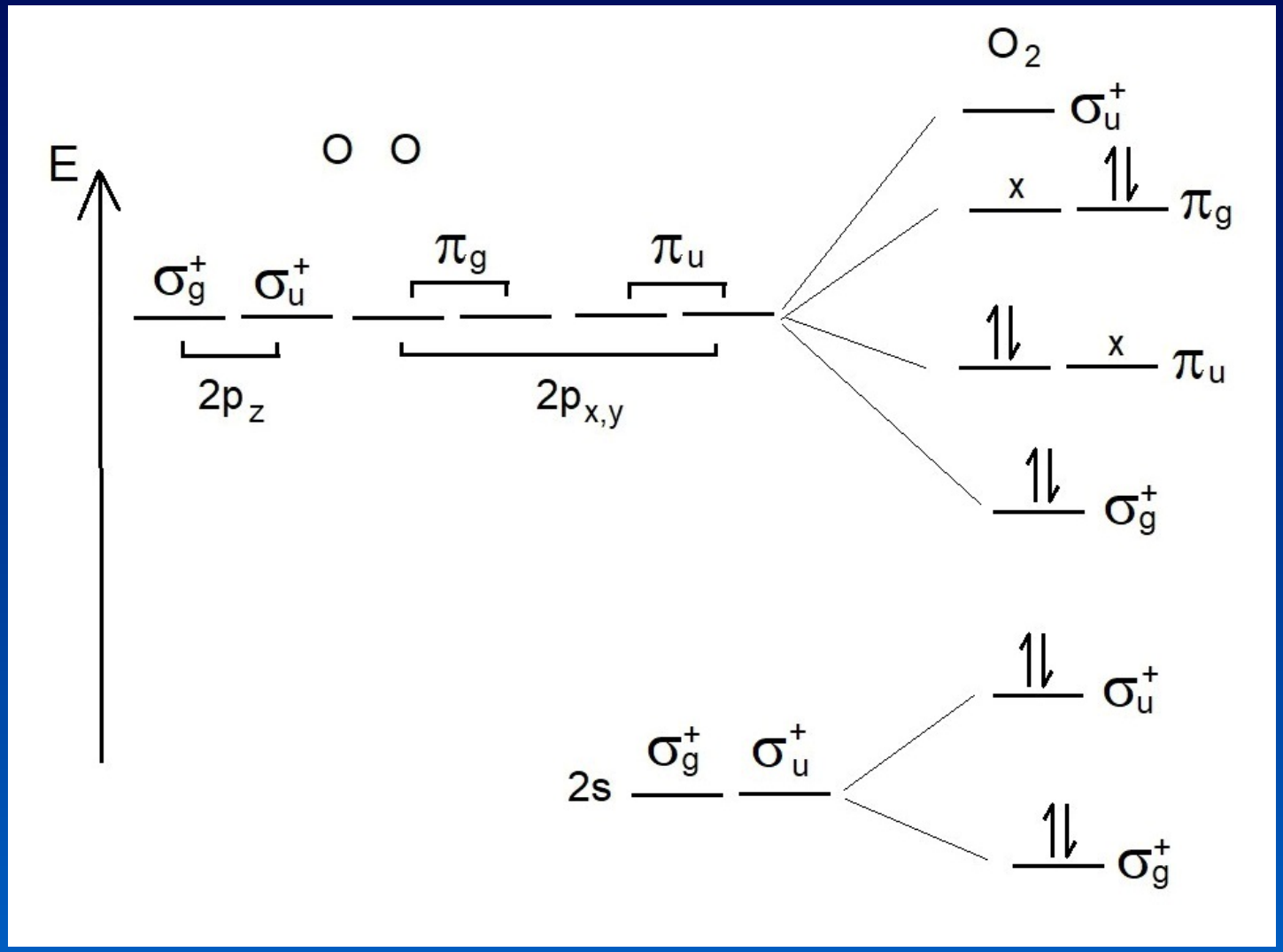
Ver espectro (Figura 7) e diagrama de energia (Figura 8) em:
Khan e Kasha, *J. Amer. Chem. Soc. 92*:3293 (1970).

Regras para nomear os níveis de energia das moléculas diatômicas[1,2]

- O estado fundamental é sempre indicado como *X*
- Utilizam-se as letras *A*, *B*, *C* ... para os estados excitados de mesma multiplicidade de spin que o estado fundamental, em ordem ascendente de energia.
- Utilizam-se as letras *a*, *b*, *c* ... para os estados excitados com multiplicidade de spin diferente do estado fundamental.
- Nas moléculas poliatômicas não lineares, utiliza-se um til (~) sobre a letra para evitar confusão com os rótulos de simetria.

1. Bernath, P. F., *Spectra of Atoms and Molecules*, 3ª ed., Oxford University Press, 2016. pg. 344.
2. Cohen, E. R. *et al*., eds., *Grandezas, Unidades de Símbolos em Físico-Química*, 3ª ed., IUPAC-SBQ, 2018. pg. 35.

O_2 - $D_{\infty h}$ (estados excitados adicionais)



$D_{\infty h}$

$D_{\infty h}$	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	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
$\Pi_g \otimes \Pi_u$	4	0	0	-4	0	0
					$\Sigma_u^+ \oplus \Sigma_u^- \oplus \Delta_u$	

O_2 - $D_{\infty h}$

Determinando os singletos e tripletos

Nesse caso, como não se trata de um estado eletrônico degenerado, todos os termos apresentam as possibilidades singleto e tripleto.

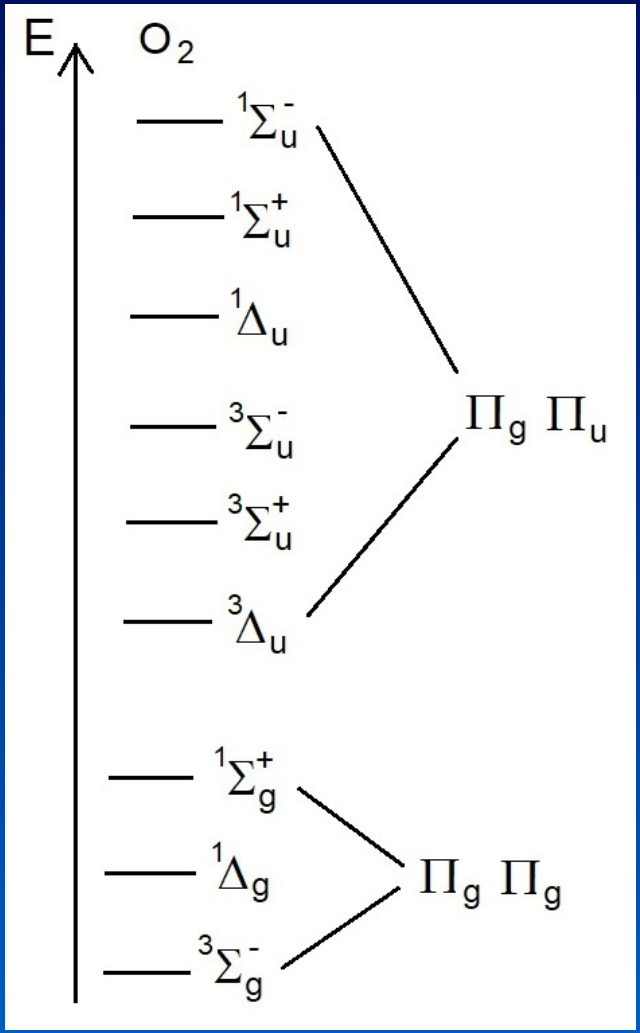
$^1\Sigma_u^+$ $^1\Sigma_u^-$ $^1\Delta_u$

$^3\Sigma_u^+$ $^3\Sigma_u^-$ $^3\Delta_u$

Harris, D. C.; Bertolucci, M. D.; *Symmetry and Spectroscopy*, Dover: Nova Iorque, 1978. pg 324

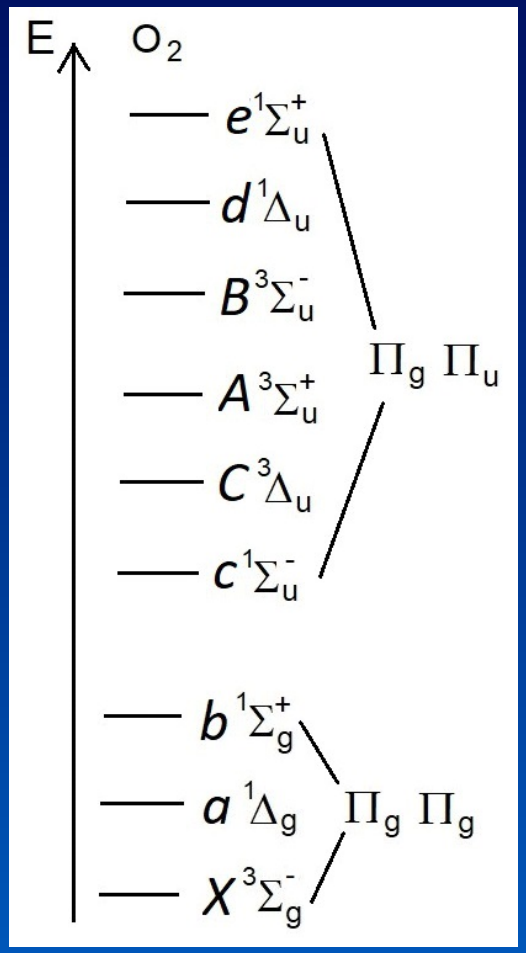
O_2 - $D_{\infty h}$

Níveis de energia incluindo estado excitado adicional



O_2 - $D_{\infty h}$

Níveis de energia incluindo estado excitado adicional



Energia da transição 0-0

cm^{-1}	nm	
49358	203	$B\ ^3\Sigma_u^-$
35007	285	$A\ ^3\Sigma_u^+$
34319	291	$C\ ^3\Delta_u$
32664	306	$c\ ^1\Sigma_u^-$
13120	762	$b\ ^1\Sigma_g^+$
7882	1268	$a\ ^1\Delta_g$
0	0	$X\ ^3\Sigma_g^-$

Descoberta depois das bandas *A* e *B*

Krupenie, P. H.; *J. Phys. Chem. Ref. Data 1*:423 (1972). Tabela 1, pg. 456-457.

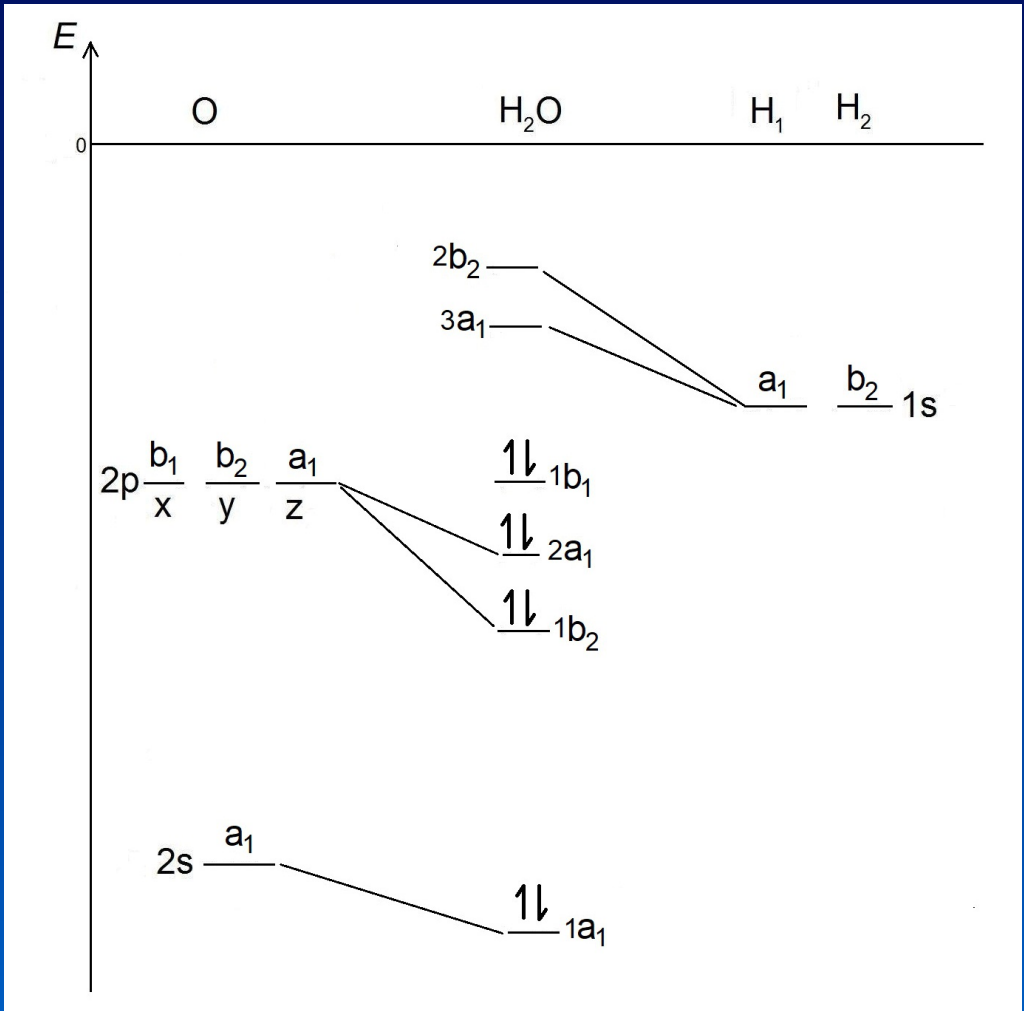
Ver espectro em Khan e Kasha, *J. Amer. Chem. Soc. 92*:3293 (1970). Figura 7, pg. 3298

Termos espectroscópicos para moléculas

Água

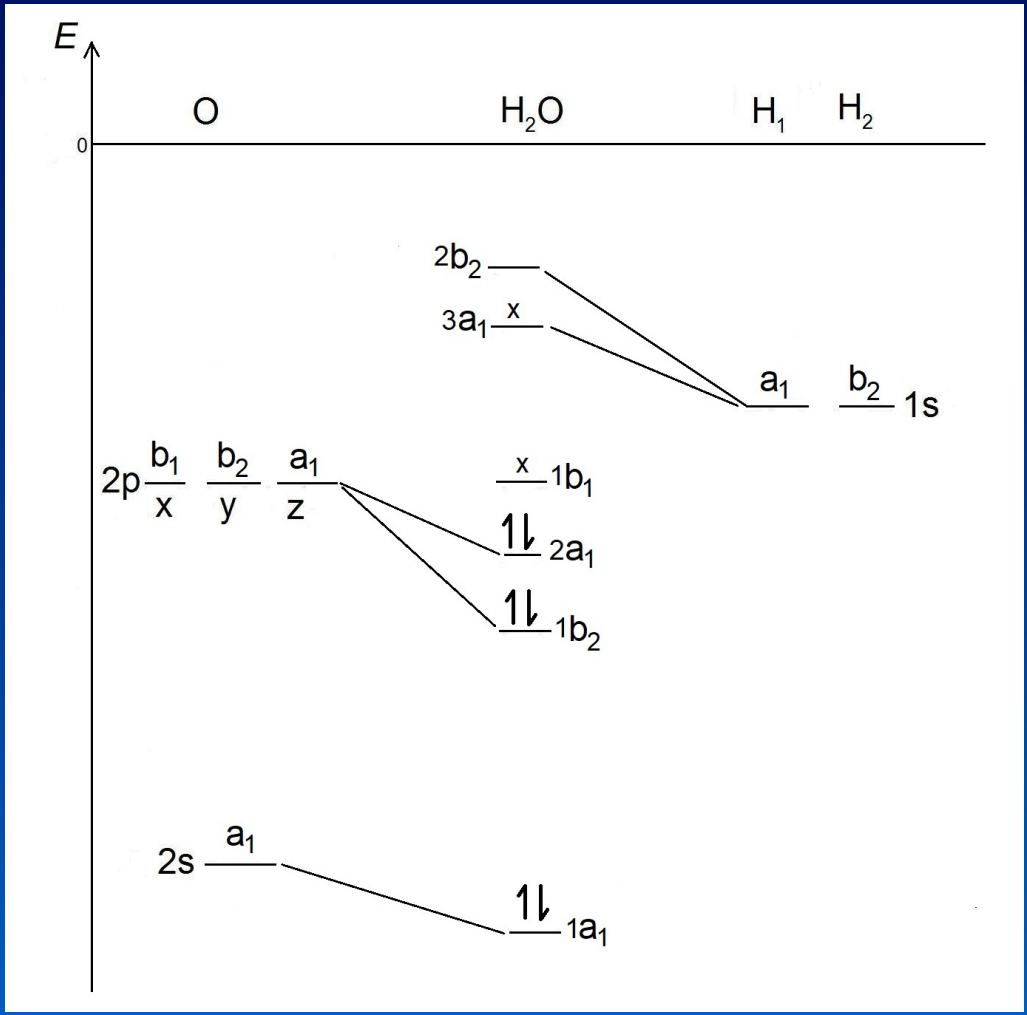
Água - C_{2v}

Diagrama de energia dos orbitais moleculares



Água - C_{2v}

Termos espectroscópicos para os estados excitados



Água - C_{2v}

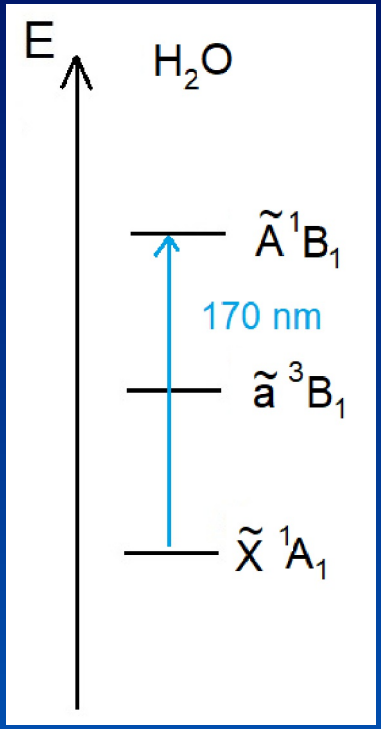
C_{2v}	E	C_2	$\sigma_v^{(xz)}$	$\sigma'_v{}^{(yz)}$	
A_1	1	1	1	1	
A_2	1	1	-1	-1	
B_1	1	-1	1	-1	
B_2	1	-1	-1	1	
$B_1 \otimes A_1$	1	-1	1	-1	B_1

Este estado excitado pode ser singleto ou tripleto

$^1B_1$ $^3B_1$

H_2O - C_{2v}

Níveis de energia da molécula

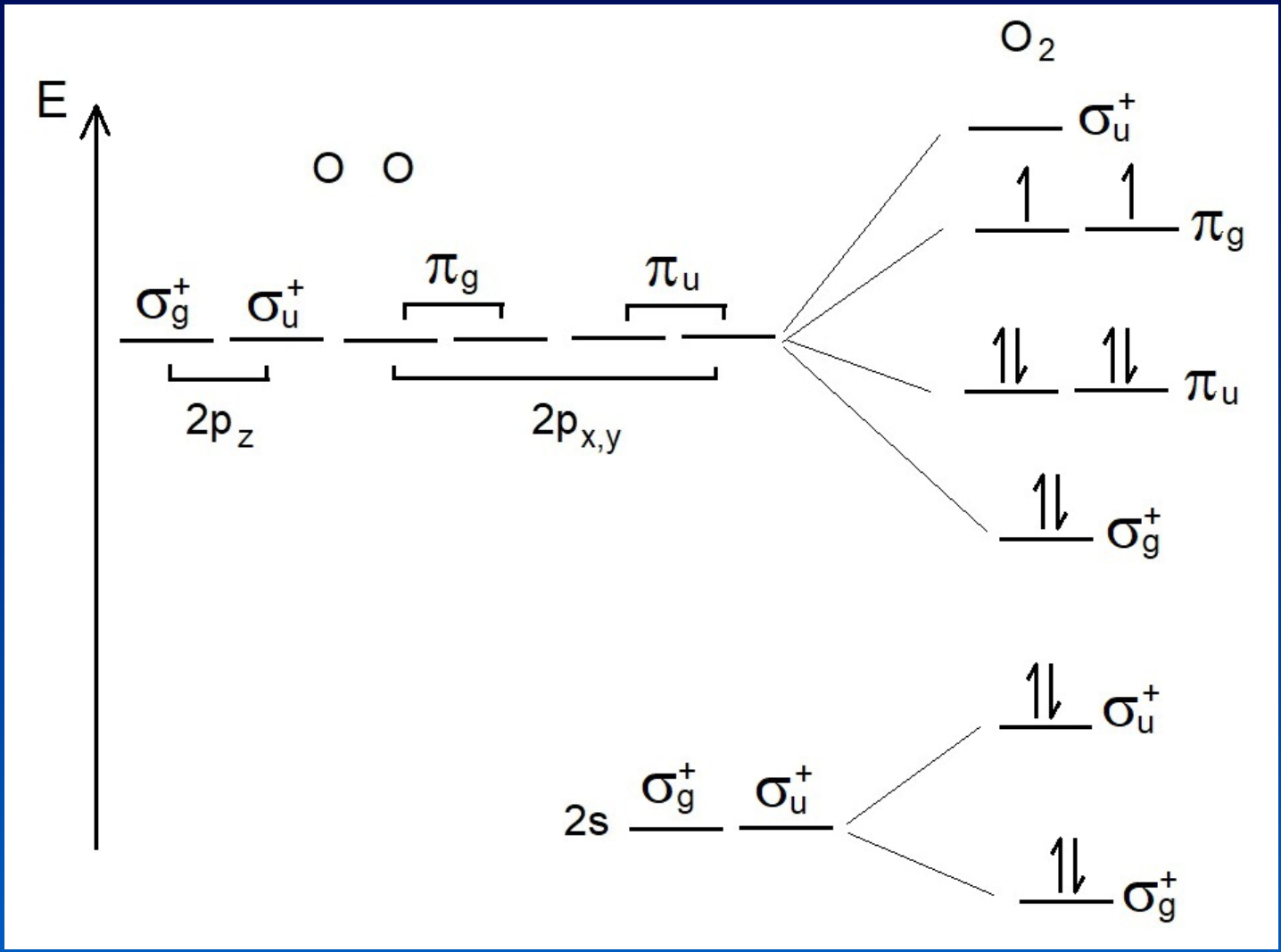


Ver espectro (Figura 1) em:
Luo *et al.* *J. Phys. Chem. A* *125*:3622 (2021)

Desenhando os orbitais moleculares

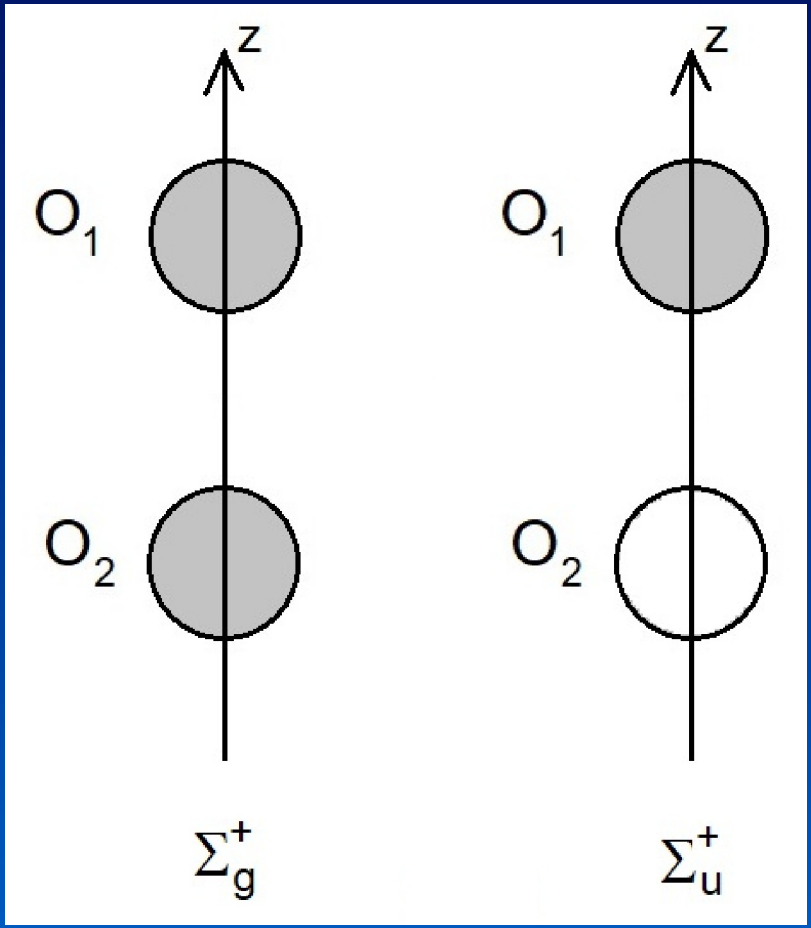
dioxigênio - O_2

O_2 - $D_{\infty h}$



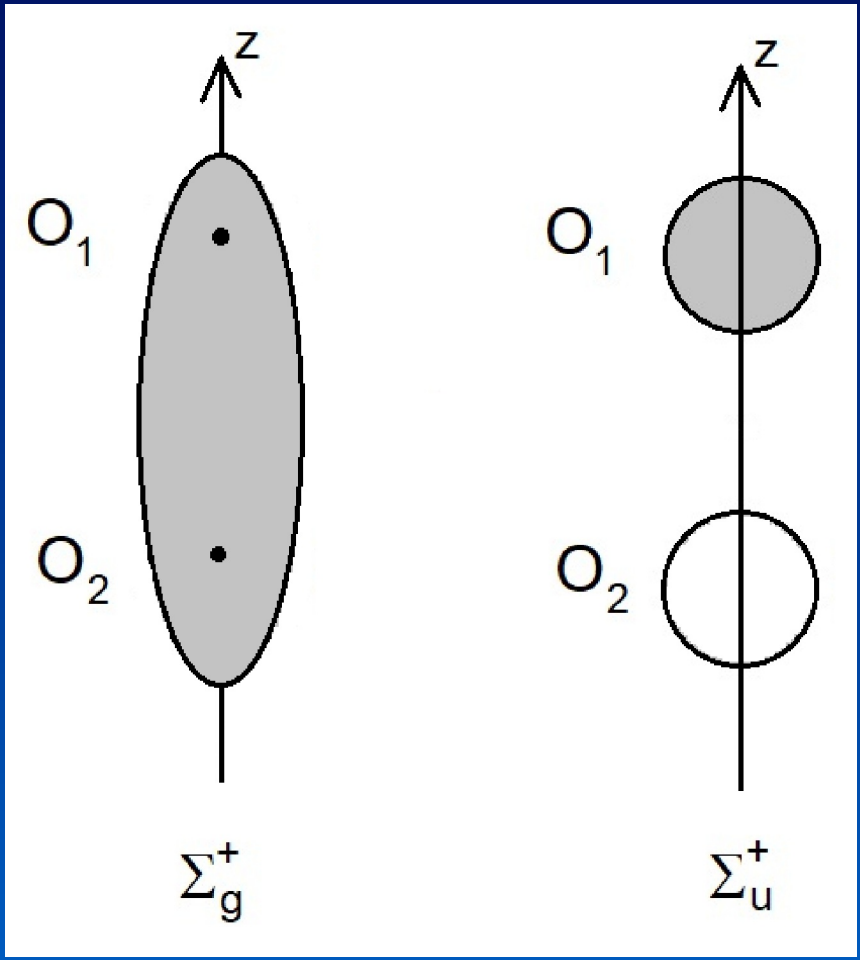
O_2 - $D_{\infty h}$

Os orbitais 2s podem formar uma combinação ligante e outra antiligante

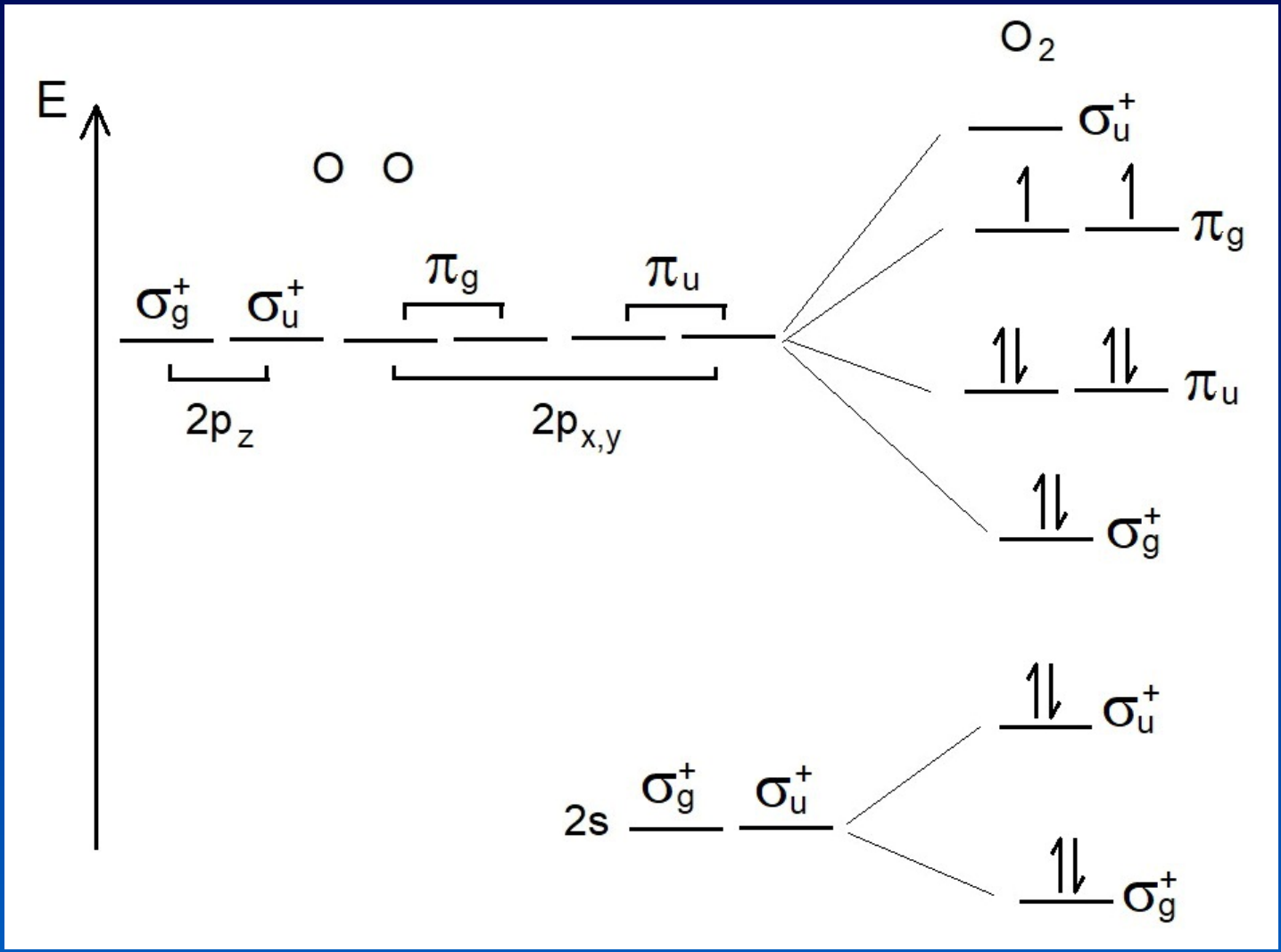


O_2 - $D_{\infty h}$

Os orbitais 2s podem formar uma combinação ligante e outra antiligante

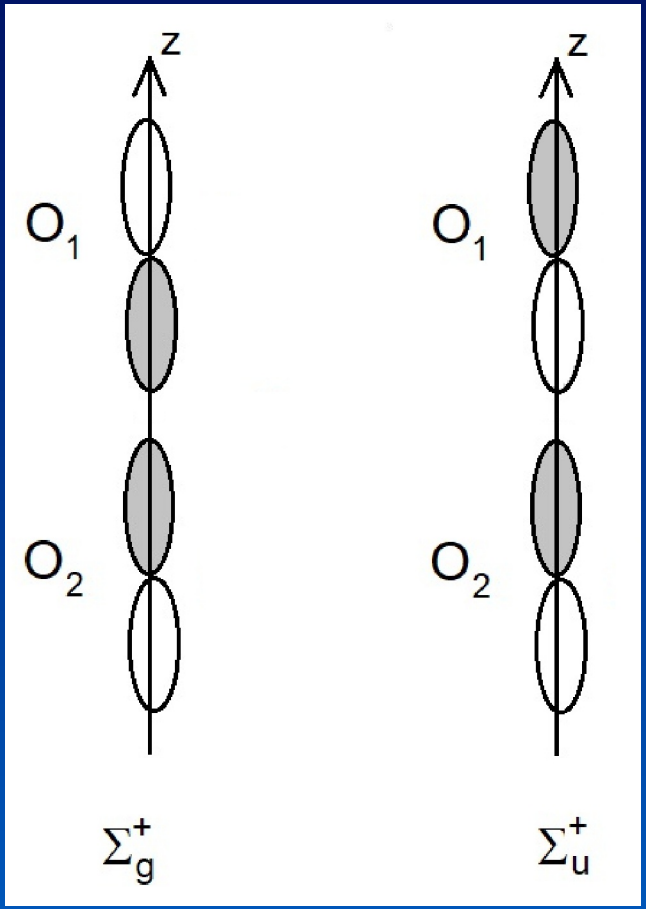


O_2 - $D_{\infty h}$



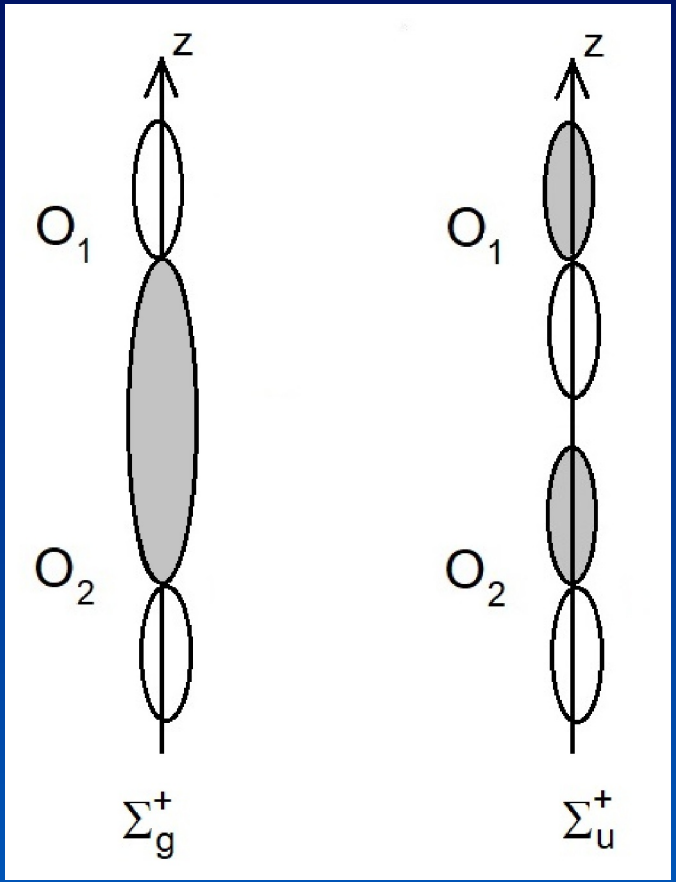
O_2 - $D_{\infty h}$

Os orbitais $2p_z$ também podem formar uma combinação σ ligante e antiligante

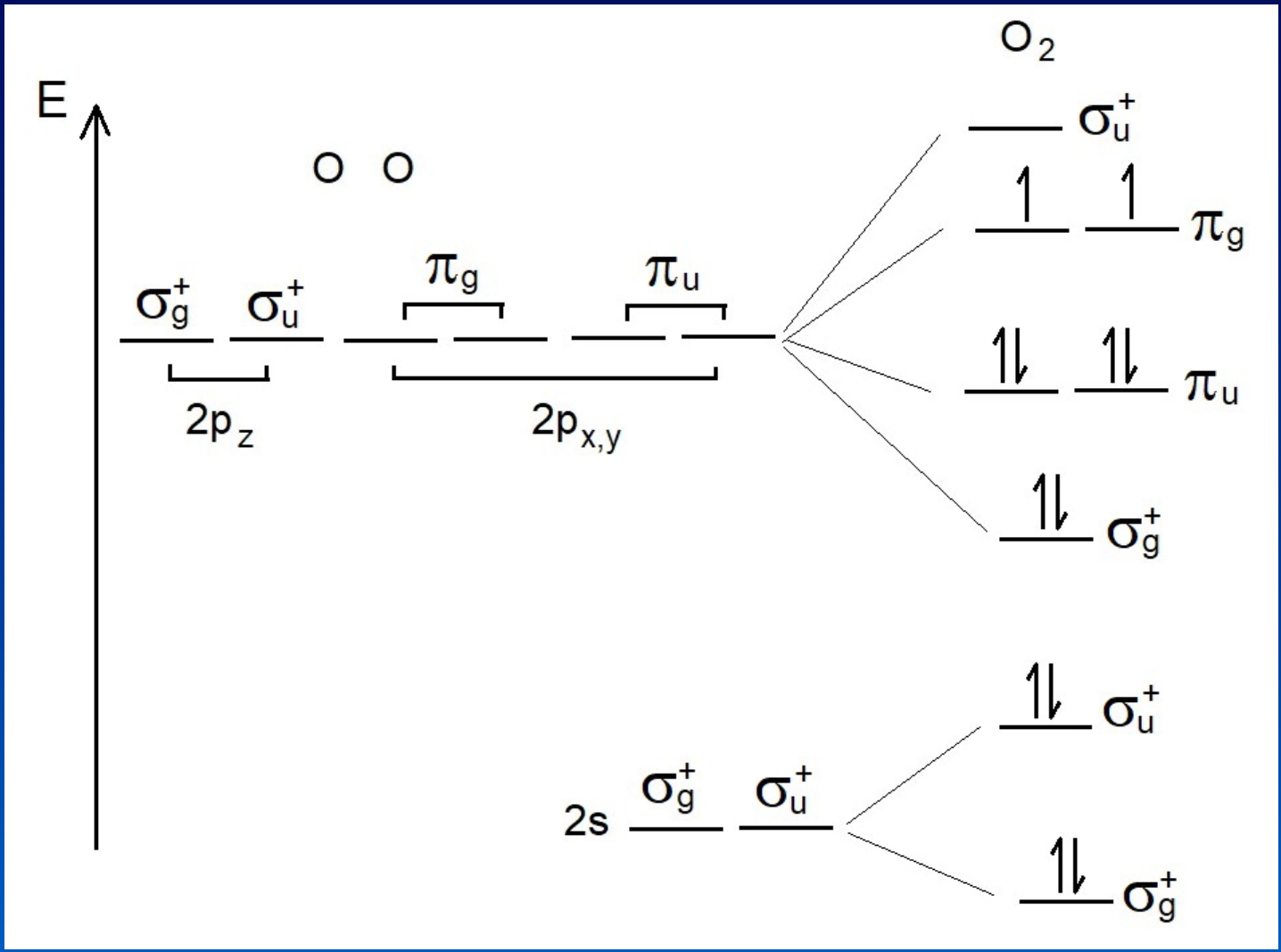


O_2 - $D_{\infty h}$

Os orbitais $2p_z$ também podem formar uma combinação σ ligante e antiligante

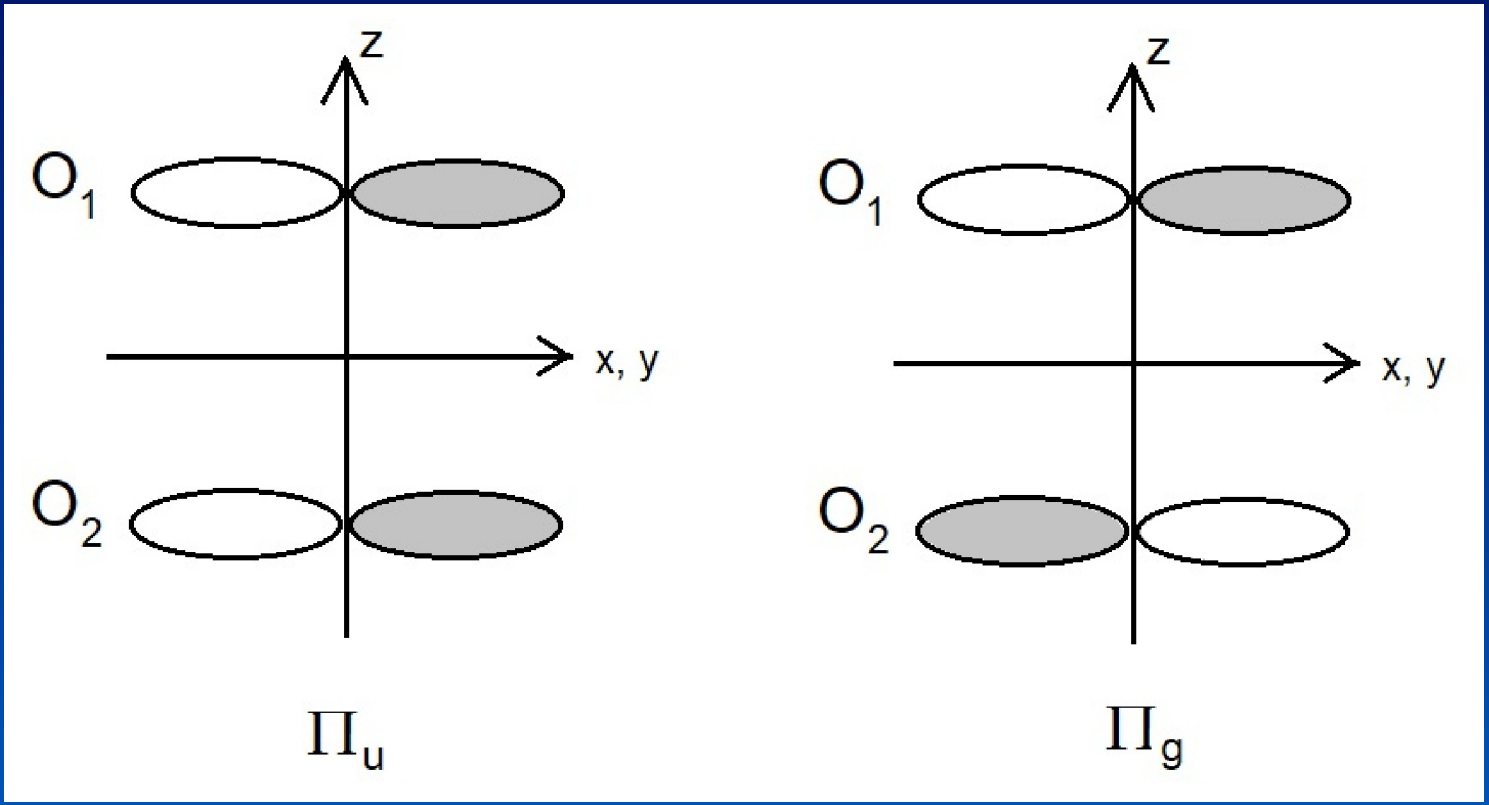


O_2 - $D_{\infty h}$



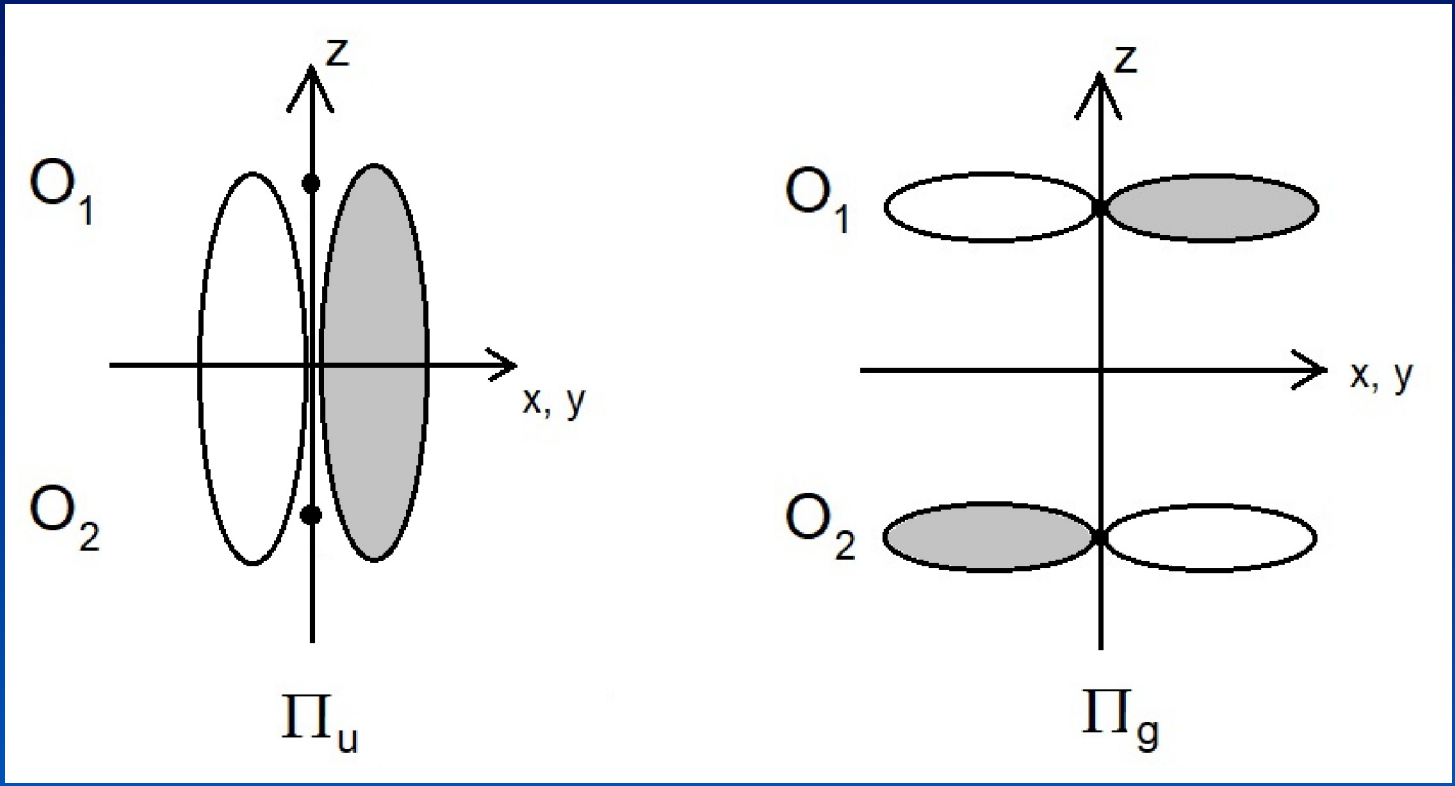
O_2 - $D_{\infty h}$

Os orbitais π (p_x,p_y) também formam combinações ligantes e antiligantes



O_2 - $D_{\infty h}$

Os orbitais π (p_x,p_y) também formam combinações ligantes e antiligantes



FIM