Organometálicos 2

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Aula 11 -Organometálicos
Simetria T_d
$[NiCl_4]^{2-}$ ⇨ $[Ni(CO)_4]$

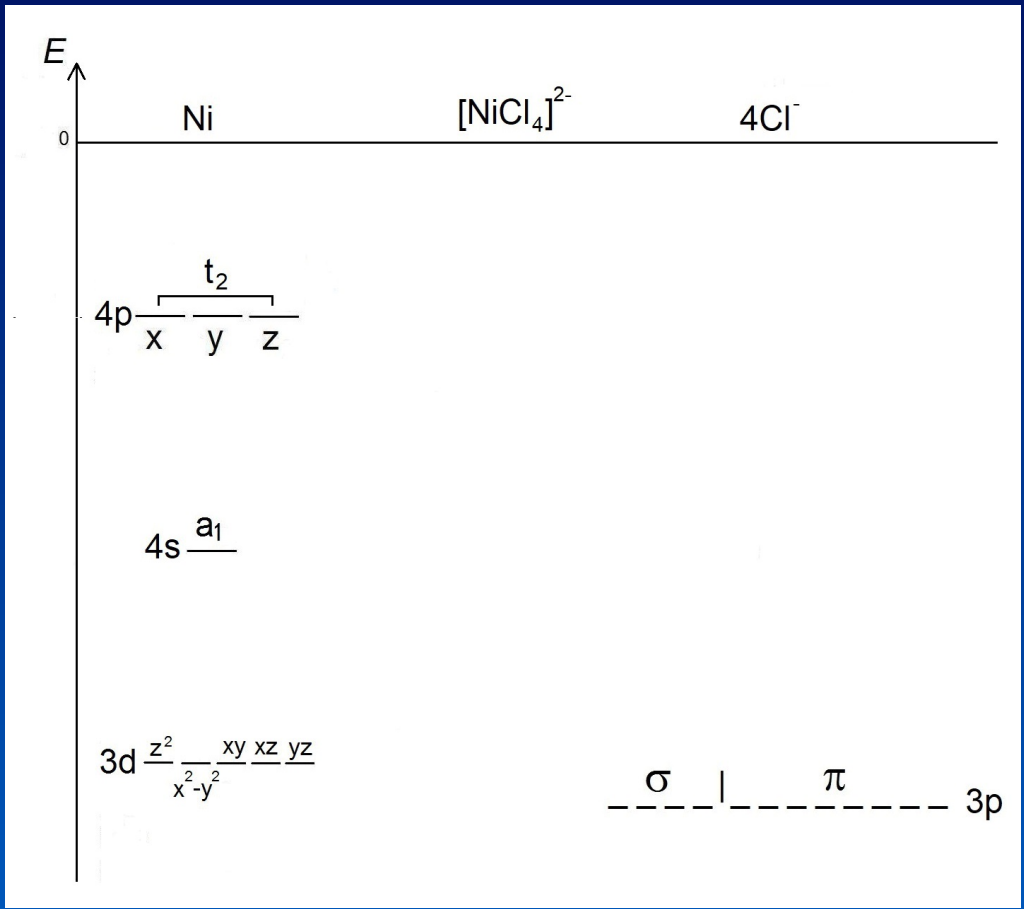
12/06/2024

$[NiCl_4]^{2-}$ - 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

$[NiCl_4]^{2-}$ - T_d

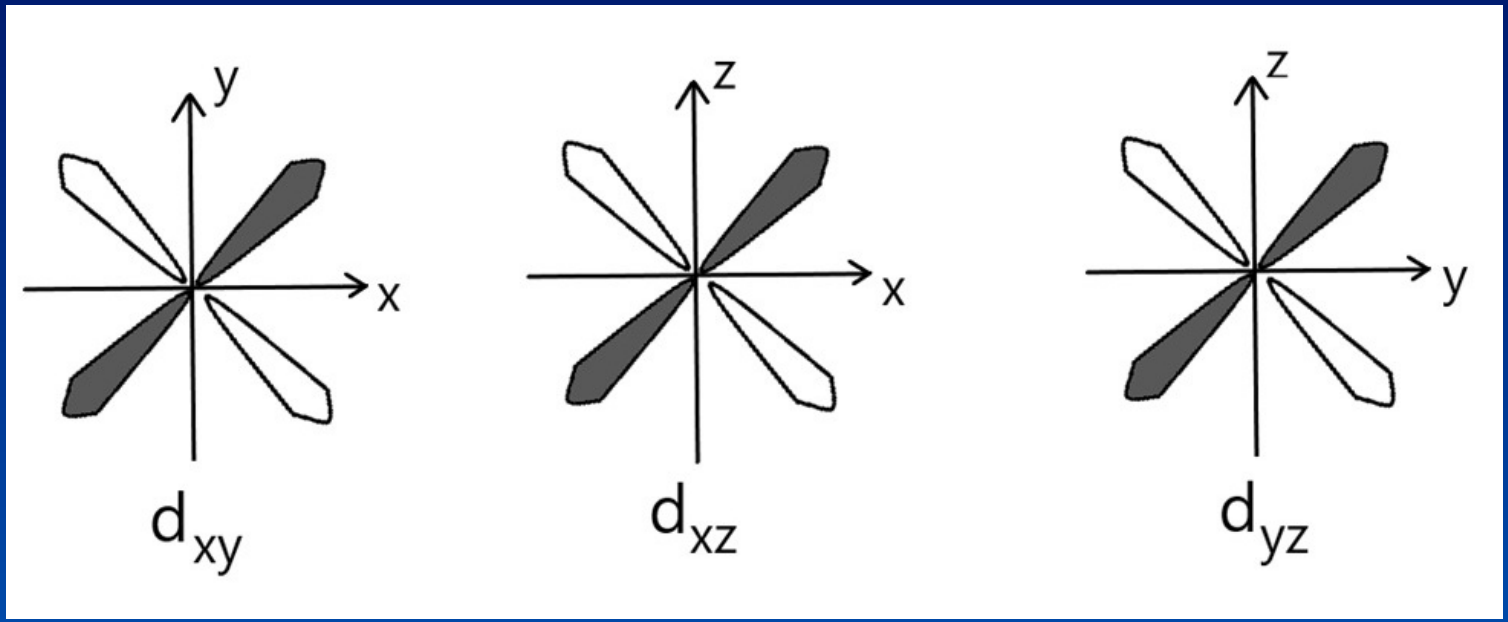
Diagrama de energia dos orbitais moleculares



Aproveitando os resultados do metano, T_d

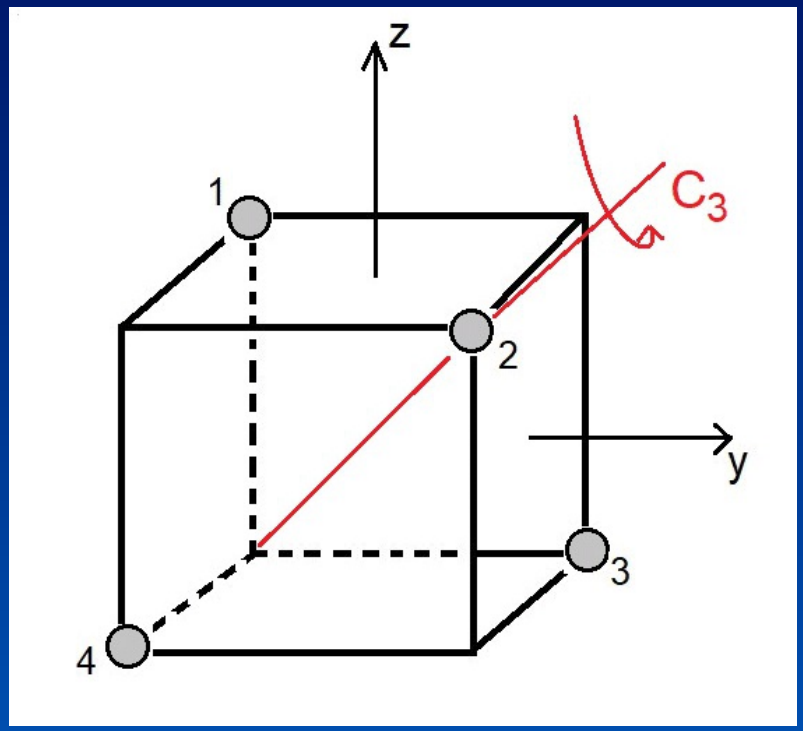
$[NiCl_4]^{2-}$ - T_d

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



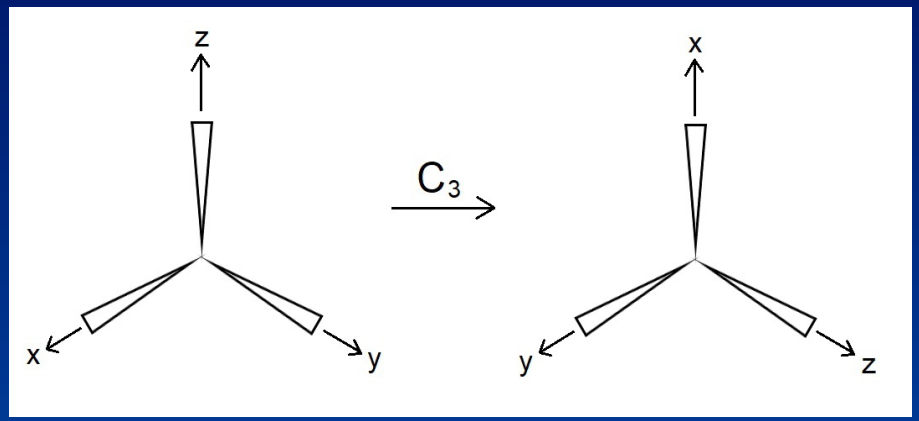
$[NiCl_4]^{2-}$ - T_d

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



$[NiCl_4]^{2-}$ - T_d

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



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

$[NiCl_4]^{2-}$ - T_d

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

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

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

	d_{xy}	d_{xz}	d_{yz}
d_{xy}	1	0	0
d_{xz}	0	1	0
d_{yz}	0	0	1

$C_3 \rightarrow$

	d_{xy}	d_{xz}	d_{yz}
d_{xy}	0	1	0
d_{xz}	0	0	1
d_{yz}	1	0	0

$\chi = 0$

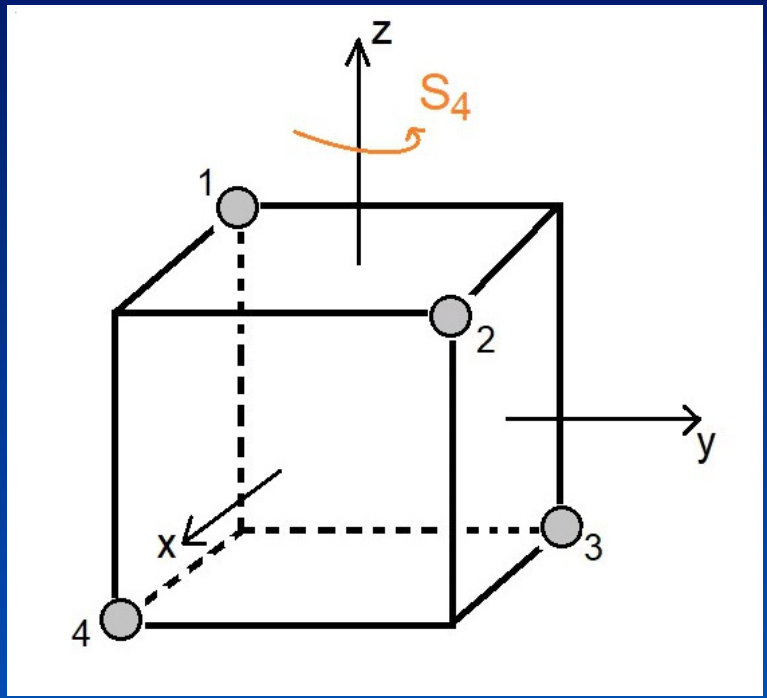
$[NiCl_4]^{2-}$ - T_d

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			

$[NiCl_4]^{2-}$ - T_d

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



$x - {}^{(z)}S_4 \rightarrow y$

$y - {}^{(z)}S_4 \rightarrow -x$

$z - {}^{(z)}S_4 \rightarrow -z$

$[NiCl_4]^{2-}$ - T_d

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

$x - {}^{(z)}S_4 \rightarrow y$

$y - {}^{(z)}S_4 \rightarrow -x$

$z - {}^{(z)}S_4 \rightarrow -z$

$d_{xy} - {}^{(z)}S_4 \rightarrow d_{y(-x)} = -d_{xy}$

$d_{xz} - {}^{(z)}S_4 \rightarrow d_{y(-z)} = -d_{yz}$

$d_{yz} - {}^{(z)}S_4 \rightarrow d_{(-x)(-z)} = d_{xz}$

	d_{xy}	d_{xz}	d_{yz}
d_{xy}	1	0	0
d_{xz}	0	1	0
d_{yz}	0	0	1

$\xrightarrow{{}^{(z)}S_4}$

	d_{xy}	d_{xz}	d_{yz}
d_{xy}	-1	0	0
d_{xz}	0	0	-1
d_{yz}	0	1	0

$\chi = -1$

$[NiCl_4]^{2-}$ - T_d

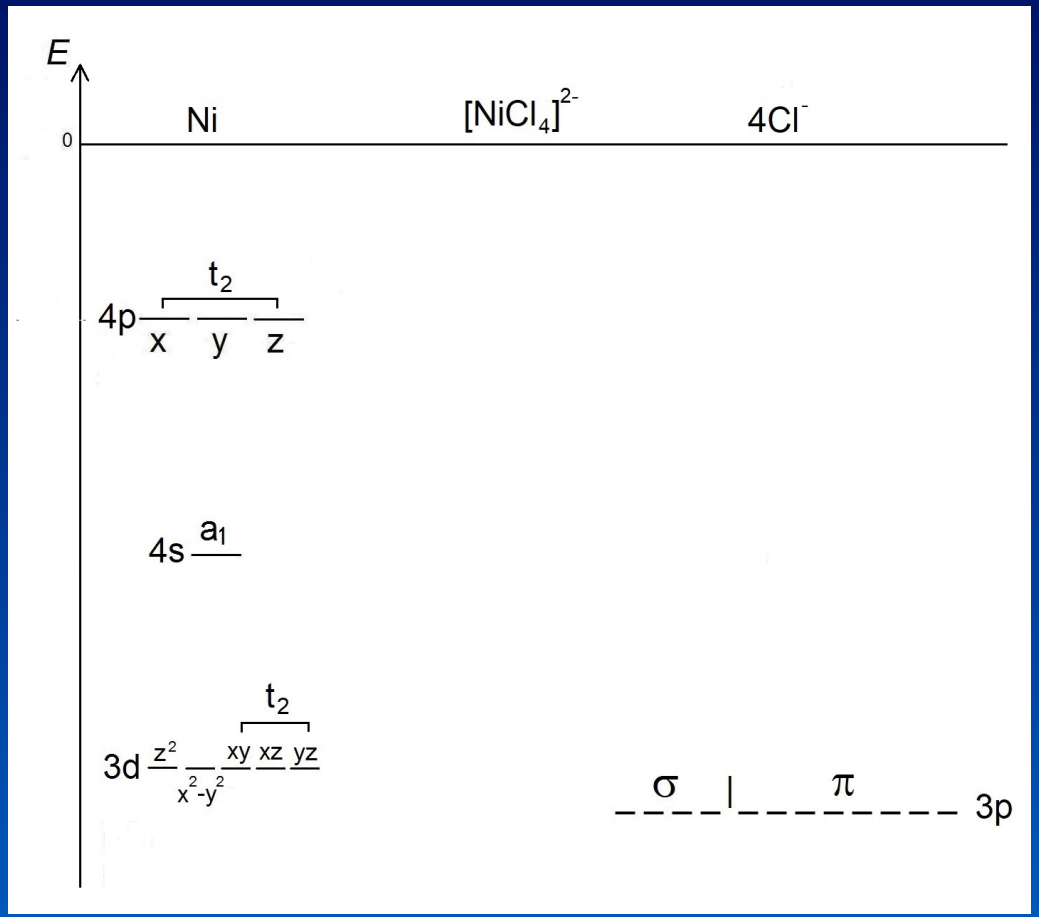
Classificando os orbitais 3d (xy,xz,yz) do Ni -INSEPARÁVEIS

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

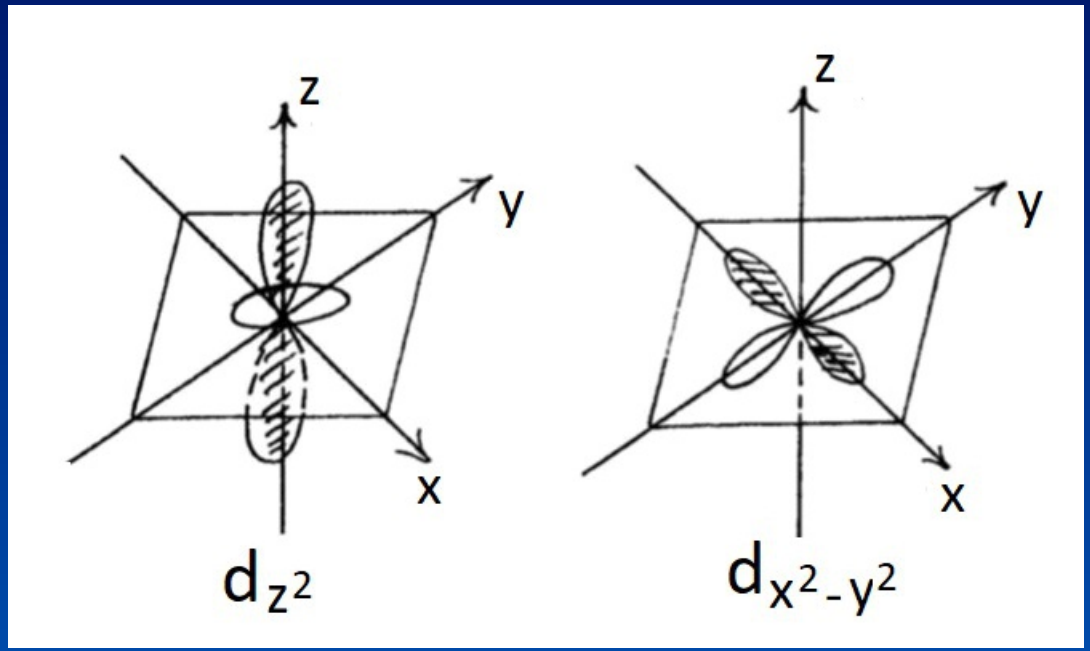
$[NiCl_4]^{2-}$ - T_d

Diagrama de energia dos orbitais moleculares



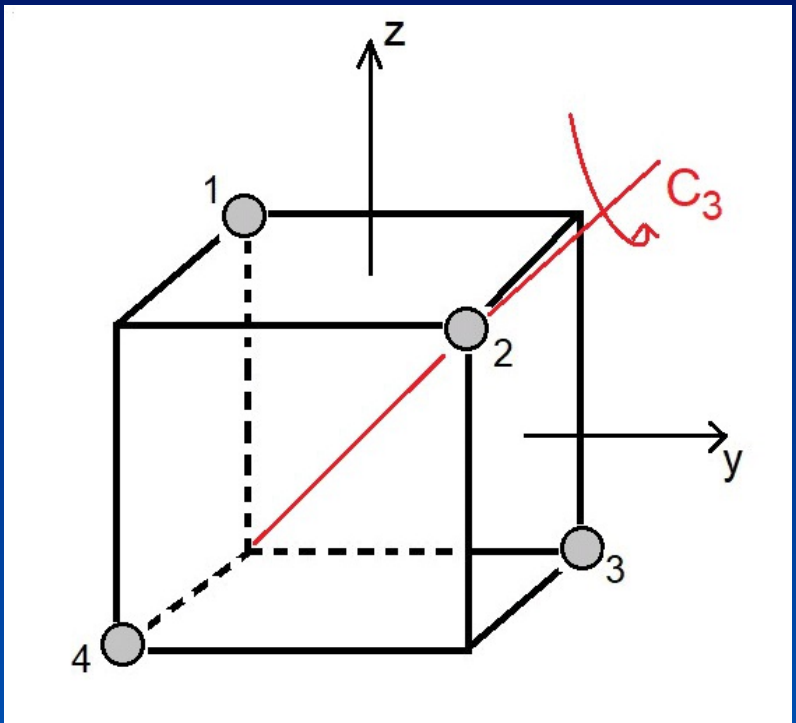
$[NiCl_4]^{2-}$ - T_d

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



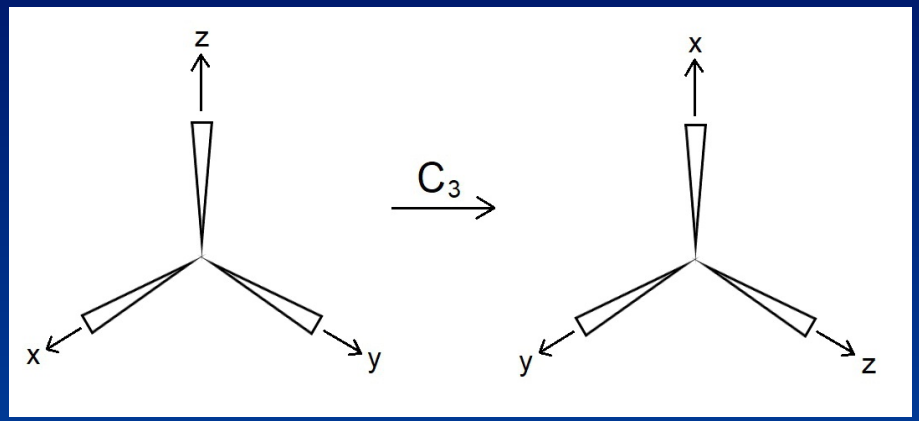
$[NiCl_4]^{2-}$ - T_d

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



$[NiCl_4]^{2-}$ - T_d

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



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

$[NiCl_4]^{2-}$ - T_d

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

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

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

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

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

$[NiCl_4]^{2-}$ - T_d

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

Pode-se mostrar que os novos orbitais d_{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}:

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

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

$[NiCl_4]^{2-}$ - T_d

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

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

$[NiCl_4]^{2-}$ - T_d

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

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

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

$[NiCl_4]^{2-}$ - T_d

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

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

$[NiCl_4]^{2-}$ - T_d

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

$\chi = -1$

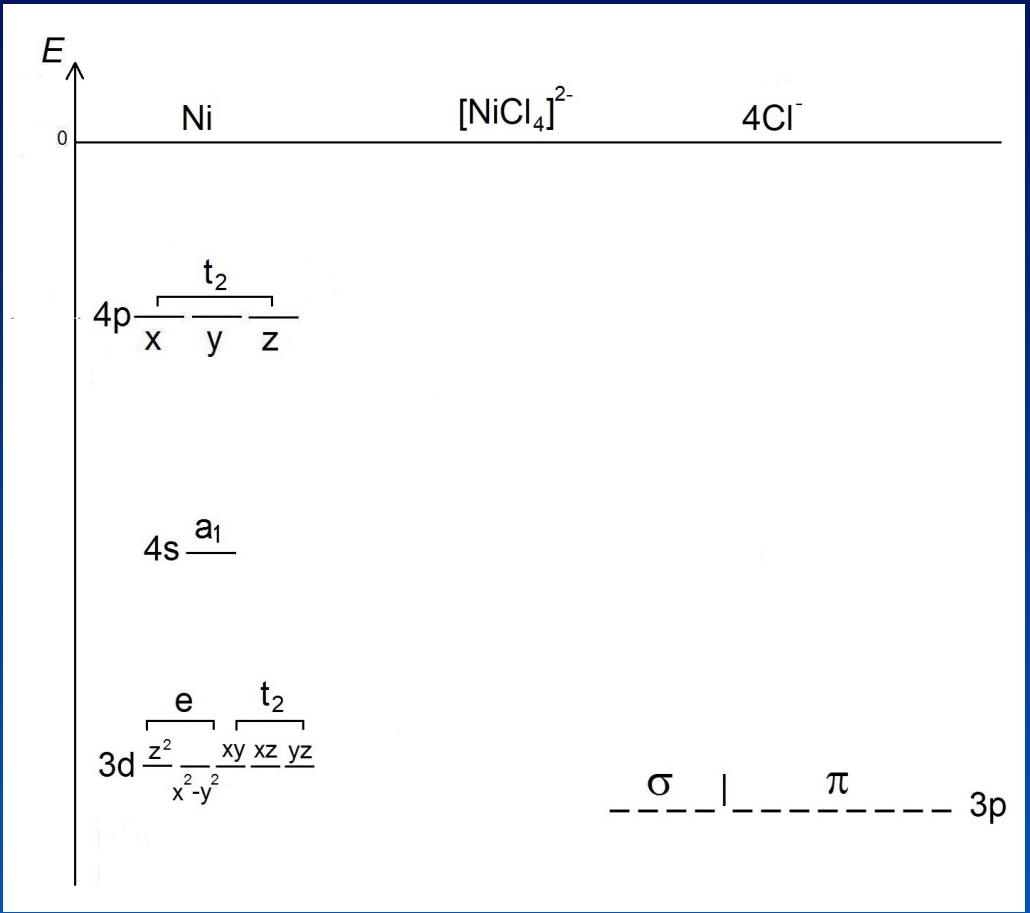
$[NiCl_4]^{2-}$ - T_d

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	
$(d_{z2,x2-y2})$	2	-1				E

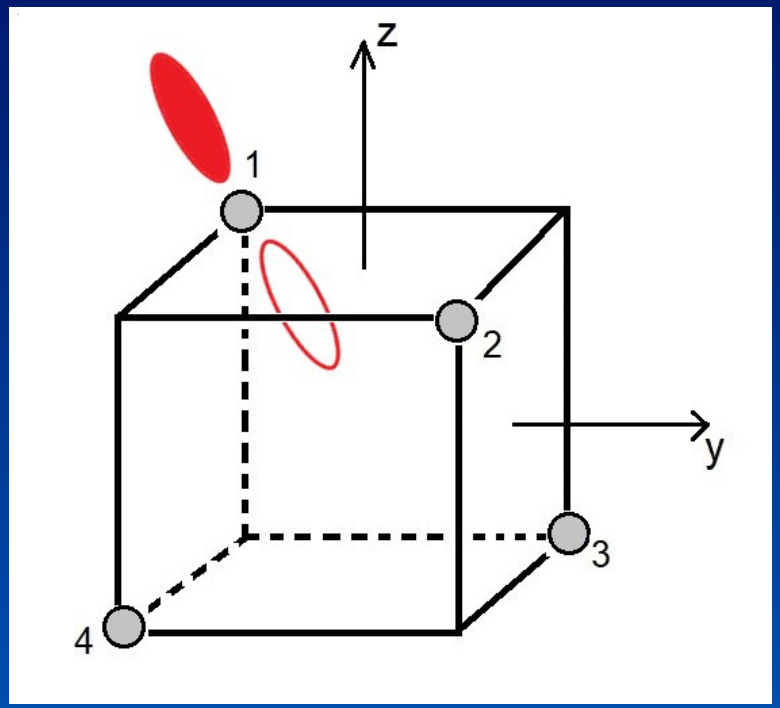
$[NiCl_4]^{2-}$ - T_d

Diagrama de energia dos orbitais moleculares



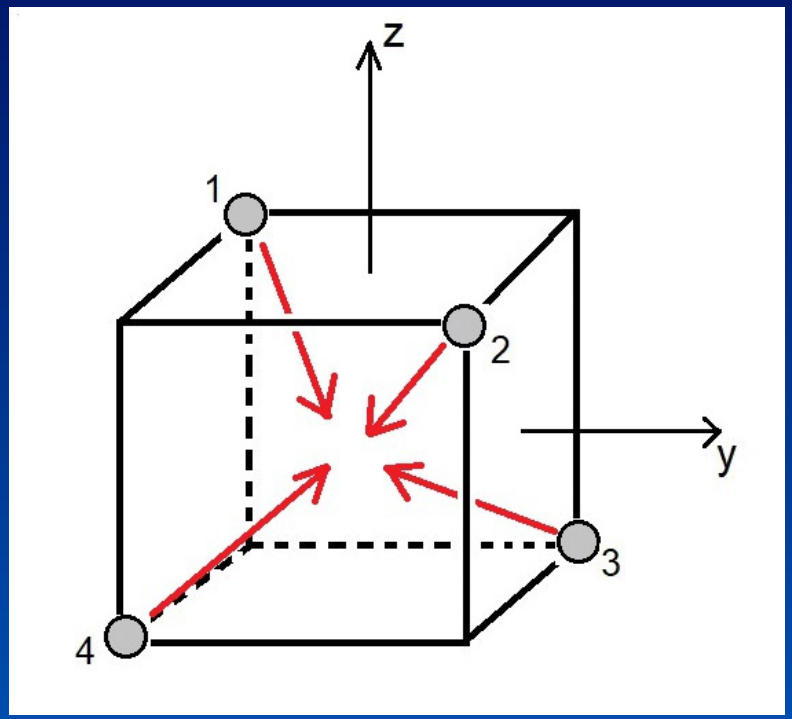
$[NiCl_4]^{2-}$ - T_d

Classificando os orbitais pσ dos ligantes cloreto -INSEPARÁVEIS



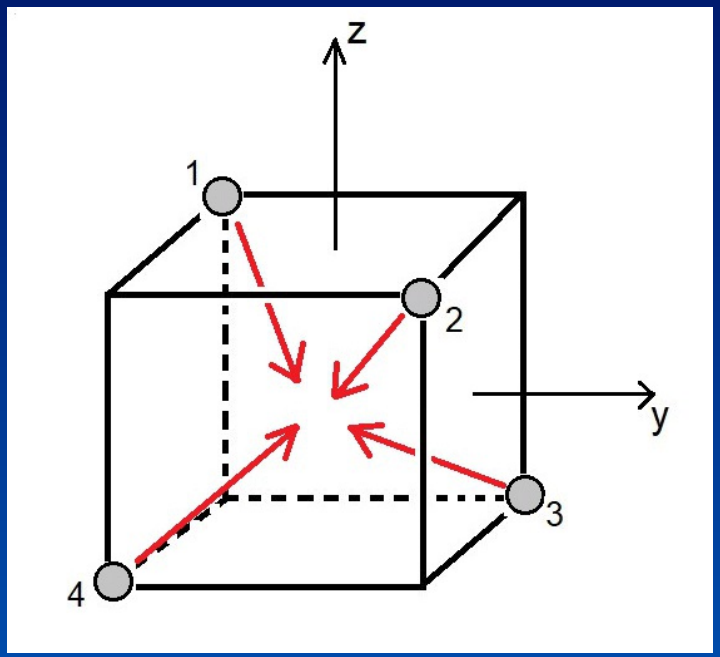
$[NiCl_4]^{2-}$ - T_d

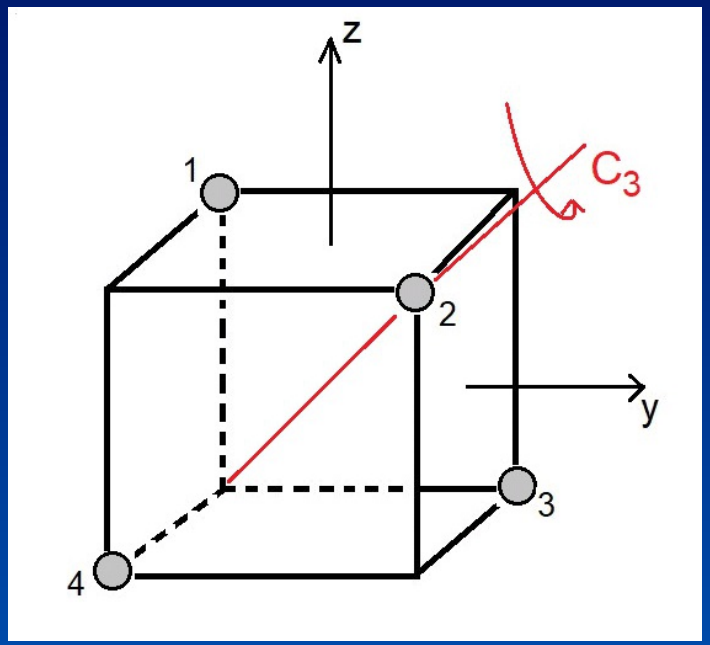
Classificando os orbitais pσ dos ligantes cloreto -INSEPARÁVEIS



$[NiCl_4]^{2-}$ - T_d

Classificando os orbitais pσ dos ligantes cloreto -INSEPARÁVEIS





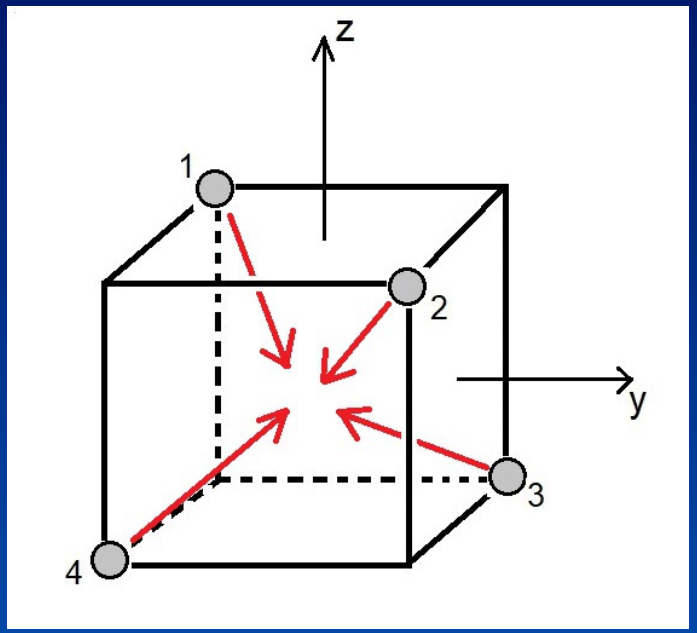
$[NiCl_4]^{2-}$ - T_d

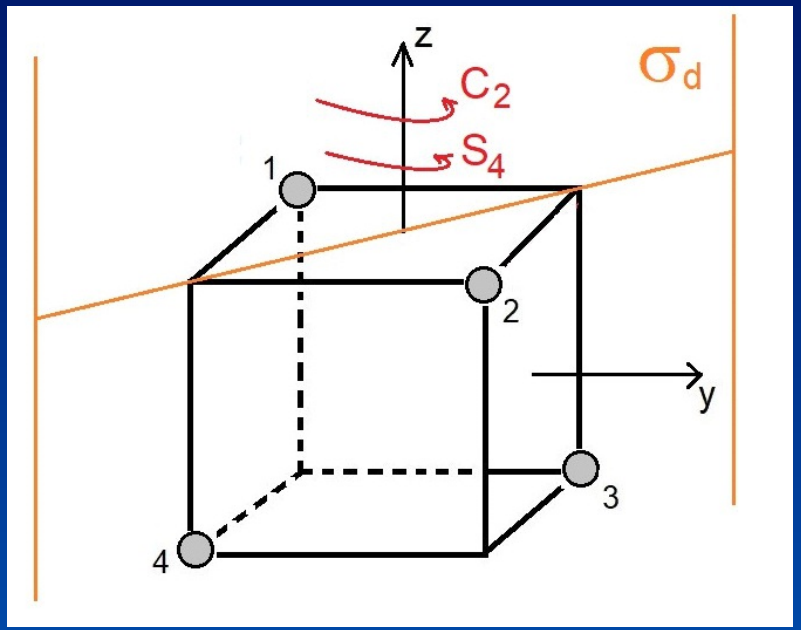
Classificando os orbitais pσ dos ligantes cloreto -INSEPARÁVEIS

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			

$[NiCl_4]^{2-}$ - T_d

Classificando os orbitais pσ dos ligantes cloreto -INSEPARÁVEIS





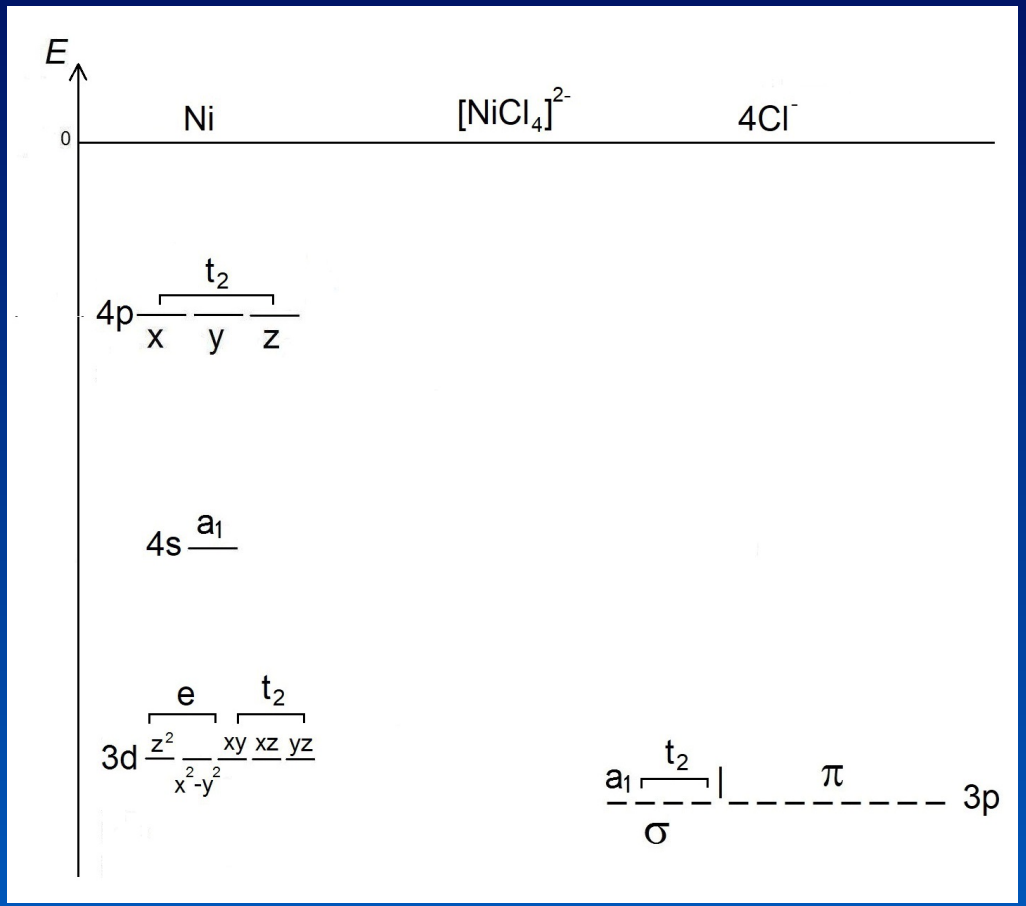
$[NiCl_4]^{2-}$ - T_d

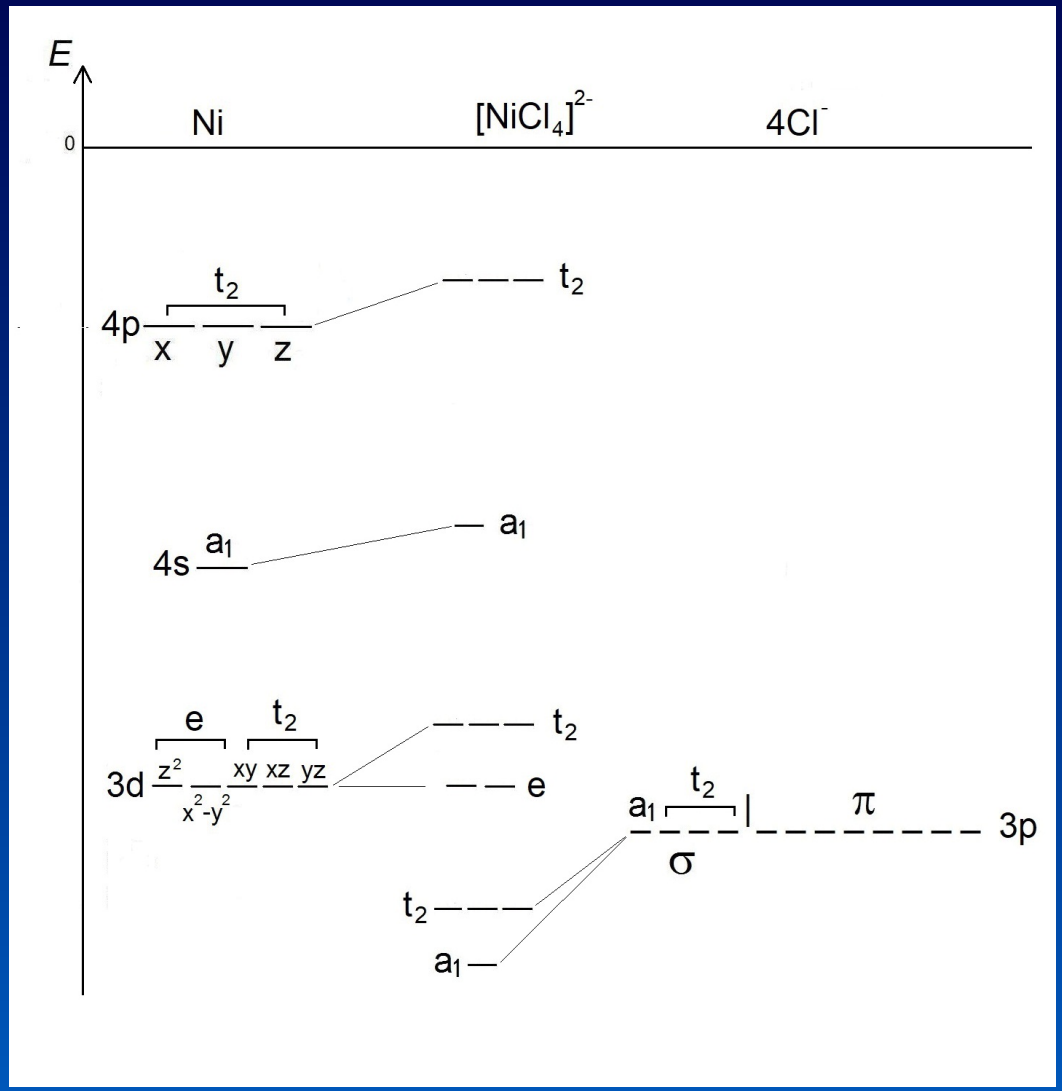
Classificando os orbitais pσ dos ligantes cloreto -INSEPARÁVEIS

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	0	0	2	$A_1 + T_2$

$[NiCl_4]^{2-}$ - T_d

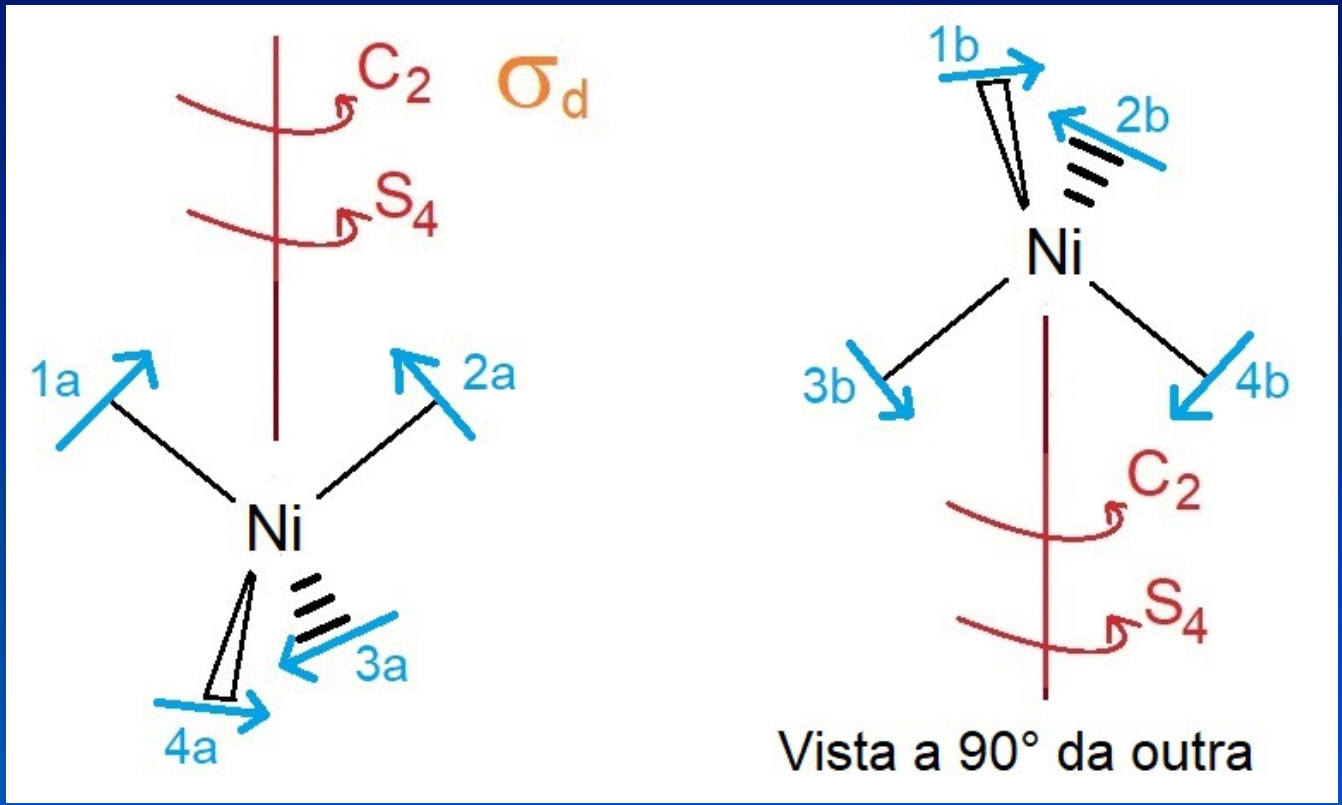
Diagrama de energia dos orbitais moleculares




E
0
Ni
[NiCl4]2-
4Cl-
4p
t2
x y z
t2
4s
a1
a1
3d
e
t2
z2
x2-y2
xy xz yz
t2
e
a1
t2
π
3p
σ
t2
a1

$[NiCl_4]^{2-}$ - T_d

Classificando os orbitais pπ dos ligantes cloreto -INSEPARÁVEIS



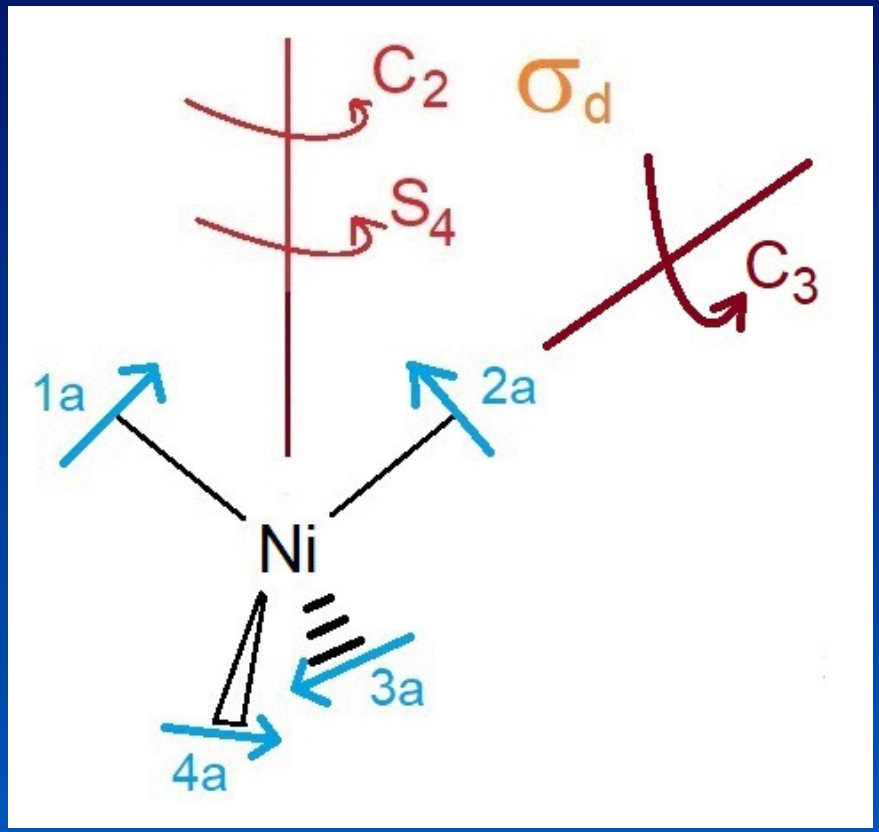
$[NiCl_4]^{2-}$ - T_d

Classificando os orbitais pπ 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
pπ(1 a 8)	8		0	0	0

$[NiCl_4]^{2-}$ - T_d

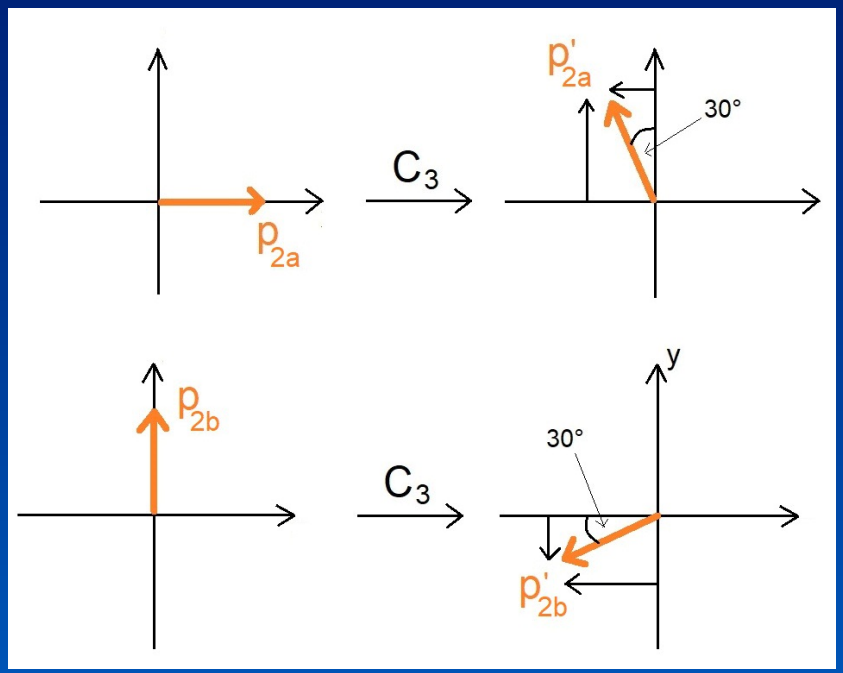
Classificando os orbitais pπ dos ligantes cloreto -INSEPARÁVEIS



$[NiCl_4]^{2-}$ - T_d

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

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



$[NiCl_4]^{2-}$ - T_d

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

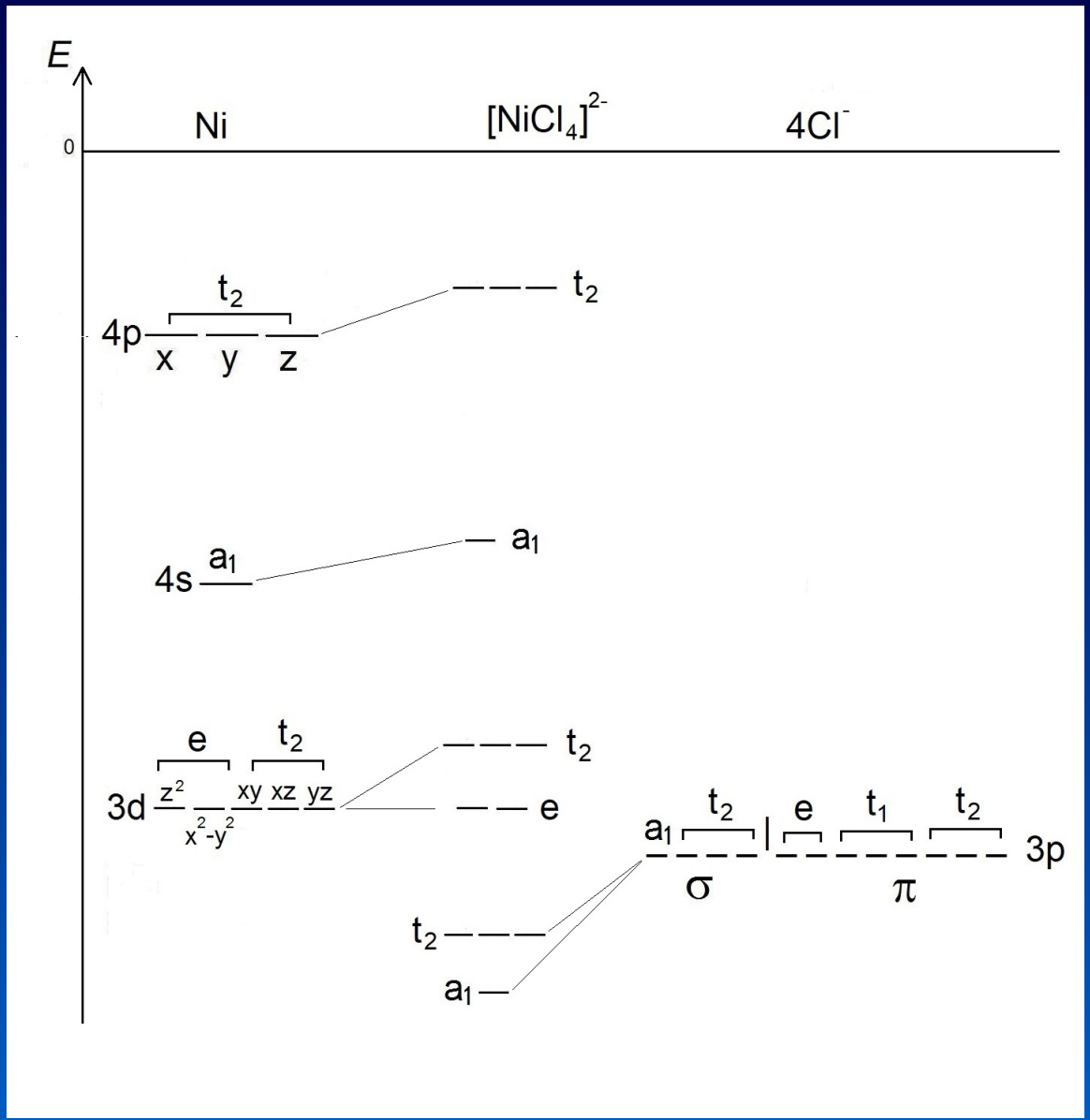
	$2p_{2a}$	$2p_{2b}$
$2p_{2a}$	1	0
$2p_{2b}$	0	1

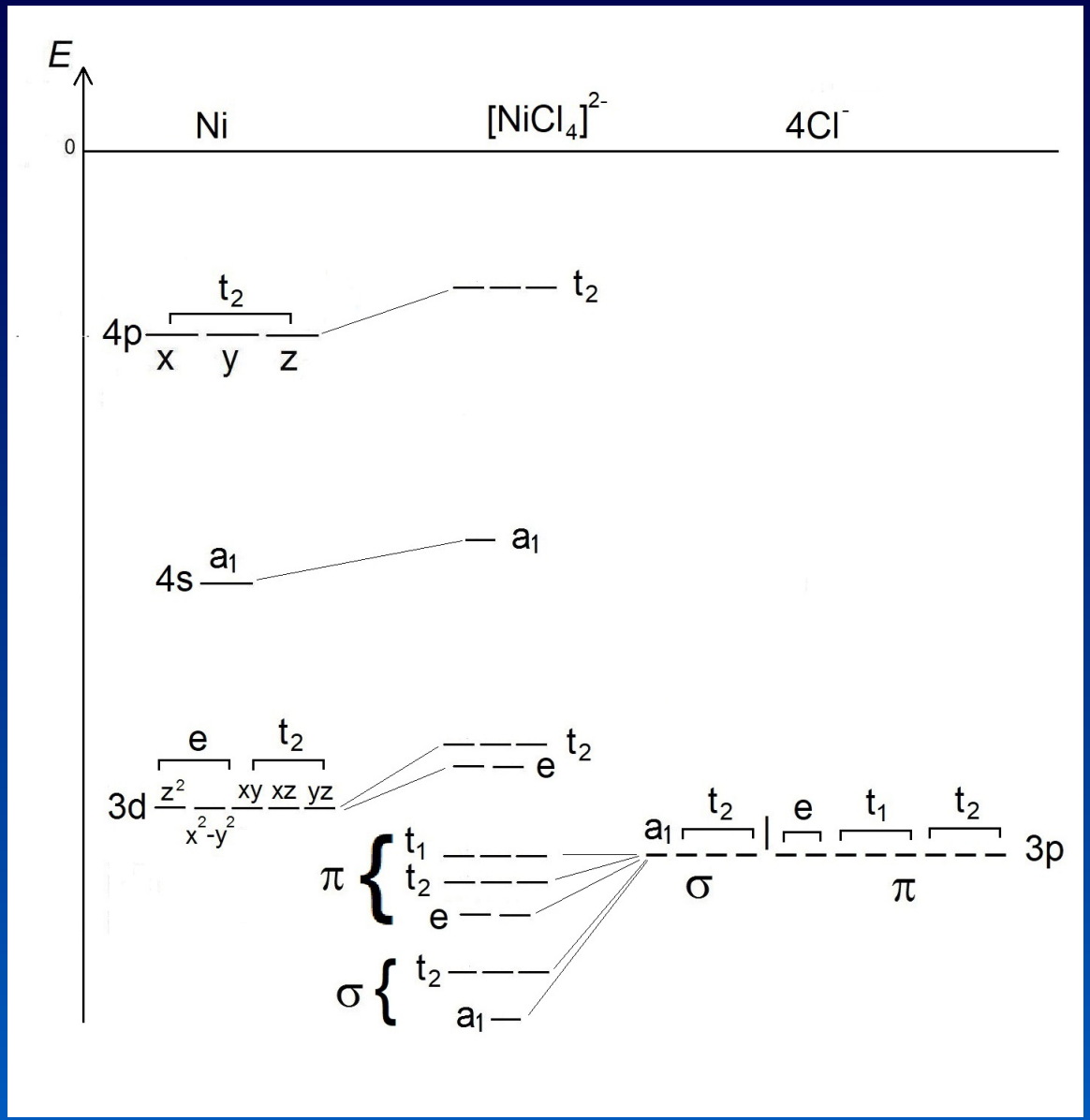
$C_3 \rightarrow$

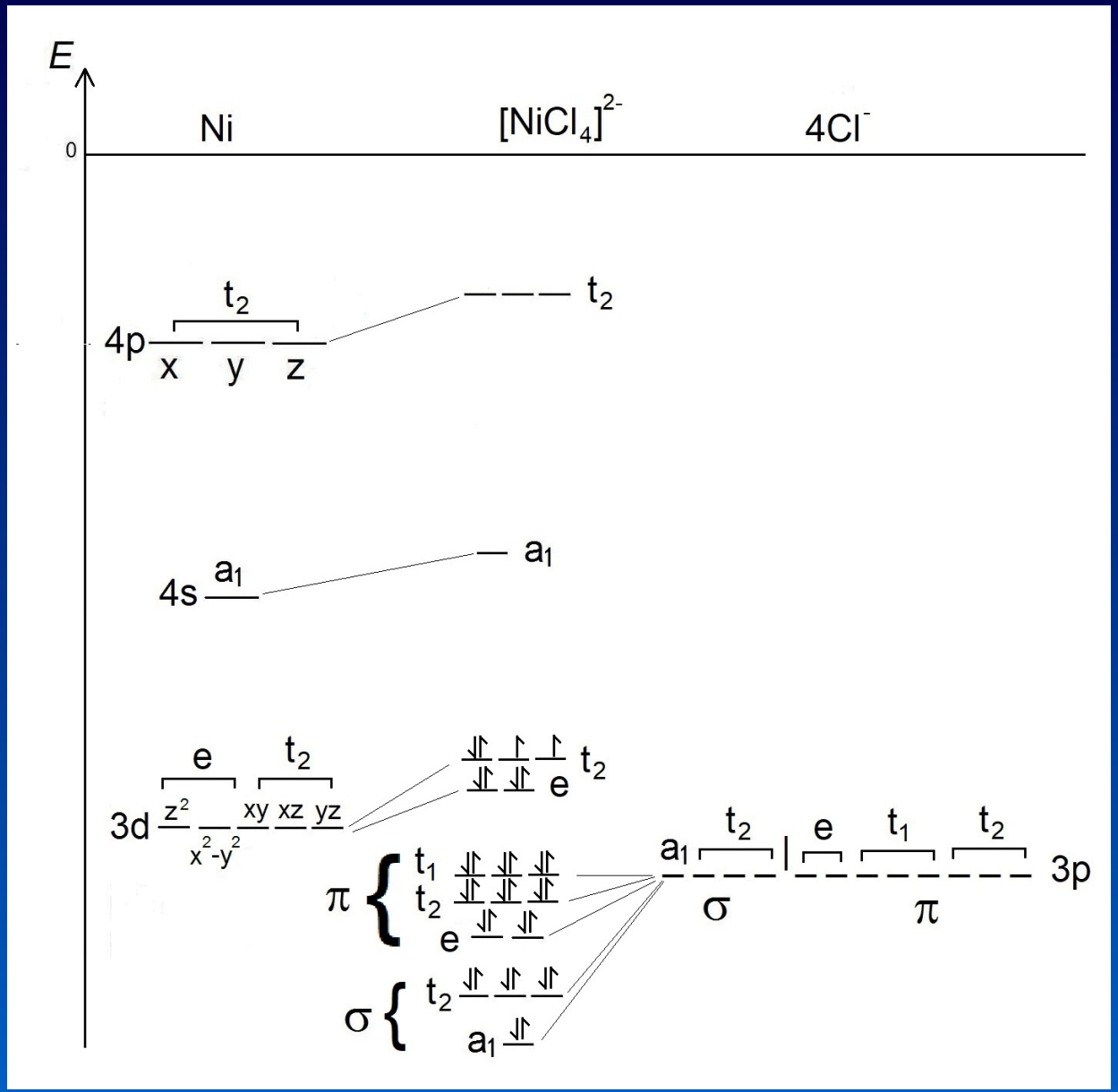
	$2p_{2a}$	$2p_{2b}$
$2p_{2a}'$	$-1/2$	$\sqrt{3}/2$
$2p_{2b}'$	$-\sqrt{3}/2$	$-1/2$

$\chi = -1$

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	
$p\pi(1 \text{ a } 8)$	8	-1	0	0	0	$E + T_1 + T_2$

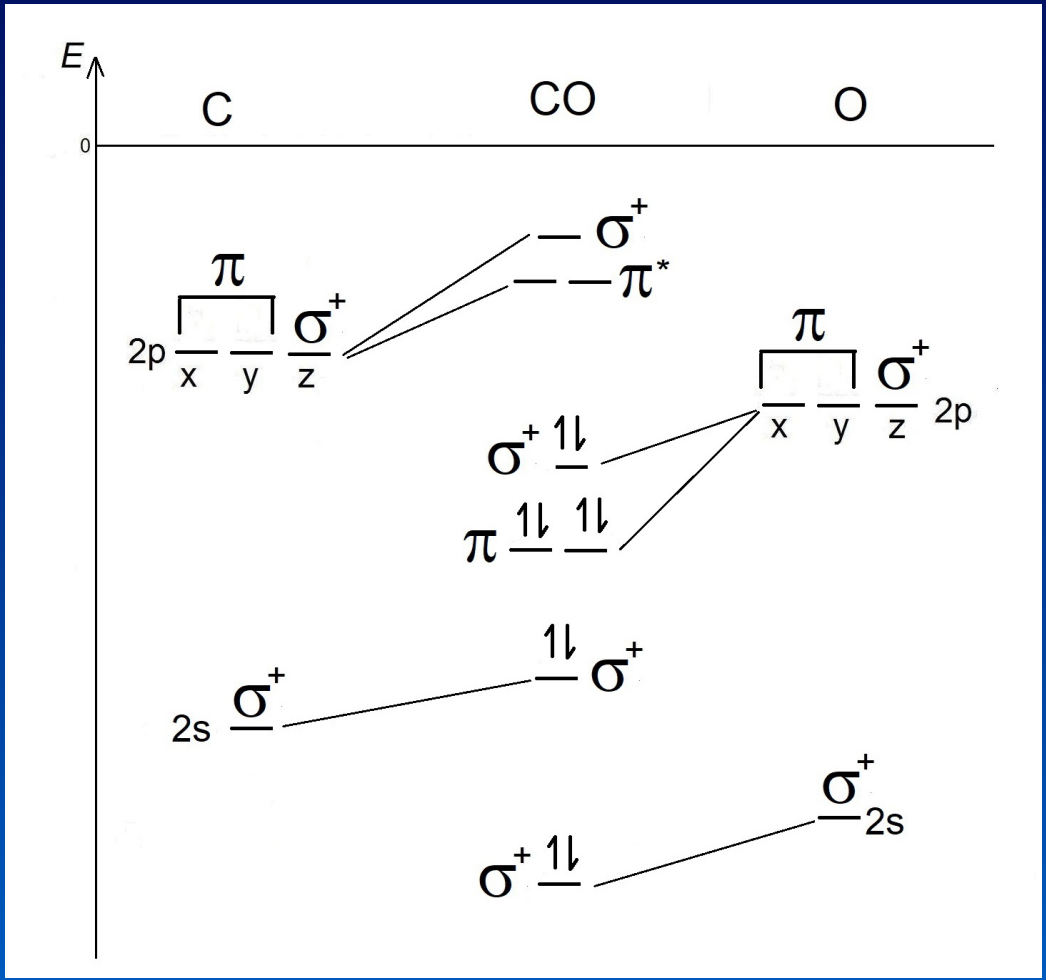

E
0
Ni
[NiCl4]2-
4Cl-
4p
t2
x
y
z
t2
4s
a1
a1
3d
e
t2
z2
x2-y2
xy
xz
yz
t2
e
t2
e
t1
t2
a1
3p
σ
π
t2
a1


E
0
Ni
$[NiCl_4]^{2-}$
$4Cl^-$
4p
t_2
x y z
t_2
4s
a_1
a_1
3d
e
t_2
z^2
x^2-y^2
xy xz yz
t_2
e
π
t_1
t_2
e
σ
t_2
a_1
a_1
t_2
e
t_1
t_2
σ
π
3p

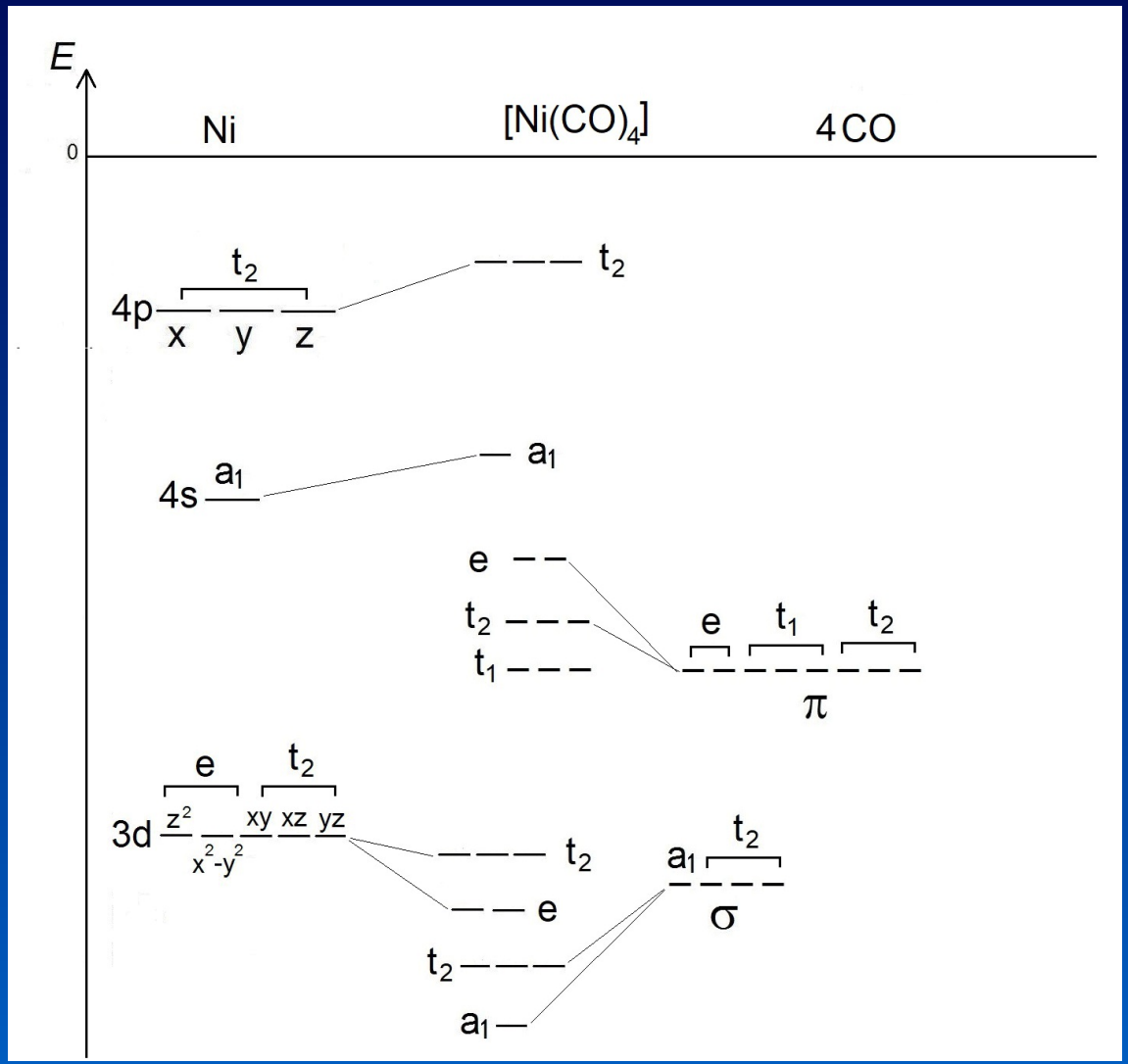

E
0
Ni
[NiCl4]2-
4Cl-
4p
t2
x y z
t2
4s
a1
a1
3d
e
t2
z2
x2-y2
xy xz yz
t2
e
π
t1
t2
e
σ
t2
a1
a1
t2
e
t1
t2
σ
π
3p

$[Ni(CO)_4]$- T_d

Diagrama de energia dos orbitais moleculares do CO

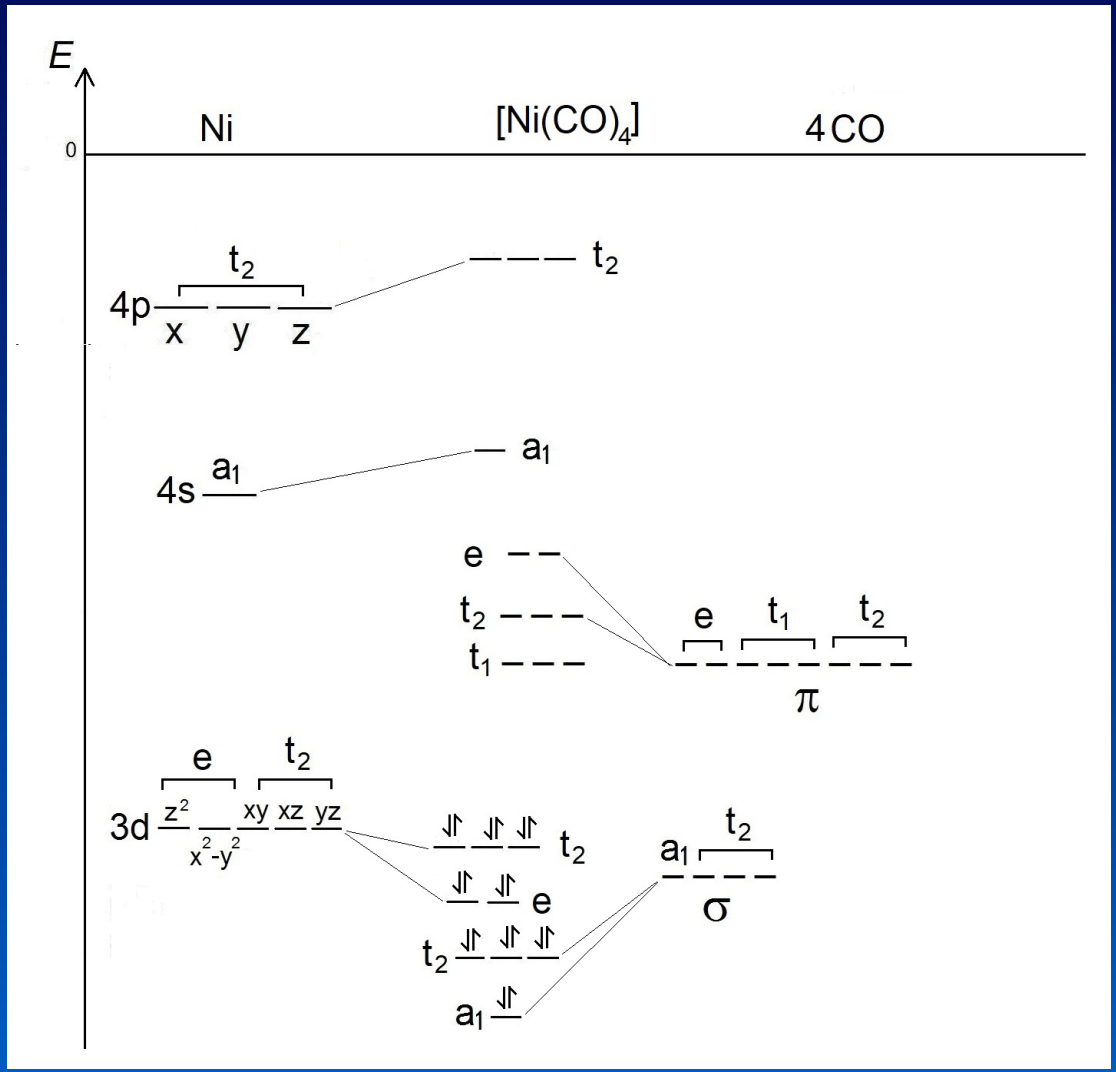


$[Ni(CO)_4]$- T_d



Aproveitando os resultados do $[NiCl_4]^{2-}$ T_d

$[Ni(CO)_4]$- T_d



18 elétrons

FIM