



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

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Aula 7



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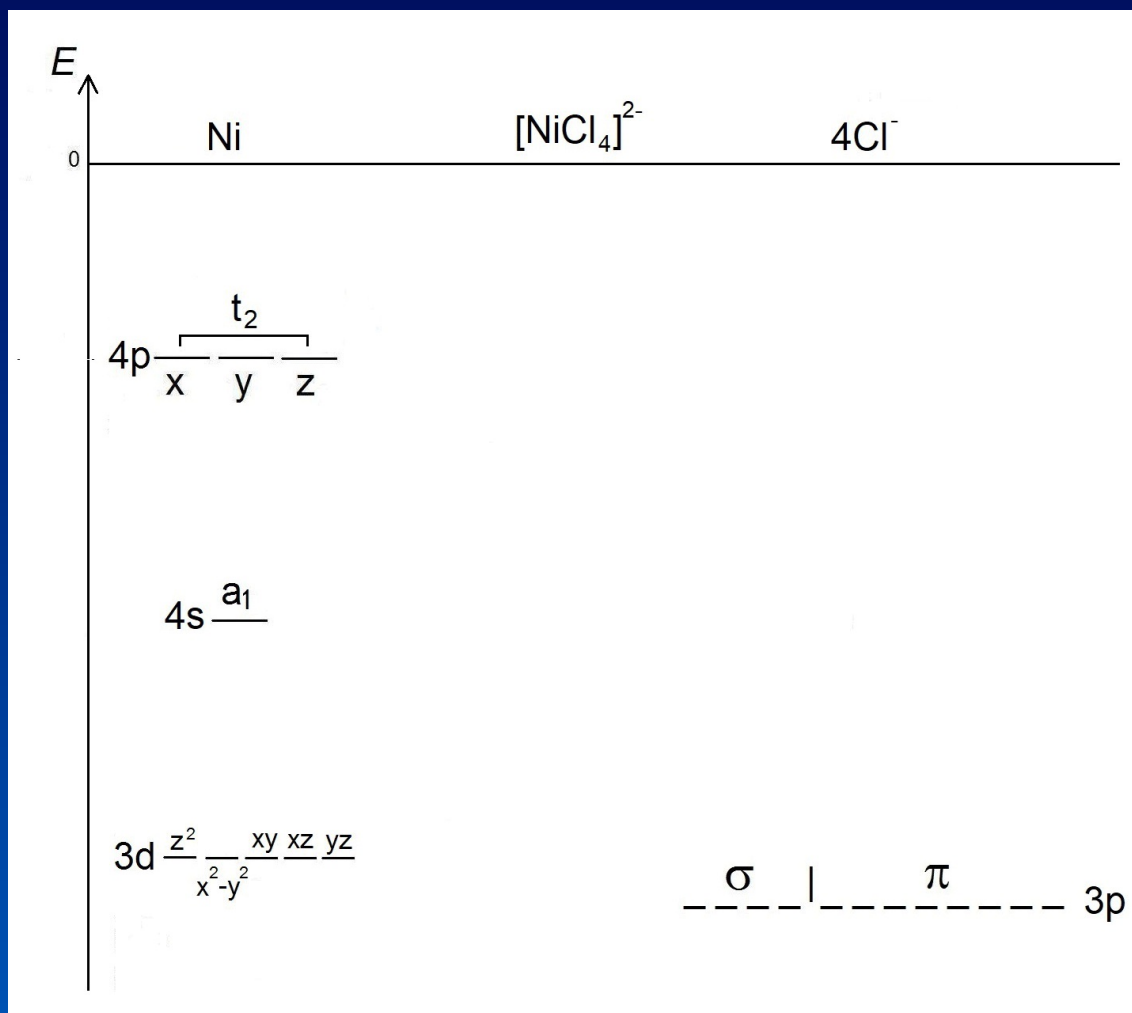
11 a 15 de março de 2024

$[\text{NiCl}_4]^{2-} - T_d$

T_d	E	$8C_3$	$3C_2$	$6S_4$	$6\sigma_d$
A_1	1	1	1	1	1
A_2	1	1	1	-1	-1
E	2	-1	2	0	0
T_1	3	0	-1	1	-1
T_2	3	0	-1	-1	1

$[\text{NiCl}_4]^{2-} - T_d$

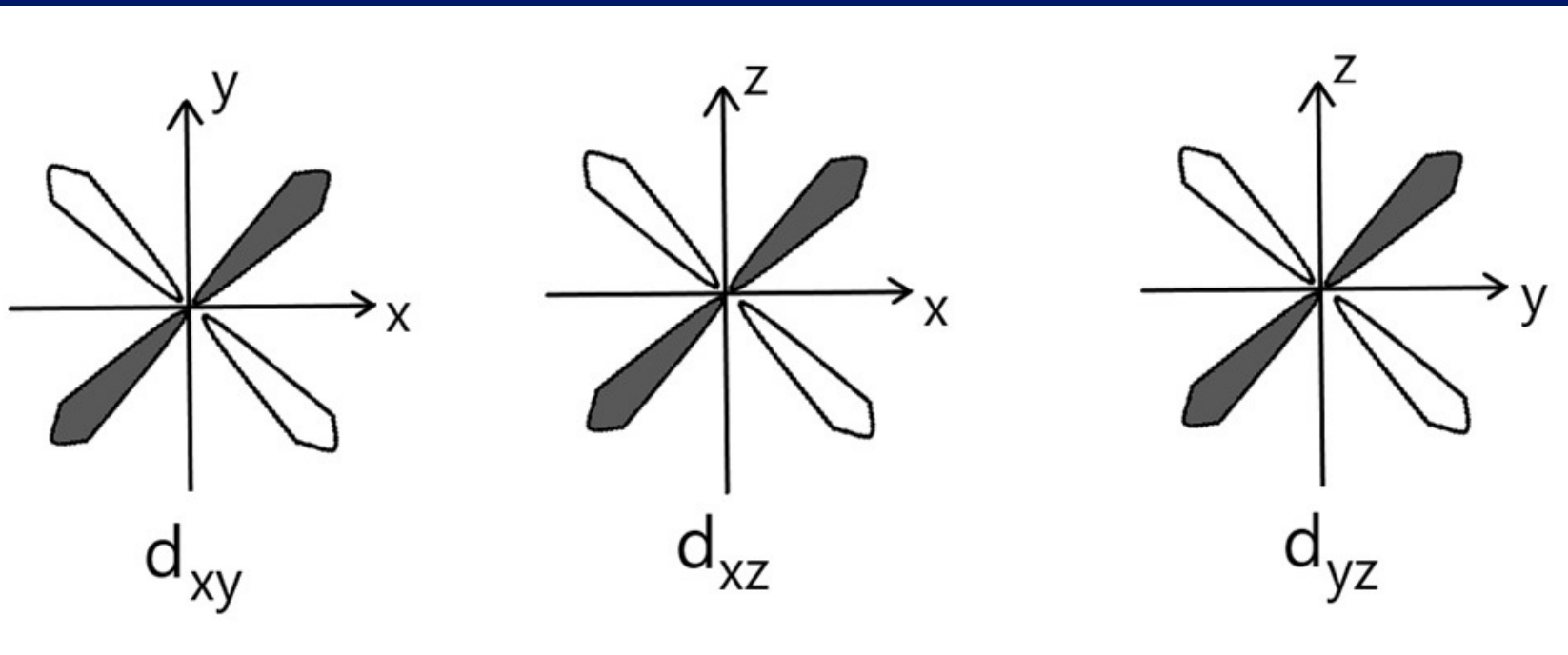
Diagrama de energia dos orbitais moleculares



Aproveitando os resultados do metano, T_d

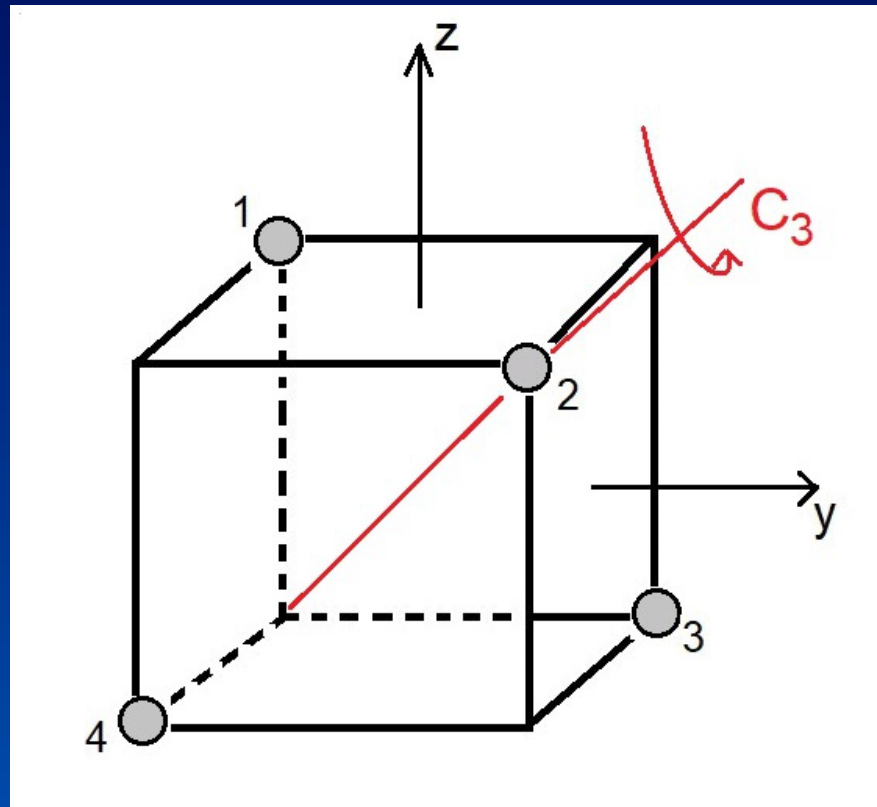
$[\text{NiCl}_4]^{2-} - T_d$

Classificando os orbitais 3d (xy,xz,yz) do Ni - INSEPARÁVEIS



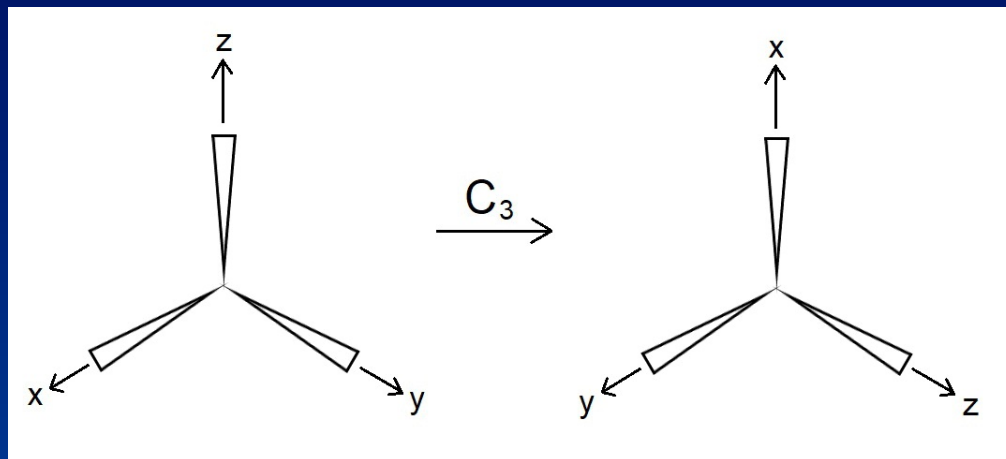
$[\text{NiCl}_4]^{2-} - T_d$

Classificando os orbitais 3d (xy,xz,yz) do Ni - INSEPARÁVEIS



$[\text{NiCl}_4]^{2-} - T_d$

Classificando os orbitais 3d (xy,xz,yz) do Ni - INSEPARÁVEIS



$$x - C_3 \rightarrow z$$

$$y - C_3 \rightarrow x$$

$$z - C_3 \rightarrow y$$

$[\text{NiCl}_4]^{2-} - \text{T}_d$

Classificando os orbitais 3d (xy,xz,yz) do Ni - INSEPARÁVEIS

$$\begin{aligned} x &-C_3 \rightarrow z \\ y &-C_3 \rightarrow x \\ z &-C_3 \rightarrow y \end{aligned}$$

$$\begin{aligned} d_{xy} &-C_3 \rightarrow d_{zx} = d_{xz} \\ d_{xz} &-C_3 \rightarrow d_{zy} = d_{yz} \\ d_{yz} &-C_3 \rightarrow d_{xy} \end{aligned}$$

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

$$\chi = 0$$

$[\text{NiCl}_4]^{2-} - T_d$

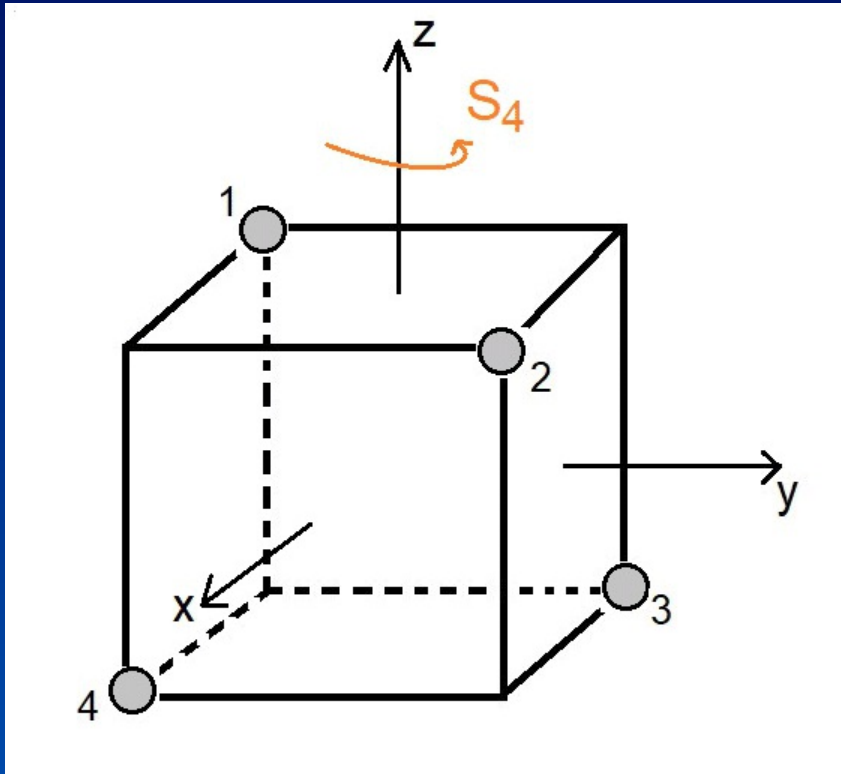
Classificando os orbitais 3d (xy,xz,yz) do Ni -INSEPARÁVEIS

T_d	E	$8C_3$	$3C_2$	$6S_4$	$6\sigma_d$
A_1	1	1	1	1	1
A_2	1	1	1	-1	-1
E	2	-1	2	0	0
T_1	3	0	-1	1	-1
T_2	3	0	-1	-1	1

$(d_{xy,xz,yz})$ 3 0

$[\text{NiCl}_4]^{2-} - T_d$

Classificando os orbitais 3d (xy,xz,yz) do Ni - INSEPARÁVEIS



$$\begin{aligned}x &- \text{}^{(z)}S_4 \rightarrow y \\y &- \text{}^{(z)}S_4 \rightarrow -x \\z &- \text{}^{(z)}S_4 \rightarrow -z\end{aligned}$$

$[\text{NiCl}_4]^{2-} - T_d$

Classificando os orbitais 3d (xy,xz,yz) do Ni - INSEPARÁVEIS

$$\begin{aligned} x &- \text{}^{(z)}S_4 \rightarrow y \\ y &- \text{}^{(z)}S_4 \rightarrow -x \\ z &- \text{}^{(z)}S_4 \rightarrow -z \end{aligned}$$

$$\begin{aligned} d_{xy} &- \text{}^{(z)}S_4 \rightarrow d_{y(-x)} = -d_{xy} \\ d_{xz} &- \text{}^{(z)}S_4 \rightarrow d_{y(-z)} = -d_{yz} \\ d_{yz} &- \text{}^{(z)}S_4 \rightarrow d_{(-x)(-z)} = d_{xz} \end{aligned}$$

$$\begin{array}{ccc} & d_{xy} & d_{xz} & d_{yz} \\ d_{xy} & 1 & 0 & 0 \\ d_{xz} & 0 & 1 & 0 \\ d_{yz} & 0 & 0 & 1 \end{array} \xrightarrow{\text{}^{(z)}S_4} \begin{array}{ccc} & d_{xy} & d_{xz} & d_{yz} \\ d_{xy} & -1 & 0 & 0 \\ d_{xz} & 0 & 0 & -1 \\ d_{yz} & 0 & 1 & 0 \end{array}$$

$$\chi = -1$$

$[\text{NiCl}_4]^{2-} - T_d$

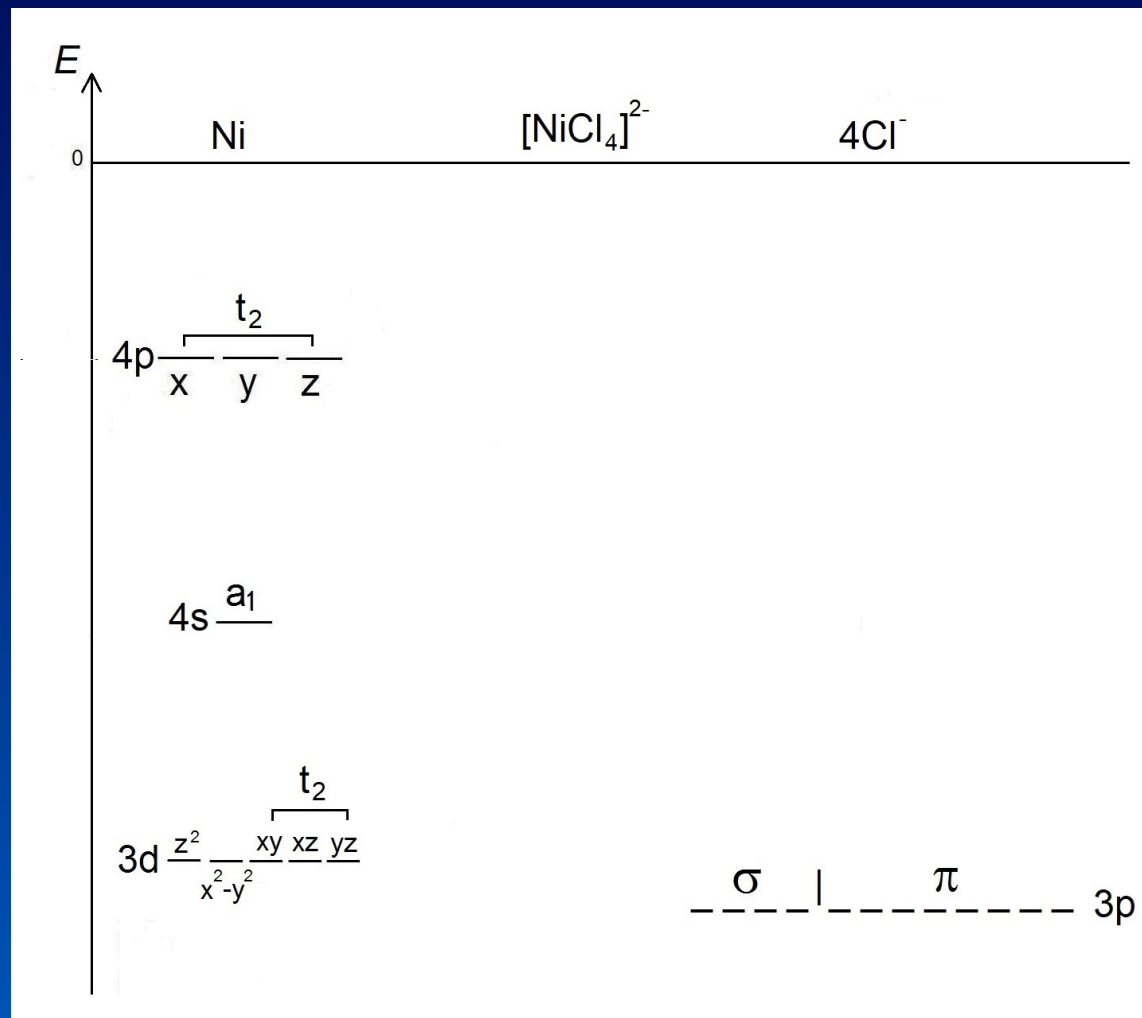
Classificando os orbitais 3d (xy,xz,yz) do Ni -INSEPARÁVEIS

T_d	E	$8C_3$	$3C_2$	$6S_4$	$6\sigma_d$
A_1	1	1	1	1	1
A_2	1	1	1	-1	-1
E	2	-1	2	0	0
T_1	3	0	-1	1	-1
T_2	3	0	-1	-1	1

$(d_{xy,xz,yz})$	3	0	-1	T_2
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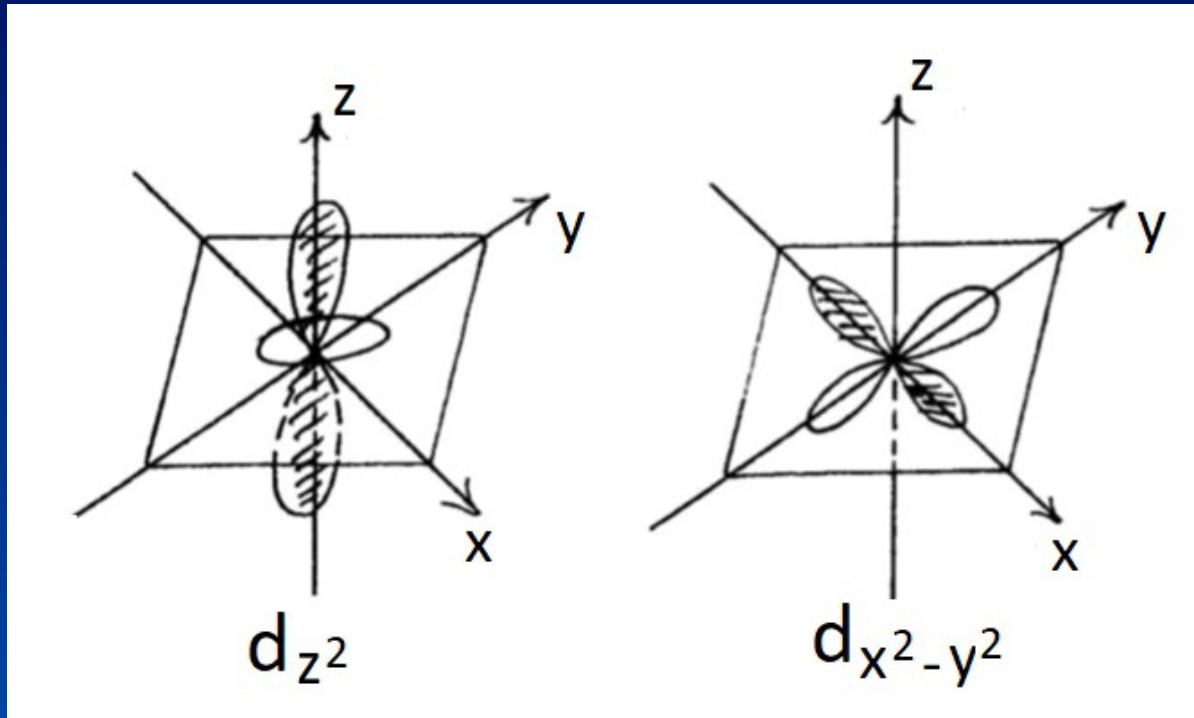
$[\text{NiCl}_4]^{2-} - T_d$

Diagrama de energia dos orbitais moleculares



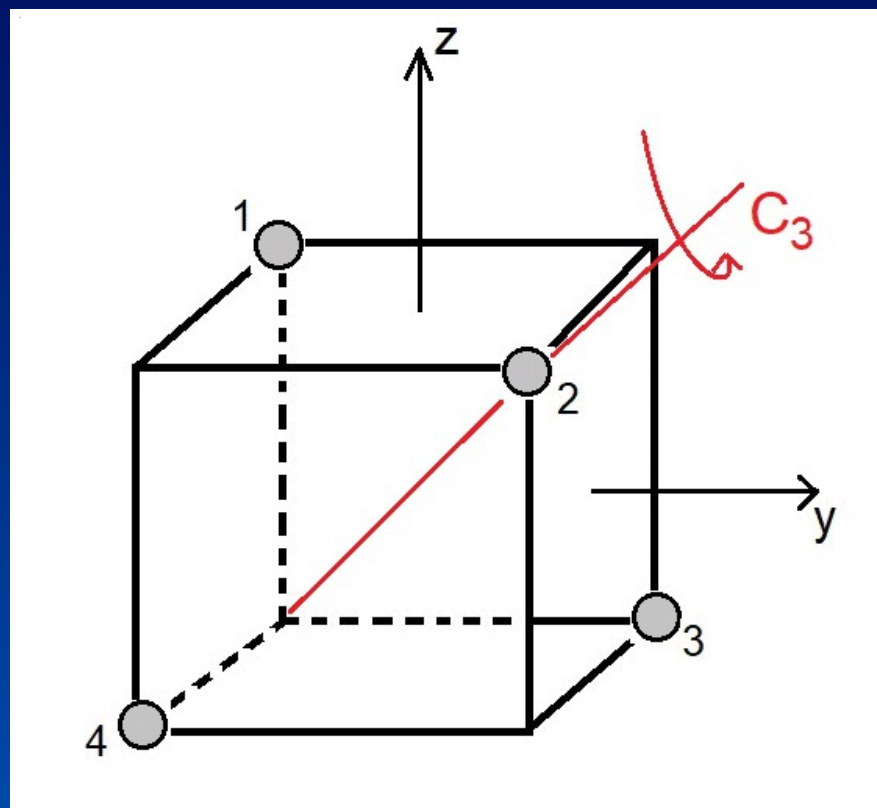
$[\text{NiCl}_4]^{2-} - T_d$

Classificando os orbitais 3d (z^2, x^2-y^2) do Ni - INSEPARÁVEIS



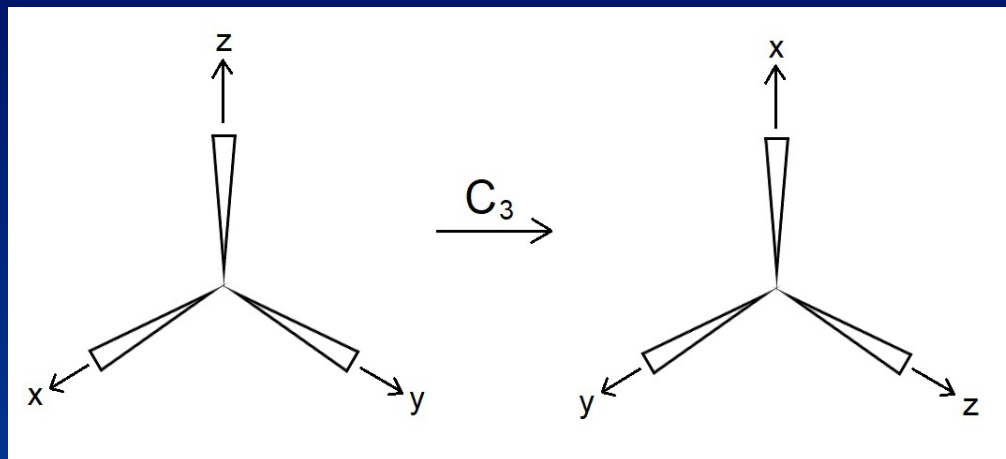
$[\text{NiCl}_4]^{2-} - T_d$

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$[\text{NiCl}_4]^{2-} - T_d$

Classificando os orbitais 3d (z^2, x^2-y^2) do Ni - INSEPARÁVEIS



$$\begin{aligned} x &-C_3 \rightarrow y \\ y &-C_3 \rightarrow z \\ z &-C_3 \rightarrow x \end{aligned}$$

$[\text{NiCl}_4]^{2-} - \text{T}_d$

Classificando os orbitais 3d (z^2, x^2-y^2) do Ni - INSEPARÁVEIS

$$\begin{aligned}x &-C_3 \rightarrow y \\y &-C_3 \rightarrow z \\z &-C_3 \rightarrow x\end{aligned}$$

$$\begin{aligned}d_{z^2} &C_3 \rightarrow d_{x^2} \\d_{x^2-y^2} &C_3 \rightarrow d_{y^2-z^2}\end{aligned}$$

Na verdade, a expressão do orbital d_{z^2} é mais complexa:

$$\begin{aligned}d_{z^2} &= (1/\sqrt{3})(2z^2 - x^2 - y^2) & C_3 \rightarrow d_{x^2} &= (1/\sqrt{3})(2x^2 - y^2 - z^2) \\d_{x^2-y^2} &= x^2 - y^2 & C_3 \rightarrow d_{y^2-z^2} &= y^2 - z^2\end{aligned}$$

$[\text{NiCl}_4]^{2-} - T_d$

Classificando os orbitais 3d (z^2, x^2-y^2) do Ni - INSEPARÁVEIS

Pode-se mostrar que os novos orbitais d_{x^2} e $d_{y^2-z^2}$ são uma combinação linear dos orbitais d_{z^2} e $d_{x^2-y^2}$.

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

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

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

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

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

$[\text{NiCl}_4]^{2-} - T_d$

Classificando os orbitais 3d (z^2, x^2-y^2) do Ni - INSEPARÁVEIS

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

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

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

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

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

$$C_{12} = (1/\sqrt{3}) + (1/2)(1/\sqrt{3}) = (\sqrt{3})/2$$

$[\text{NiCl}_4]^{2-} - T_d$

Classificando os orbitais 3d (z^2, x^2-y^2) do Ni - INSEPARÁVEIS

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

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

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

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

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

$[\text{NiCl}_4]^{2-} - T_d$

Classificando os orbitais 3d (z^2, x^2-y^2) do Ni - INSEPARÁVEIS

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

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

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

$$\begin{aligned} 1 &= -C_{21} (1/\sqrt{3}) - C_{22} \\ 1 &= (\sqrt{3}/2)(1/\sqrt{3}) - C_{22} \\ C_{22} &= -1 + 1/2 = \mathbf{-1/2} \end{aligned}$$

$[\text{NiCl}_4]^{2-} - T_d$

Classificando os orbitais 3d (z^2, x^2-y^2) do Ni - INSEPARÁVEIS

$$\begin{array}{cc} & \begin{array}{c} d_{z^2} \\ d_{x^2-y^2} \end{array} \\ \begin{array}{c} d_{z^2} \\ d_{x^2-y^2} \end{array} & \begin{array}{cc} 1 & 0 \\ 0 & 1 \end{array} \end{array} \xrightarrow{C_3} \begin{array}{cc} & \begin{array}{c} d_{z^2} \\ d_{x^2-y^2} \end{array} \\ \begin{array}{c} d_{z^2} \\ d_{x^2-y^2} \end{array} & \begin{array}{cc} -1/2 & (\sqrt{3})/2 \\ -(\sqrt{3})/2 & -1/2 \end{array} \end{array}$$

$$\chi = -1$$

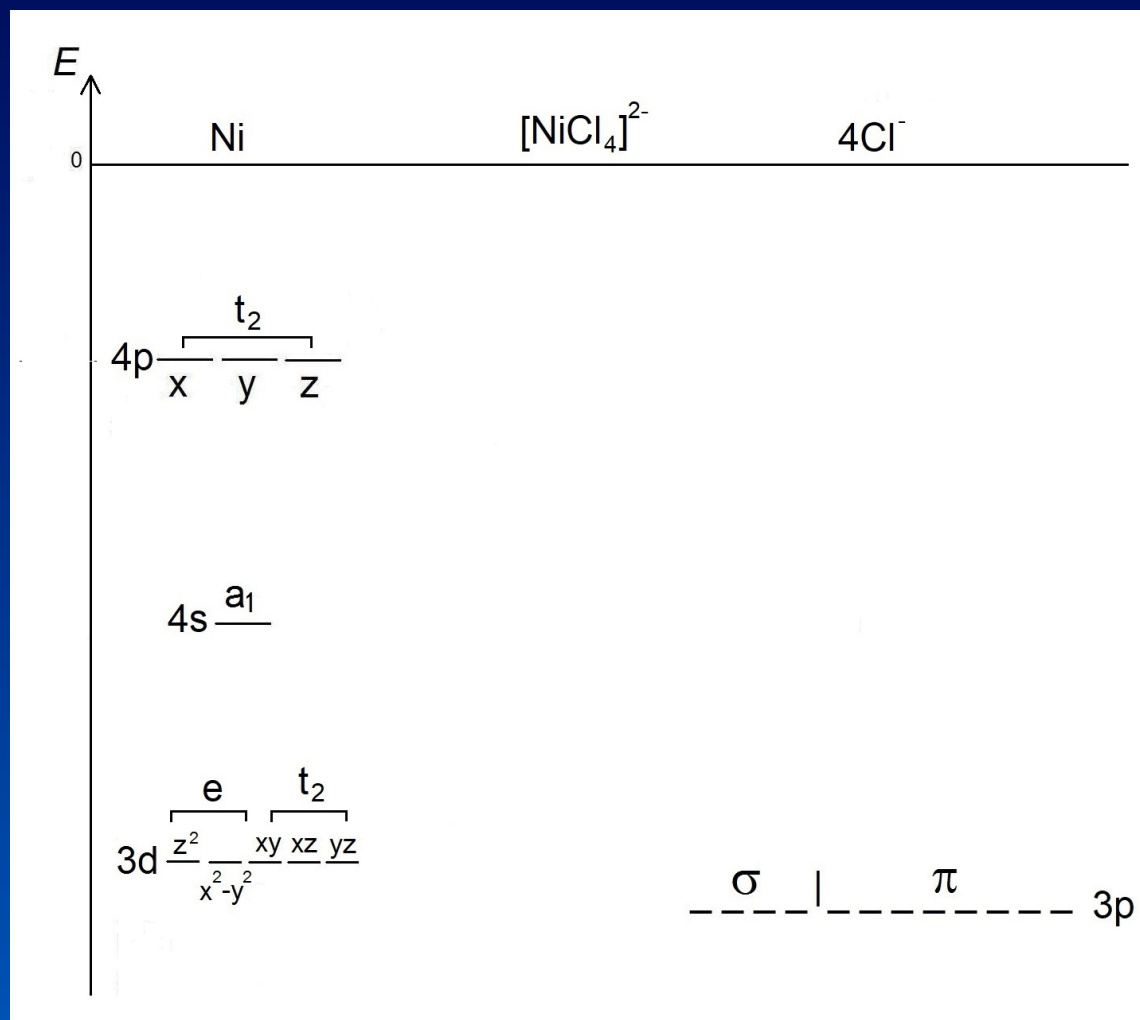
$[\text{NiCl}_4]^{2-} - T_d$

Classificando os orbitais 3d (z^2, x^2-y^2) do Ni -INSEPARÁVEIS

T_d	E	$8C_3$	$3C_2$	$6S_4$	$6\sigma_d$
A_1	1	1	1	1	1
A_2	1	1	1	-1	-1
E	2	-1	2	0	0
T_1	3	0	-1	1	-1
T_2	3	0	-1	-1	1
<hr/>					
(d_{z^2, x^2-y^2})	2	-1			E

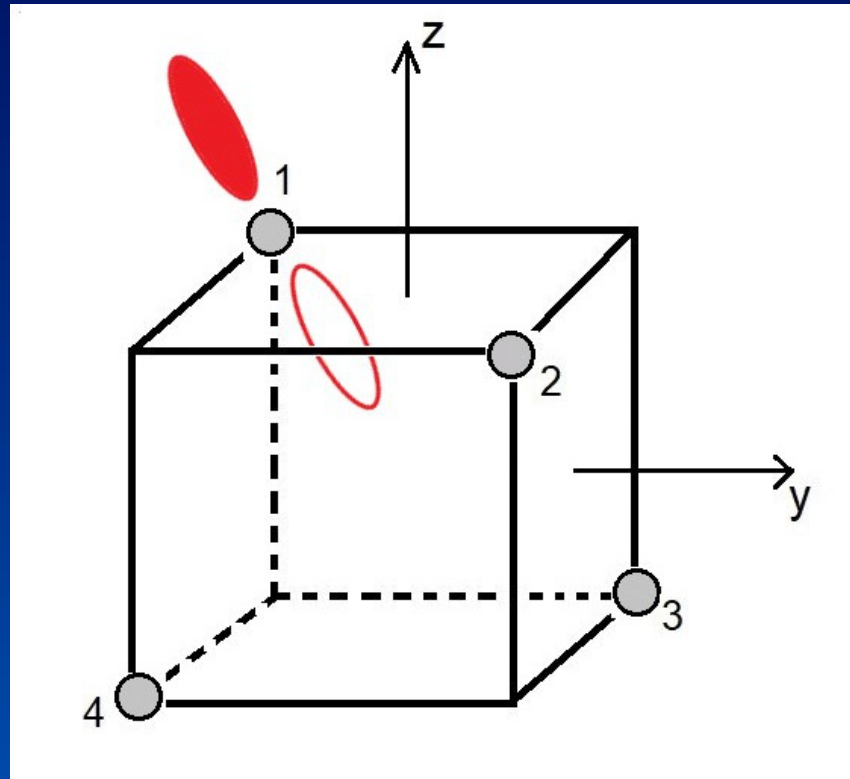


Diagrama de energia dos orbitais moleculares



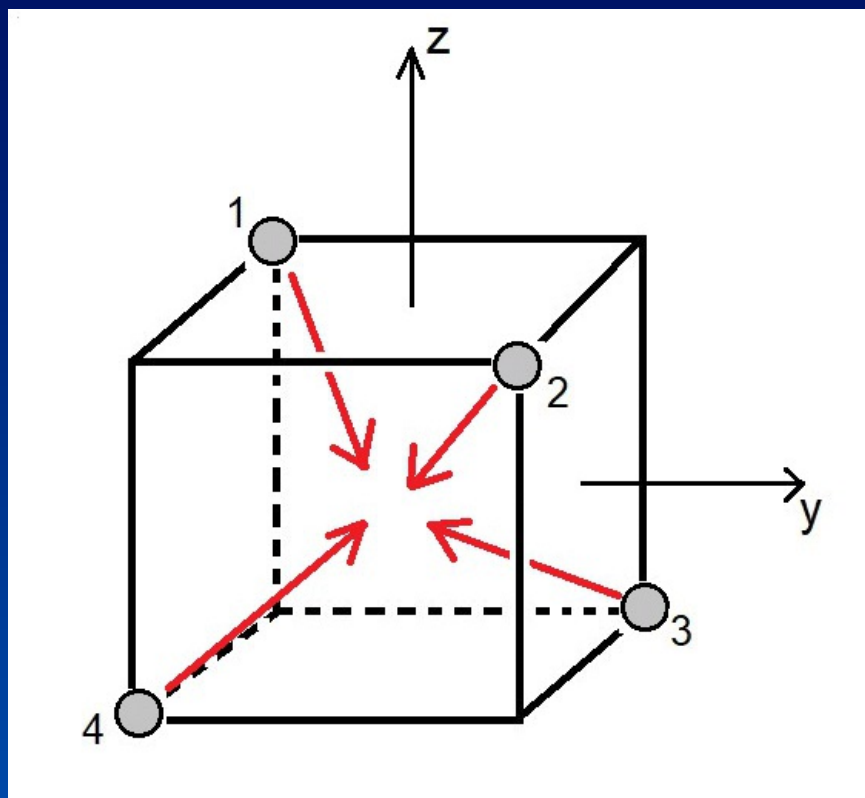


Classificando os orbitais $p\sigma$ dos ligantes cloreto -INSEPARÁVEIS



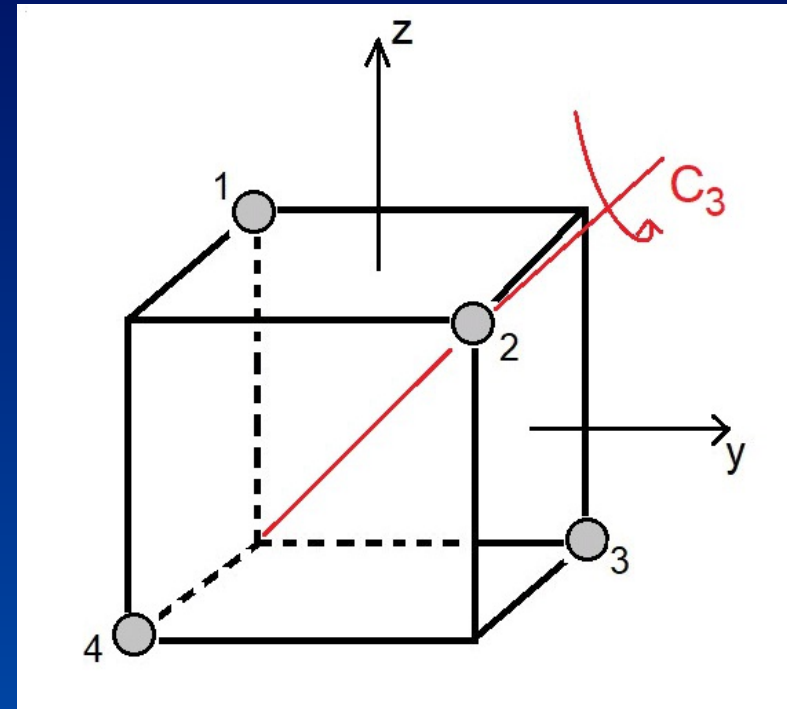
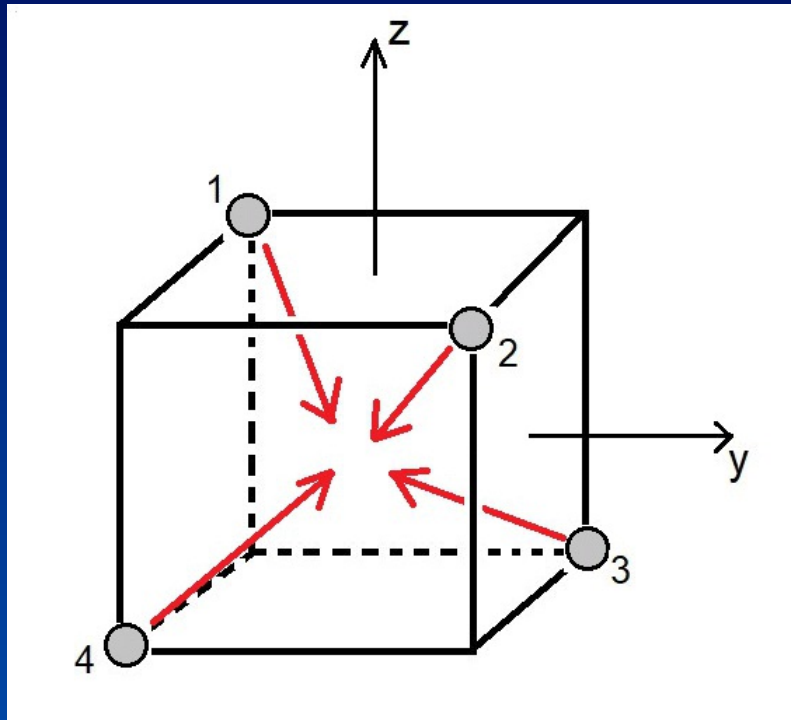


Classificando os orbitais $p\sigma$ dos ligantes cloreto -INSEPARÁVEIS



$[\text{NiCl}_4]^{2-} - T_d$

Classificando os orbitais $p\sigma$ dos ligantes cloreto -INSEPARÁVEIS



$[\text{NiCl}_4]^{2-} - T_d$

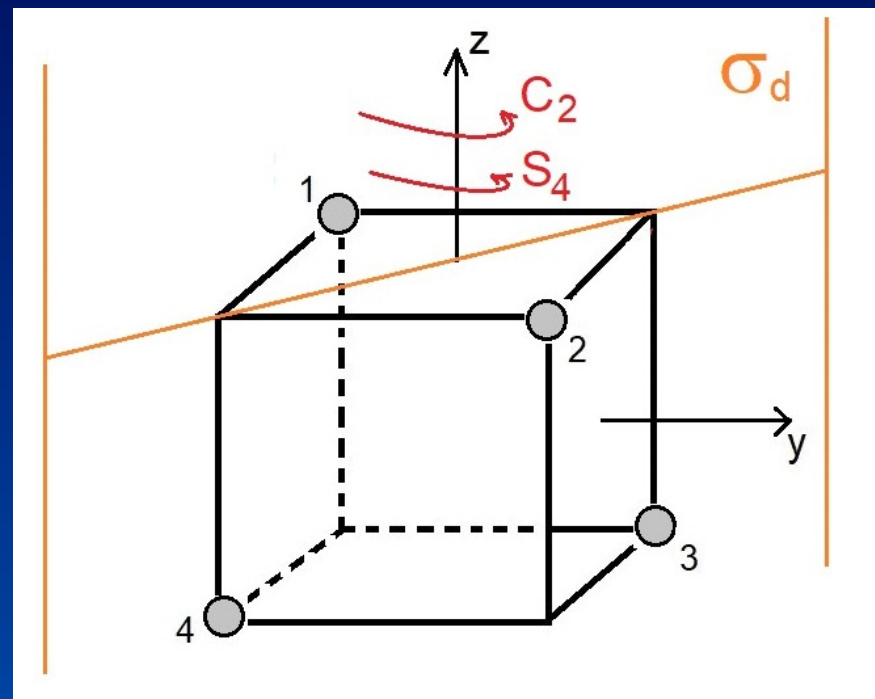
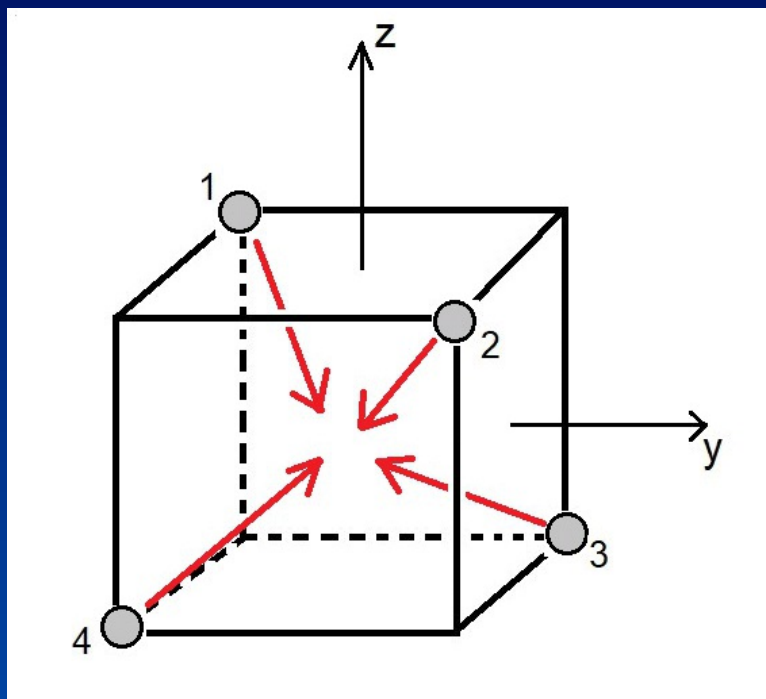
Classificando os orbitais $p\sigma$ dos ligantes cloreto -INSEPARÁVEIS

T_d	E	$8C_3$	$3C_2$	$6S_4$	$6\sigma_d$
A_1	1	1	1	1	1
A_2	1	1	1	-1	-1
E	2	-1	2	0	0
T_1	3	0	-1	1	-1
T_2	3	0	-1	-1	1

$p\sigma(1,2,3,4)$	4	1
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$[\text{NiCl}_4]^{2-} - T_d$

Classificando os orbitais $p\sigma$ dos ligantes cloreto -INSEPARÁVEIS



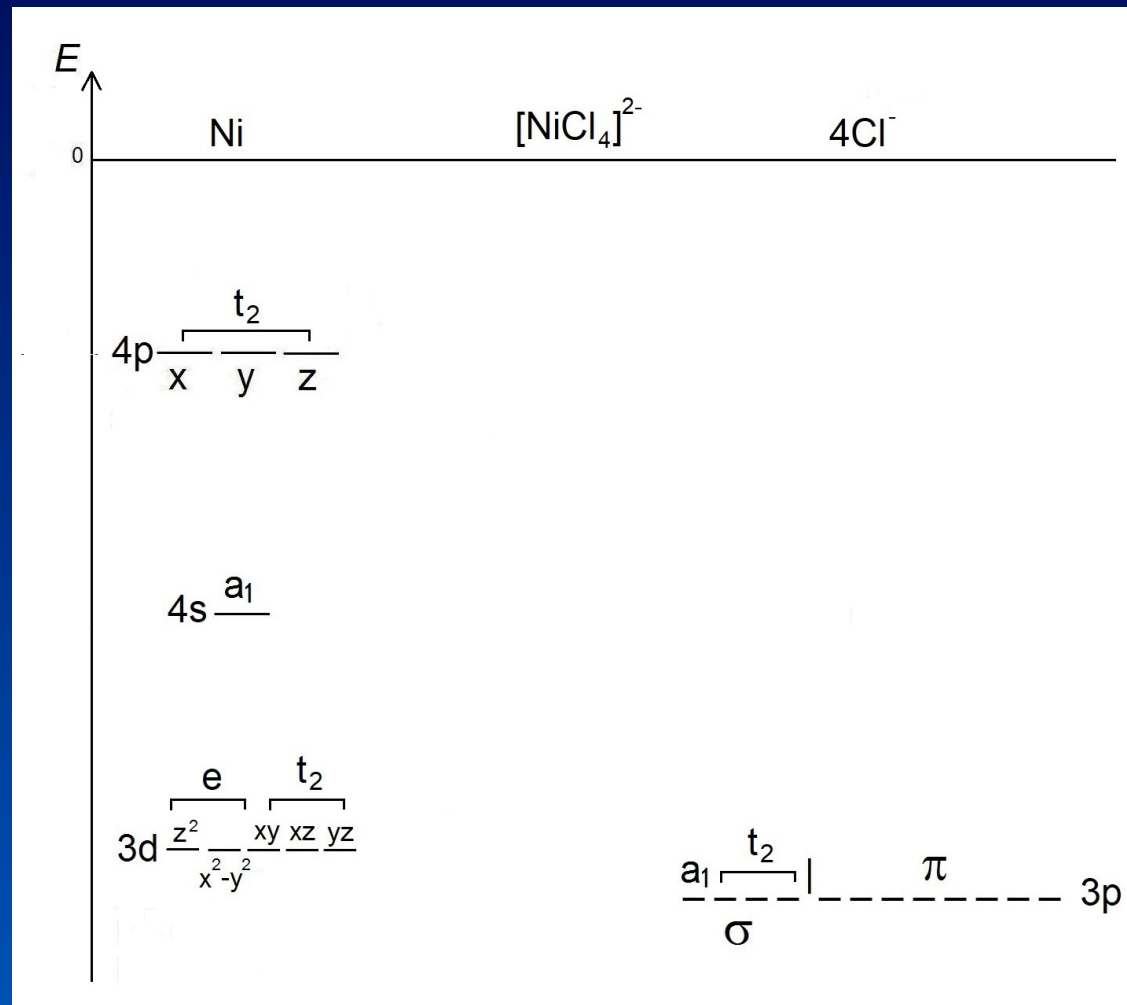
$[\text{NiCl}_4]^{2-} - \text{T}_d$

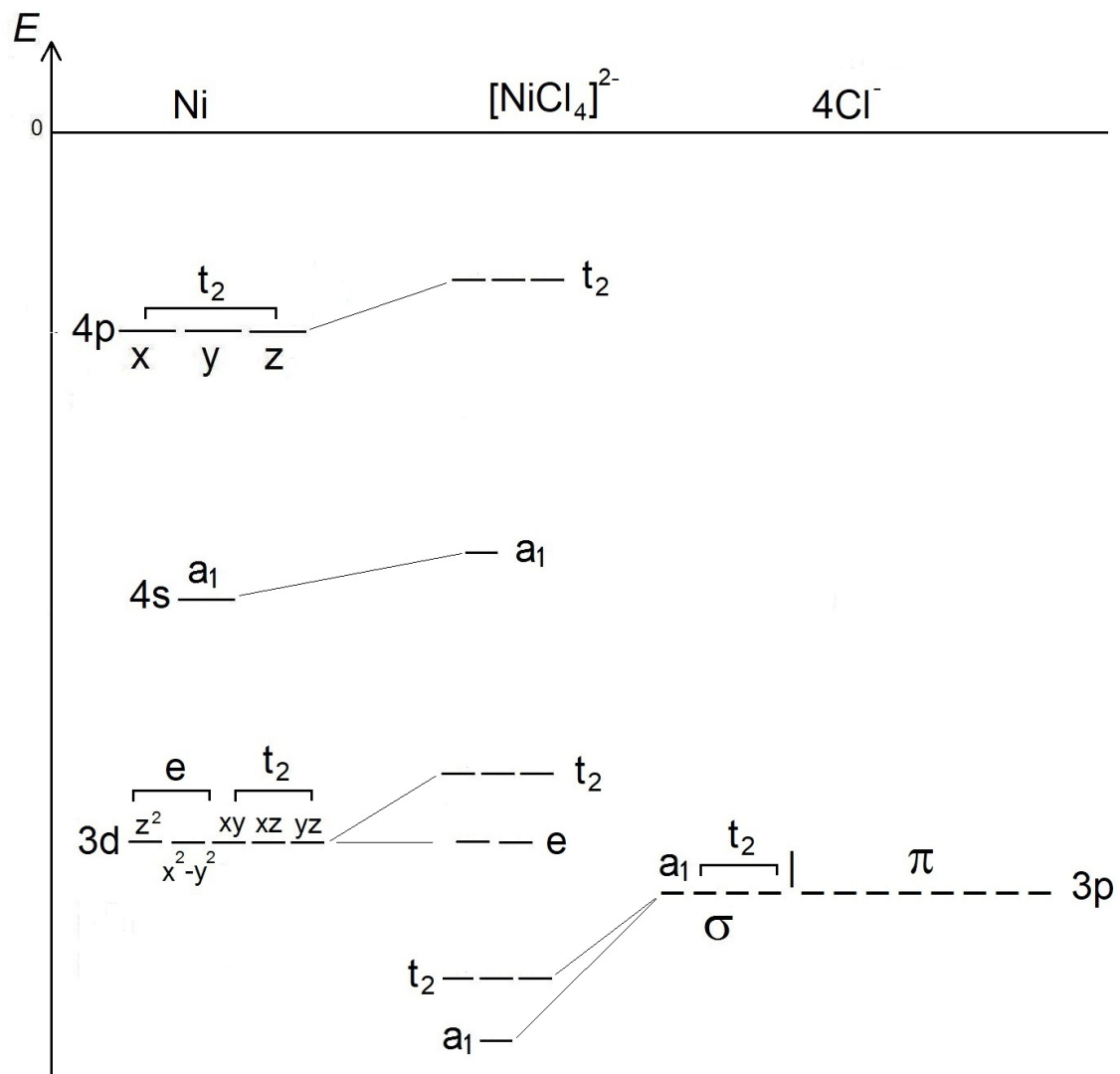
Classificando os orbitais $p\sigma$ dos ligantes cloreto -INSEPARÁVEIS

T_d	E	8C_3	3C_2	6S_4	$6\sigma_d$	
A_1	1	1	1	1	1	
A_2	1	1	1	-1	-1	
E	2	-1	2	0	0	
T_1	3	0	-1	1	-1	
T_2	3	0	-1	-1	1	
<hr/>						
$p\sigma(1,2,3,4)$	4	1	0	0	2	$\text{A}_1 + \text{T}_2$

$[\text{NiCl}_4]^{2-} - \text{T}_d$

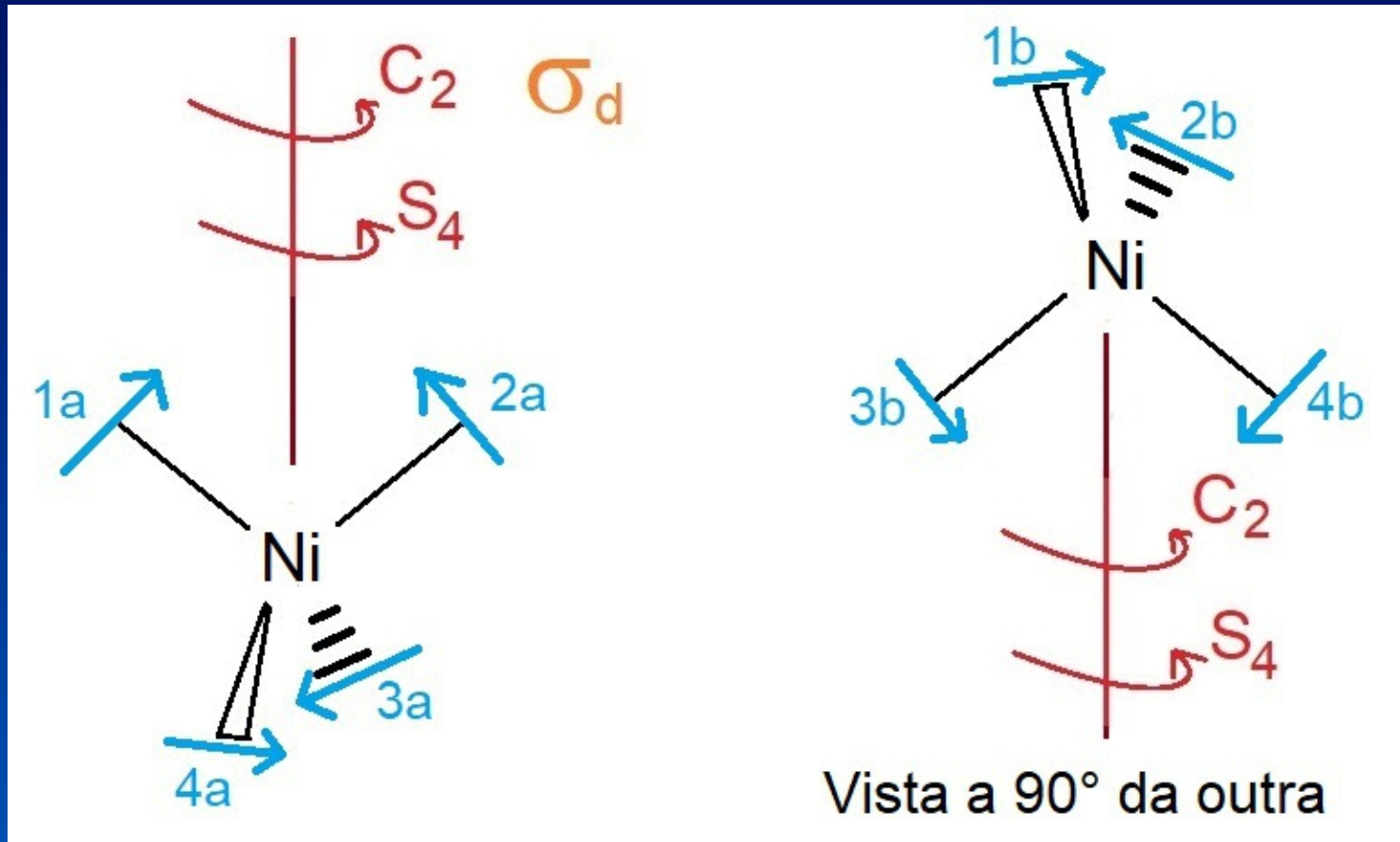
Diagrama de energia dos orbitais moleculares





$[\text{NiCl}_4]^{2-} - T_d$

Classificando os orbitais $p\pi$ dos ligantes cloreto -INSEPARÁVEIS



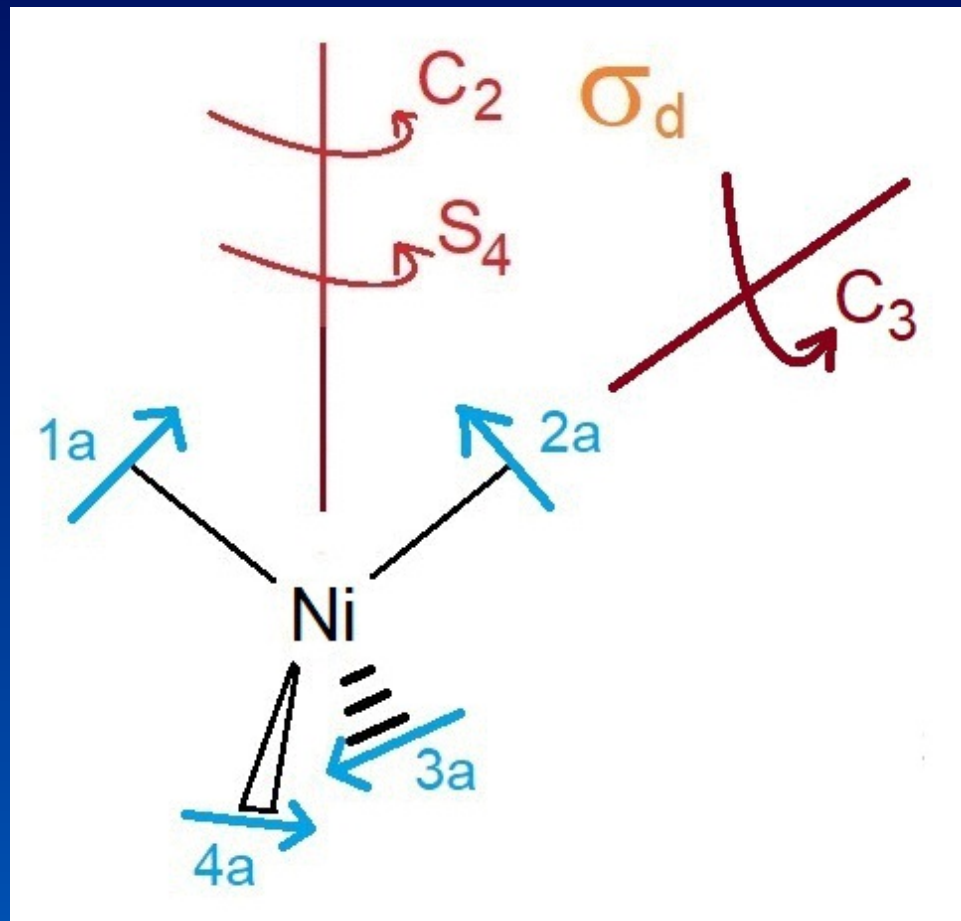
$[\text{NiCl}_4]^{2-} - \text{T}_d$

Classificando os orbitais $p\pi$ dos ligantes cloreto -INSEPARÁVEIS

T_d	E	8C_3	3C_2	6S_4	$6\sigma_d$
A_1	1	1	1	1	1
A_2	1	1	1	-1	-1
E	2	-1	2	0	0
T_1	3	0	-1	1	-1
T_2	3	0	-1	-1	1
<hr/>					
$p\pi(1 \text{ a } 8)$	8		0	0	0

$[\text{NiCl}_4]^{2-} - T_d$

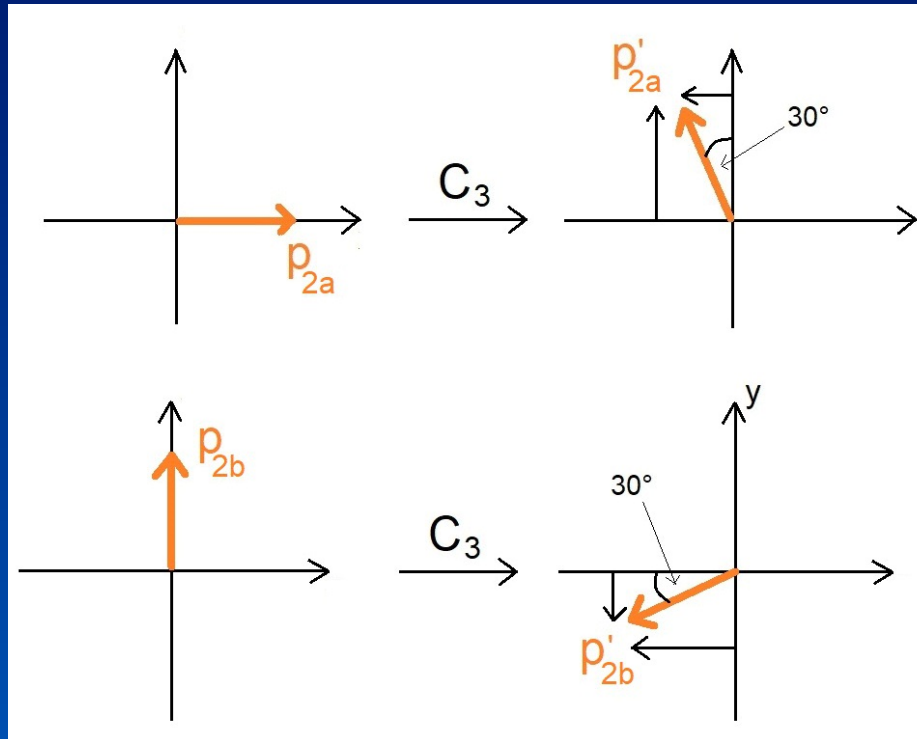
Classificando os orbitais $p\pi$ dos ligantes cloreto -INSEPARÁVEIS



$[\text{NiCl}_4]^{2-} - T_d$

Os orbitais p_{2a} e p_{2b} do Cl são **INSEPARÁVEIS**

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



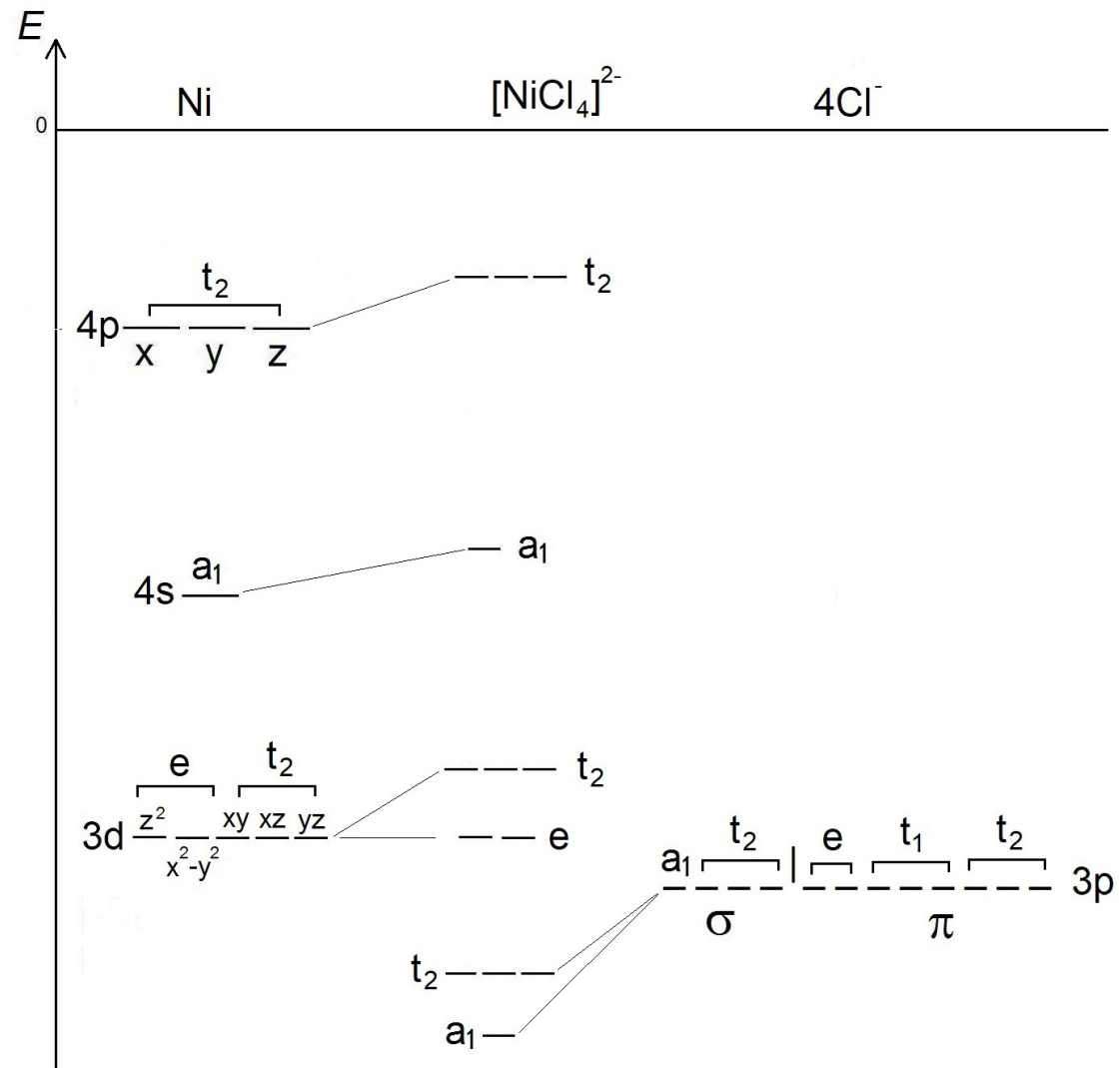
[NiCl₄]²⁻ - T_d

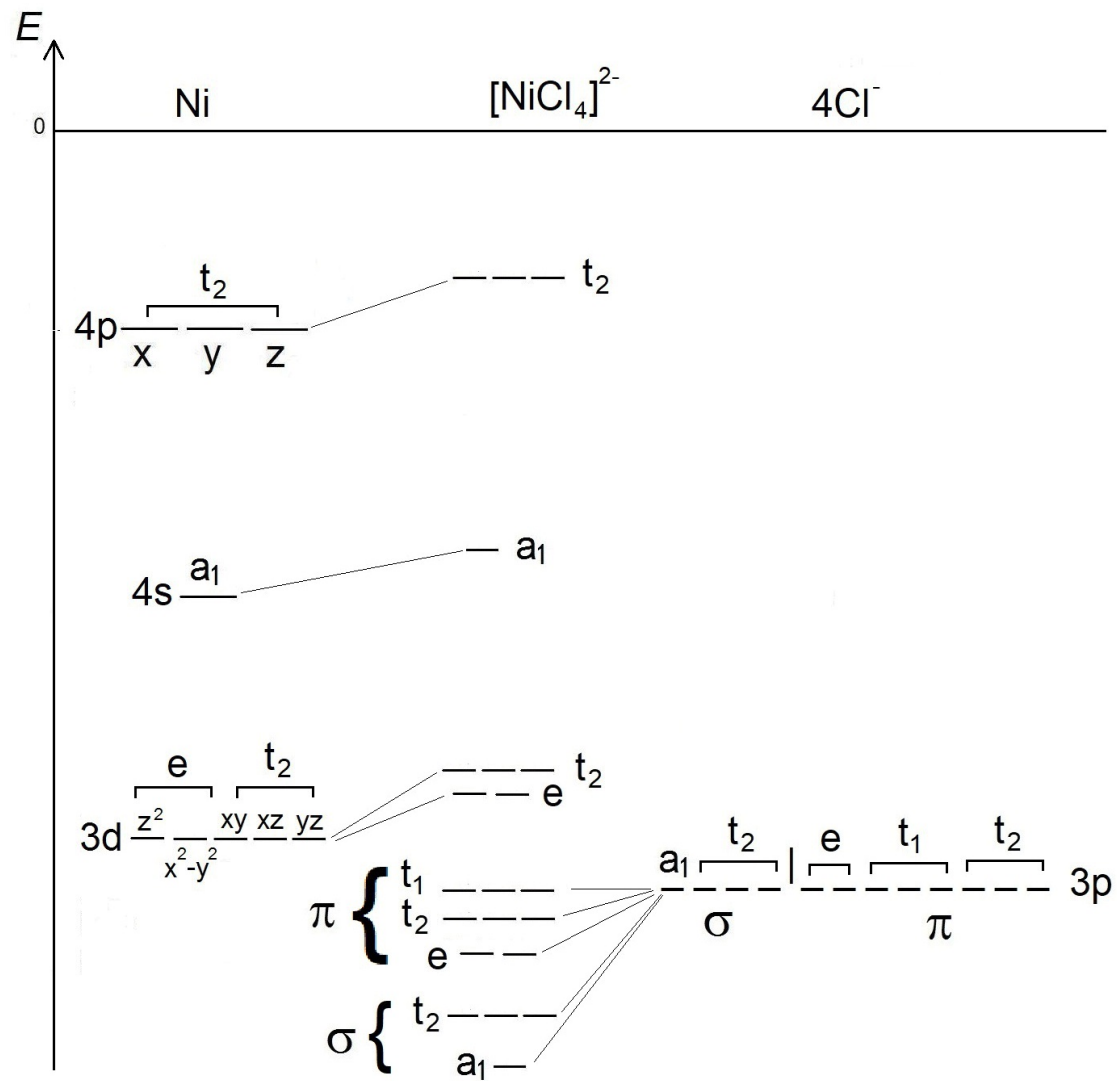
Os orbitais p_{2a} e p_{2b} do Cl são **INSEPARÁVEIS**

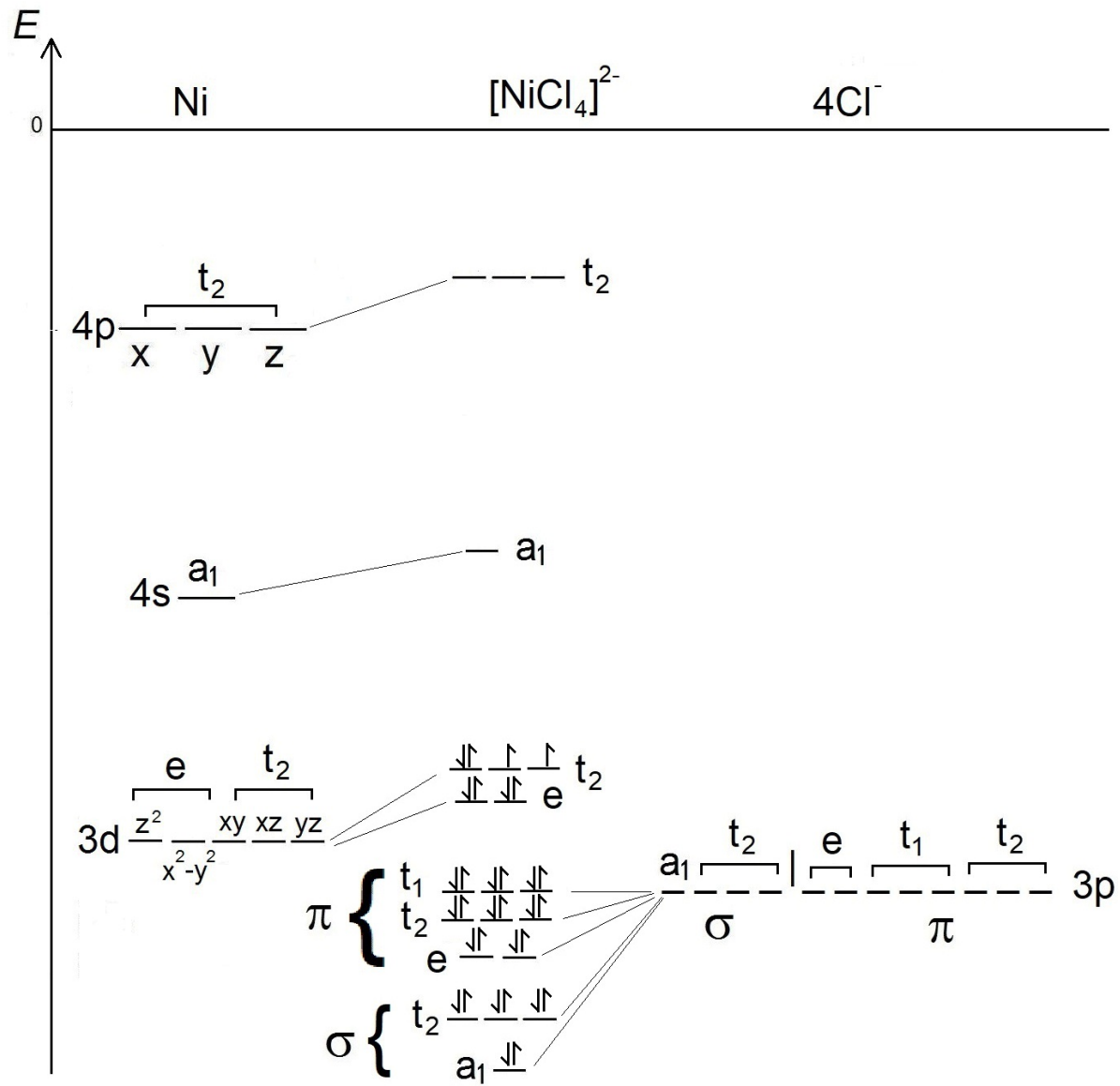
$$\begin{array}{cc}
 & \begin{array}{cc} 2p_{2a} & 2p_{2b} \end{array} \\
 \begin{array}{c} 2p_{2a} \\ 2p_{2b} \end{array} & \begin{array}{cc} 1 & 0 \\ 0 & 1 \end{array}
 \end{array}
 \xrightarrow{C_3}
 \begin{array}{cc}
 & \begin{array}{cc} 2p_{2a}' & 2p_{2b}' \end{array} \\
 \begin{array}{c} 2p_{2a}' \\ 2p_{2b}' \end{array} & \begin{array}{cc} -1/2 & \sqrt{3}/2 \\ -\sqrt{3}/2 & -1/2 \end{array}
 \end{array}
 \chi = -1$$

T _d	E	8C ₃	3C ₂	6S ₄	6σ _d
A ₁	1	1	1	1	1
A ₂	1	1	1	-1	-1
E	2	-1	2	0	0
T ₁	3	0	-1	1	-1
T ₂	3	0	-1	-1	1

$$\begin{array}{cccccc}
 p\pi(1 \text{ a } 8) & 8 & -1 & 0 & 0 & 0
 \end{array}
 \quad E + T_1 + T_2$$







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