Química Inorgânica Avançada
IQU-708

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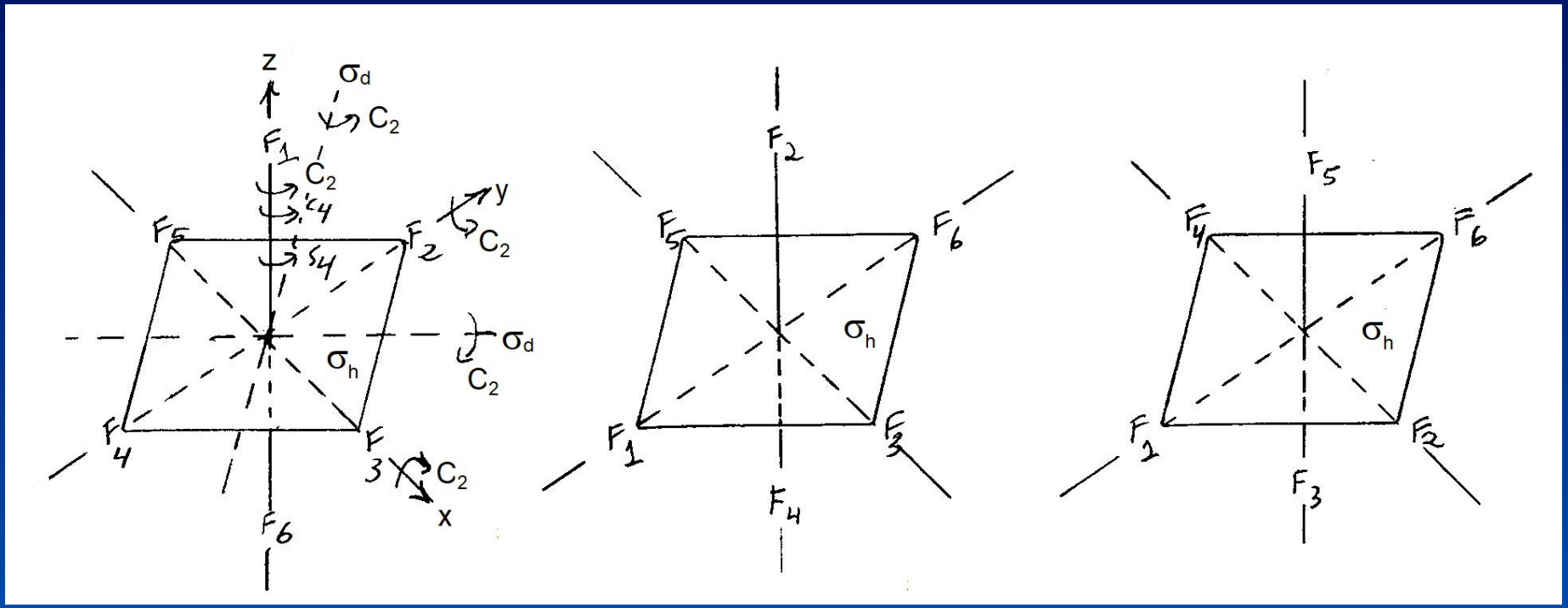
Simetria - Aula 5 - Geometria octaédrica
Complexos com ligantes de campo fraco, forte e intermediário
Transições eletrônicas

10/06/2024

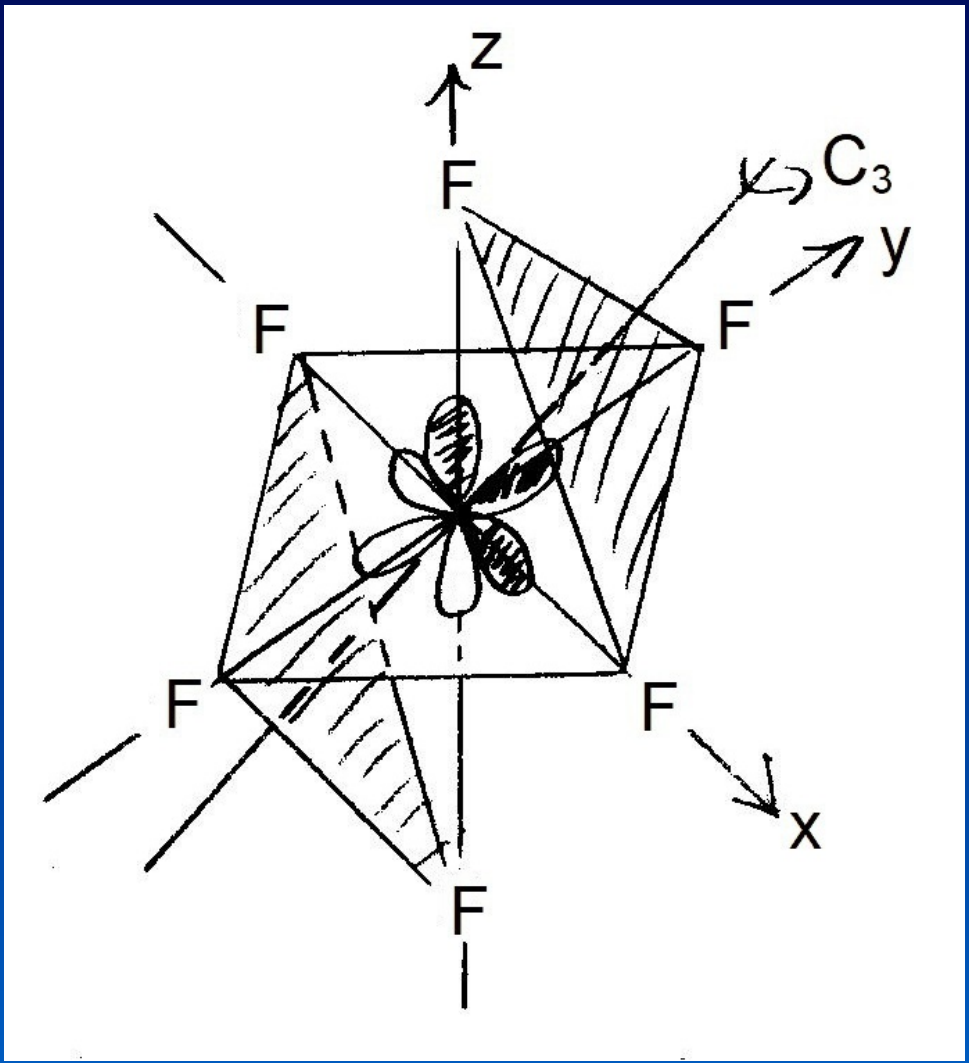
$[CoF_6]^{3-}$ - O_h

O_h	E	$8C_3$	$6C_2$	$6C_4$	$3C_2(=C_4^2)$	i	$6S_4$	$8S_6$	$3\sigma_h$	$6\sigma_d$	(x,y,z)
A_{1g}	1	1	1	1	1	1	1	1	1	1	
A_{2g}	1	1	-1	-1	1	1	-1	1	1	-1	
E_g	2	-1	0	0	2	2	0	-1	2	0	
T_{1g}	3	0	-1	1	-1	3	1	0	-1	-1	
T_{2g}	3	0	1	-1	-1	3	-1	0	-1	1	
A_{1u}	1	1	1	1	1	-1	-1	-1	-1	-1	
A_{2u}	1	1	-1	-1	1	-1	1	-1	-1	1	
E_u	2	-1	0	0	2	-2	0	1	-2	0	
T_{1u}	3	0	-1	1	-1	-3	-1	0	1	1	
T_{2u}	3	0	1	-1	-1	-3	1	0	1	-1	

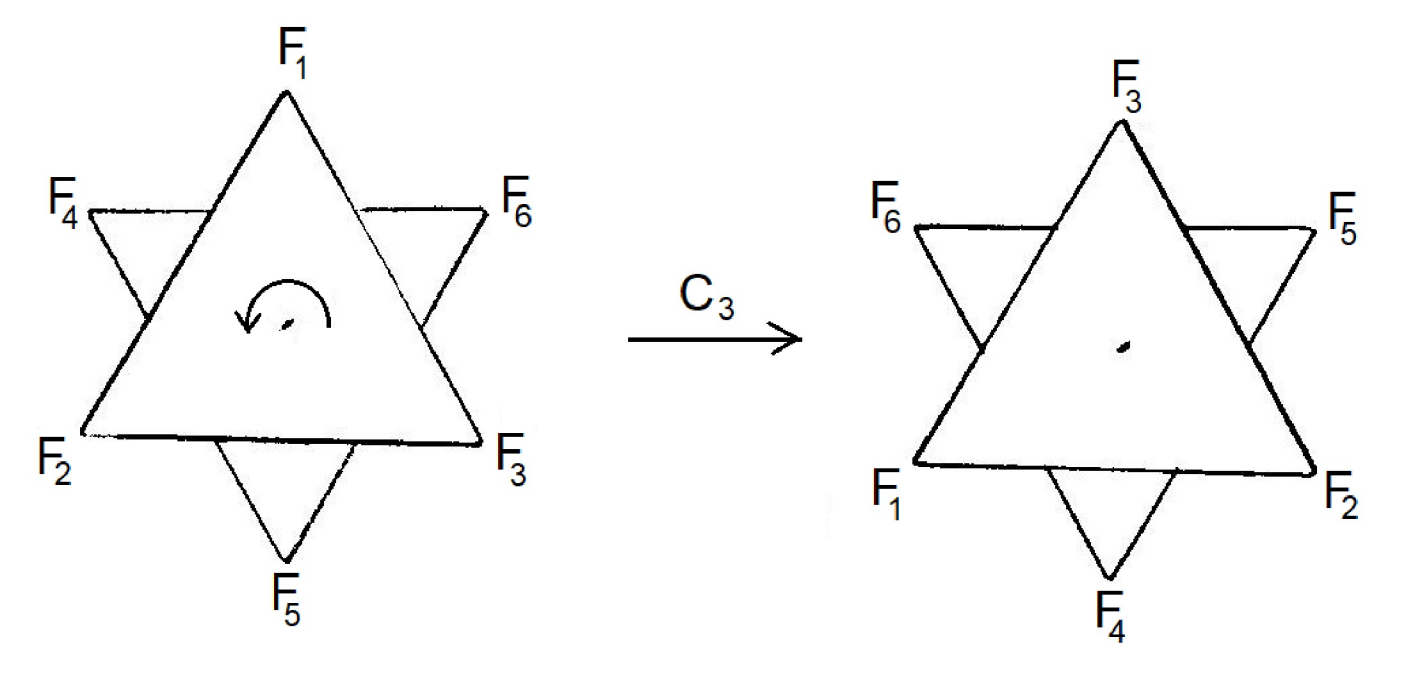
$[CoF_6]^{3-}$ - O_h


z
σd
C2
F1
C2
S4
y
F5
F2
C2
S4
σd
σh
C2
F4
F3
C2
x
F6
F2
F5
F6
σh
F1
F3
F4
F5
F4
F6
σh
F1
F2
F3

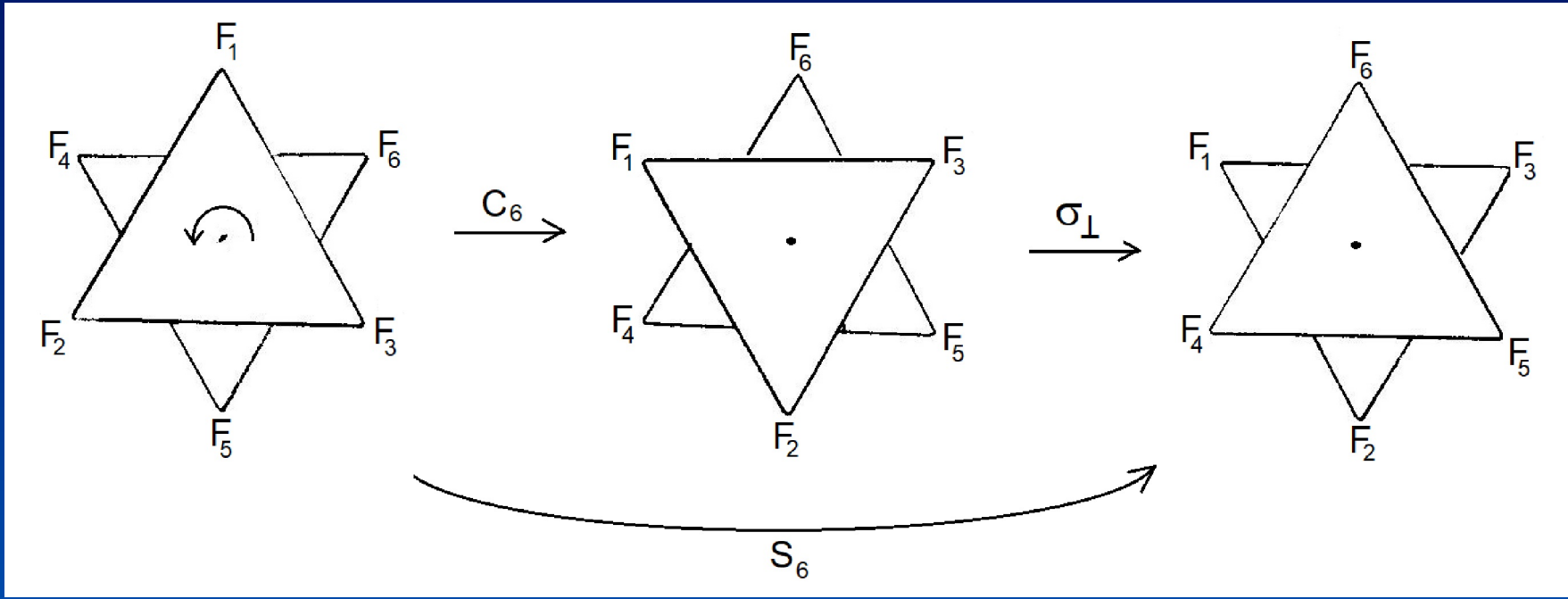
$[CoF_6]^{3-}$ - O_h



$[CoF_6]^{3-}$ - O_h



$[CoF_6]^{3-}$ - O_h

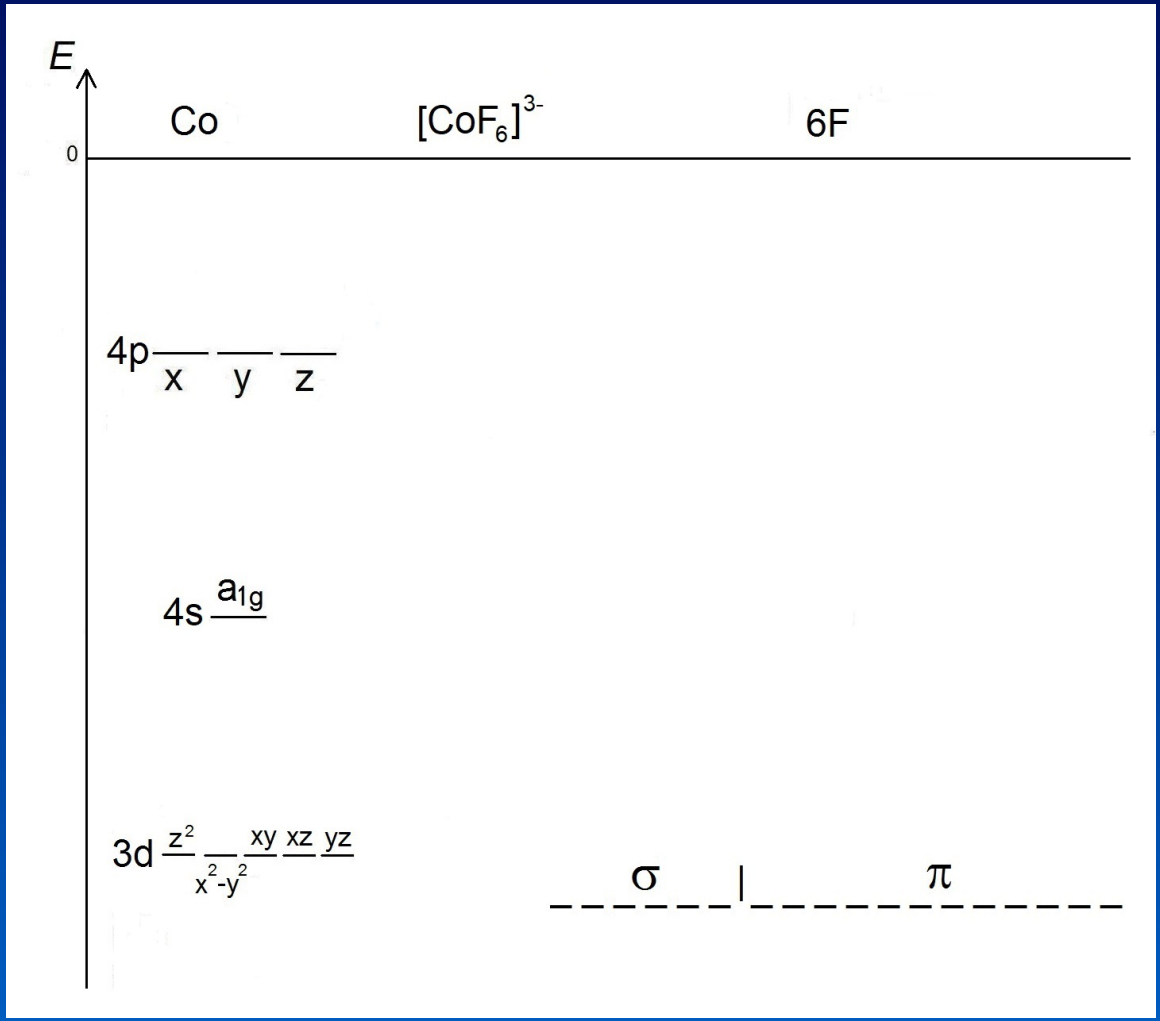


Classificando o orbital 4s do Co

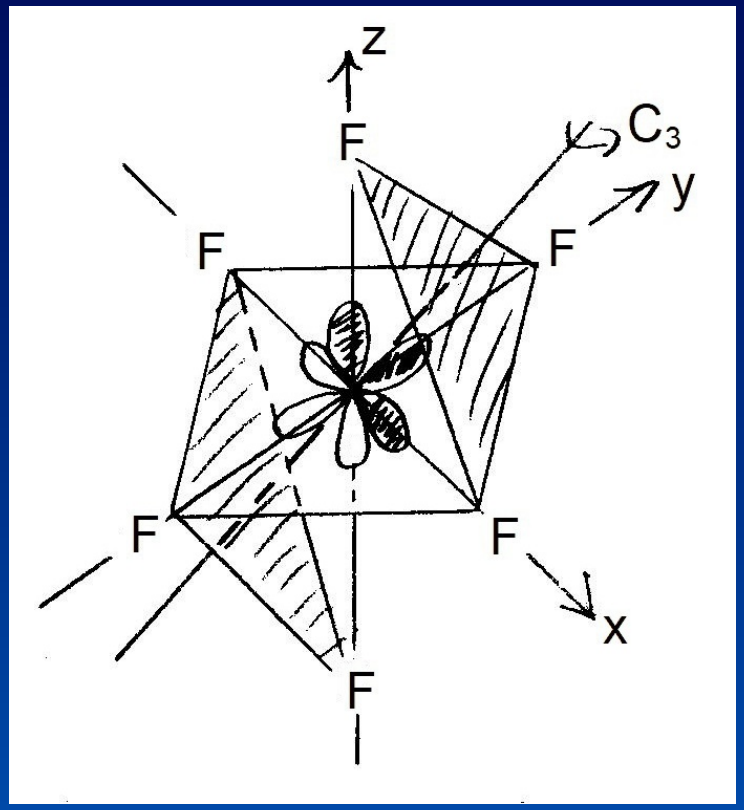
O_h	E	$8C_3$	$6C_2$	$6C_4$	$3C_2(=C_4^2)$	i	$6S_4$	$8S_6$	$3\sigma_h$	$6\sigma_d$	(x,y,z)
A_{1g}	1	1	1	1	1	1	1	1	1	1	
A_{2g}	1	1	-1	-1	1	1	-1	1	1	-1	
E_g	2	-1	0	0	2	2	0	-1	2	0	
T_{1g}	3	0	-1	1	-1	3	1	0	-1	-1	
T_{2g}	3	0	1	-1	-1	3	-1	0	-1	1	
A_{1u}	1	1	1	1	1	-1	-1	-1	-1	-1	
A_{2u}	1	1	-1	-1	1	-1	1	-1	-1	1	
E_u	2	-1	0	0	2	-2	0	1	-2	0	
T_{1u}	3	0	-1	1	-1	-3	-1	0	1	1	
T_{2u}	3	0	1	-1	-1	-3	1	0	1	-1	
4s	1	1	1	1	1	1	1	1	1	1	A_{1g}

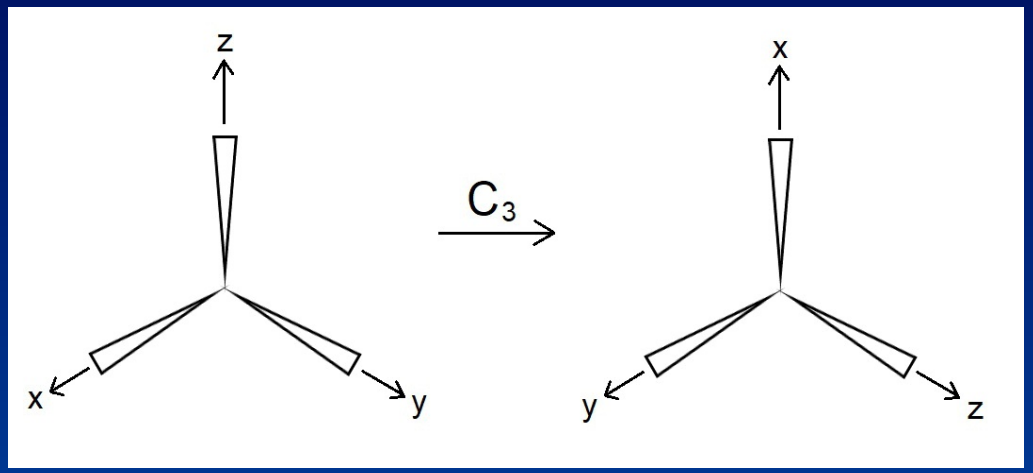
$[CoF_6]^{3-}$ - O_h

Construindo o diagrama de energia dos orbitais moleculares



Classificando os orbitais 4p do Co - INSEPARÁVEIS





$$x \xrightarrow{-C_3} y$$
$$y \xrightarrow{-C_3} z$$
$$z \xrightarrow{-C_3} x$$

$[CoF_6]^{3-}$ - O_h

Classificando os orbitais 4p do Co - INSEPARÁVEIS

$$
\begin{array}{c|ccc}
 & 2p_x & 2p_y & 2p_z \\
\hline
2p_x & 1 & 0 & 0 \\
2p_y & 0 & 1 & 0 \\
2p_z & 0 & 0 & 1
\end{array}
\quad \xrightarrow{C_3} \quad
\begin{array}{c|ccc}
 & 2p_x & 2p_y & 2p_z \\
\hline
2p_x & 0 & 1 & 0 \\
2p_y & 0 & 0 & 1 \\
2p_z & 1 & 0 & 0
\end{array}
$$

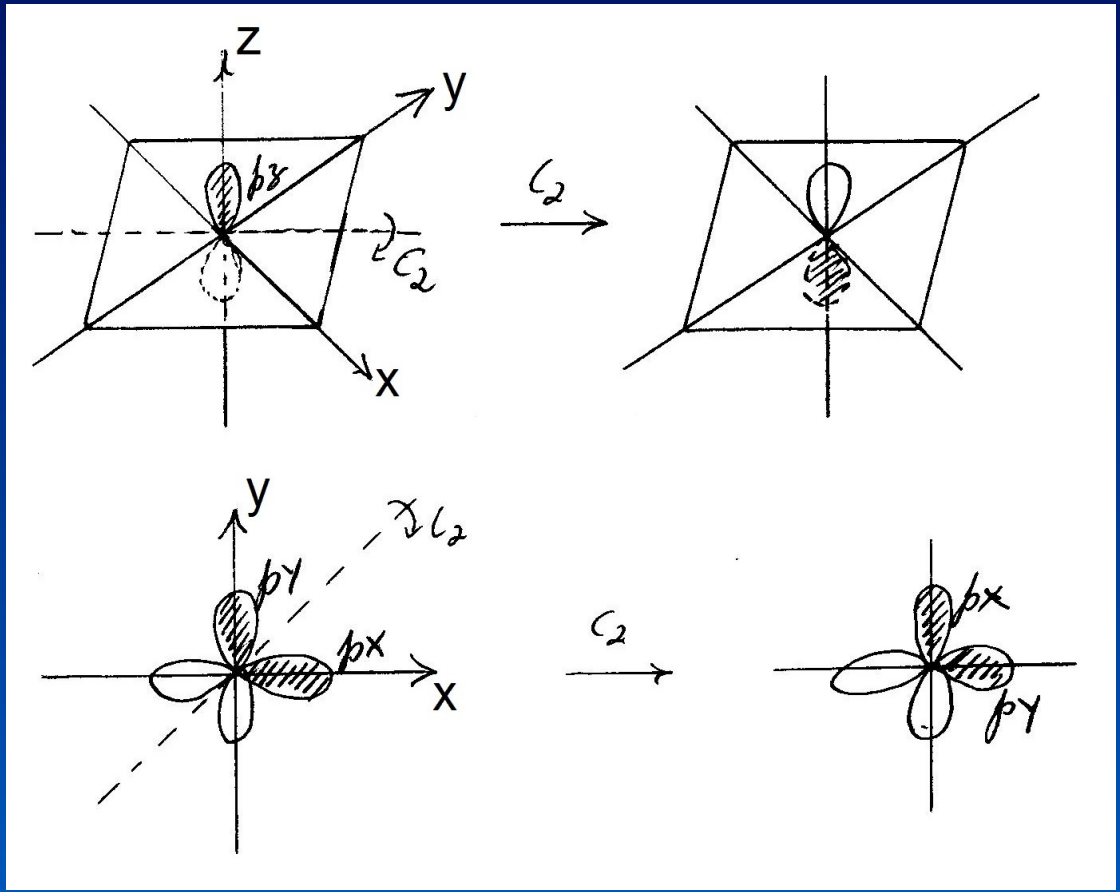
$\chi = 0$

Classificando os orbitais 4p do Co - INSEPARÁVEIS

O_h	E	$8C_3$	$6C_2$	$6C_4$	$3C_2(=C_4^2)$	i	$6S_4$	$8S_6$	$3\sigma_h$	$6\sigma_d$	(x,y,z)
A_{1g}	1	1	1	1	1	1	1	1	1	1	
A_{2g}	1	1	-1	-1	1	1	-1	1	1	-1	
E_g	2	-1	0	0	2	2	0	-1	2	0	
T_{1g}	3	0	-1	1	-1	3	1	0	-1	-1	
T_{2g}	3	0	1	-1	-1	3	-1	0	-1	1	
A_{1u}	1	1	1	1	1	-1	-1	-1	-1	-1	
A_{2u}	1	1	-1	-1	1	-1	1	-1	-1	1	
E_u	2	-1	0	0	2	-2	0	1	-2	0	
T_{1u}	3	0	-1	1	-1	-3	-1	0	1	1	
T_{2u}	3	0	1	-1	-1	-3	1	0	1	-1	
4p	3	0									

$[CoF_6]^{3-}$ - O_h

Classificando os orbitais 4p do Co - INSEPARÁVEIS



$[CoF_6]^{3-}$ - O_h

Classificando os orbitais 4p do Co - INSEPARÁVEIS

$$
\begin{array}{c|ccc}
 & 2p_x & 2p_y & 2p_z \\
\hline
2p_x & 1 & 0 & 0 \\
2p_y & 0 & 1 & 0 \\
2p_z & 0 & 0 & 1
\end{array}
\quad \xrightarrow{C_2} \quad
\begin{array}{c|ccc}
 & 2p_x & 2p_y & 2p_z \\
\hline
2p_x & 0 & 1 & 0 \\
2p_y & 1 & 0 & 0 \\
2p_z & 0 & 0 & -1
\end{array}
$$

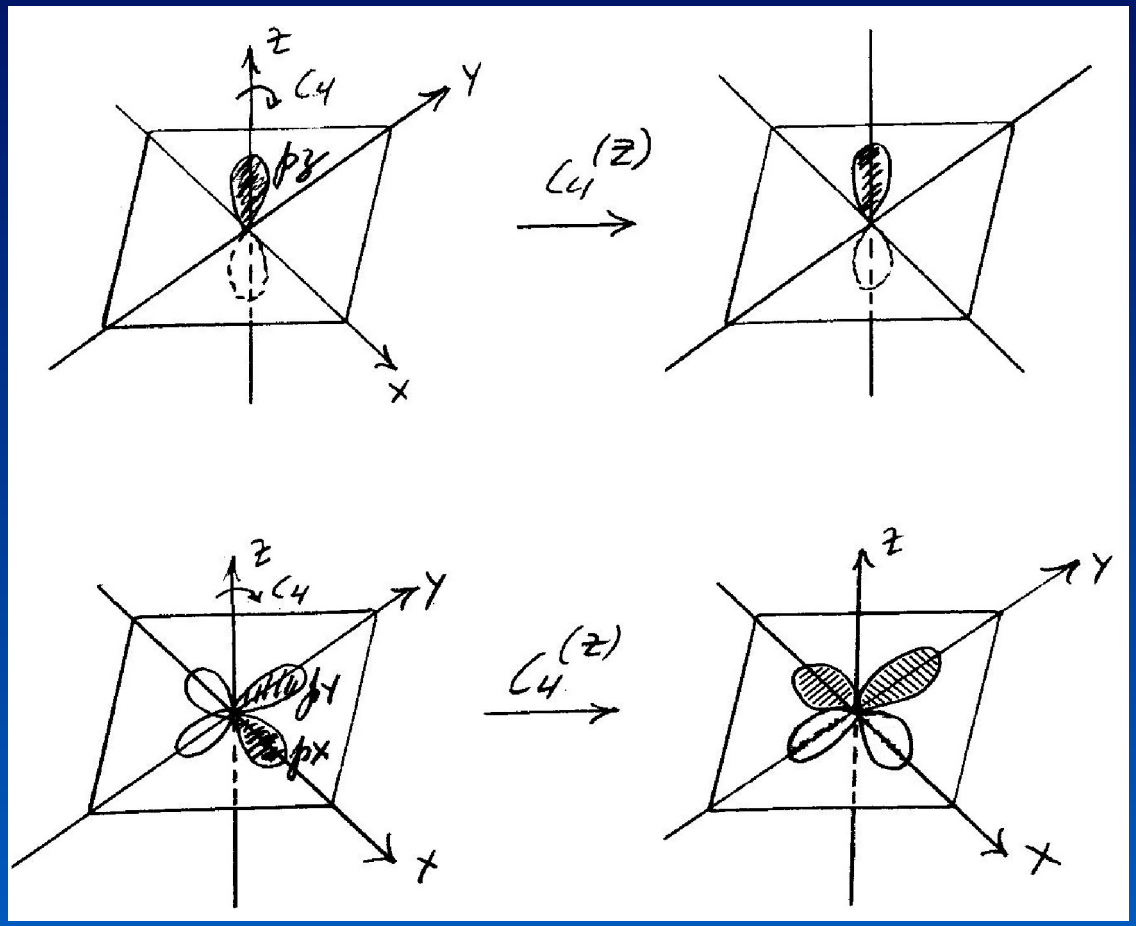
$\chi = -1$

Classificando os orbitais 4p do Co - INSEPARÁVEIS

O_h	E	$8C_3$	$6C_2$	$6C_4$	$3C_2(=C_4^2)$	i	$6S_4$	$8S_6$	$3\sigma_h$	$6\sigma_d$	(x,y,z)
A_{1g}	1	1	1	1	1	1	1	1	1	1	
A_{2g}	1	1	-1	-1	1	1	-1	1	1	-1	
E_g	2	-1	0	0	2	2	0	-1	2	0	
T_{1g}	3	0	-1	1	-1	3	1	0	-1	-1	
T_{2g}	3	0	1	-1	-1	3	-1	0	-1	1	
A_{1u}	1	1	1	1	1	-1	-1	-1	-1	-1	
A_{2u}	1	1	-1	-1	1	-1	1	-1	-1	1	
E_u	2	-1	0	0	2	-2	0	1	-2	0	
T_{1u}	3	0	-1	1	-1	-3	-1	0	1	1	
T_{2u}	3	0	1	-1	-1	-3	1	0	1	-1	
4p	3	0	-1								

$[CoF_6]^{3-}$ - O_h

Classificando os orbitais 4p do Co - INSEPARÁVEIS



$[CoF_6]^{3-}$ - O_h

Classificando os orbitais 4p do Co - INSEPARÁVEIS

$$
\begin{array}{c|ccc}
 & 2p_x & 2p_y & 2p_z \\
\hline
2p_x & 1 & 0 & 0 \\
2p_y & 0 & 1 & 0 \\
2p_z & 0 & 0 & 1
\end{array}
\quad \xrightarrow{C_4} \quad
\begin{array}{c|ccc}
 & 2p_x & 2p_y & 2p_z \\
\hline
2p_x & 0 & 1 & 0 \\
2p_y & -1 & 0 & 0 \\
2p_z & 0 & 0 & 1
\end{array}
$$

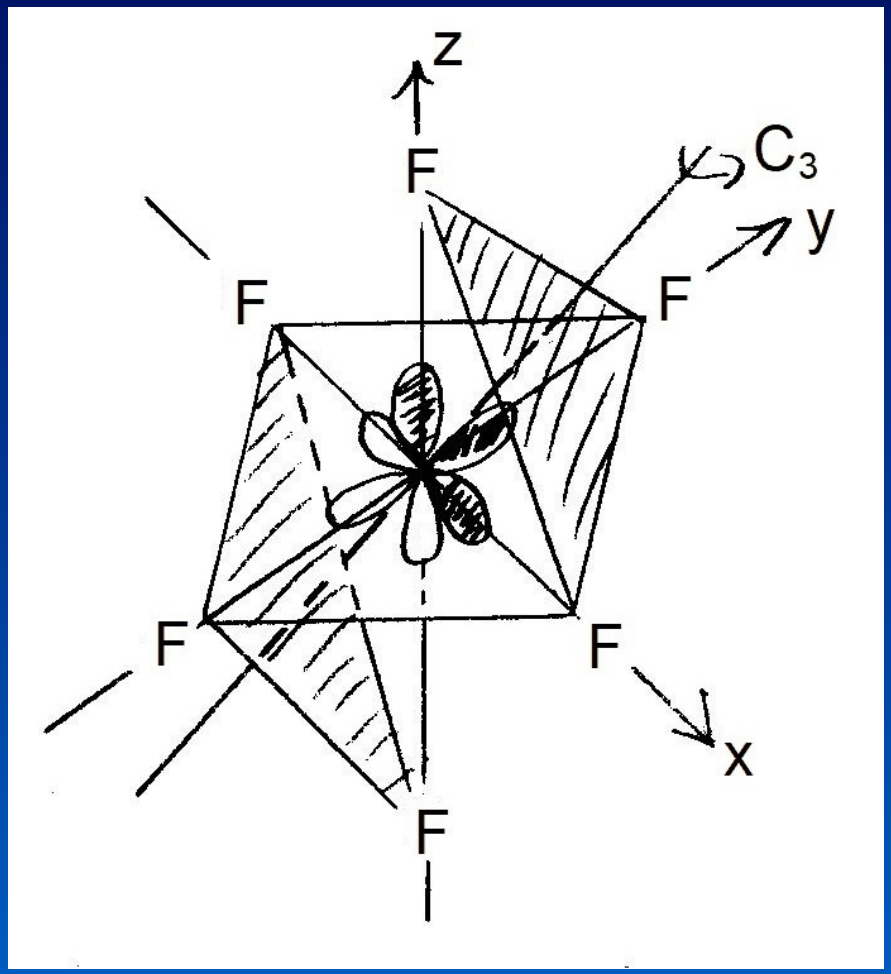
$\chi = 1$

Classificando os orbitais 4p do Co - INSEPARÁVEIS

O_h	E	$8C_3$	$6C_2$	$6C_4$	$3C_2(=C_4^2)$	i	$6S_4$	$8S_6$	$3\sigma_h$	$6\sigma_d$	(x,y,z)
A_{1g}	1	1	1	1	1	1	1	1	1	1	
A_{2g}	1	1	-1	-1	1	1	-1	1	1	-1	
E_g	2	-1	0	0	2	2	0	-1	2	0	
T_{1g}	3	0	-1	1	-1	3	1	0	-1	-1	
T_{2g}	3	0	1	-1	-1	3	-1	0	-1	1	
A_{1u}	1	1	1	1	1	-1	-1	-1	-1	-1	
A_{2u}	1	1	-1	-1	1	-1	1	-1	-1	1	
E_u	2	-1	0	0	2	-2	0	1	-2	0	
T_{1u}	3	0	-1	1	-1	-3	-1	0	1	1	
T_{2u}	3	0	1	-1	-1	-3	1	0	1	-1	
4p	3	0	-1	1							

$[CoF_6]^{3-}$ - O_h

Classificando os orbitais 4p do Co - INSEPARÁVEIS



i = centro de inversão

$[CoF_6]^{3-}$ - O_h

Classificando os orbitais 4p do Co - INSEPARÁVEIS

	$2p_x$	$2p_y$	$2p_z$			$2p_x$	$2p_y$	$2p_z$
$2p_x$	1	0	0	i	$2p_x$	-1	0	0
$2p_y$	0	1	0	→	$2p_y$	0	-1	0
$2p_z$	0	0	1		$2p_z$	0	0	-1

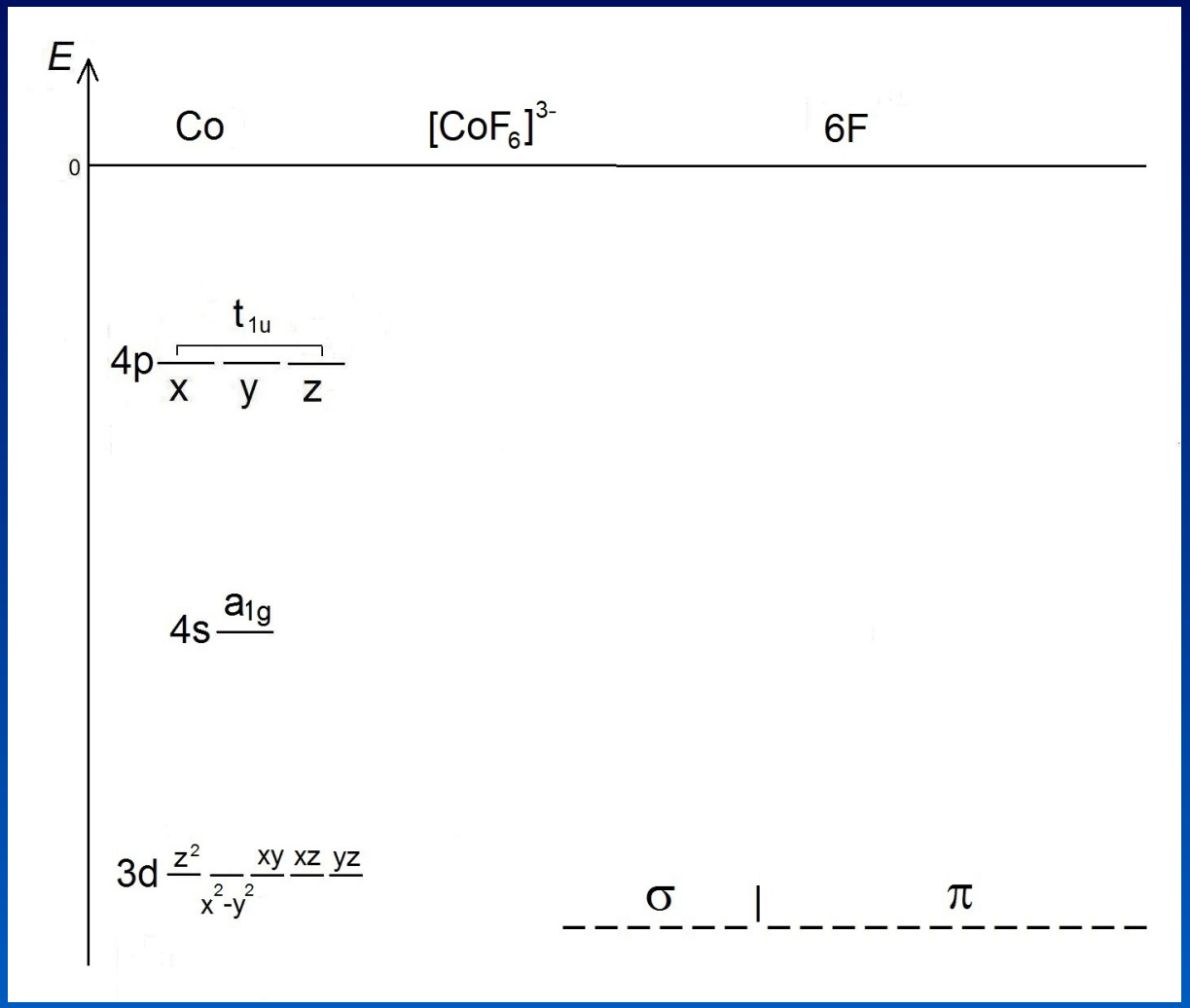
$\chi = -3$

Classificando os orbitais 4p do Co - INSEPARÁVEIS

O_h	E	$8C_3$	$6C_2$	$6C_4$	$3C_2(=C_4^2)$	i	$6S_4$	$8S_6$	$3\sigma_h$	$6\sigma_d$	(x,y,z)
A_{1g}	1	1	1	1	1	1	1	1	1	1	
A_{2g}	1	1	-1	-1	1	1	-1	1	1	-1	
E_g	2	-1	0	0	2	2	0	-1	2	0	
T_{1g}	3	0	-1	1	-1	3	1	0	-1	-1	
T_{2g}	3	0	1	-1	-1	3	-1	0	-1	1	
A_{1u}	1	1	1	1	1	-1	-1	-1	-1	-1	
A_{2u}	1	1	-1	-1	1	-1	1	-1	-1	1	
E_u	2	-1	0	0	2	-2	0	1	-2	0	
T_{1u}	3	0	-1	1	-1	-3	-1	0	1	1	
T_{2u}	3	0	1	-1	-1	-3	1	0	1	-1	
4p	3	0	-1	1		-3					T_{1u}

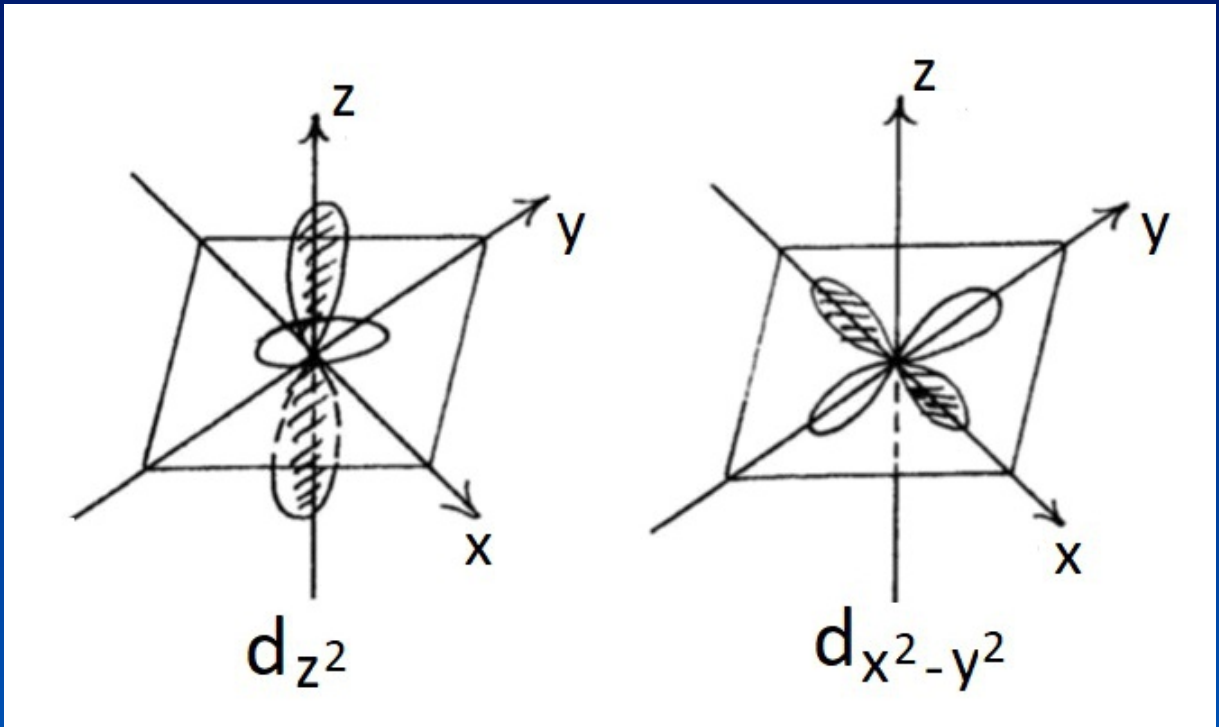
$[CoF_6]^{3-}$ - O_h

Construindo o diagrama de energia dos orbitais moleculares



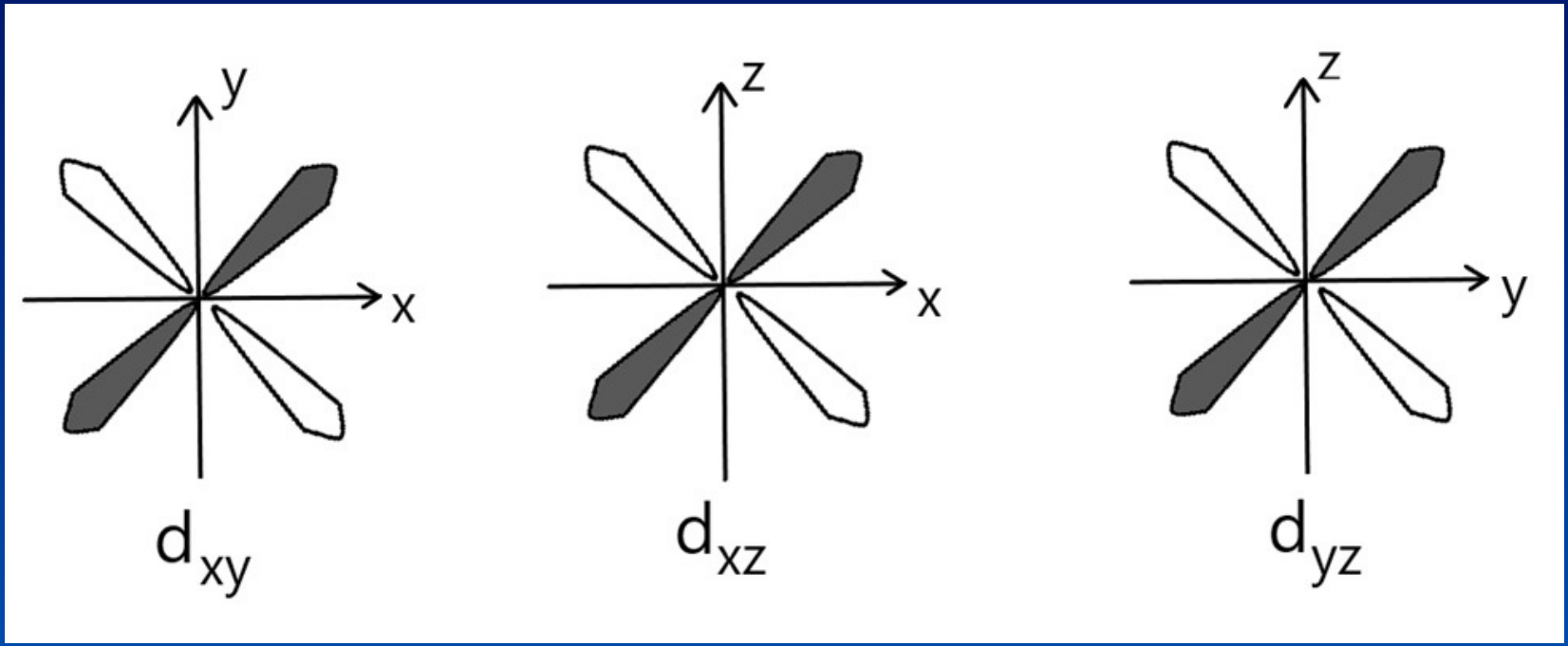
$[CoF_6]^{3-}$ - O_h

Os orbitais $3d_{z2}$ e $3d_{x2-y2}$ do Co



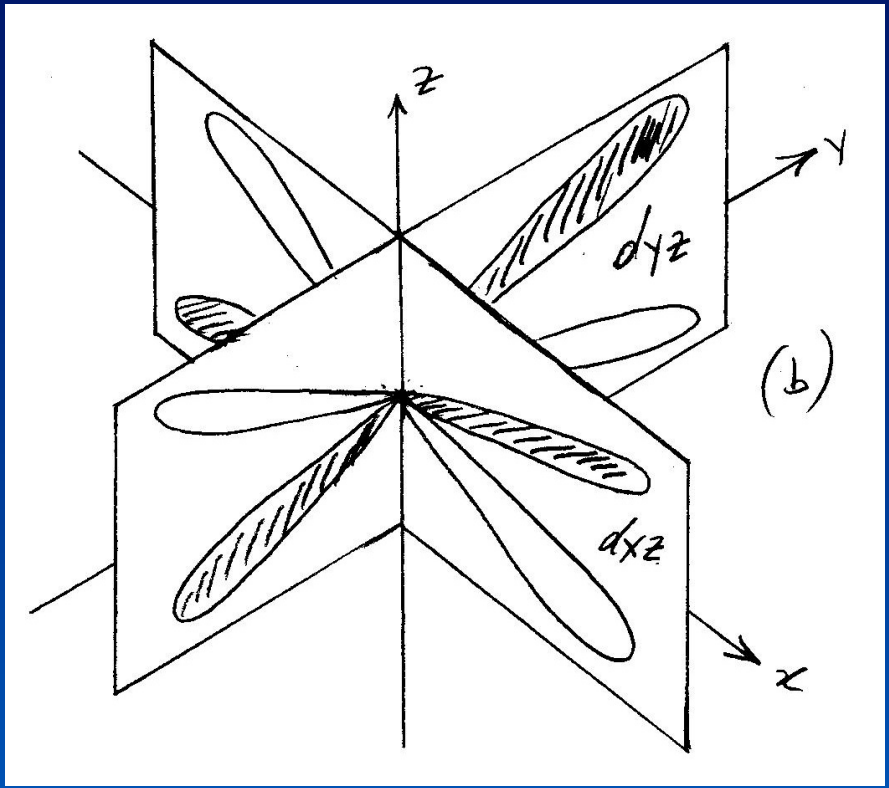
$[CoF_6]^{3-}$ - O_h

Os orbitais $3d_{xy}$, $3d_{xz}$ e $3d_{yz}$ do Co

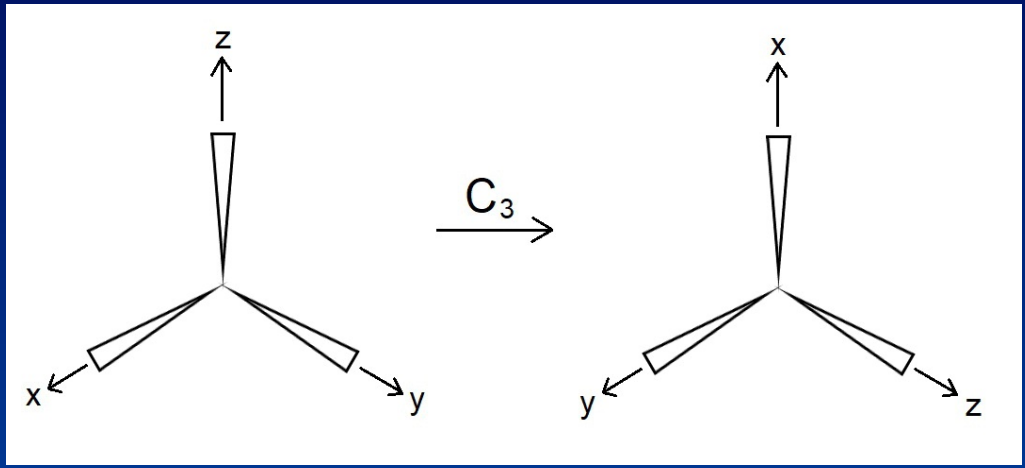


$[CoF_6]^{3-}$ - O_h

Os orbitais $3d_{xz}$ e $3d_{yz}$ do Co



Transformação dos eixos na operação C_3



$$x \xrightarrow{-C_3} y$$
$$y \xrightarrow{-C_3} z$$
$$z \xrightarrow{-C_3} x$$

$[CoF_6]^{3-}$ - O_h

Classificando os orbitais $3d_{xy}$, $3d_{xz}$, $3d_{yz}$ do Co -INSEPARÁVEIS

$$x \xrightarrow{-C_3} y \qquad y \xrightarrow{-C_3} z \qquad z \xrightarrow{-C_3} x$$

$$d_{xy} \xrightarrow{-C_3} d_{yz} \qquad d_{xz} \xrightarrow{-C_3} d_{yx} = d_{xy} \qquad d_{yz} \xrightarrow{-C_3} d_{zx} = d_{xz}$$

$$\begin{array}{c|ccc} & d_{xy} & d_{xz} & d_{yz} \\ \hline d_{xy} & 1 & 0 & 0 \\ d_{xz} & 0 & 1 & 0 \\ d_{yz} & 0 & 0 & 1 \end{array} \xrightarrow{C_3} \begin{array}{c|ccc} & d_{xy} & d_{xz} & d_{yz} \\ \hline d_{xy} & 0 & 0 & 1 \\ d_{xz} & 1 & 0 & 0 \\ d_{yz} & 0 & 1 & 0 \end{array}$$

$$\chi = 0$$

Classificando os orbitais d_{xy}, d_{xz}, d_{xz} do Co -INSEPARÁVEIS

(x,y,z)

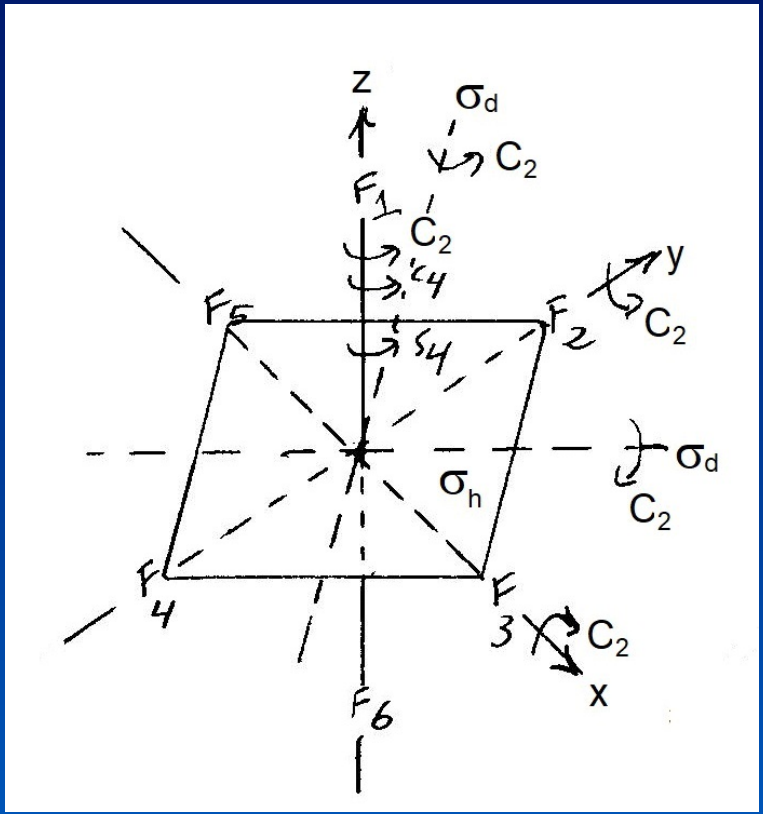
O_h	E	$8C_3$	$6C_2$	$6C_4$	$3C_2(=C_4^2)$	i	$6S_4$	$8S_6$	$3\sigma_h$	$6\sigma_d$
A_{1g}	1	1	1	1	1	1	1	1	1	1
A_{2g}	1	1	-1	-1	1	1	-1	1	1	-1
E_g	2	-1	0	0	2	2	0	-1	2	0
T_{1g}	3	0	-1	1	-1	3	1	0	-1	-1
T_{2g}	3	0	1	-1	-1	3	-1	0	-1	1
A_{1u}	1	1	1	1	1	-1	-1	-1	-1	-1
A_{2u}	1	1	-1	-1	1	-1	1	-1	-1	1
E_u	2	-1	0	0	2	-2	0	1	-2	0
T_{1u}	3	0	-1	1	-1	-3	-1	0	1	1
T_{2u}	3	0	1	-1	-1	-3	1	0	1	-1
$3d_{mn}$	3	0								

$[CoF_6]^{3-}$ - O_h

Classificando os orbitais $3d_{xy}$, $3d_{xz}$, $3d_{yz}$ do Co -INSEPARÁVEIS

$C_2 \neq x, y, z$

$x - C_2 \rightarrow y$
$y - C_2 \rightarrow x$
$z - C_2 \rightarrow -z$



$[CoF_6]^{3-}$ - O_h

Classificando os orbitais $3d_{xy}$, $3d_{xz}$, $3d_{yz}$ do Co -INSEPARÁVEIS

$$x \quad C_2 \rightarrow y$$
$$y \quad C_2 \rightarrow x$$
$$z \quad C_2 \rightarrow -z$$

$$d_{xy} \quad C_2 \rightarrow d_{yx} = d_{xy}$$
$$d_{xz} \quad C_2 \rightarrow d_{y(-z)} = -d_{yz}$$
$$d_{yz} \quad C_2 \rightarrow d_{x(-z)} = -d_{xz}$$

$$\begin{array}{c|ccc} & d_{xy} & d_{xz} & d_{yz} \\ \hline d_{xy} & 1 & 0 & 0 \\ d_{xz} & 0 & 1 & 0 \\ d_{yz} & 0 & 0 & 1 \end{array} \quad \xrightarrow{C_2} \quad \begin{array}{c|ccc} & d_{xy} & d_{xz} & d_{yz} \\ \hline d_{xy} & 1 & 0 & 0 \\ d_{xz} & 0 & 0 & -1 \\ d_{yz} & 0 & -1 & 0 \end{array}$$

$$\chi = 1$$

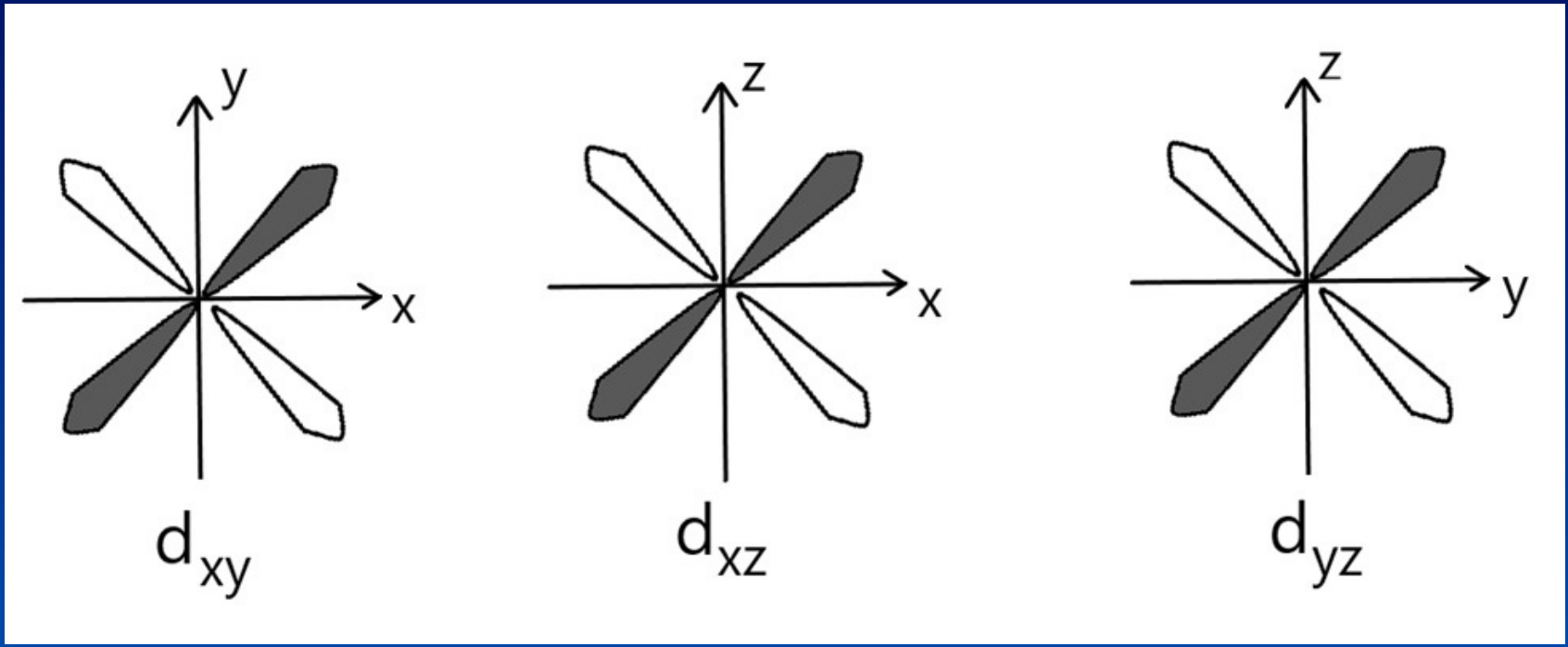
Classificando os orbitais d_{xy}, d_{xz}, d_{xz} do Co -INSEPARÁVEIS

(x,y,z)

O_h	E	$8C_3$	$6C_2$	$6C_4$	$3C_2(=C_4^2)$	i	$6S_4$	$8S_6$	$3\sigma_h$	$6\sigma_d$
A_{1g}	1	1	1	1	1	1	1	1	1	1
A_{2g}	1	1	-1	-1	1	1	-1	1	1	-1
E_g	2	-1	0	0	2	2	0	-1	2	0
T_{1g}	3	0	-1	1	-1	3	1	0	-1	-1
T_{2g}	3	0	1	-1	-1	3	-1	0	-1	1
A_{1u}	1	1	1	1	1	-1	-1	-1	-1	-1
A_{2u}	1	1	-1	-1	1	-1	1	-1	-1	1
E_u	2	-1	0	0	2	-2	0	1	-2	0
T_{1u}	3	0	-1	1	-1	-3	-1	0	1	1
T_{2u}	3	0	1	-1	-1	-3	1	0	1	-1
$3d_{mn}$	3	0	1							

$[CoF_6]^{3-}$ - O_h

Classificando os orbitais $3d_{xy}$, $3d_{xz}$, $3d_{yz}$ do Co -INSEPARÁVEIS



i = centro de inversão

$[CoF_6]^{3-}$ - O_h

Classificando os orbitais $3d_{xy}$, $3d_{xz}$, $3d_{yz}$ do Co -INSEPARÁVEIS

$$\begin{array}{c|ccc} & d_{xy} & d_{xz} & d_{yz} \\ \hline d_{xy} & 1 & 0 & 0 \\ d_{xz} & 0 & 1 & 0 \\ d_{yz} & 0 & 0 & 1 \end{array} \quad \xrightarrow{i} \quad \begin{array}{c|ccc} & d_{xy} & d_{xz} & d_{yz} \\ \hline d_{xy} & 1 & 0 & 0 \\ d_{xz} & 0 & 1 & 0 \\ d_{yz} & 0 & 0 & 1 \end{array}$$

$\chi = 3$

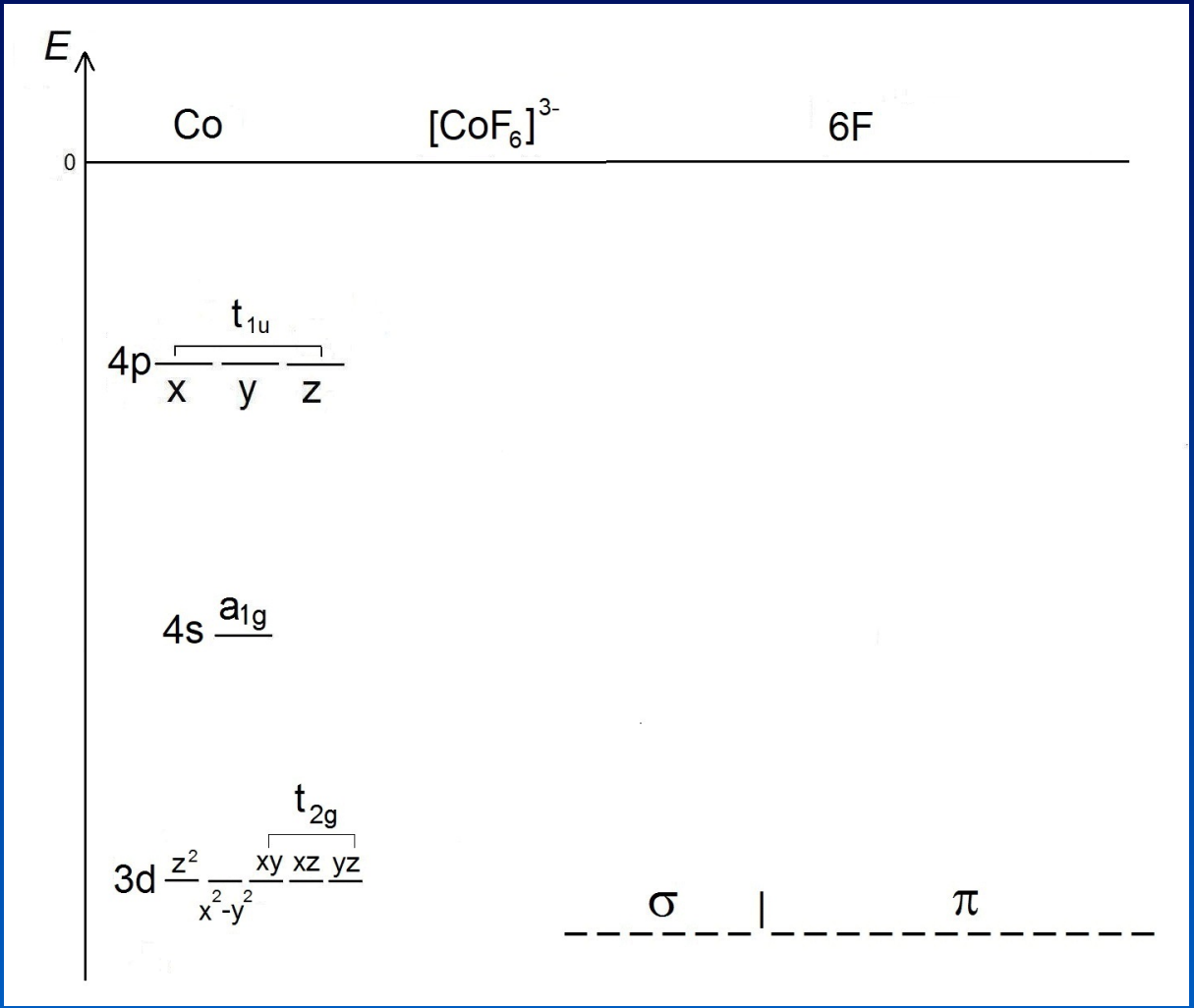
Classificando os orbitais d_{xy}, d_{xz}, d_{xz} do Co -INSEPARÁVEIS

(x,y,z)

O_h	E	$8C_3$	$6C_2$	$6C_4$	$3C_2(=C_4^2)$	i	$6S_4$	$8S_6$	$3\sigma_h$	$6\sigma_d$
A_{1g}	1	1	1	1	1	1	1	1	1	1
A_{2g}	1	1	-1	-1	1	1	-1	1	1	-1
E_g	2	-1	0	0	2	2	0	-1	2	0
T_{1g}	3	0	-1	1	-1	3	1	0	-1	-1
T_{2g}	3	0	1	-1	-1	3	-1	0	-1	1
A_{1u}	1	1	1	1	1	-1	-1	-1	-1	-1
A_{2u}	1	1	-1	-1	1	-1	1	-1	-1	1
E_u	2	-1	0	0	2	-2	0	1	-2	0
T_{1u}	3	0	-1	1	-1	-3	-1	0	1	1
T_{2u}	3	0	1	-1	-1	-3	1	0	1	-1
$3d_{mn}$	3	0	1			3				T_{2g}

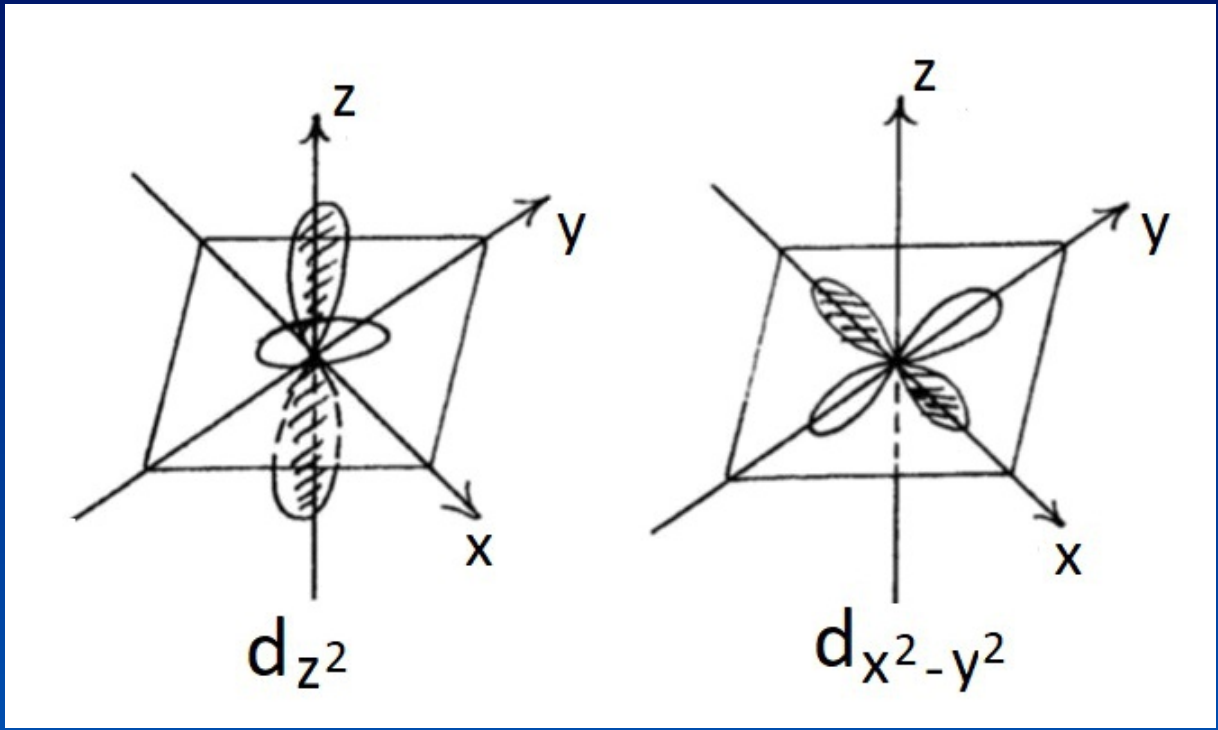
$[CoF_6]^{3-}$ - O_h

Construindo o diagrama de energia dos orbitais moleculares



$[CoF_6]^{3-}$ - O_h

Classificando os orbitais $3d_{z2}$, $3d_{x2-y2}$ do Co, INSEPARÁVEIS(!)



$[CoF_6]^{3-}$ - O_h

Classificando os orbitais $3d_{z2}$, $3d_{x2-y2}$ do Co, INSEPARÁVEIS(!)

$x \; -C_3 \rightarrow y$
$y \; -C_3 \rightarrow z$
$z \; -C_3 \rightarrow x$

$d_{z2} \quad C_3 \rightarrow d_{x2}$
$d_{x2-y2} \quad C_3 \rightarrow d_{y2-z2}$

Na verdade, a expressão do orbital d_{z2} é mais complexa:

$d_{z2} = (1/\sqrt{3})(2z^2 - x^2 - y^2) \quad C_3 \rightarrow d_{x2} = (1/\sqrt{3})(2x^2 - y^2 - z^2)$
$d_{x2-y2} = x^2 - y^2 \quad C_3 \rightarrow d_{y2-z2} = y^2 - z^2$

$[CoF_6]^{3-}$ - O_h

Classificando os orbitais $3d_{z2}$, $3d_{x2-y2}$ do Co -INSEPARÁVEIS

Pode-se mostrar que os novos orbitais d_{x2} e d_{y2-z2} são uma combinação linear dos orbitais d_{z2} e d_{x2-y2}.

$$d_{x2} = (1/\sqrt{3})(2x^2 - y^2 - z^2) = C_{11}\,(1/\sqrt{3})(2z^2 - x^2 - y^2) + C_{12}(x^2 - y^2)$$

$$d_{y2-z2} = y^2 - z^2 = C_{21}\,(1/\sqrt{3})(2z^2 - x^2 - y^2) + C_{22}(x^2 - y^2)$$

Colecionando-se os termos de z^2 da primeira equação, obtém-se o valor de C_{11}:

$$-(1/\sqrt{3}) = C_{11}\,(1/\sqrt{3}) \times 2$$

$$C_{11} = \mathbf{-1/2}$$

$[CoF_6]^{3-}$ - O_h

Classificando os orbitais $3d_{z2}$, $3d_{x2-y2}$ do Co -INSEPARÁVEIS

$$d_{x2} = (1/\sqrt{3})(2x^2 - y^2 - z^2) = C_{11}\,(1/\sqrt{3})(2z^2 - x^2 - y^2) + C_{12}(x^2 - y^2)$$

$$d_{y2-z2} = y^2 - z^2 = C_{21}\,(1/\sqrt{3})(2z^2 - x^2 - y^2) + C_{22}(x^2 - y^2)$$

Colecionando-se os termos de y^2 da primeira equação, obtém-se o valor de C_{12}:

$$-(1/\sqrt{3}) = -C_{11}\,(1/\sqrt{3}) - C_{12}$$
$$-(1/\sqrt{3}) = -(-1/2)(1/\sqrt{3}) - C_{12}$$
$$C_{12} = -(1/\sqrt{3}) - (1/2)(1/\sqrt{3}) = \mathbf{(\sqrt{3})/2}$$

$[CoF_6]^{3-}$ - O_h

Classificando os orbitais $3d_{z2}$, $3d_{x2-y2}$ do Co -INSEPARÁVEIS

$$d_{x2} = (1/\sqrt{3})(2x^2 - y^2 - z^2) = C_{11}\,(1/\sqrt{3})(2z^2 - x^2 - y^2) + C_{12}(x^2 - y^2)$$

$$d_{y2-z2} = y^2 - z^2 = C_{21}\,(1/\sqrt{3})(2z^2 - x^2 - y^2) + C_{22}(x^2 - y^2)$$

Colecionando-se os termos de z^2 da segunda equação, obtém-se o valor de C_{21}:

$$-1 = C_{21}\,(2/\sqrt{3})$$

$$C_{21} = \mathbf{-(\sqrt{3})/2}$$

$[CoF_6]^{3-}$ - O_h

Classificando os orbitais $3d_{z2}$, $3d_{x2-y2}$ do Co -INSEPARÁVEIS

$$d_{x2} = (1/\sqrt{3})(2x^2 - y^2 - z^2) = C_{11}\,(1/\sqrt{3})(2z^2 - x^2 - y^2) + C_{12}(x^2 - y^2)$$

$$d_{y2-z2} = y^2 - z^2 = C_{21}\,(1/\sqrt{3})(2z^2 - x^2 - y^2) + C_{22}(x^2 - y^2)$$

Colecionando-se os termos de y^2 da segunda equação, obtém-se o valor de C_{22}:

$1 = -C_{21}\,(1/\sqrt{3}) - C_{22}$
$1 = (\sqrt{3}/2)(1/\sqrt{3}) - C_{22}$
$C_{22} = -1 + 1/2 \quad = \mathbf{-1/2}$

$[CoF_6]^{3-}$ - O_h

Classificando os orbitais $3d_{z2}$, $3d_{x2-y2}$ do Co -INSEPARÁVEIS

	d_{z2}	d_{x2-y2}			d_{z2}	d_{x2-y2}
d_{z2}	1	0	C_3	d_{z2}	-1/2	$(\sqrt{3})/2$
d_{x2-y2}	0	1	$\rightarrow$	d_{x2-y2}	$-(\sqrt{3})/2$	-1/2

$\chi = -1$

Classificando os orbitais d_{z2}, d_{x2-y2} do Co -INSEPARÁVEIS

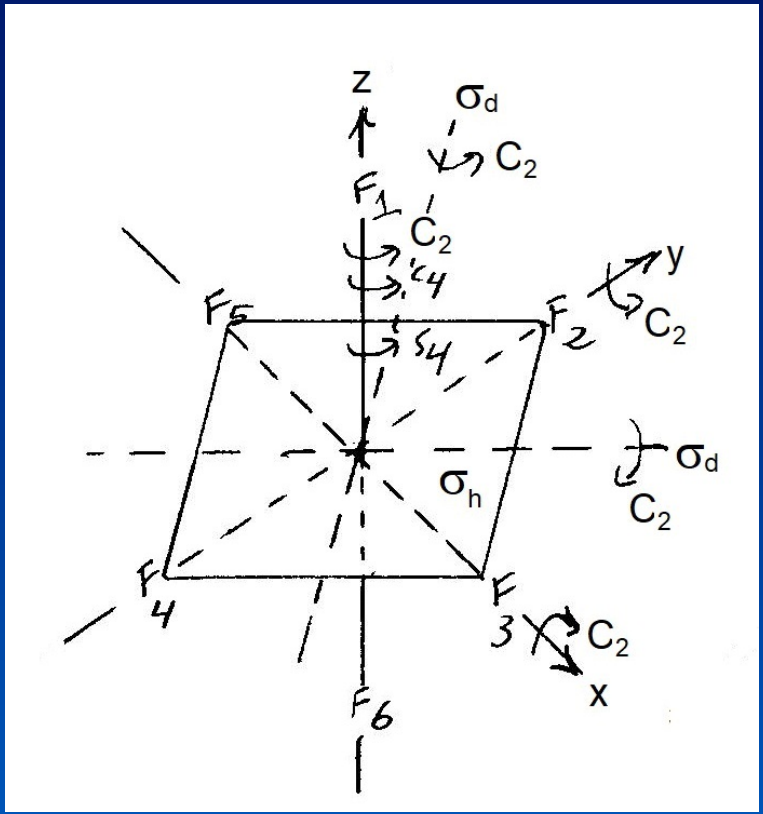
O_h	E	$8C_3$	$6C_2$	$6C_4$	$3C_2(=C_4^2)$	i	$6S_4$	$8S_6$	$3\sigma_h$	$6\sigma_d$	(x,y,z)
A_{1g}	1	1	1	1	1	1	1	1	1	1	
A_{2g}	1	1	-1	-1	1	1	-1	1	1	-1	
E_g	2	-1	0	0	2	2	0	-1	2	0	
T_{1g}	3	0	-1	1	-1	3	1	0	-1	-1	
T_{2g}	3	0	1	-1	-1	3	-1	0	-1	1	
A_{1u}	1	1	1	1	1	-1	-1	-1	-1	-1	
A_{2u}	1	1	-1	-1	1	-1	1	-1	-1	1	
E_u	2	-1	0	0	2	-2	0	1	-2	0	
T_{1u}	3	0	-1	1	-1	-3	-1	0	1	1	
T_{2u}	3	0	1	-1	-1	-3	1	0	1	-1	
z2,x2-y2	2	-1									

$[CoF_6]^{3-}$ - O_h

Classificando os orbitais $3d_{z2}$ e $3d_{x2-y2}$, do Co, INSEPARÁVEIS

$C_2 \neq x, y, z$

x $C_2 \rightarrow y$
y $C_2 \rightarrow x$
z $C_2 \rightarrow -z$



$[CoF_6]^{3-}$ - O_h

Classificando os orbitais $3d_{z2}$, $3d_{x2-y2}$ do Co, INSEPARÁVEIS

$x \quad C_2 \rightarrow y$

$y \quad C_2 \rightarrow x$

$z \quad C_2 \rightarrow -z$

$d_{z2} \quad C_2 \rightarrow d_{(-z)(-z)} = d_{z2}$

$d_{x2-y2} \quad C_2 \rightarrow d_{y2-x2} = -d_{x2-y2}$

$$\begin{array}{cccc} & d_{z2} & d_{x2-y2} & \\ d_{z2} & 1 & 0 & \\ d_{x2-y2} & 0 & 1 & \end{array} \xrightarrow{C_2} \begin{array}{ccc} & d_{z2} & d_{x2-y2} \\ d_{z2} & 1 & 0 \\ d_{x2-y2} & 0 & -1 \end{array}$$

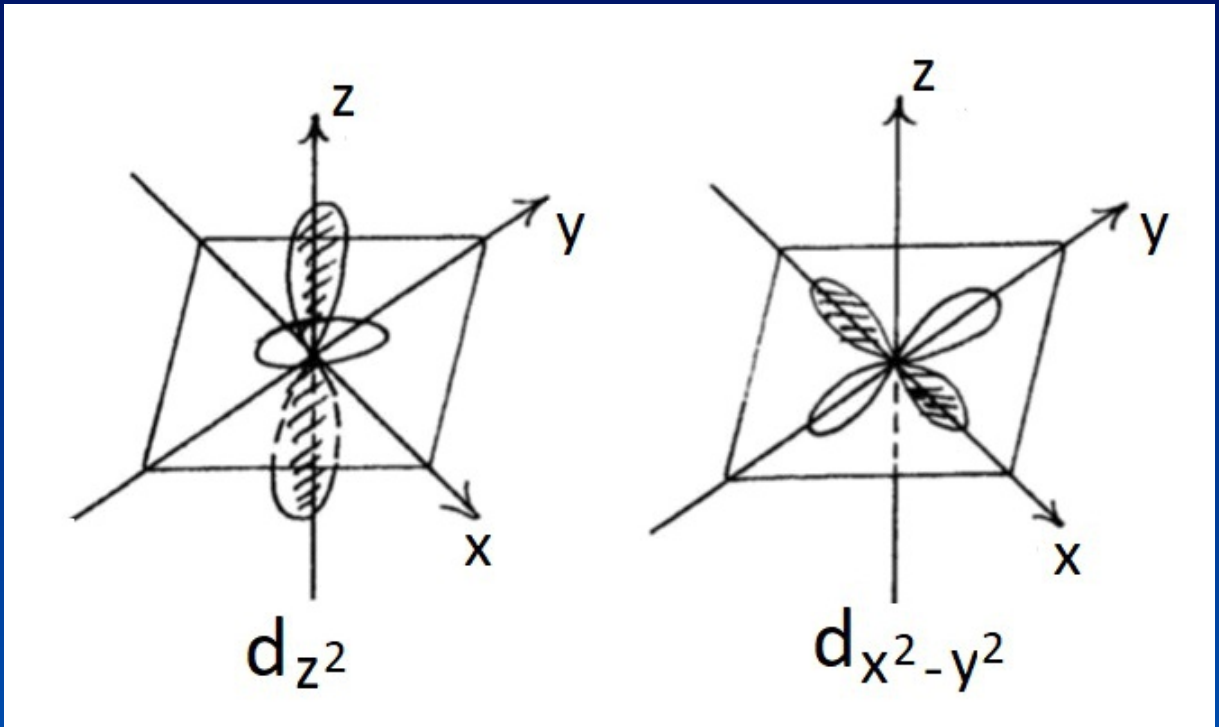
$\chi = 2$ $\qquad$ $\chi = 0$

Classificando os orbitais d_{z2}, d_{x2-y2} do Co -INSEPARÁVEIS

O_h	E	$8C_3$	$6C_2$	$6C_4$	$3C_2(=C_4^2)$	i	$6S_4$	$8S_6$	$3\sigma_h$	$6\sigma_d$	(x,y,z)
A_{1g}	1	1	1	1	1	1	1	1	1	1	
A_{2g}	1	1	-1	-1	1	1	-1	1	1	-1	
E_g	2	-1	0	0	2	2	0	-1	2	0	
T_{1g}	3	0	-1	1	-1	3	1	0	-1	-1	
T_{2g}	3	0	1	-1	-1	3	-1	0	-1	1	
A_{1u}	1	1	1	1	1	-1	-1	-1	-1	-1	
A_{2u}	1	1	-1	-1	1	-1	1	-1	-1	1	
E_u	2	-1	0	0	2	-2	0	1	-2	0	
T_{1u}	3	0	-1	1	-1	-3	-1	0	1	1	
T_{2u}	3	0	1	-1	-1	-3	1	0	1	-1	
z2,x2-y2	2	-1	0								

$[CoF_6]^{3-}$ - O_h

Classificando os orbitais $3d_{z2}$, $3d_{x2-y2}$ do Co -INSEPARÁVEIS



i = centro de inversão

$[CoF_6]^{3-}$ - O_h

Classificando os orbitais $3d_{z2}$, $3d_{x2-y2}$ do Co -INSEPARÁVEIS

	d_{z2}	d_{x2-y2}			d_{z2}	d_{x2-y2}
d_{z2}	1	0	i	d_{z2}	1	0
d_{x2-y2}	0	1	$\rightarrow$	d_{x2-y2}	0	1

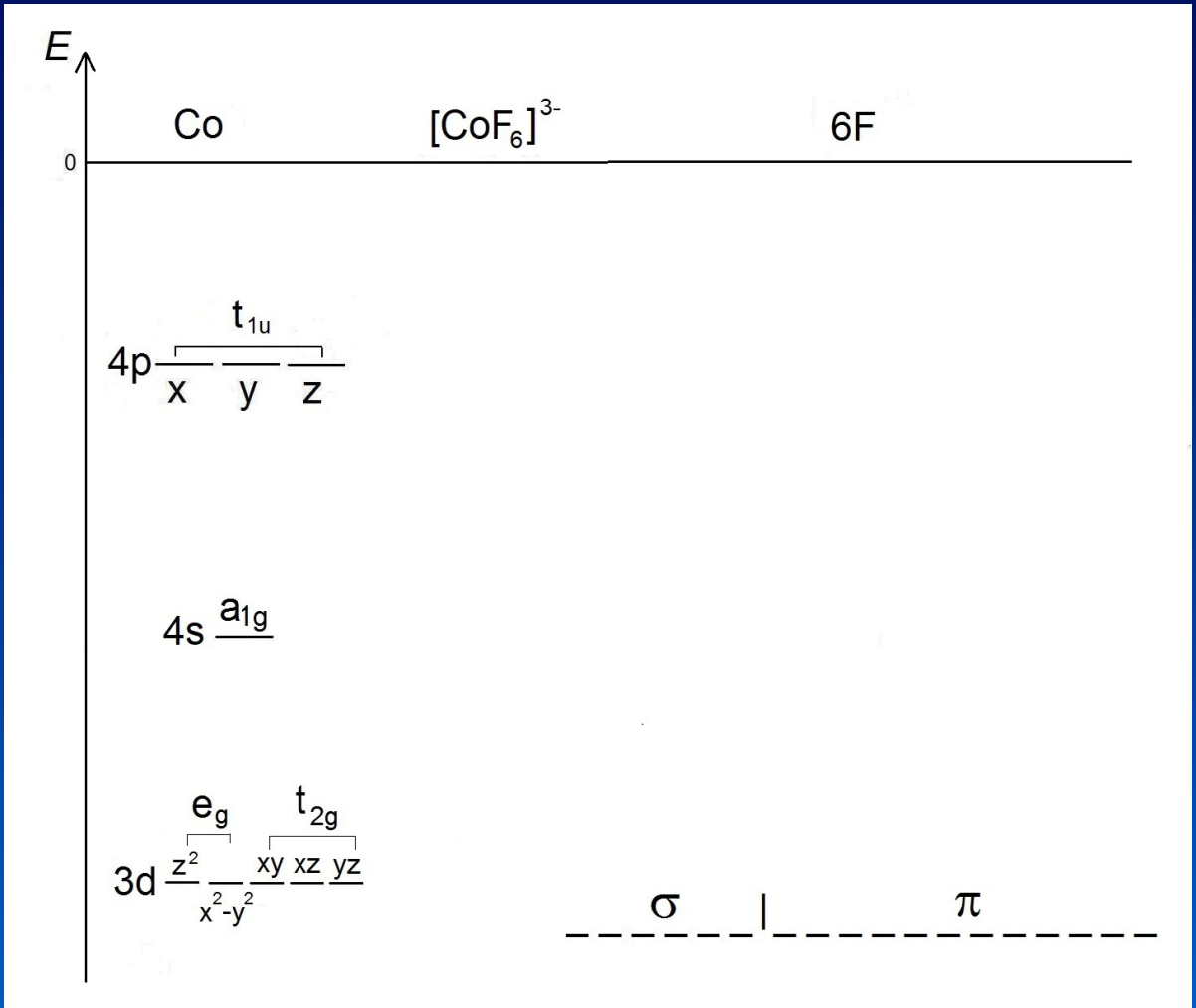
$\chi = 2$

Classificando os orbitais d_{z2}, d_{x2-y2} do Co -INSEPARÁVEIS

O_h	E	$8C_3$	$6C_2$	$6C_4$	$3C_2(=C_4^2)$	i	$6S_4$	$8S_6$	$3\sigma_h$	$6\sigma_d$	(x,y,z)
A_{1g}	1	1	1	1	1	1	1	1	1	1	
A_{2g}	1	1	-1	-1	1	1	-1	1	1	-1	
E_g	2	-1	0	0	2	2	0	-1	2	0	
T_{1g}	3	0	-1	1	-1	3	1	0	-1	-1	
T_{2g}	3	0	1	-1	-1	3	-1	0	-1	1	
A_{1u}	1	1	1	1	1	-1	-1	-1	-1	-1	
A_{2u}	1	1	-1	-1	1	-1	1	-1	-1	1	
E_u	2	-1	0	0	2	-2	0	1	-2	0	
T_{1u}	3	0	-1	1	-1	-3	-1	0	1	1	
T_{2u}	3	0	1	-1	-1	-3	1	0	1	-1	
z2,x2-y2	2	-1	0			2					E_g

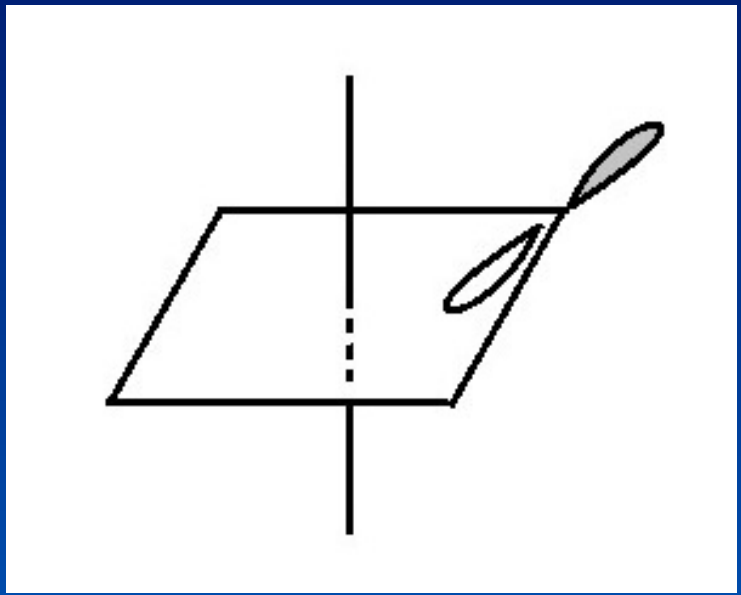
$[CoF_6]^{3-}$ - O_h

Construindo o diagrama de energia dos orbitais moleculares



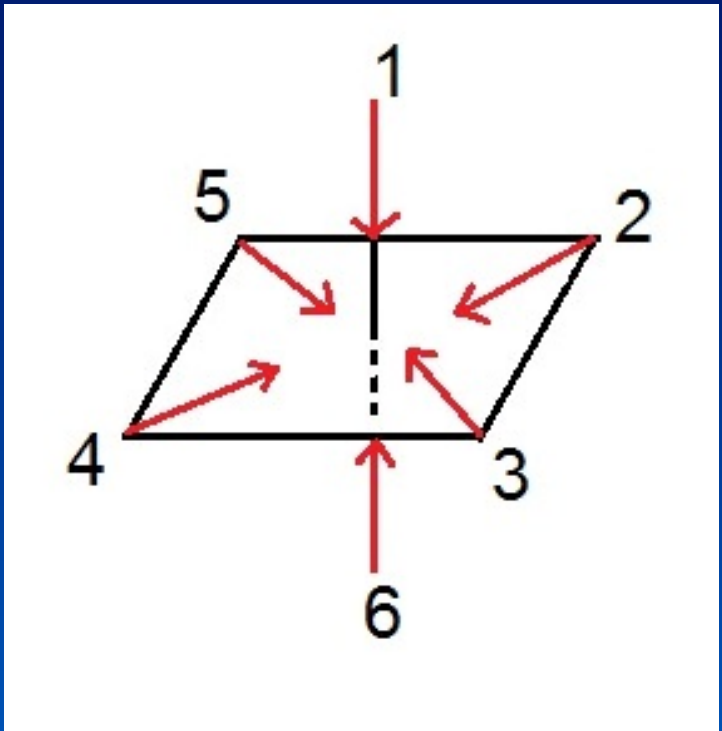
$[CoF_6]^{3-}$ - O_h

Classificando os orbitais 2pσ dos 6F - INSEPARÁVEIS

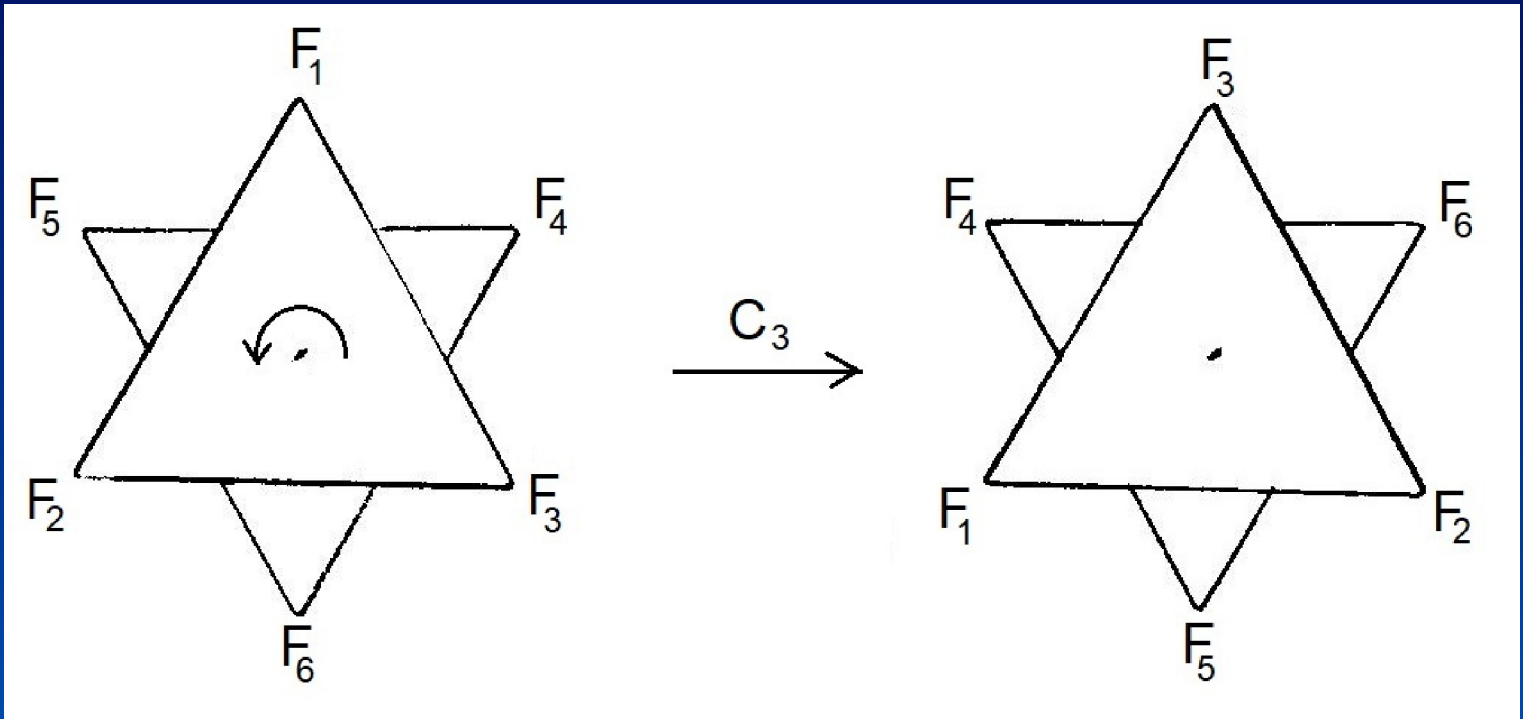


$[CoF_6]^{3-}$ - O_h

Classificando os orbitais 2pσ dos 6F - INSEPARÁVEIS



$[CoF_6]^{3-}$ - O_h



$[CoF_6]^{3-}$ - O_h

Classificando os orbitais 2pσ dos 6F - INSEPARÁVEIS

$$
\begin{array}{c|cccccc}
 & \sigma_1 & \sigma_2 & \sigma_3 & \sigma_4 & \sigma_5 & \sigma_6 \\
\hline
\sigma_1 & 1 & 0 & 0 & 0 & 0 & 0 \\
\sigma_2 & 0 & 1 & 0 & 0 & 0 & 0 \\
\sigma_3 & 0 & 0 & 1 & 0 & 0 & 0 \\
\sigma_4 & 0 & 0 & 0 & 1 & 0 & 0 \\
\sigma_5 & 0 & 0 & 0 & 0 & 1 & 0 \\
\sigma_6 & 0 & 0 & 0 & 0 & 0 & 1
\end{array}
\quad \xrightarrow{C_3} \quad
\begin{array}{c|cccccc}
 & \sigma_1 & \sigma_2 & \sigma_3 & \sigma_4 & \sigma_5 & \sigma_6 \\
\hline
\sigma_1 & 0 & 1 & 0 & 0 & 0 & 0 \\
\sigma_2 & 0 & 0 & 1 & 0 & 0 & 0 \\
\sigma_3 & 1 & 0 & 0 & 0 & 0 & 0 \\
\sigma_4 & 0 & 0 & 0 & 0 & 1 & 0 \\
\sigma_5 & 0 & 0 & 0 & 0 & 0 & 1 \\
\sigma_6 & 1 & 0 & 0 & 0 & 0 & 0
\end{array}
$$

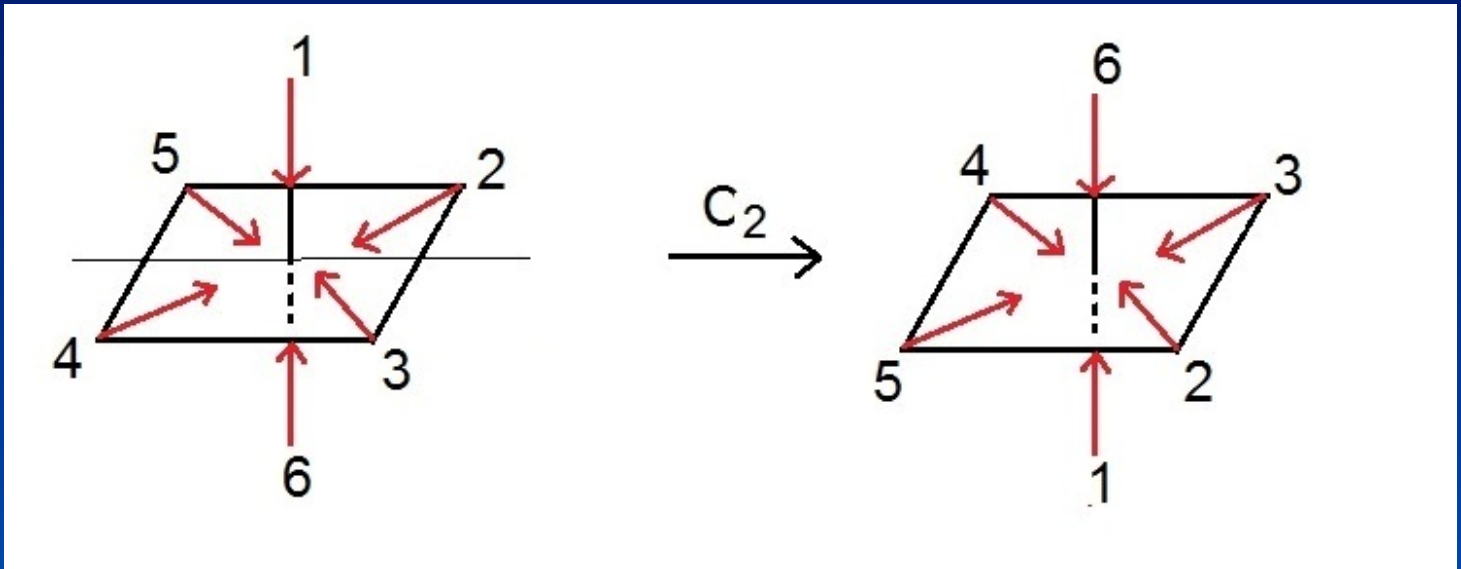
$\chi = 6$ $\qquad$ $\chi = 0$

Classificando os orbitais 2pσ dos 6F - INSEPARÁVEIS

					(x,y,z)					
O_h	E	$8C_3$	$6C_2$	$6C_4$	$3C_2(=C_4^2)$	i	$6S_4$	$8S_6$	$3\sigma_h$	$6\sigma_d$
A_{1g}	1	1	1	1	1	1	1	1	1	1
A_{2g}	1	1	-1	-1	1	1	-1	1	1	-1
E_g	2	-1	0	0	2	2	0	-1	2	0
T_{1g}	3	0	-1	1	-1	3	1	0	-1	-1
T_{2g}	3	0	1	-1	-1	3	-1	0	-1	1
A_{1u}	1	1	1	1	1	-1	-1	-1	-1	-1
A_{2u}	1	1	-1	-1	1	-1	1	-1	-1	1
E_u	2	-1	0	0	2	-2	0	1	-2	0
T_{1u}	3	0	-1	1	-1	-3	-1	0	1	1
T_{2u}	3	0	1	-1	-1	-3	1	0	1	-1
pσ	6	0								

$[CoF_6]^{3-}$ - O_h

Classificando os orbitais 2pσ dos 6F - INSEPARÁVEIS



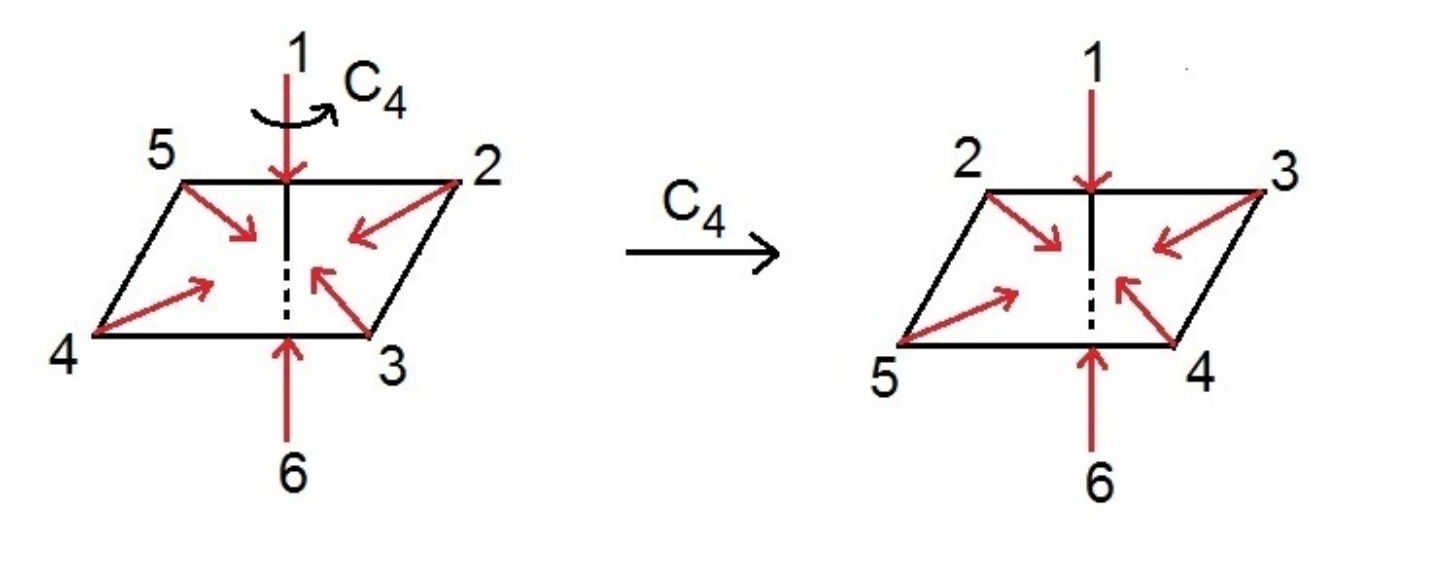
Classificando os orbitais 2pσ dos 6F - INSEPARÁVEIS

(x,y,z)

O_h	E	$8C_3$	$6C_2$	$6C_4$	$3C_2(=C_4^2)$	i	$6S_4$	$8S_6$	$3\sigma_h$	$6\sigma_d$
A_{1g}	1	1	1	1	1	1	1	1	1	1
A_{2g}	1	1	-1	-1	1	1	-1	1	1	-1
E_g	2	-1	0	0	2	2	0	-1	2	0
T_{1g}	3	0	-1	1	-1	3	1	0	-1	-1
T_{2g}	3	0	1	-1	-1	3	-1	0	-1	1
A_{1u}	1	1	1	1	1	-1	-1	-1	-1	-1
A_{2u}	1	1	-1	-1	1	-1	1	-1	-1	1
E_u	2	-1	0	0	2	-2	0	1	-2	0
T_{1u}	3	0	-1	1	-1	-3	-1	0	1	1
T_{2u}	3	0	1	-1	-1	-3	1	0	1	-1
pσ	6	0	0							

$[CoF_6]^{3-}$ - O_h

Classificando os orbitais 2pσ dos 6F - INSEPARÁVEIS



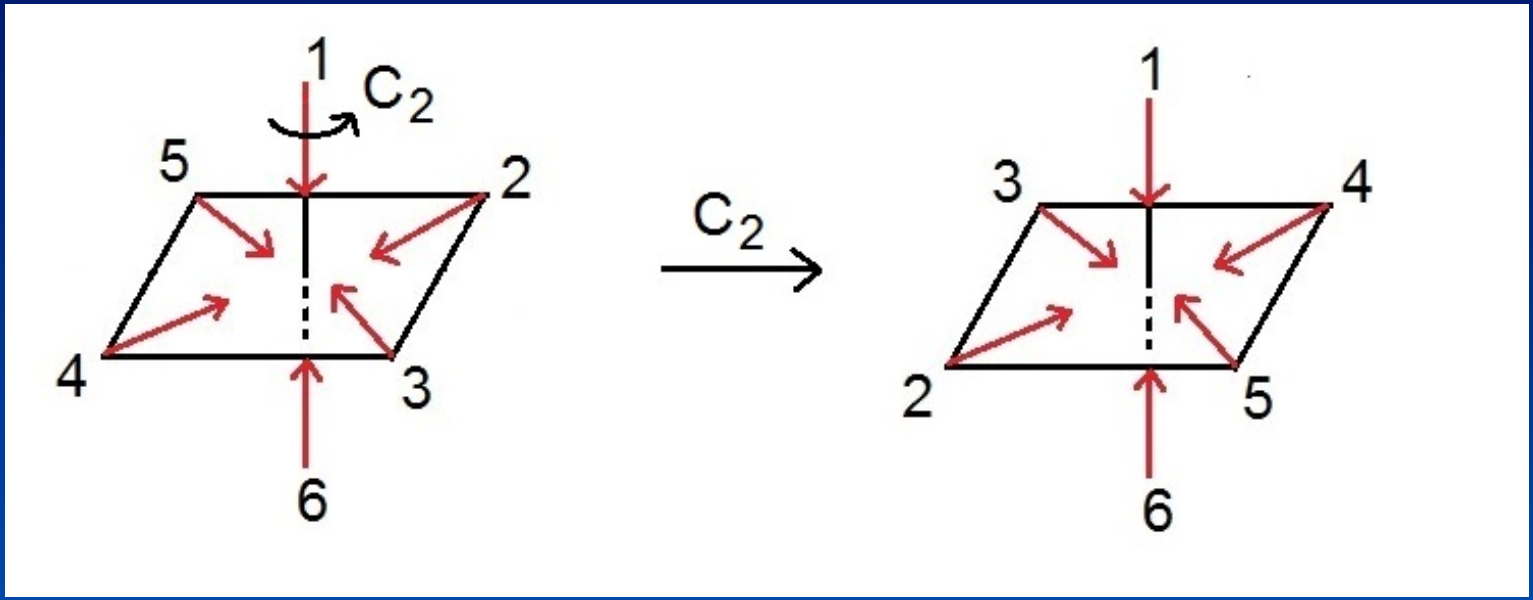
Classificando os orbitais 2pσ dos 6F - INSEPARÁVEIS

(x,y,z)

O_h	E	$8C_3$	$6C_2$	$6C_4$	$3C_2(=C_4^2)$	i	$6S_4$	$8S_6$	$3\sigma_h$	$6\sigma_d$
A_{1g}	1	1	1	1	1	1	1	1	1	1
A_{2g}	1	1	-1	-1	1	1	-1	1	1	-1
E_g	2	-1	0	0	2	2	0	-1	2	0
T_{1g}	3	0	-1	1	-1	3	1	0	-1	-1
T_{2g}	3	0	1	-1	-1	3	-1	0	-1	1
A_{1u}	1	1	1	1	1	-1	-1	-1	-1	-1
A_{2u}	1	1	-1	-1	1	-1	1	-1	-1	1
E_u	2	-1	0	0	2	-2	0	1	-2	0
T_{1u}	3	0	-1	1	-1	-3	-1	0	1	1
T_{2u}	3	0	1	-1	-1	-3	1	0	1	-1
pσ	6	0	0	2						

$[CoF_6]^{3-}$ - O_h

Classificando os orbitais 2pσ dos 6F - INSEPARÁVEIS



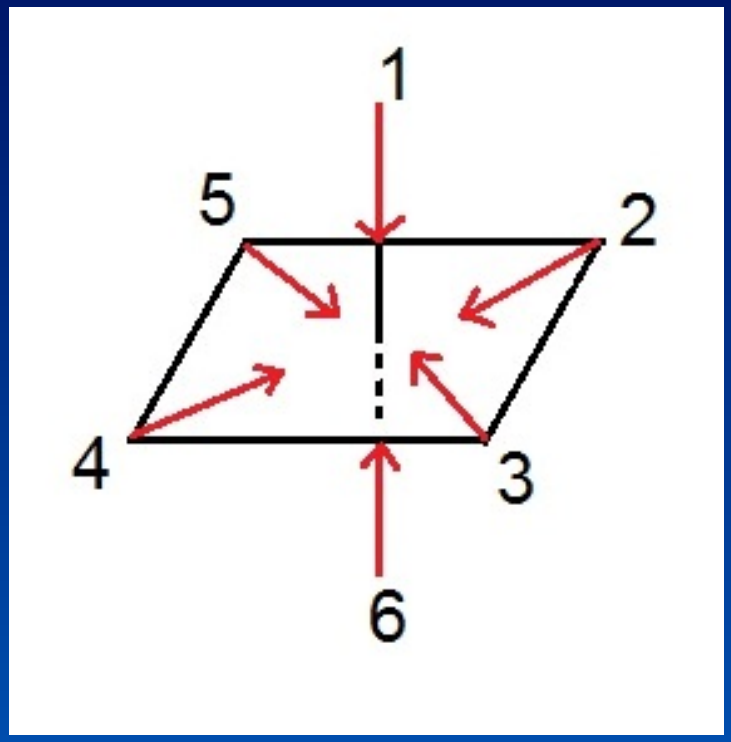
Classificando os orbitais 2pσ dos 6F - INSEPARÁVEIS

(x,y,z)

O_h	E	$8C_3$	$6C_2$	$6C_4$	$3C_2(=C_4^2)$	i	$6S_4$	$8S_6$	$3\sigma_h$	$6\sigma_d$
A_{1g}	1	1	1	1	1	1	1	1	1	1
A_{2g}	1	1	-1	-1	1	1	-1	1	1	-1
E_g	2	-1	0	0	2	2	0	-1	2	0
T_{1g}	3	0	-1	1	-1	3	1	0	-1	-1
T_{2g}	3	0	1	-1	-1	3	-1	0	-1	1
A_{1u}	1	1	1	1	1	-1	-1	-1	-1	-1
A_{2u}	1	1	-1	-1	1	-1	1	-1	-1	1
E_u	2	-1	0	0	2	-2	0	1	-2	0
T_{1u}	3	0	-1	1	-1	-3	-1	0	1	1
T_{2u}	3	0	1	-1	-1	-3	1	0	1	-1
pσ	6	0	0	2	2					

$[CoF_6]^{3-}$ - O_h

Classificando os orbitais 2pσ dos 6F - INSEPARÁVEIS



i = centro de inversão

todos saem do lugar
e da diagonal da matriz 6×6

$\chi = 0$

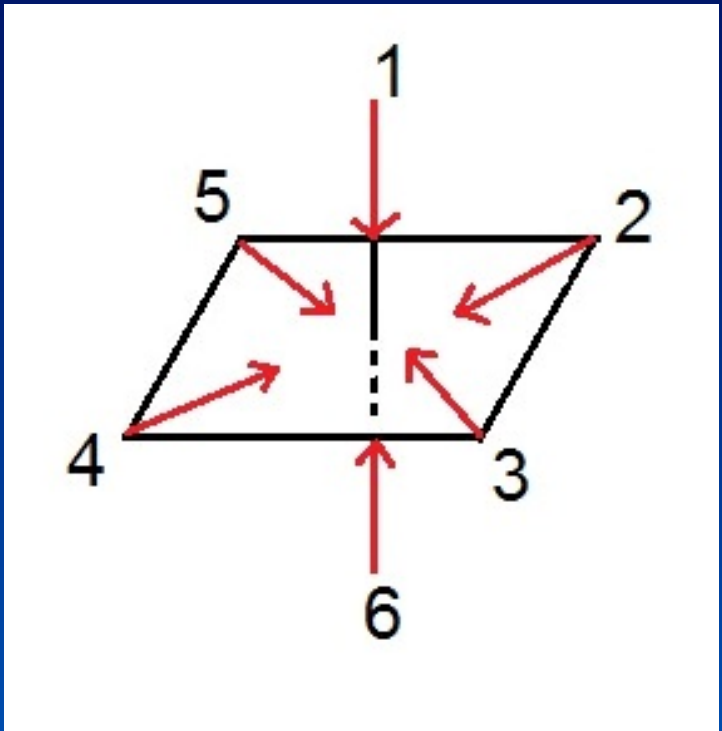
Classificando os orbitais 2pσ dos 6F - INSEPARÁVEIS

(x,y,z)

O_h	E	$8C_3$	$6C_2$	$6C_4$	$3C_2(=C_4^2)$	i	$6S_4$	$8S_6$	$3\sigma_h$	$6\sigma_d$
A_{1g}	1	1	1	1	1	1	1	1	1	1
A_{2g}	1	1	-1	-1	1	1	-1	1	1	-1
E_g	2	-1	0	0	2	2	0	-1	2	0
T_{1g}	3	0	-1	1	-1	3	1	0	-1	-1
T_{2g}	3	0	1	-1	-1	3	-1	0	-1	1
A_{1u}	1	1	1	1	1	-1	-1	-1	-1	-1
A_{2u}	1	1	-1	-1	1	-1	1	-1	-1	1
E_u	2	-1	0	0	2	-2	0	1	-2	0
T_{1u}	3	0	-1	1	-1	-3	-1	0	1	1
T_{2u}	3	0	1	-1	-1	-3	1	0	1	-1
pσ	6	0	0	2	2	0				

$[CoF_6]^{3-}$ - O_h

Classificando os orbitais 2pσ dos 6F - INSEPARÁVEIS



S_4

todos saem do lugar
e da diagonal da matriz 6×6

$\chi = 0$

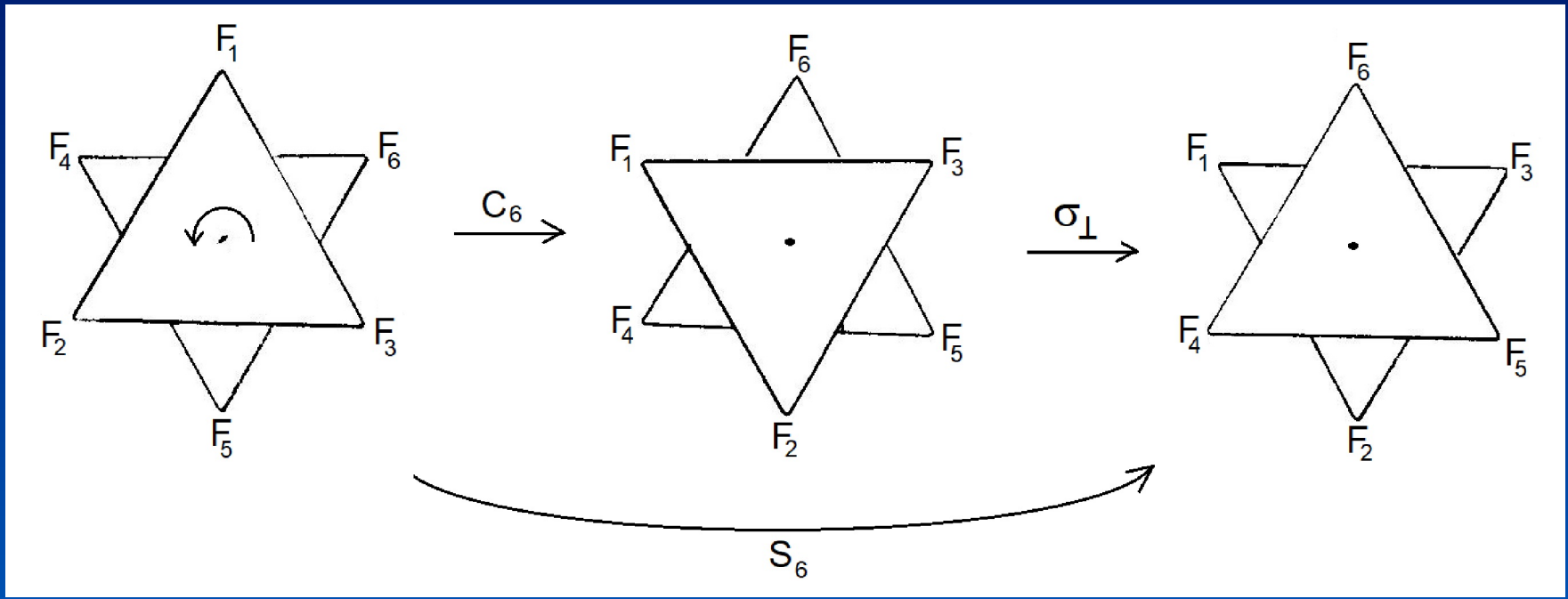
Classificando os orbitais 2pσ dos 6F - INSEPARÁVEIS

(x,y,z)

O_h	E	$8C_3$	$6C_2$	$6C_4$	$3C_2(=C_4^2)$	i	$6S_4$	$8S_6$	$3\sigma_h$	$6\sigma_d$
A_{1g}	1	1	1	1	1	1	1	1	1	1
A_{2g}	1	1	-1	-1	1	1	-1	1	1	-1
E_g	2	-1	0	0	2	2	0	-1	2	0
T_{1g}	3	0	-1	1	-1	3	1	0	-1	-1
T_{2g}	3	0	1	-1	-1	3	-1	0	-1	1
A_{1u}	1	1	1	1	1	-1	-1	-1	-1	-1
A_{2u}	1	1	-1	-1	1	-1	1	-1	-1	1
E_u	2	-1	0	0	2	-2	0	1	-2	0
T_{1u}	3	0	-1	1	-1	-3	-1	0	1	1
T_{2u}	3	0	1	-1	-1	-3	1	0	1	-1
pσ	6	0	0	2	2	0	0			

$[CoF_6]^{3-}$ - O_h

$$S_6 = C_6 + \sigma_\perp$$



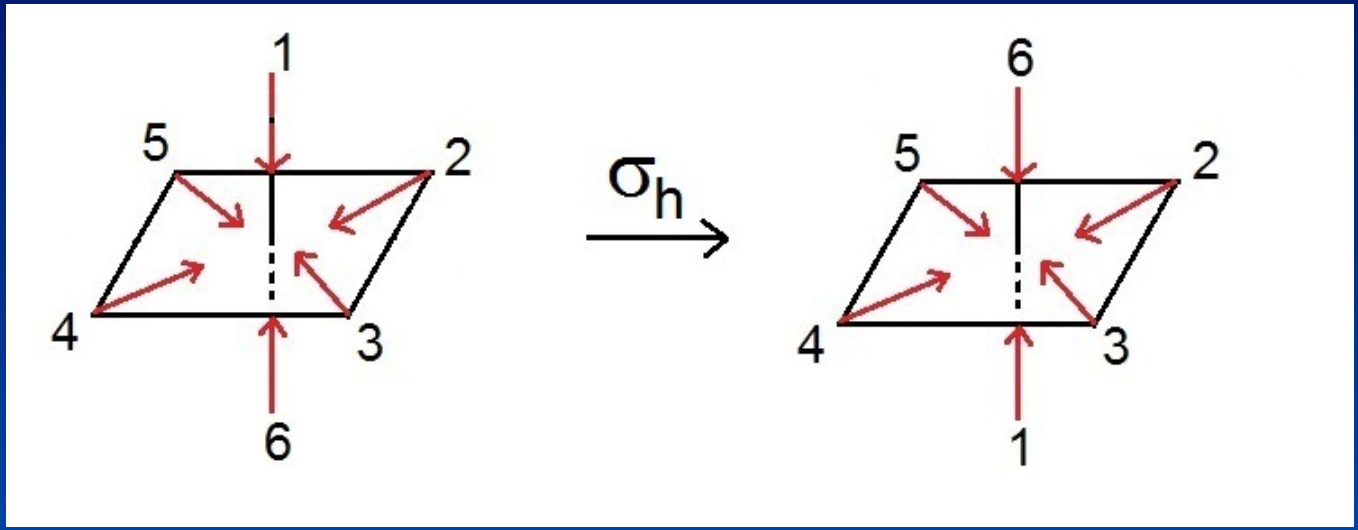
Classificando os orbitais 2pσ dos 6F - INSEPARÁVEIS

(x,y,z)

O_h	E	$8C_3$	$6C_2$	$6C_4$	$3C_2(=C_4^2)$	i	$6S_4$	$8S_6$	$3\sigma_h$	$6\sigma_d$
A_{1g}	1	1	1	1	1	1	1	1	1	1
A_{2g}	1	1	-1	-1	1	1	-1	1	1	-1
E_g	2	-1	0	0	2	2	0	-1	2	0
T_{1g}	3	0	-1	1	-1	3	1	0	-1	-1
T_{2g}	3	0	1	-1	-1	3	-1	0	-1	1
A_{1u}	1	1	1	1	1	-1	-1	-1	-1	-1
A_{2u}	1	1	-1	-1	1	-1	1	-1	-1	1
E_u	2	-1	0	0	2	-2	0	1	-2	0
T_{1u}	3	0	-1	1	-1	-3	-1	0	1	1
T_{2u}	3	0	1	-1	-1	-3	1	0	1	-1
pσ	6	0	0	2	2	0	0	0		

$[CoF_6]^{3-}$ - O_h

Classificando os orbitais 2pσ dos 6F - INSEPARÁVEIS



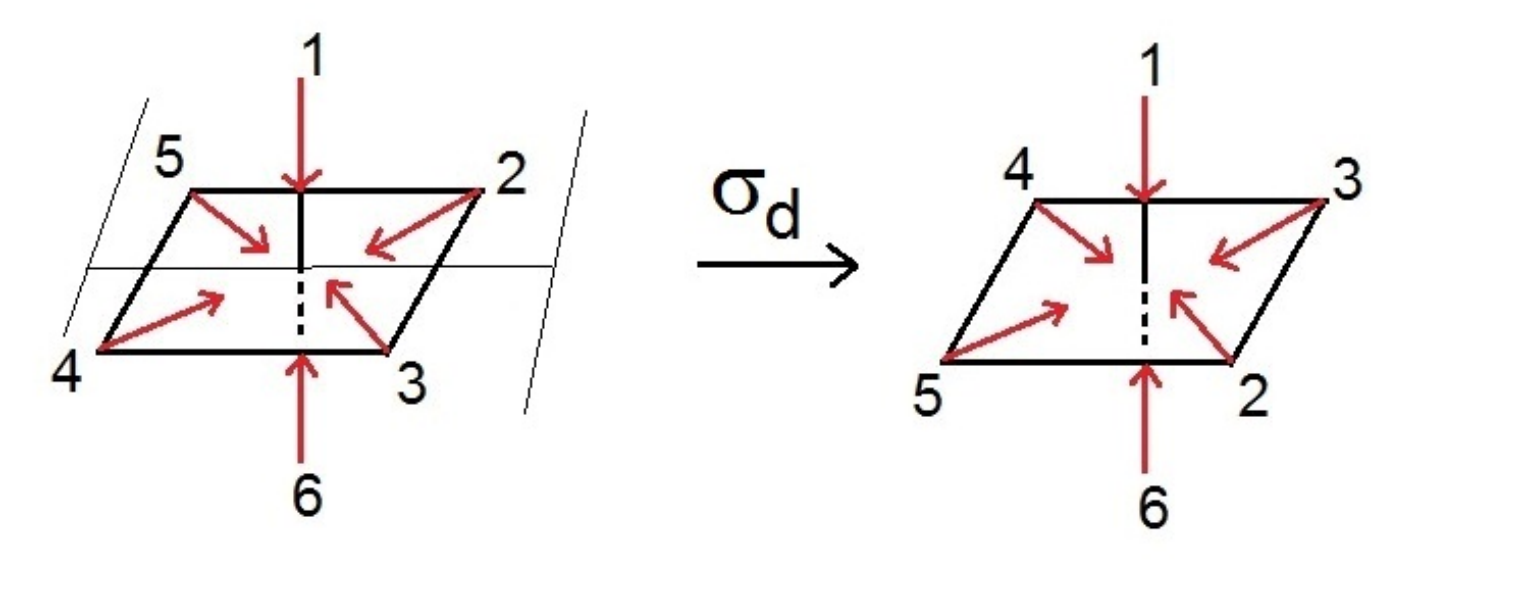
Classificando os orbitais 2pσ dos 6F - INSEPARÁVEIS

(x,y,z)

O_h	E	$8C_3$	$6C_2$	$6C_4$	$3C_2(=C_4^2)$	i	$6S_4$	$8S_6$	$3\sigma_h$	$6\sigma_d$
A_{1g}	1	1	1	1	1	1	1	1	1	1
A_{2g}	1	1	-1	-1	1	1	-1	1	1	-1
E_g	2	-1	0	0	2	2	0	-1	2	0
T_{1g}	3	0	-1	1	-1	3	1	0	-1	-1
T_{2g}	3	0	1	-1	-1	3	-1	0	-1	1
A_{1u}	1	1	1	1	1	-1	-1	-1	-1	-1
A_{2u}	1	1	-1	-1	1	-1	1	-1	-1	1
E_u	2	-1	0	0	2	-2	0	1	-2	0
T_{1u}	3	0	-1	1	-1	-3	-1	0	1	1
T_{2u}	3	0	1	-1	-1	-3	1	0	1	-1
pσ	6	0	0	2	2	0	0	0	4	

$[CoF_6]^{3-}$ - O_h

Classificando os orbitais 2pσ dos 6F - INSEPARÁVEIS



Classificando os orbitais 2pσ dos 6F - INSEPARÁVEIS

O_h	E	$8C_3$	$6C_2$	$6C_4$	$3C_2(=C_4^2)$	i	$6S_4$	$8S_6$	$3\sigma_h$	$6\sigma_d$
					(x,y,z)					
A_{1g}	1	1	1	1	1	1	1	1	1	1
A_{2g}	1	1	-1	-1	1	1	-1	1	1	-1
E_g	2	-1	0	0	2	2	0	-1	2	0
T_{1g}	3	0	-1	1	-1	3	1	0	-1	-1
T_{2g}	3	0	1	-1	-1	3	-1	0	-1	1
A_{1u}	1	1	1	1	1	-1	-1	-1	-1	-1
A_{2u}	1	1	-1	-1	1	-1	1	-1	-1	1
E_u	2	-1	0	0	2	-2	0	1	-2	0
T_{1u}	3	0	-1	1	-1	-3	-1	0	1	1
T_{2u}	3	0	1	-1	-1	-3	1	0	1	-1
pσ	6	0	0	2	2	0	0	0	4	2

Fórmula de decomposição de Representações Redutíveis

$$a_i = \frac{1}{h} \sum_R \chi_{redutível}(R)\ \chi_i(R)$$

O_h	E	$8C_3$	$6C_2$	$6C_4$	$3C_2(=C_4^2)$ (x,y,z)	i	$6S_4$	$8S_6$	$3\sigma_h$	$6\sigma_d$
A_{1g}	1	1	1	1	1	1	1	1	1	1
$p\sigma$	6	0	0	2	2	0	0	0	4	2

$$48a_i = 6 + 0 + 0 + 2\times6 + 2\times3 + 0 + 0 + 0 + 4\times3 + 2\times6 = 48$$

$$a(A_{1g}) = 1$$

Fórmula de decomposição de Representações Redutíveis

$$a_i = \frac{1}{h} \sum_R \chi_{redutível}(R)\ \chi_i(R)$$

O_h	E	$8C_3$	$6C_2$	$6C_4$	$3C_2(=C_4^2)$ (x,y,z)	i	$6S_4$	$8S_6$	$3\sigma_h$	$6\sigma_d$
A_{2g}	1	1	-1	-1	1	1	-1	1	1	-1
$p\sigma$	6	0	0	2	2	0	0	0	4	2

$$48a_i = 6 + 0 + 0 - 2\times6 + 2\times3 + 0 + 0 + 0 + 4\times3 - 2\times6 = 0$$

$$a(A_{2g}) = 0$$

Fórmula de decomposição de Representações Redutíveis

$$a_i = \frac{1}{h} \sum_R \chi_{redutível}(R)\ \chi_i(R)$$

					(x,y,z)					
O_h	E	$8C_3$	$6C_2$	$6C_4$	$3C_2(=C_4^2)$	i	$6S_4$	$8S_6$	$3\sigma_h$	$6\sigma_d$
E_g	2	-1	0	0	2	2	0	-1	2	0
$p\sigma$	6	0	0	2	2	0	0	0	4	2

$$48a_i = 12 + 0 + 0 + 0 + 4\times3 + 0 + 0 + 0 + 8\times3 + 0 = 48$$

$$a(E_g) = 1$$

Fórmula de decomposição de Representações Redutíveis

$$a_i = \frac{1}{h} \sum_R \chi_{redutível}(R)\ \chi_i(R)$$

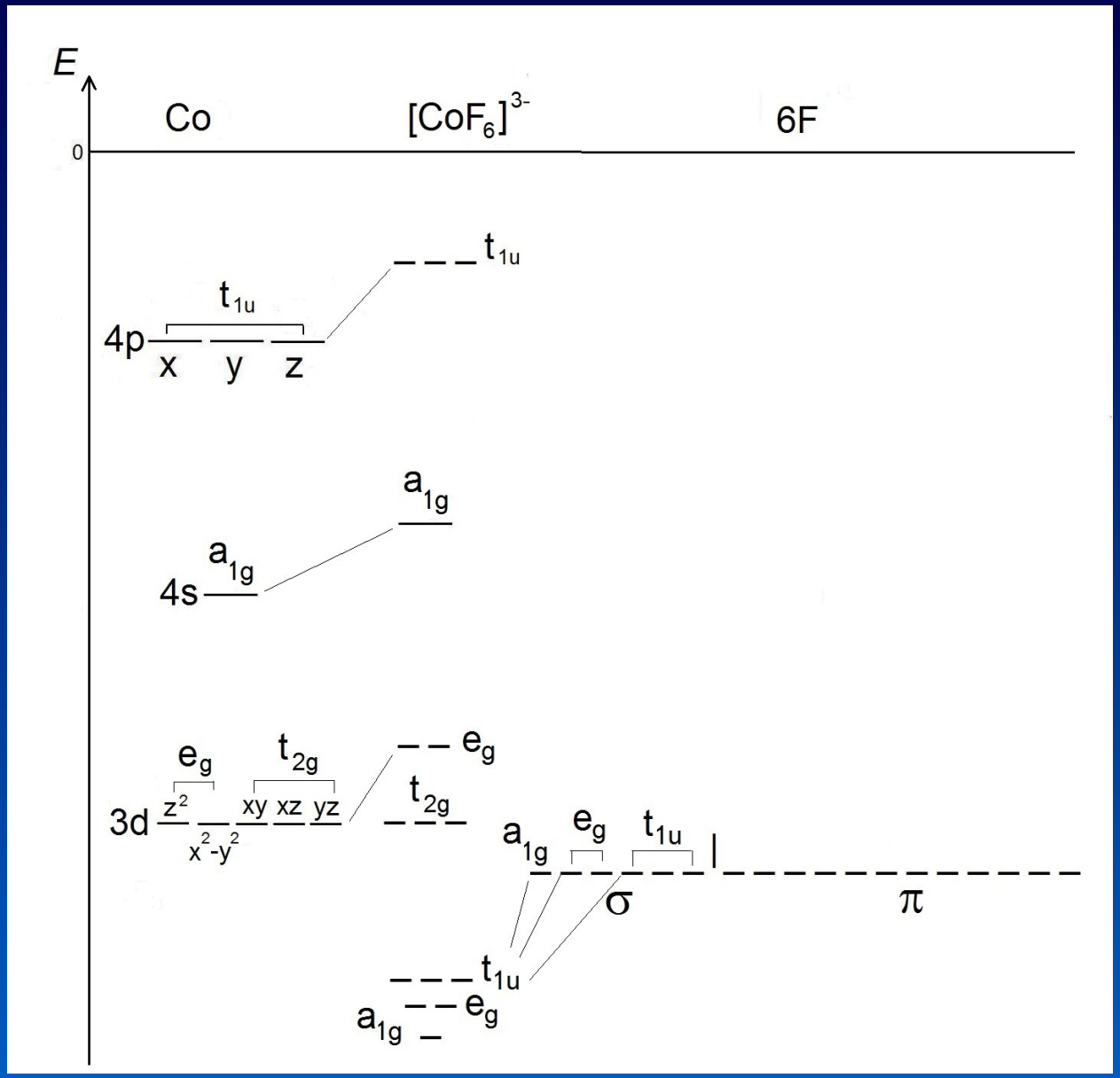
					(x,y,z)					
O_h	E	$8C_3$	$6C_2$	$6C_4$	$3C_2(=C_4^2)$	i	$6S_4$	$8S_6$	$3\sigma_h$	$6\sigma_d$
T_{1u}	3	0	-1	1	-1	-3	-1	0	1	1
$p\sigma$	6	0	0	2	2	0	0	0	4	2

$$48a_i = 18 + 0 + 0 + 2\times6 - 2\times3 + 0 + 0 + 0 + 4\times3 + 2\times6 = 48$$

$$a(T_{1u}) = 1$$

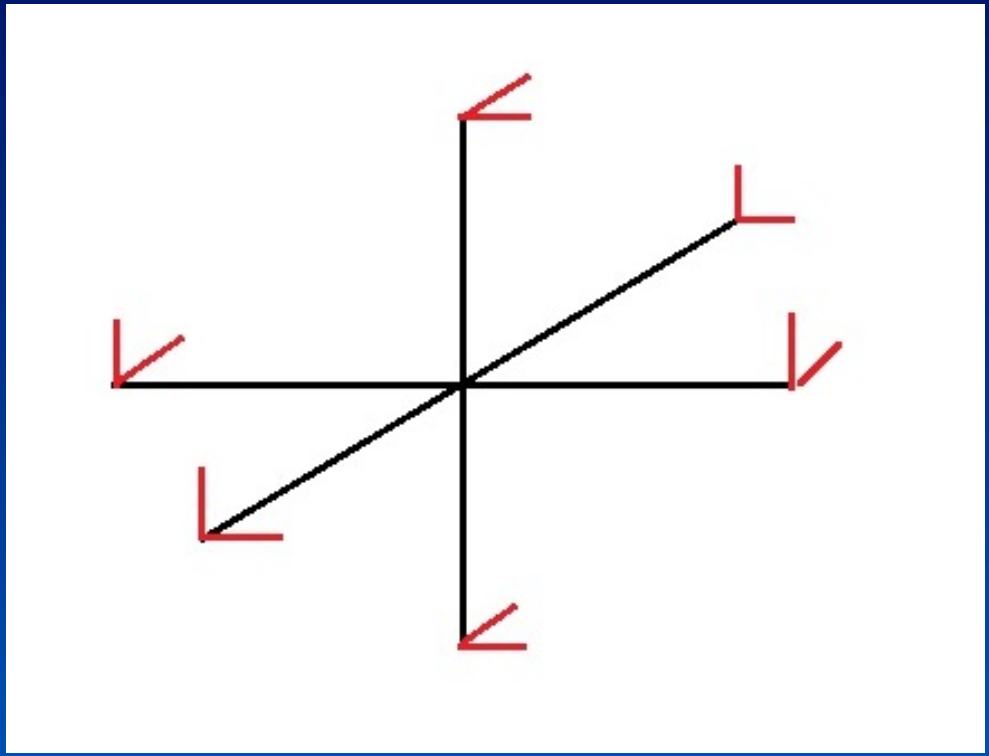
Classificando os orbitais 2pσ dos 6F - INSEPARÁVEIS

					(x,y,z)					
O_h	E	$8C_3$	$6C_2$	$6C_4$	$3C_2(=C_4^2)$	i	$6S_4$	$8S_6$	$3\sigma_h$	$6\sigma_d$
A_{1g}	1	1	1	1	1	1	1	1	1	1
E_g	2	-1	0	0	2	2	0	-1	2	0
T_{1u}	3	0	-1	1	-1	-3	-1	0	1	1
pσ	6	0	0	2	2	0	0	0	4	2


E
Co
[CoF6]3-
6F
0
t1u
t1u
4p
x
y
z
a1g
a1g
4s
eg
t2g
eg
t2g
3d
z2
x2-y2
xy
xz
yz
a1g
eg
t1u
σ
π
t1u
a1g
eg

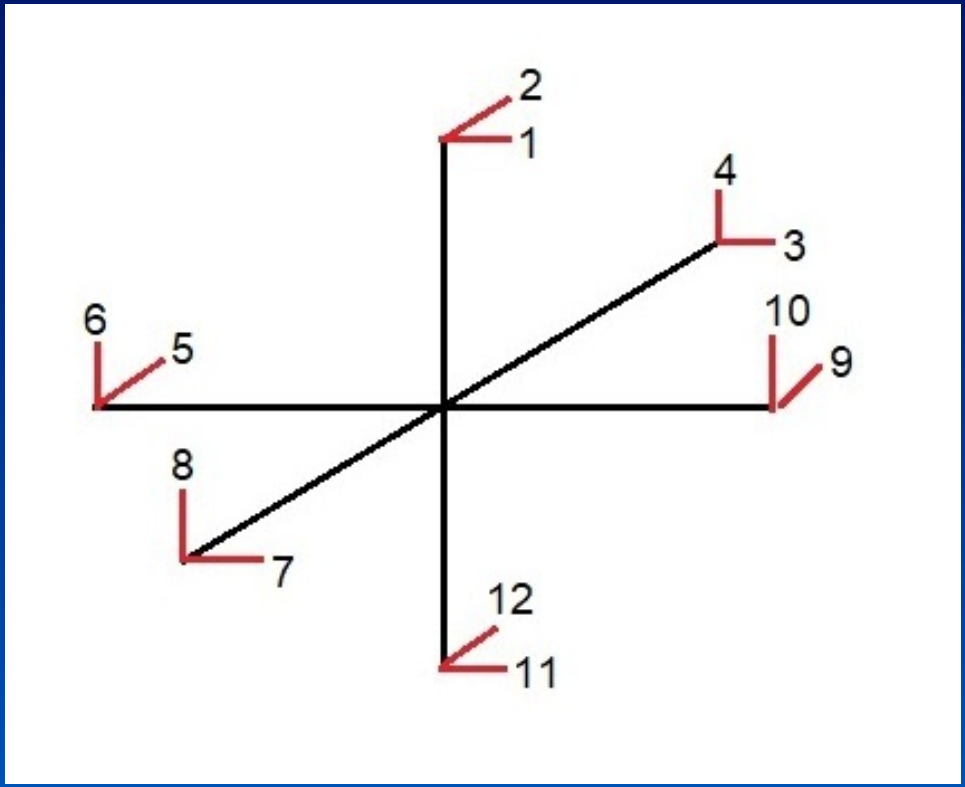
$[CoF_6]^{3-}$ - O_h

Classificando os orbitais 2pπ dos 6F - INSEPARÁVEIS



$[CoF_6]^{3-}$ - O_h

Classificando os orbitais 2pπ dos 6F - INSEPARÁVEIS



Classificando os 12 orbitais 2pπ dos 6F - INSEPARÁVEIS

(x,y,z)

O_h	E	$8C_3$	$6C_2$	$6C_4$	$3C_2(=C_4^2)$	i	$6S_4$	$8S_6$	$3\sigma_h$	$6\sigma_d$
pπ	12	?	?	?	?	?	?	?	?	?

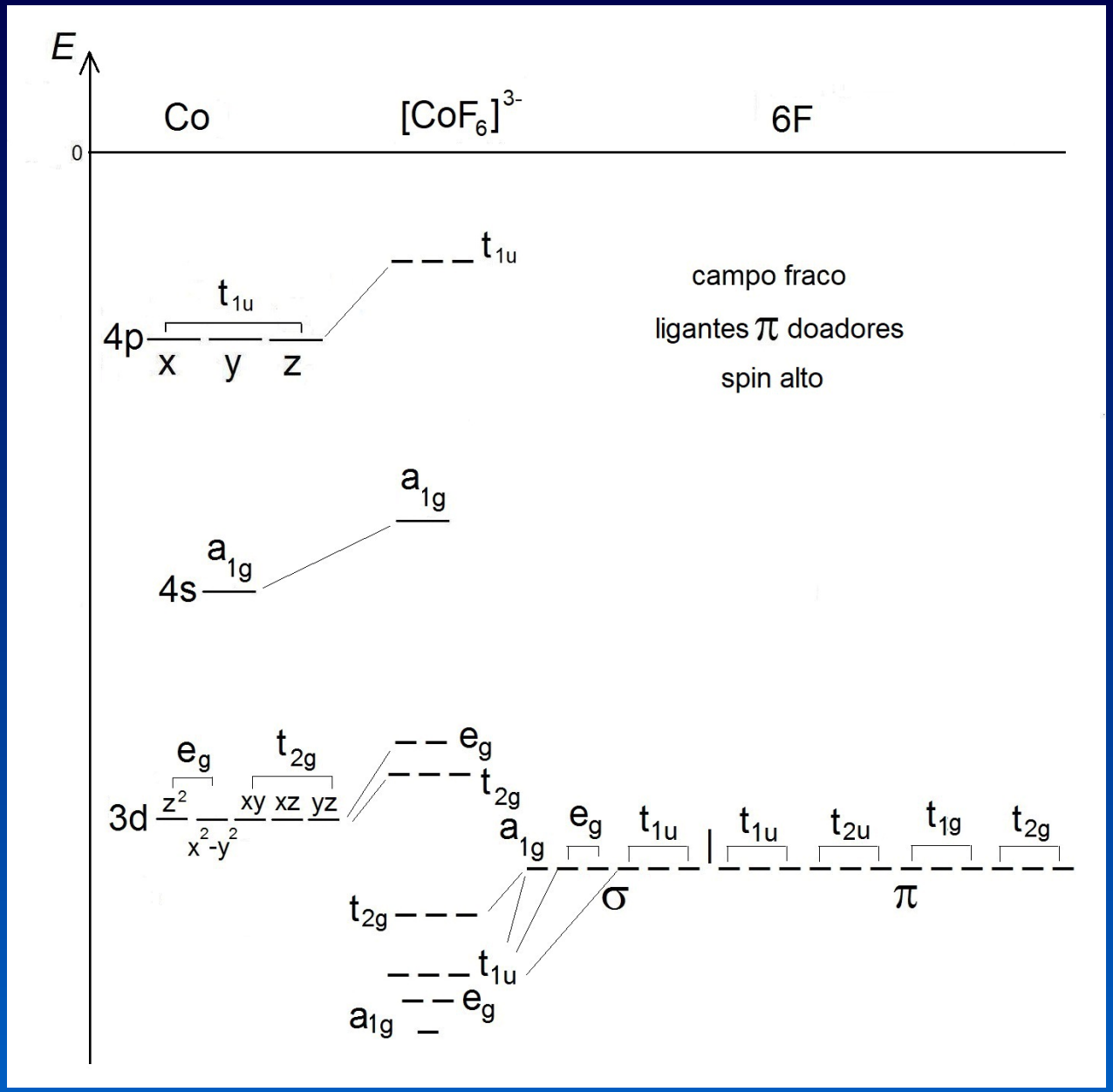
Classificando os 12 orbitais 2pπ dos 6F - INSEPARÁVEIS

(x,y,z)

O_h	E	$8C_3$	$6C_2$	$6C_4$	$3C_2(=C_4^2)$	i	$6S_4$	$8S_6$	$3\sigma_h$	$6\sigma_d$
pπ	12	0	0	0	-4	0	0	0	0	0

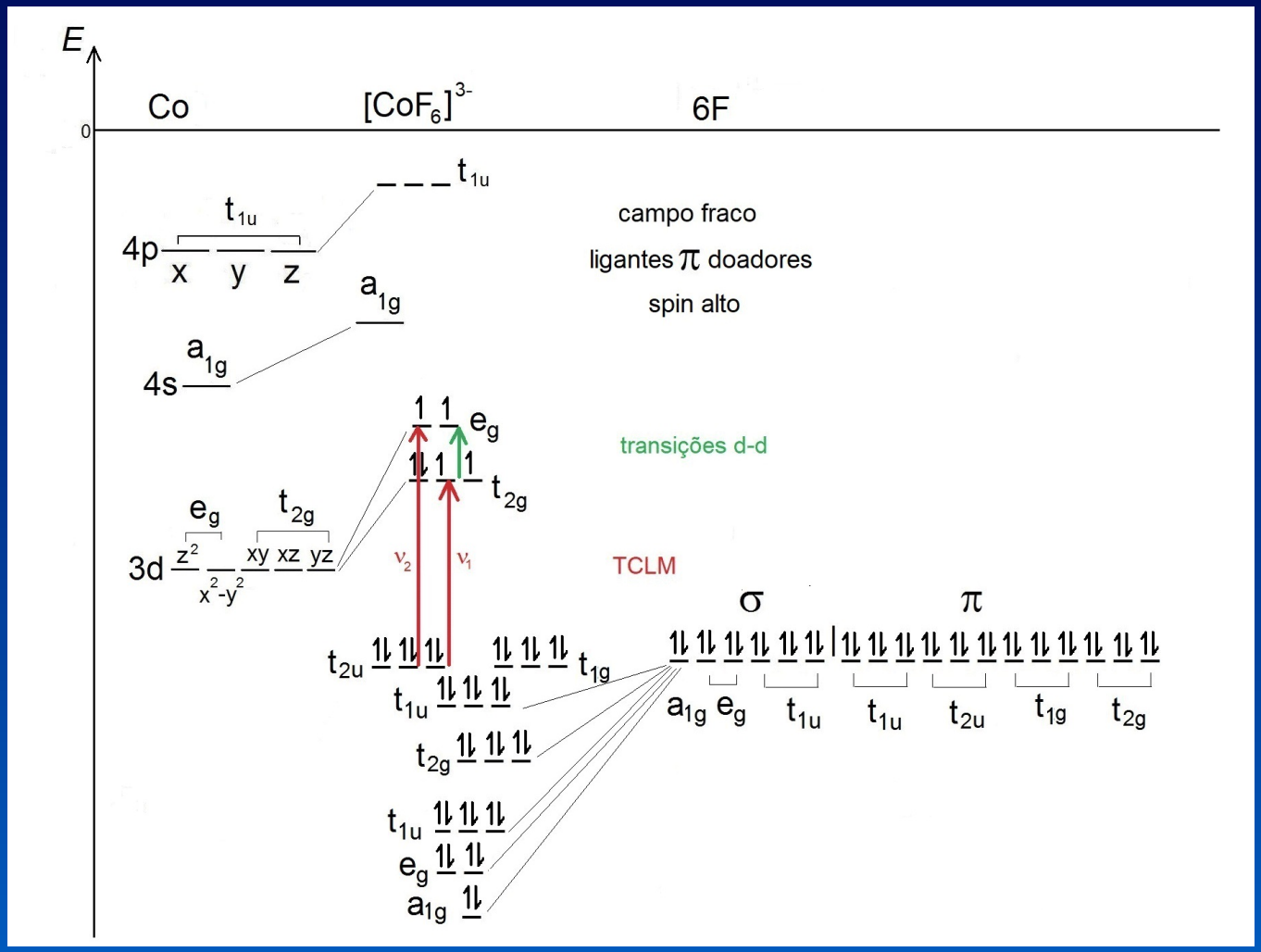
Classificando os orbitais 2pσ dos 6F - INSEPARÁVEIS

					(x,y,z)					
O_h	E	$8C_3$	$6C_2$	$6C_4$	$3C_2(=C_4^2)$	i	$6S_4$	$8S_6$	$3\sigma_h$	$6\sigma_d$
T_{1g}	3	0	-1	1	-1	3	1	0	-1	-1
T_{2g}	3	0	1	-1	-1	3	-1	0	-1	1
T_{1u}	3	0	-1	1	-1	-3	-1	0	1	1
T_{2u}	3	0	1	-1	-1	-3	1	0	1	-1
pπ	12	0	0	0	-4	0	0	0	0	0

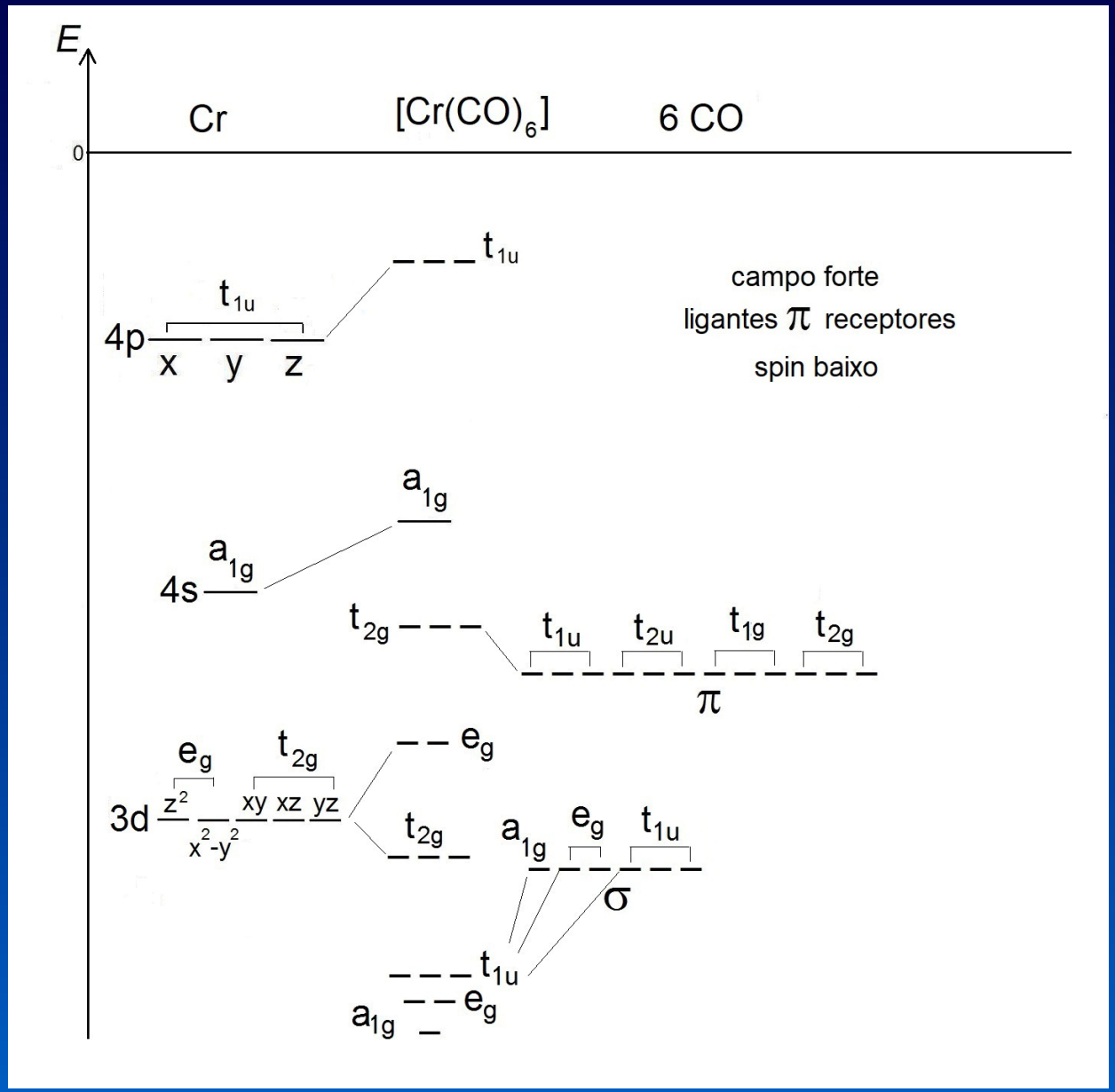


Com ligantes π de campo fraco

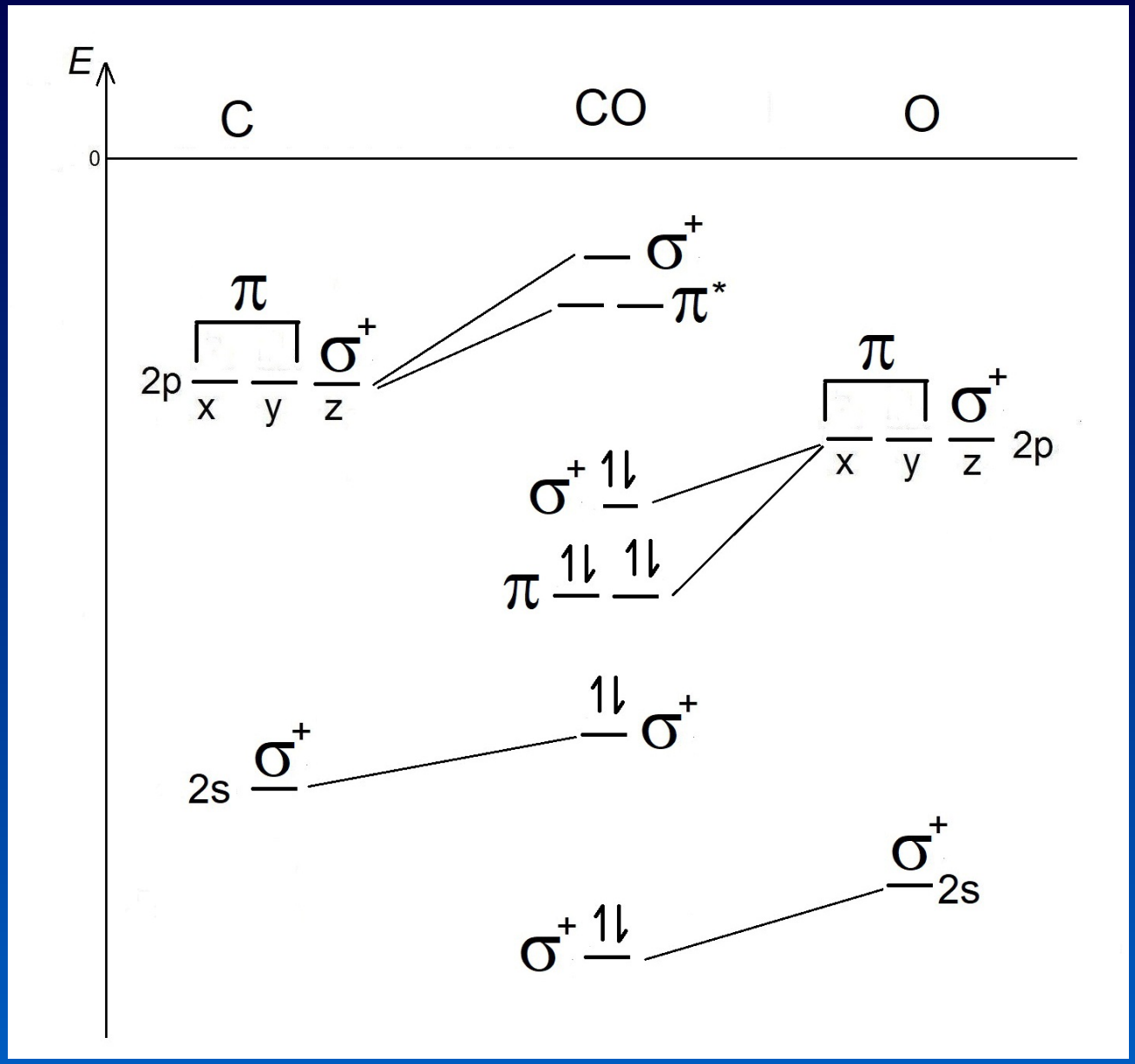
Transições eletrônicas e espectroscopia



Com ligantes π de campo fraco

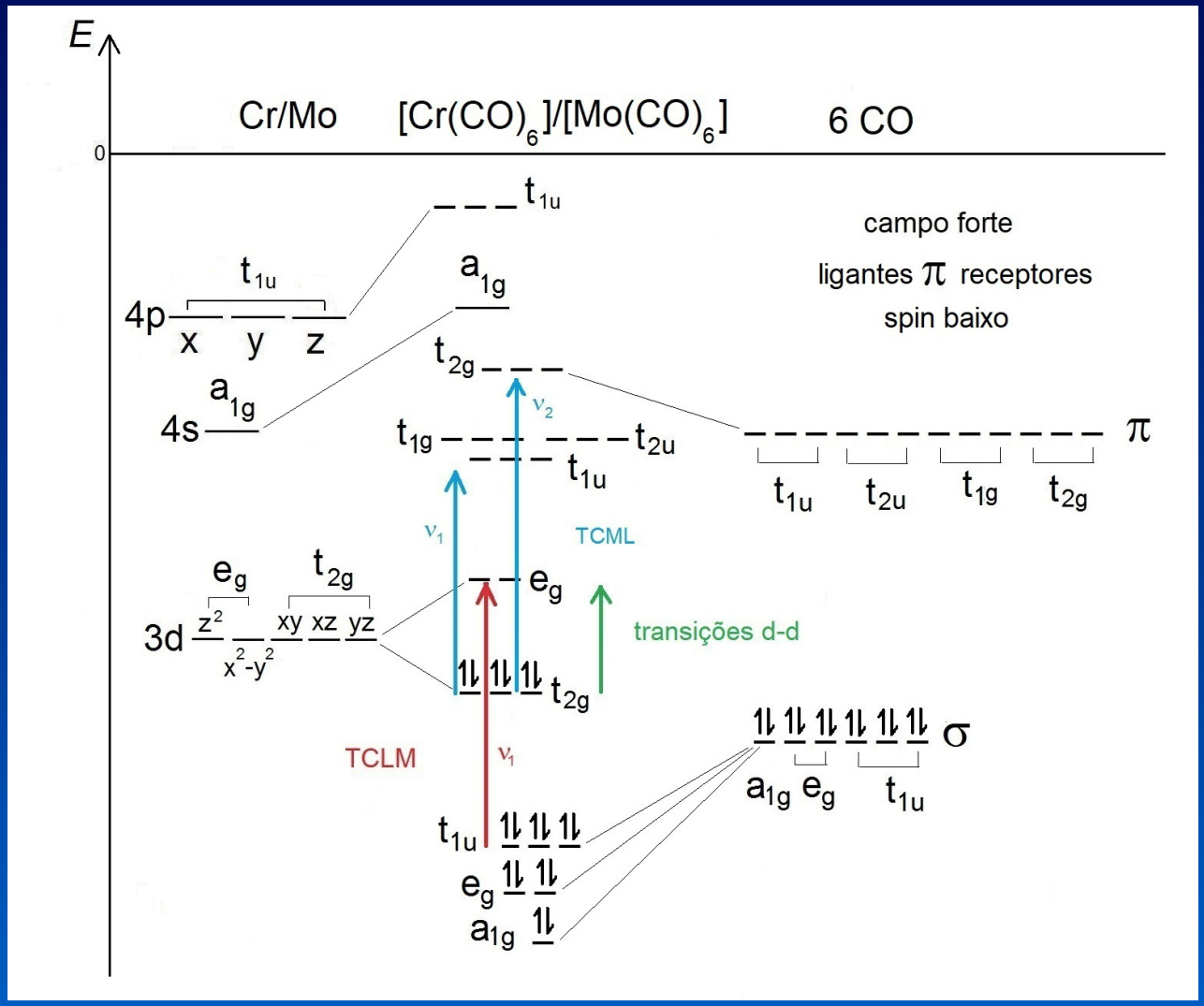


Com ligantes π de campo forte

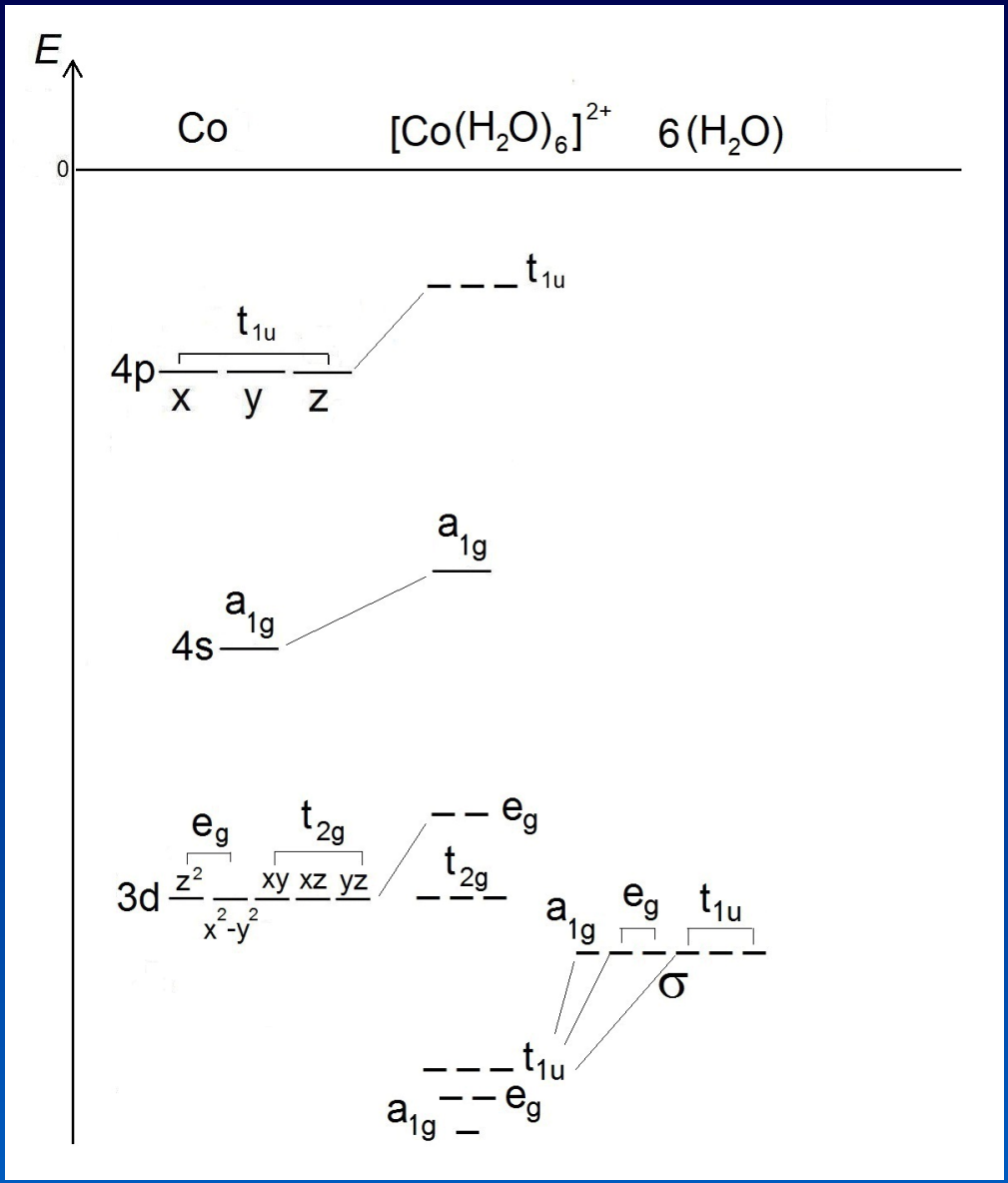


Orbitais moleculares do CO

Transições eletrônicas e espectroscopia

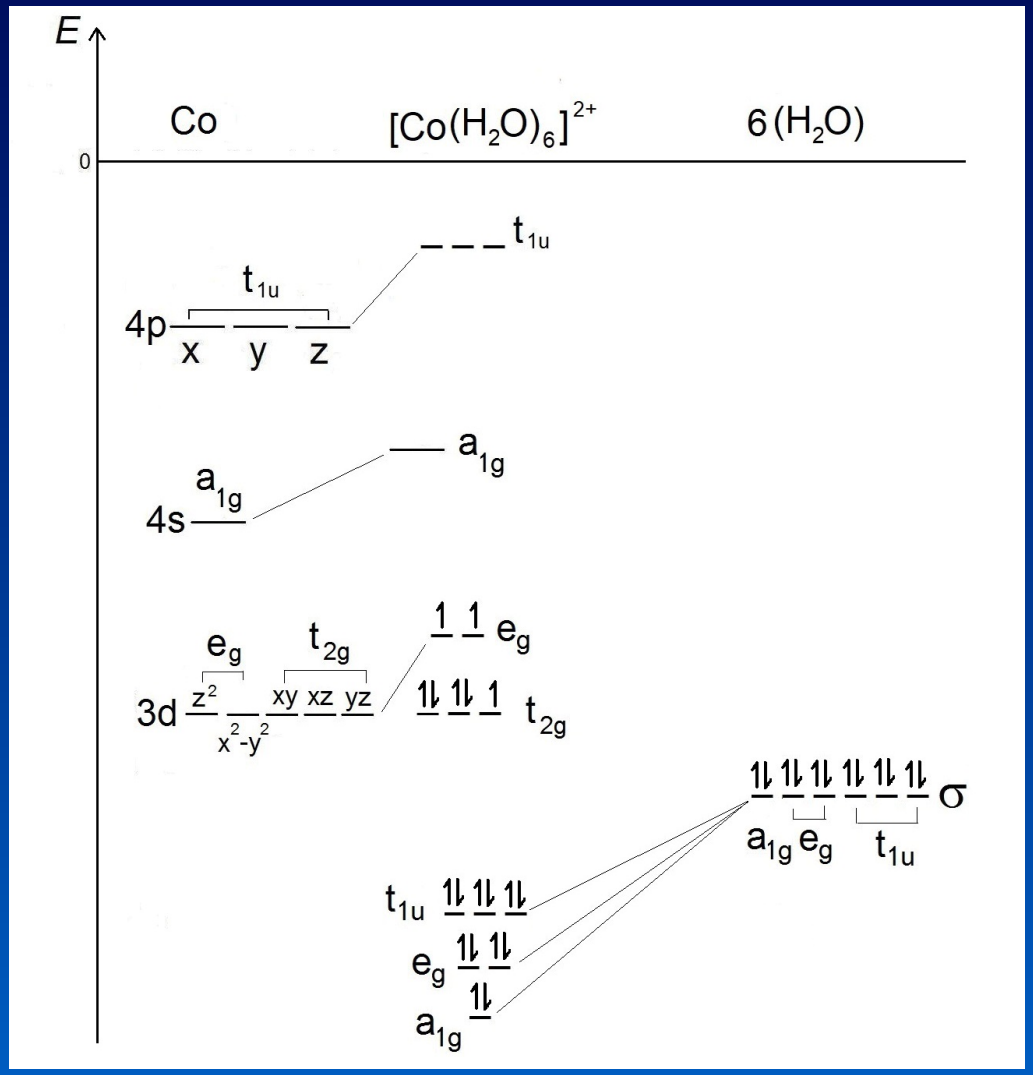


Com ligantes π de campo forte



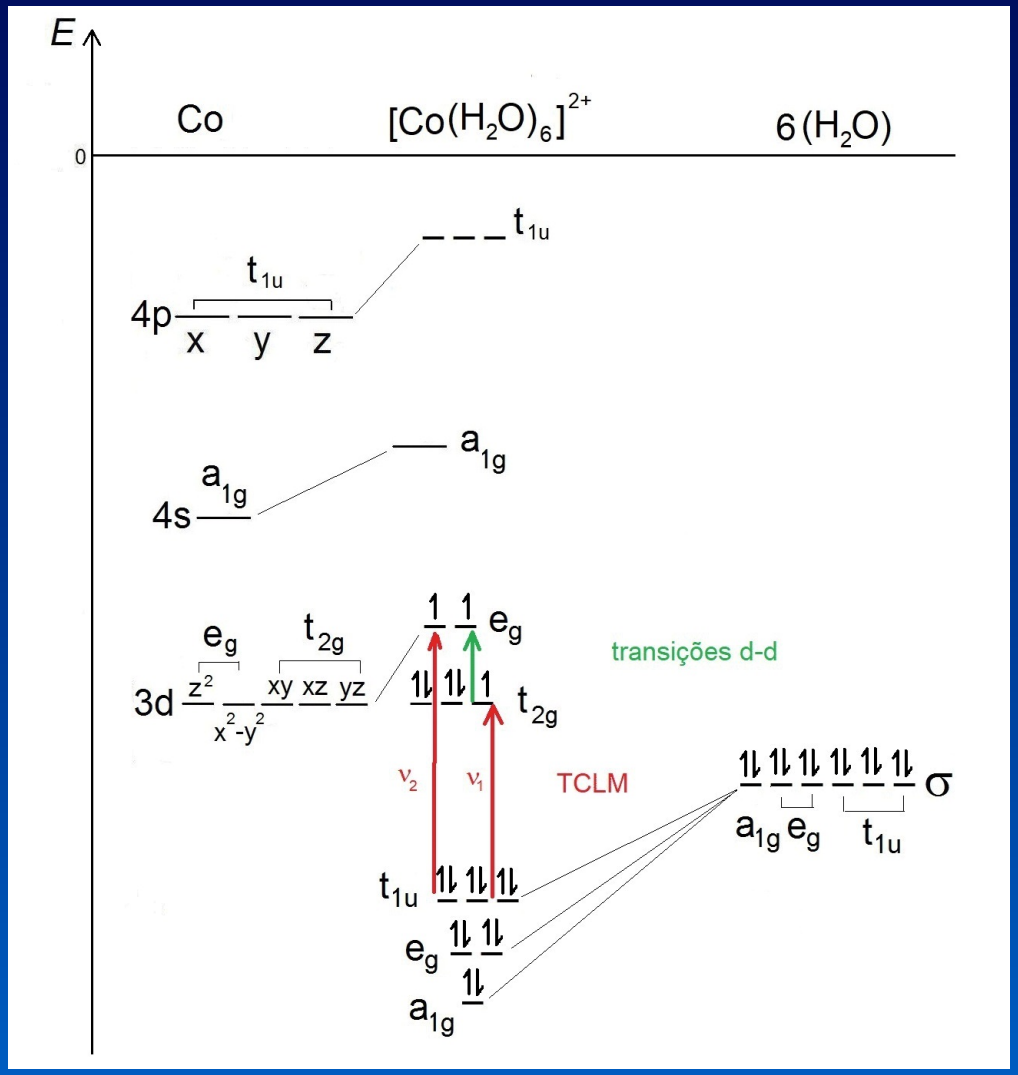
Sem ligantes π

Transições eletrônicas e espectroscopia



Sem ligantes π

Transições eletrônicas e espectroscopia



Sem ligantes π

FIM