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

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Aula 2
Amônia e Metano

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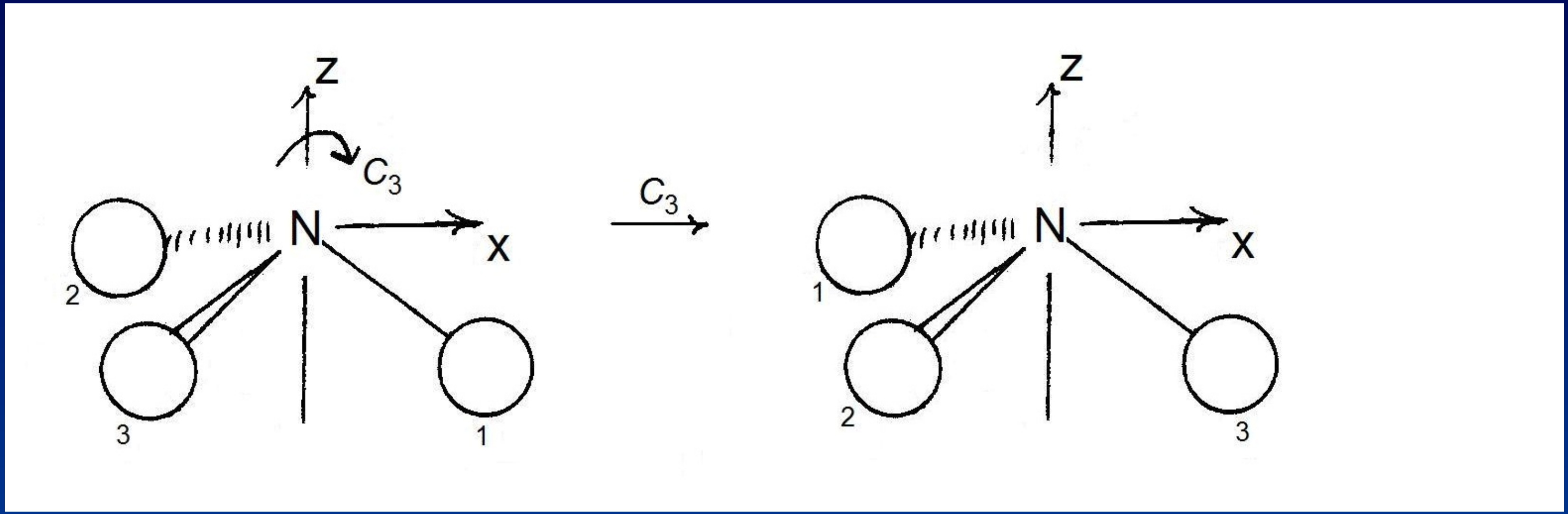
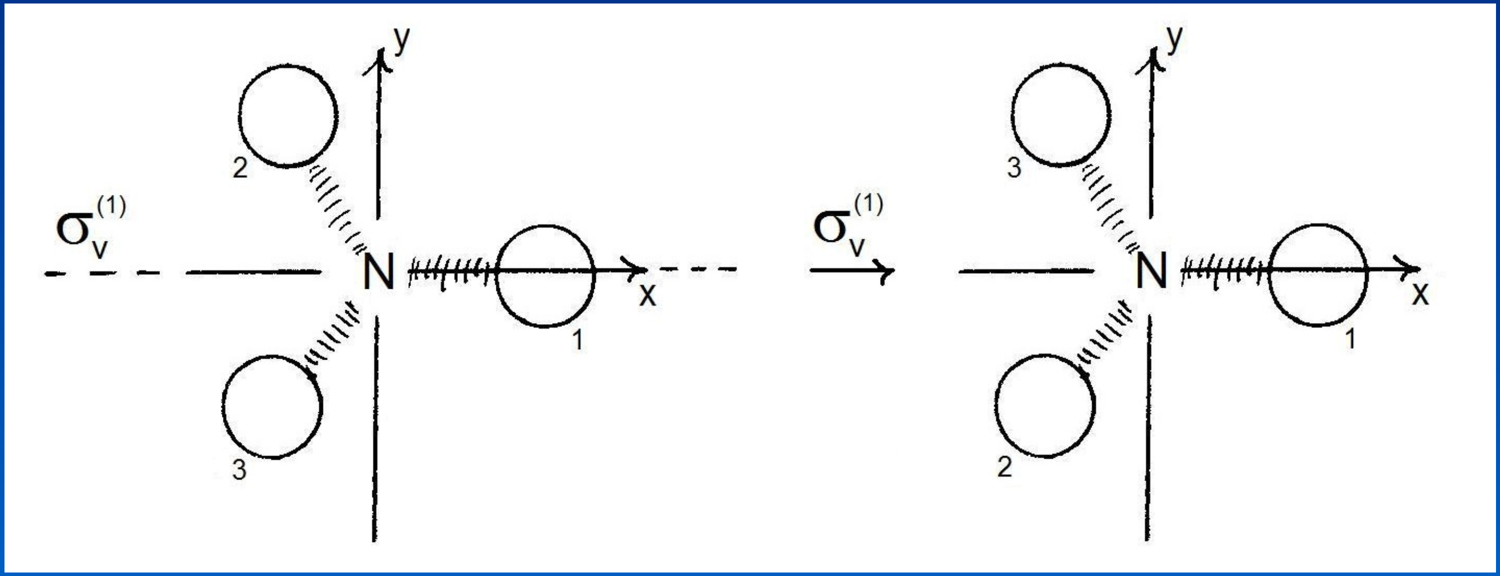
Amônia, NH_3 - C_{3v}

C_{3v}	E	$2C_3$	$3\sigma_v$
A_1	1	1	1
A_2	1	1	-1
E	2	-1	0

Amônia, NH_3 - C_{3v}

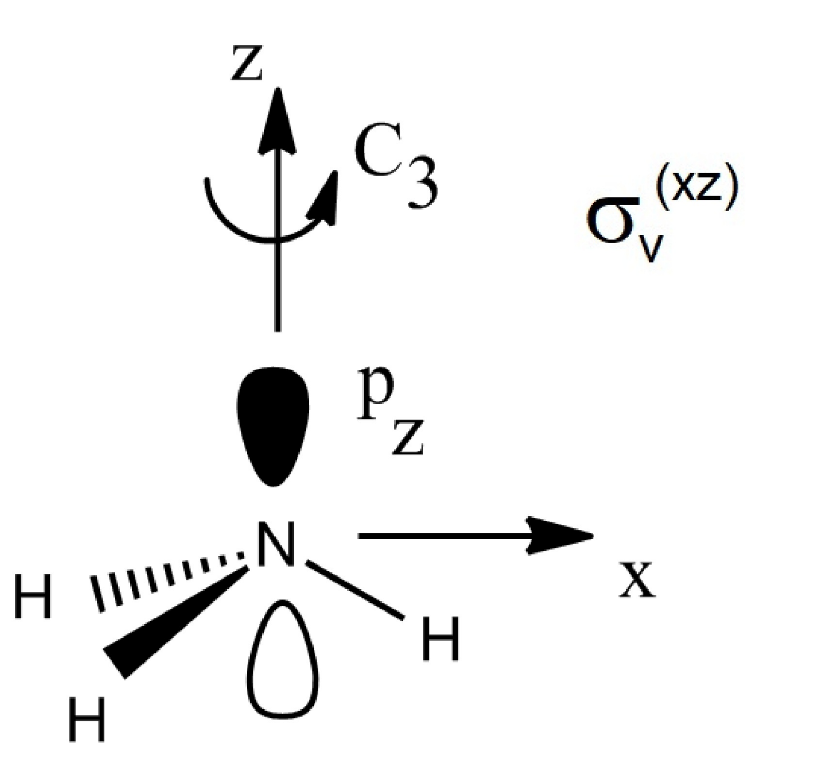




Amônia, NH_3 - C_{3v}

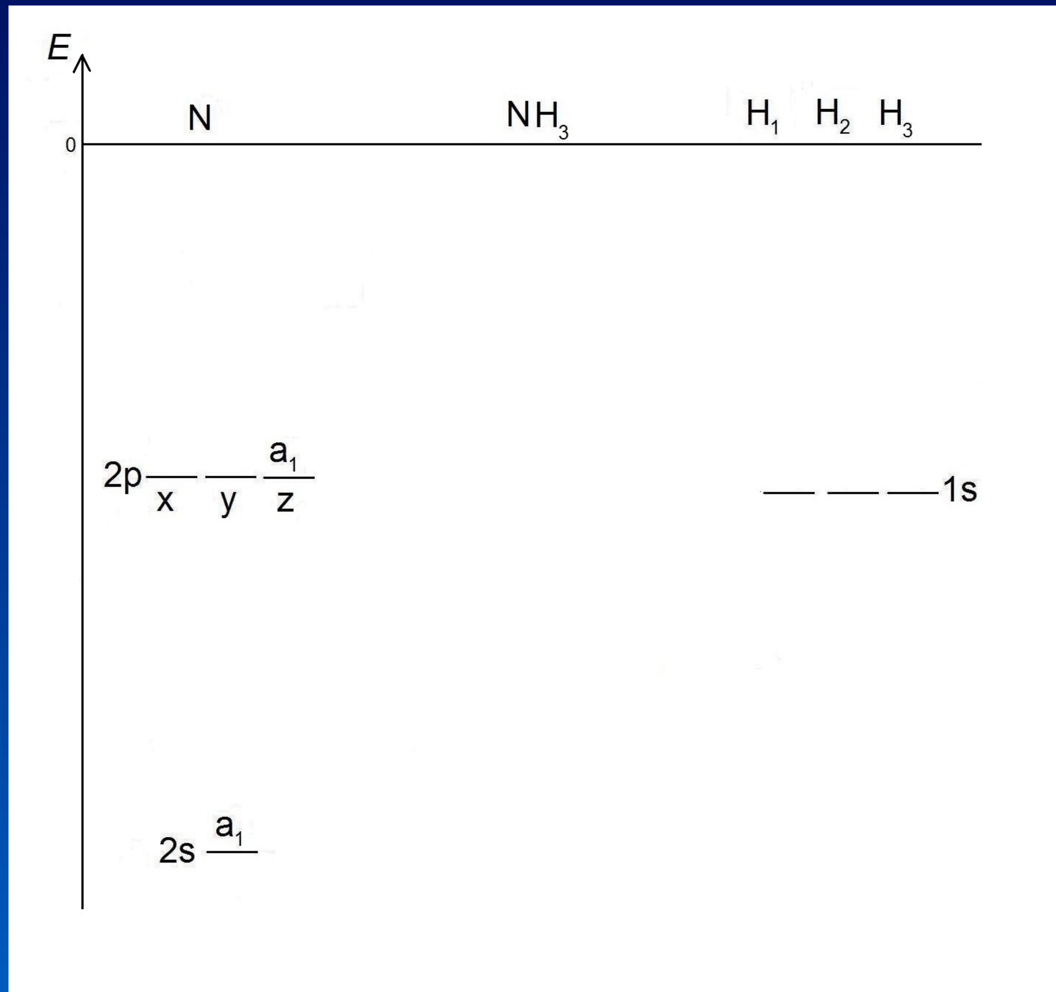
Classificando os orbitais 2s e $2p_z$ do N

C_{3v}	E	$2C_3$	$3\sigma_v$
A_1	1	1	1
A_2	1	1	-1
E	2	-1	0
2s	1	1	1
$2p_z$	1	1	1



Amônia, NH_3 - C_{3v}

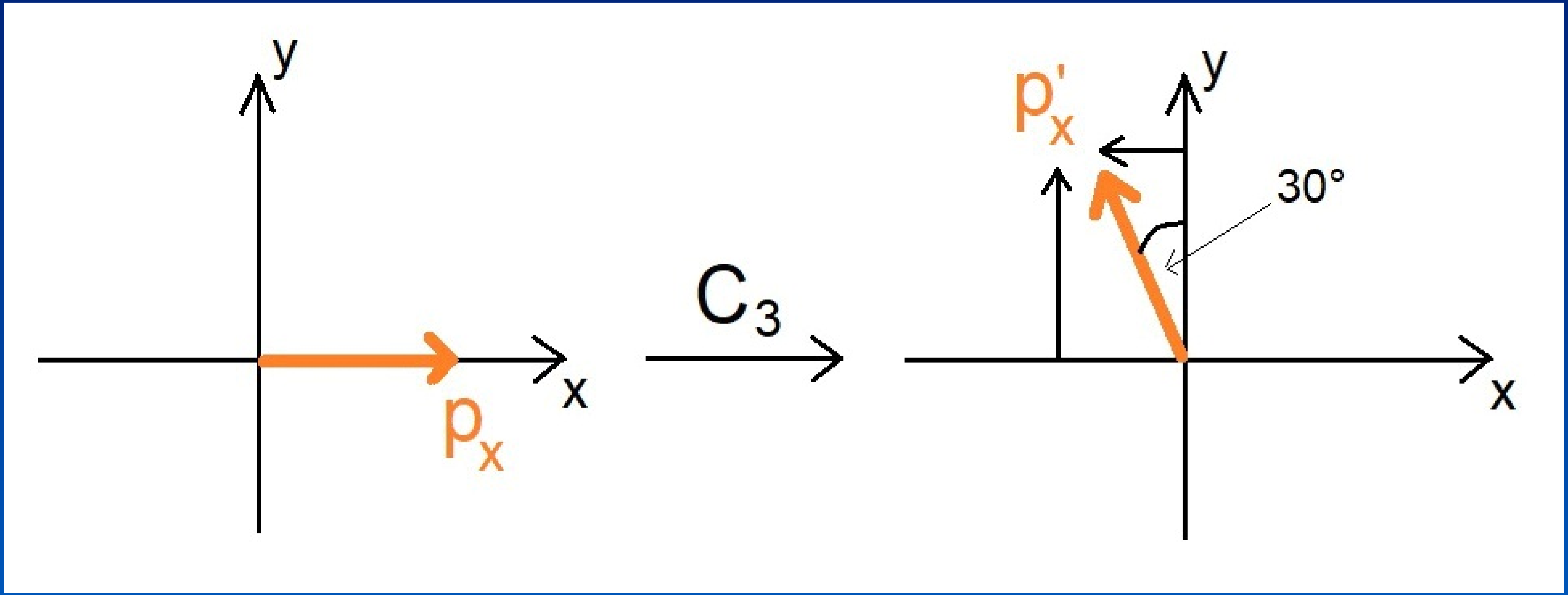
Construindo o diagrama de energia dos orbitais moleculares



Amônia, NH_3 - C_{3v}

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

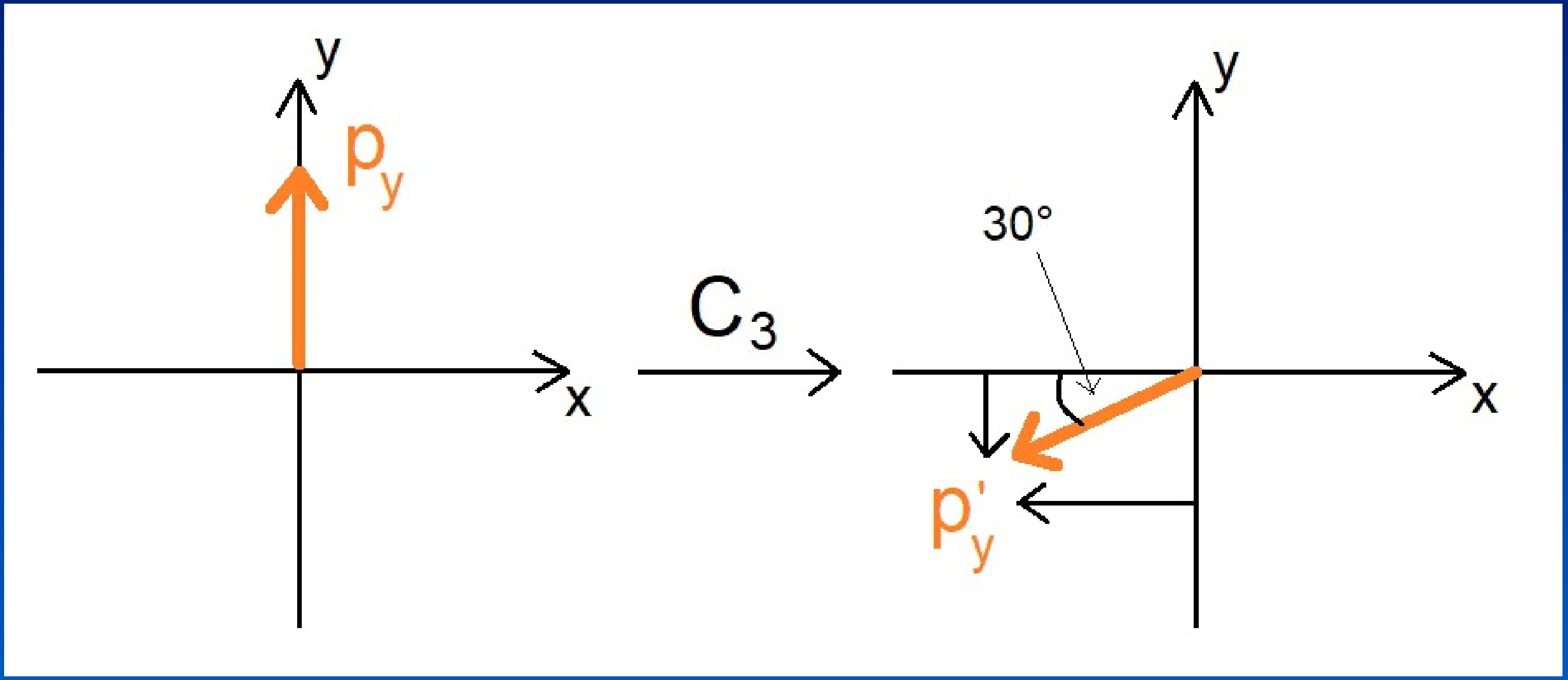
$$p_x' = -p_x \text{ sen } 30° + p_y \cos 30° = (-1/2)p_x + (\sqrt{3}/2)p_y$$



Amônia, NH_3 - C_{3v}

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

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



Amônia, NH_3 - C_{3v}

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

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

$$\xrightarrow{C_3}$$

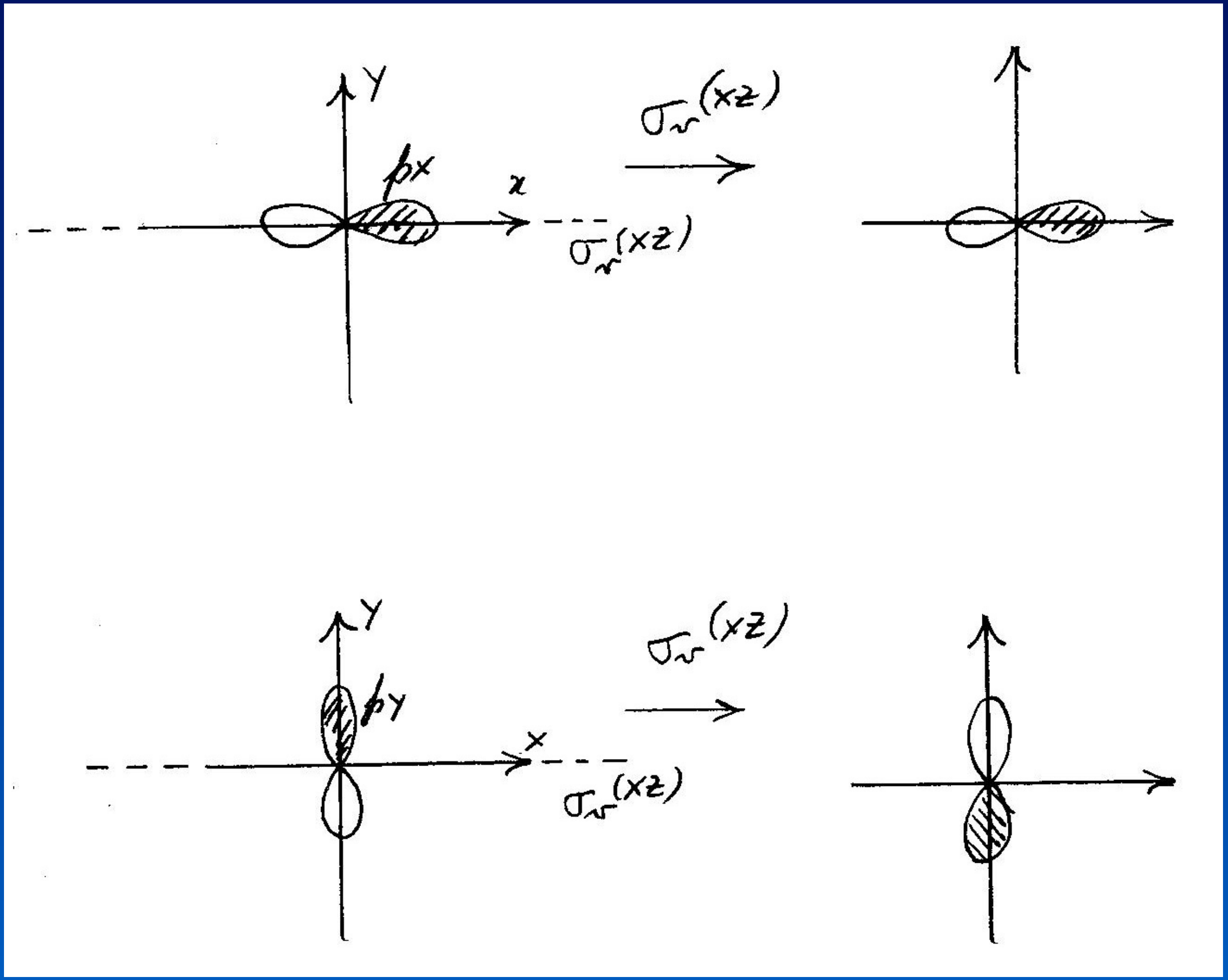
	$2p_x$	$2p_y$
$2p_x'$	$-1/2$	$\sqrt{3}/2$
$2p_y'$	$-\sqrt{3}/2$	$-1/2$

$$\chi = -1$$

C_{3v}	E	$2C_3$	$3\sigma_v$
A_1	1	1	1
A_2	1	1	-1
E	2	-1	0
(p_x,p_y)	2	-1	

Amônia, NH_3 - C_{3v}

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



Amônia, NH_3 - C_{3v}

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

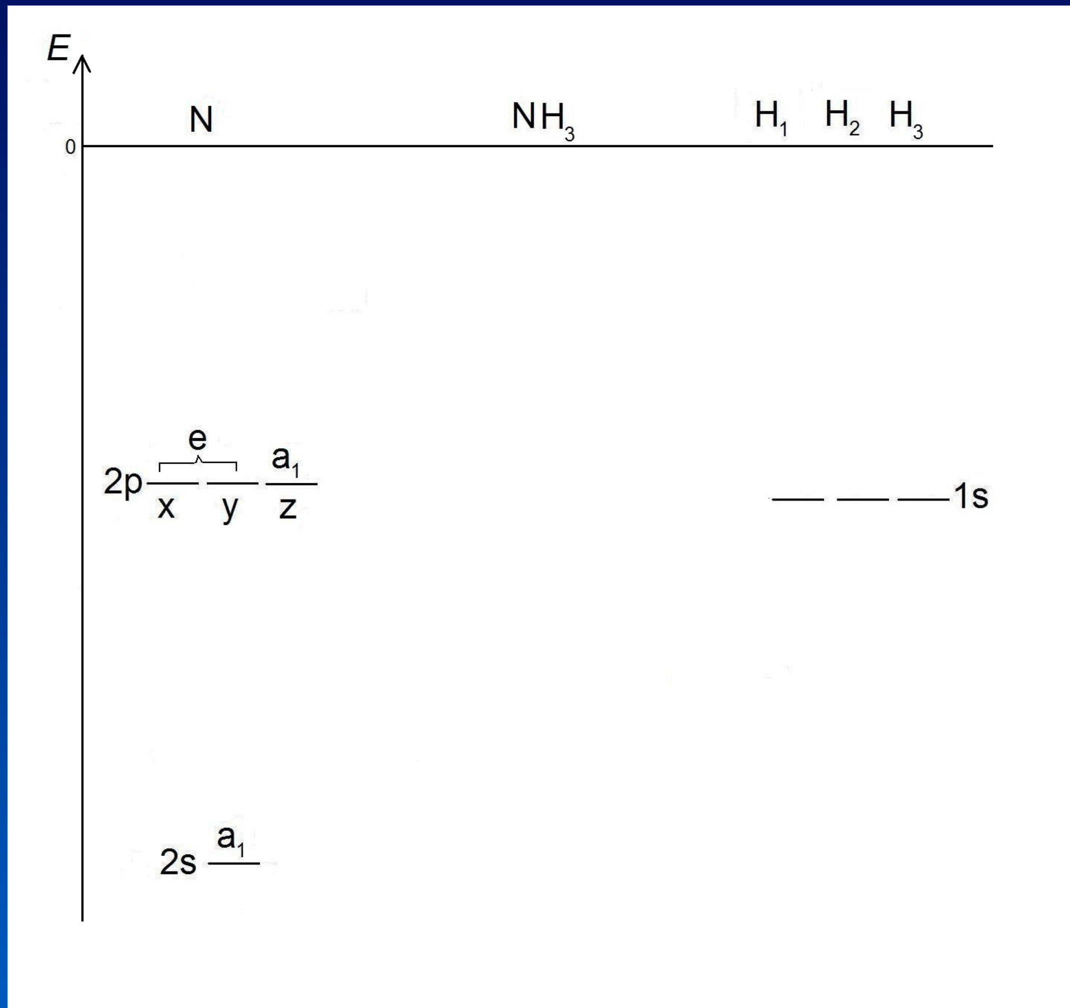
$$\begin{array}{ccc} & 2p_x & 2p_y \\ 2p_x & 1 & 0 \\ 2p_y & 0 & 1 \end{array} \quad \overset{\sigma_v^{(xz)}}{\longrightarrow} \quad \begin{array}{ccc} & 2p_x & 2p_y \\ 2p_x' & 1 & 0 \\ 2p_y' & 0 & -1 \end{array}$$

$\chi = 0$

C_{3v}	E	$2C_3$	$3\sigma_v$
A_1	1	1	1
A_2	1	1	-1
E	2	-1	0
(p_x,p_y)	2	-1	0

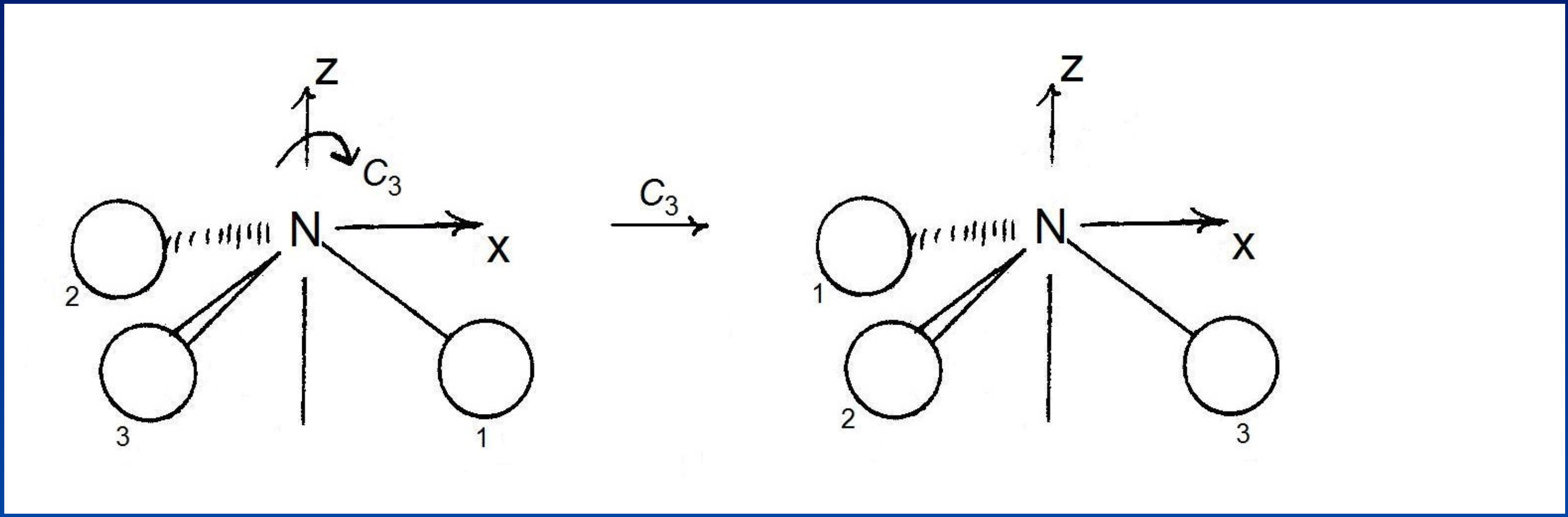
Amônia, NH_3 - C_{3v}

Construindo o diagrama de energia dos orbitais moleculares



Amônia, NH_3 - C_{3v}

Os orbitais 1s dos H são **INSEPARÁVEIS**



Amônia, NH_3 - C_{3v}

Classificando os orbitais 1s dos H

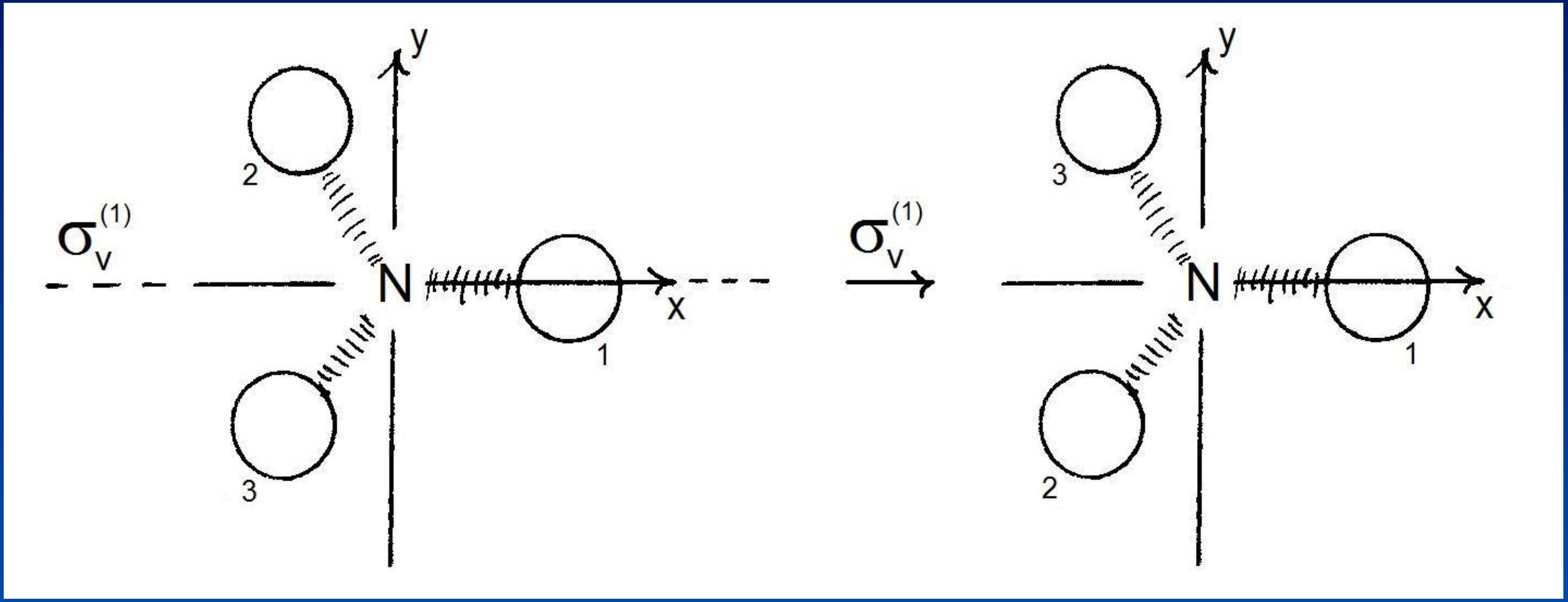
	$1sH_1$	$1sH_2$	$1sH_3$			$1sH_1$	$1sH_2$	$1sH_3$
$1sH_1$	1	0	0	C_3	$1sH_1$	0	1	0
$1sH_2$	0	1	0	$\rightarrow$	$1sH_2$	0	0	1
$1sH_3$	0	0	1		$1sH_3$	1	0	0

$\chi = 0$

C_{3v}	E	$2C_3$	$3\sigma_v$
A_1	1	1	1
A_2	1	1	-1
E	2	-1	0
(H_1,H_2,H_3)	3	0	

Amônia, NH_3 - C_{3v}

Classificando os orbitais 1s dos H



Amônia, NH_3 - C_{3v}

Classificando os orbitais 1s dos H

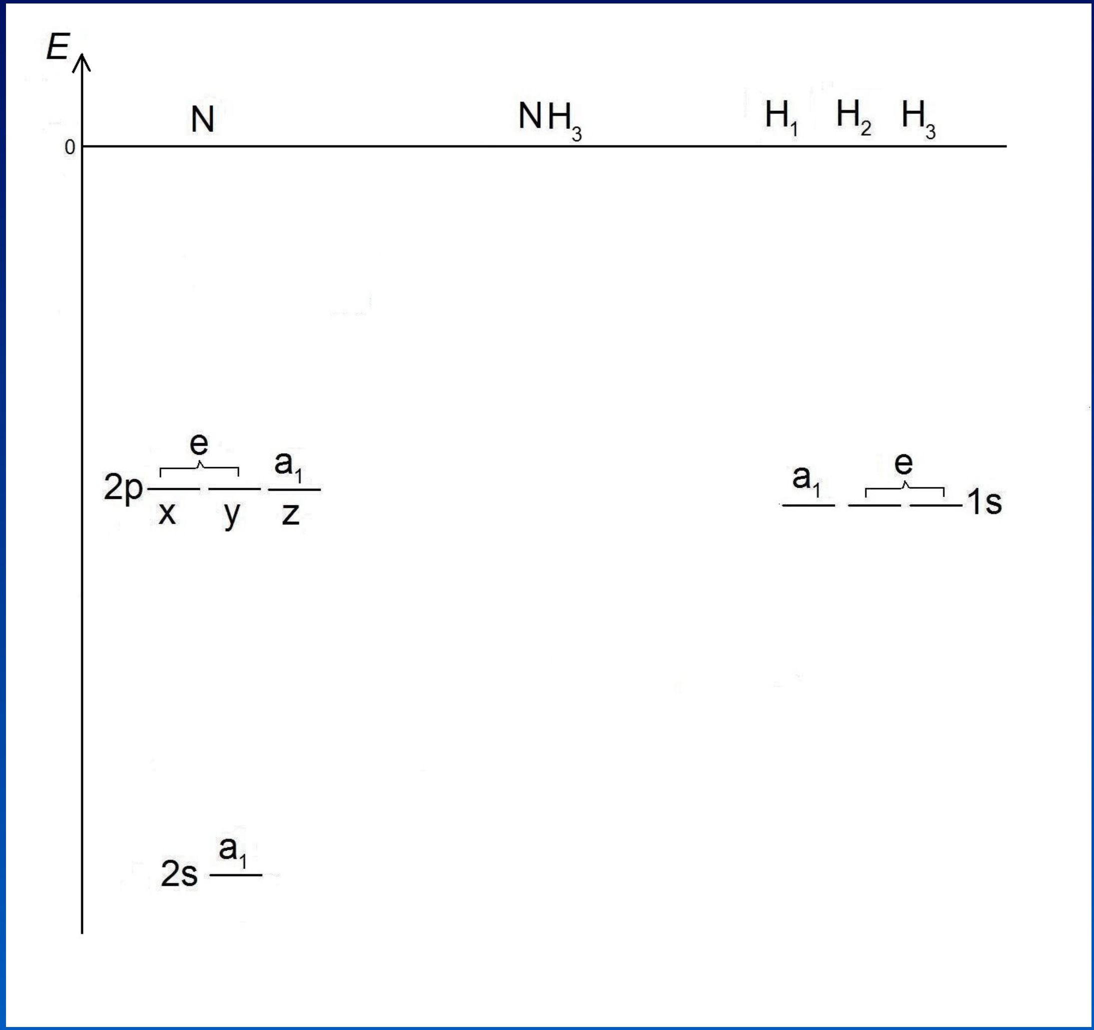
	$1sH_1$	$1sH_2$	$1sH_3$			$1sH_1$	$1sH_2$	$1sH_3$
$1sH_1$	1	0	0	$\sigma_v^{(1)}$	$1sH_1$	1	0	0
$1sH_2$	0	1	0	$\rightarrow$	$1sH_2$	0	0	1
$1sH_3$	0	0	1		$1sH_3$	0	1	0

$\chi = 1$

C_{3v}	E	$2C_3$	$3\sigma_v$	
A_1	1	1	1	
A_2	1	1	-1	
E	2	-1	0	
(H_1,H_2,H_3)	3	0	1	$A_1 + E$

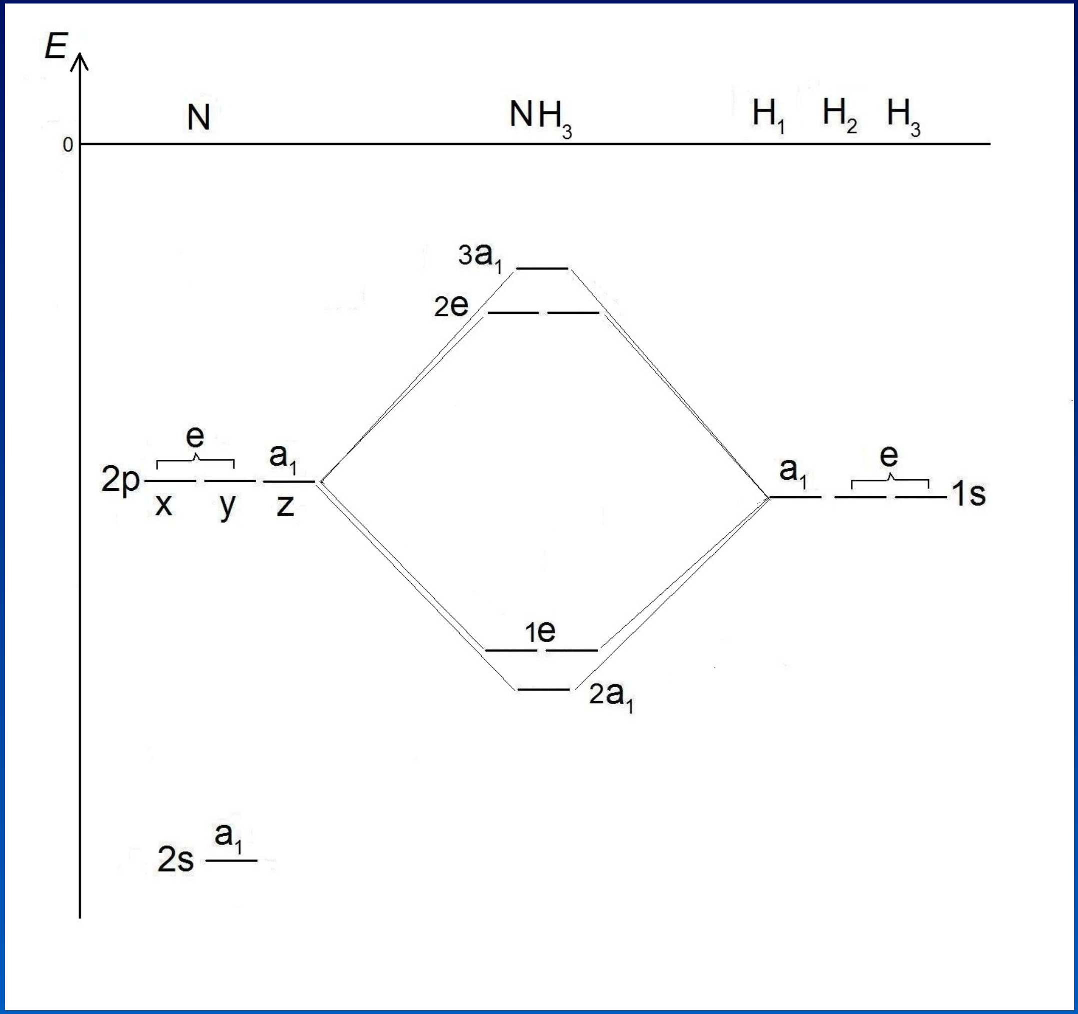
Amônia, NH_3 - C_{3v}

Construindo o diagrama de energia dos orbitais moleculares



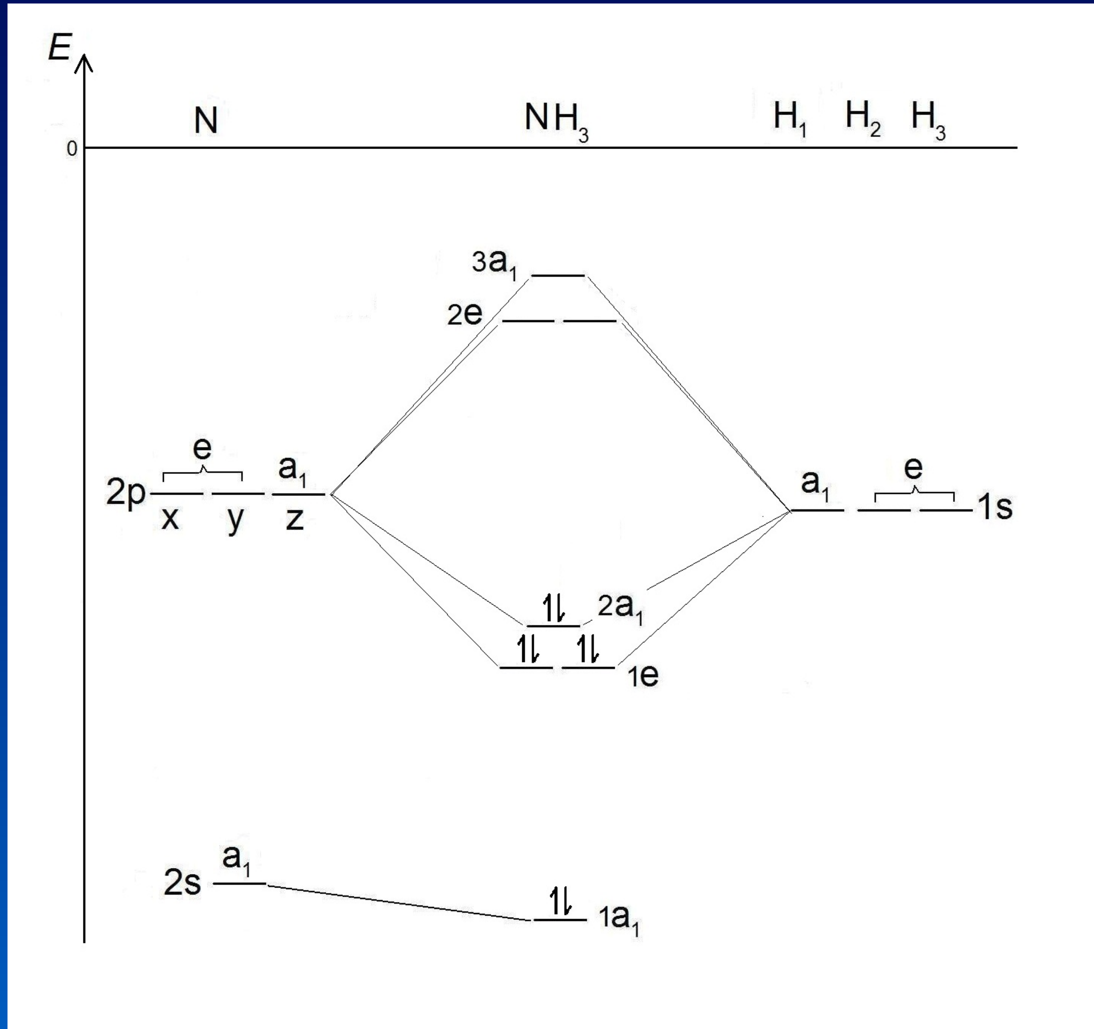
Amônia, NH_3 - C_{3v}

Construindo o diagrama de energia dos orbitais moleculares

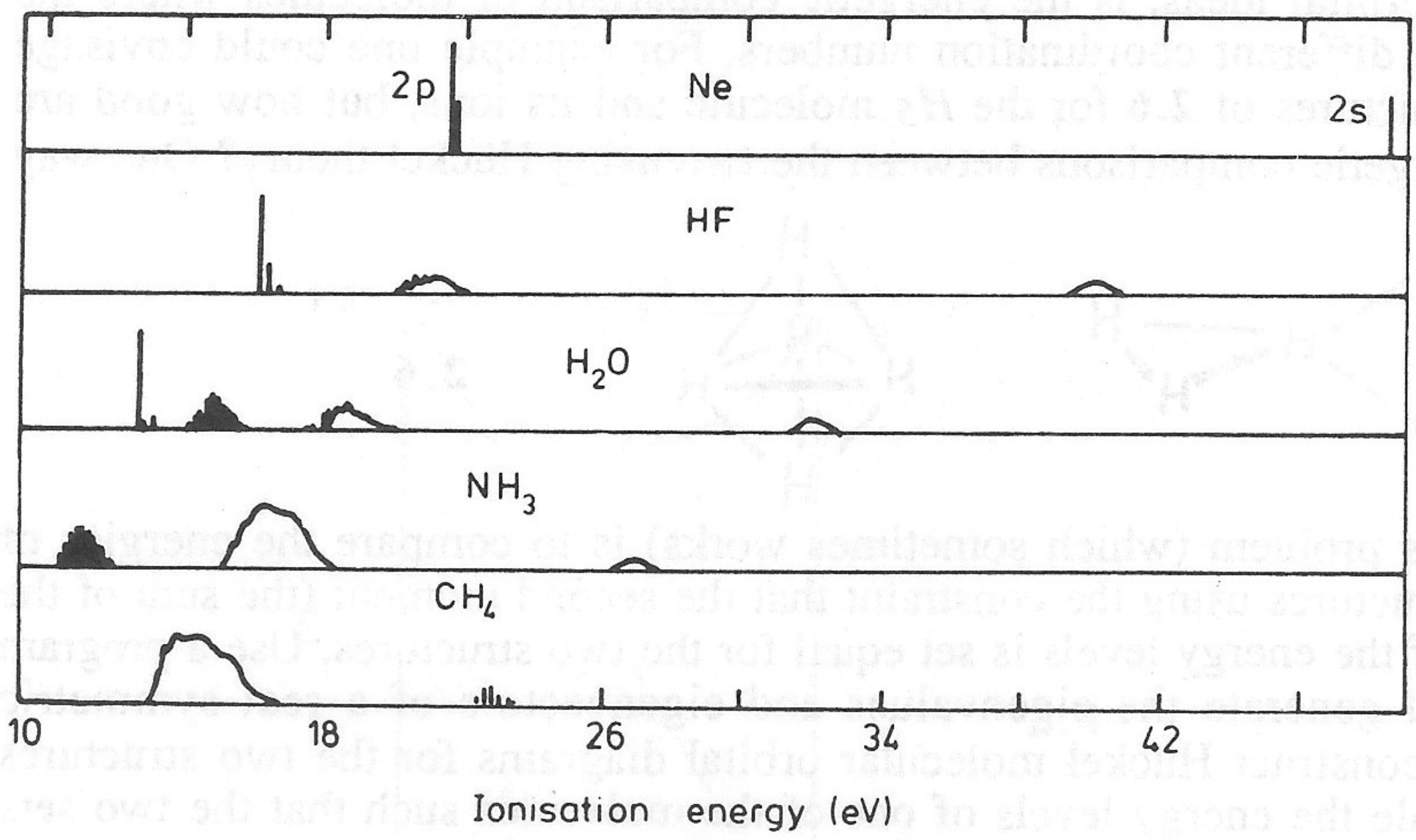


Amônia, NH_3 - C_{3v}

Construindo o diagrama de energia dos orbitais moleculares

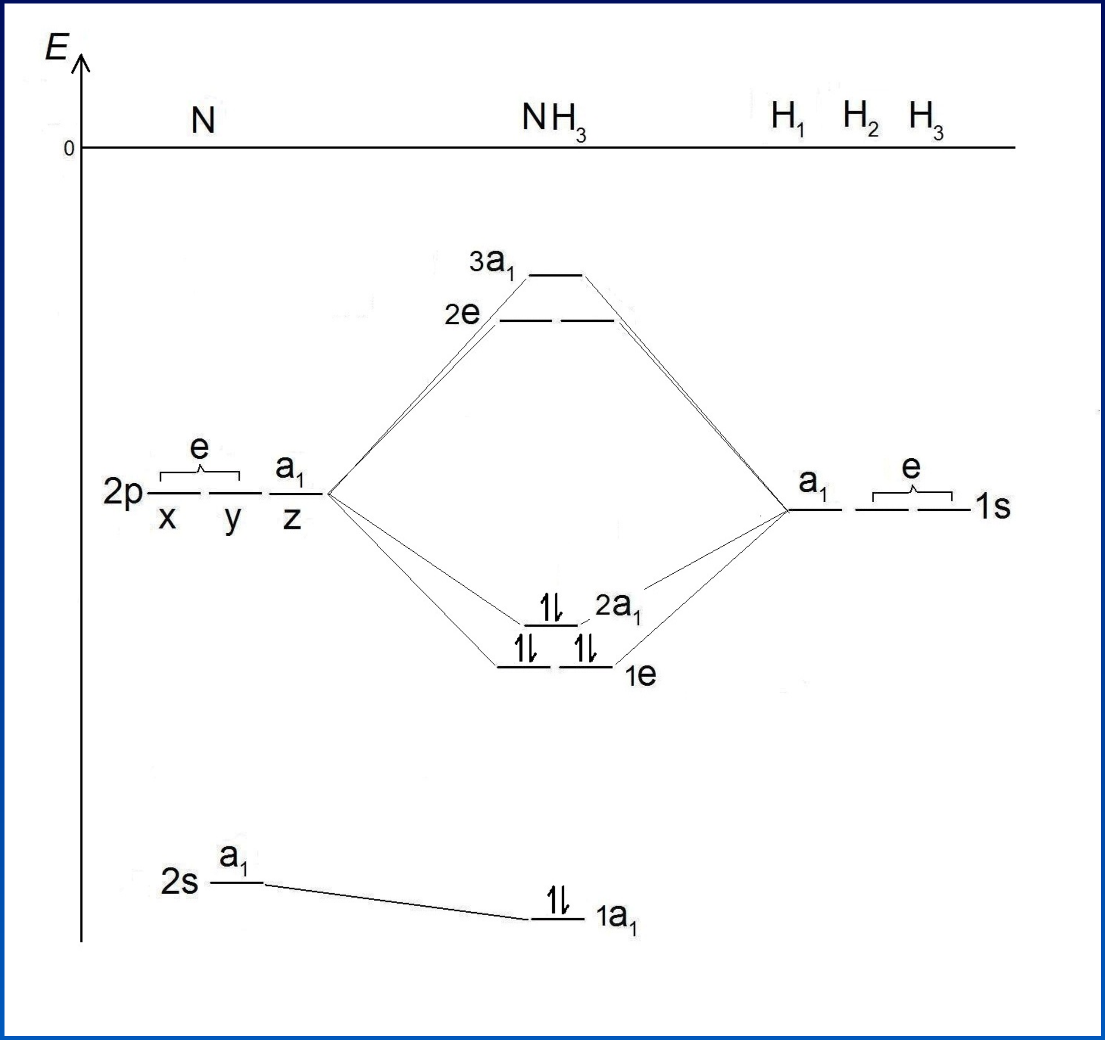


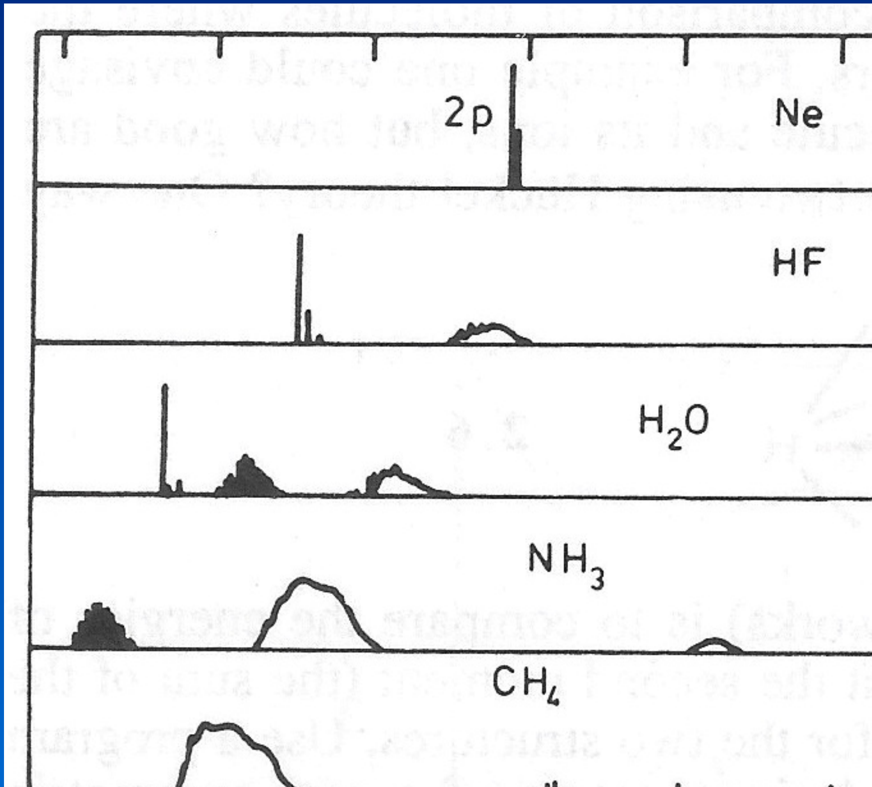
Espectros de fotoelétron



Albright, T. A.; Burdett, J. K. *Problems in Molecular Orbital Theory*, Oxford University Press, 1992. pg. 32

Espectros de fotoelétron





Espectros de fotoelétron

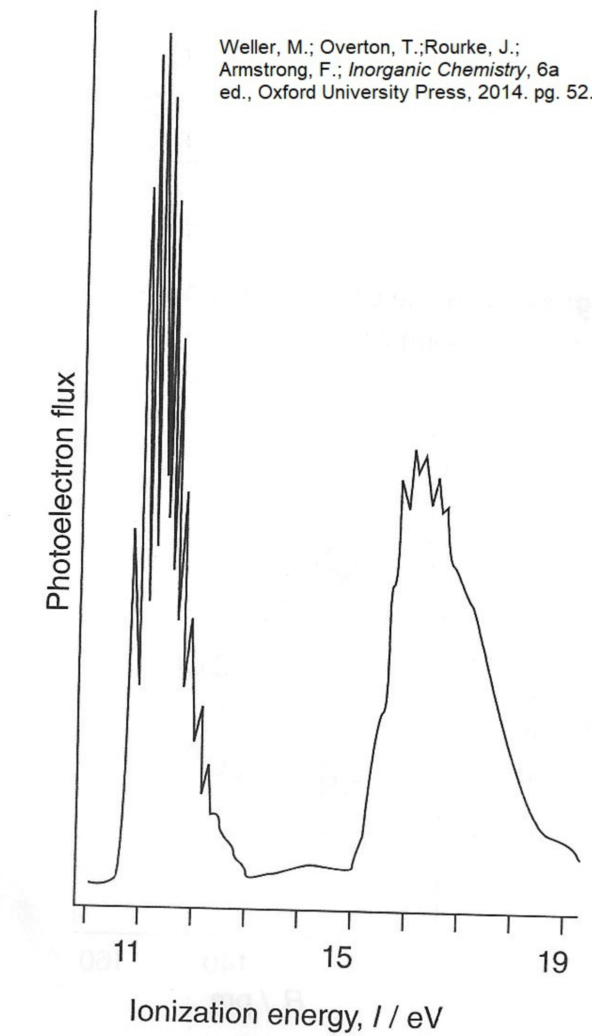


Figure 2.28 The UV photoelectron spectrum of NH_3, obtained using He 21 eV radiation.

Desenhando os orbitais moleculares

Método do Operador Projeção

Amônia, NH_3 - C_{3v}

Calculando as combinações lineares dos orbitais 1s dos H pelo
MÉTODO DO OPERADOR PROJEÇÃO

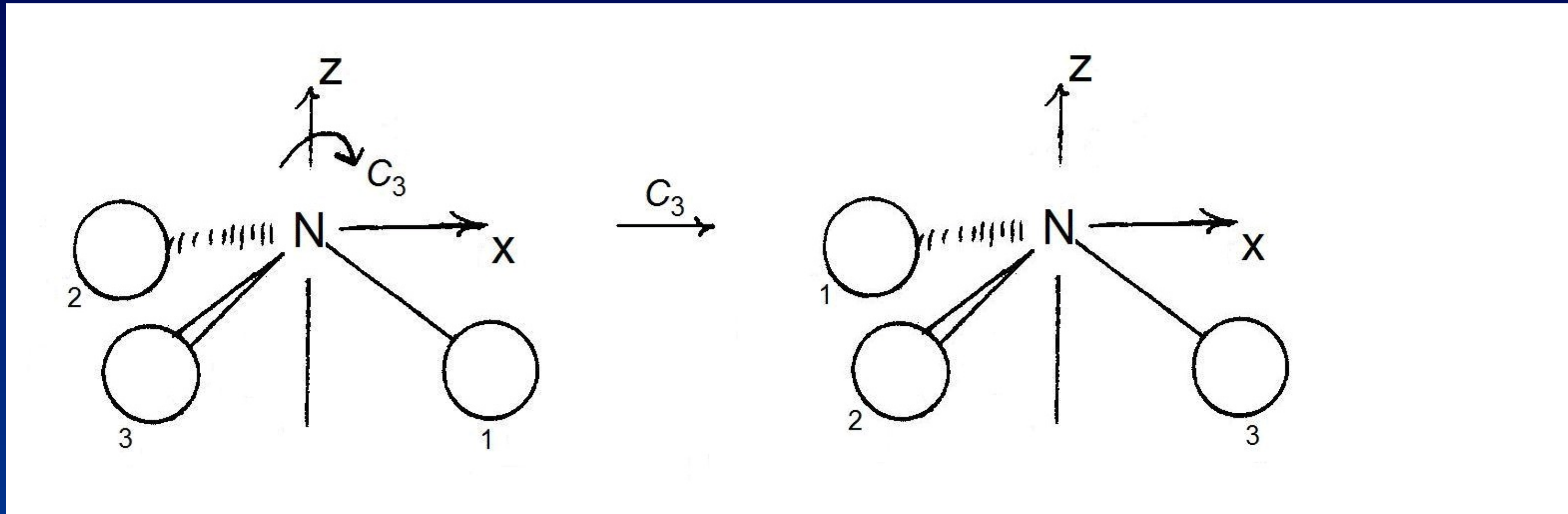
$$\hat{P}(\varphi_i) = \sum_R \chi_R \hat{R}(\varphi_i)$$

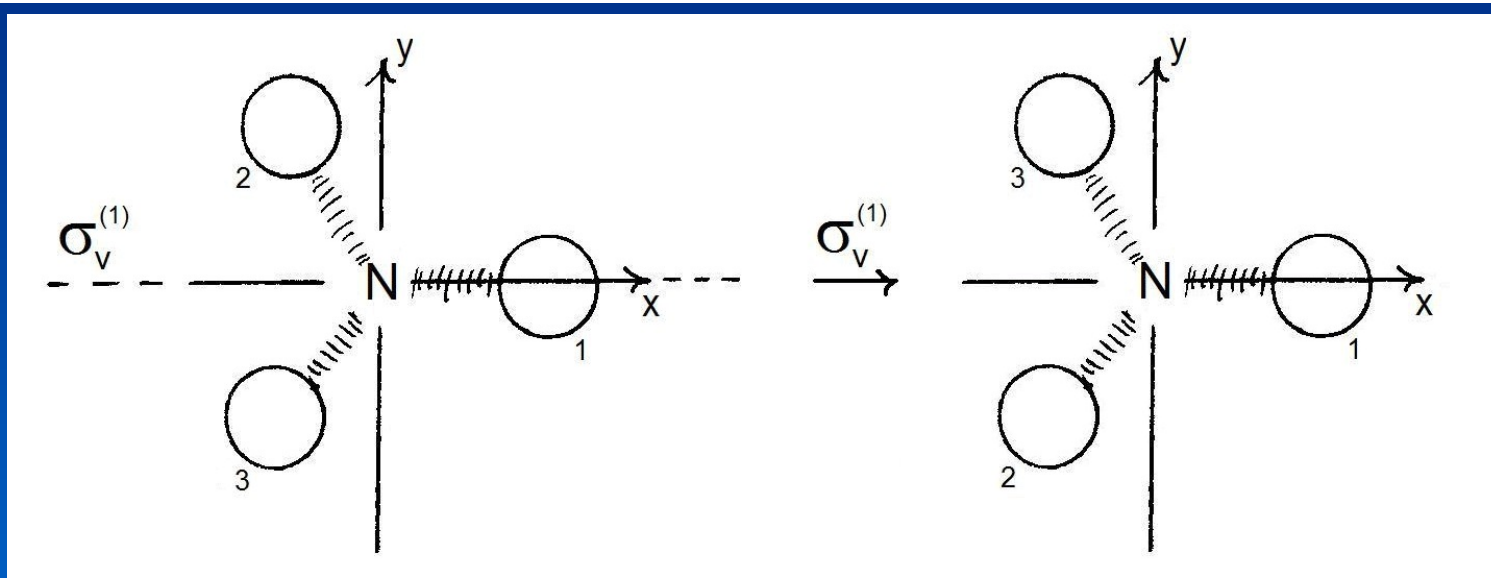
Amônia, NH_3 - C_{3v}

MÉTODO DO OPERADOR PROJEÇÃO
Lista das projeções

E	φ_1
C_3	φ_2
C_3^2	φ_3
$\sigma_v^{(1)}$	φ_1
$\sigma_v^{(2)}$	φ_3
$\sigma_v^{(3)}$	φ_2

Amônia, NH_3 - C_{3v}





Amônia, NH_3 - C_{3v}

		A_1
E	φ_1	1
C_3	φ_2	1
C_3^2	φ_3	1
$\sigma_v^{(1)}$	φ_1	1
$\sigma_v^{(2)}$	φ_3	1
$\sigma_v^{(3)}$	φ_2	1

C_{3v}	E	$2C_3$	$3\sigma_v$
A_1	1	1	1
A_2	1	1	-1
E	2	-1	0

$$\hat{P}_{A_1}(\varphi_1) = 1\times\varphi_1 + 1\times\varphi_2 + 1\times\varphi_3 + 1\times\varphi_1 + 1\times\varphi_3 + 1\times\varphi_2$$

Amônia, NH_3 - C_{3v}

		A_1
E	φ_1	1
C_3	φ_2	1
C_3^2	φ_3	1
$\sigma_v^{(1)}$	φ_1	1
$\sigma_v^{(2)}$	φ_3	1
$\sigma_v^{(3)}$	φ_2	1

C_{3v}	E	$2C_3$	$3\sigma_v$
A_1	1	1	1
A_2	1	1	-1
E	2	-1	0

$$\hat{P}_{A_1}(\varphi_1) = 2\varphi_1 + 2\varphi_2 + 2\varphi_3$$

Amônia, NH_3 - C_{3v}

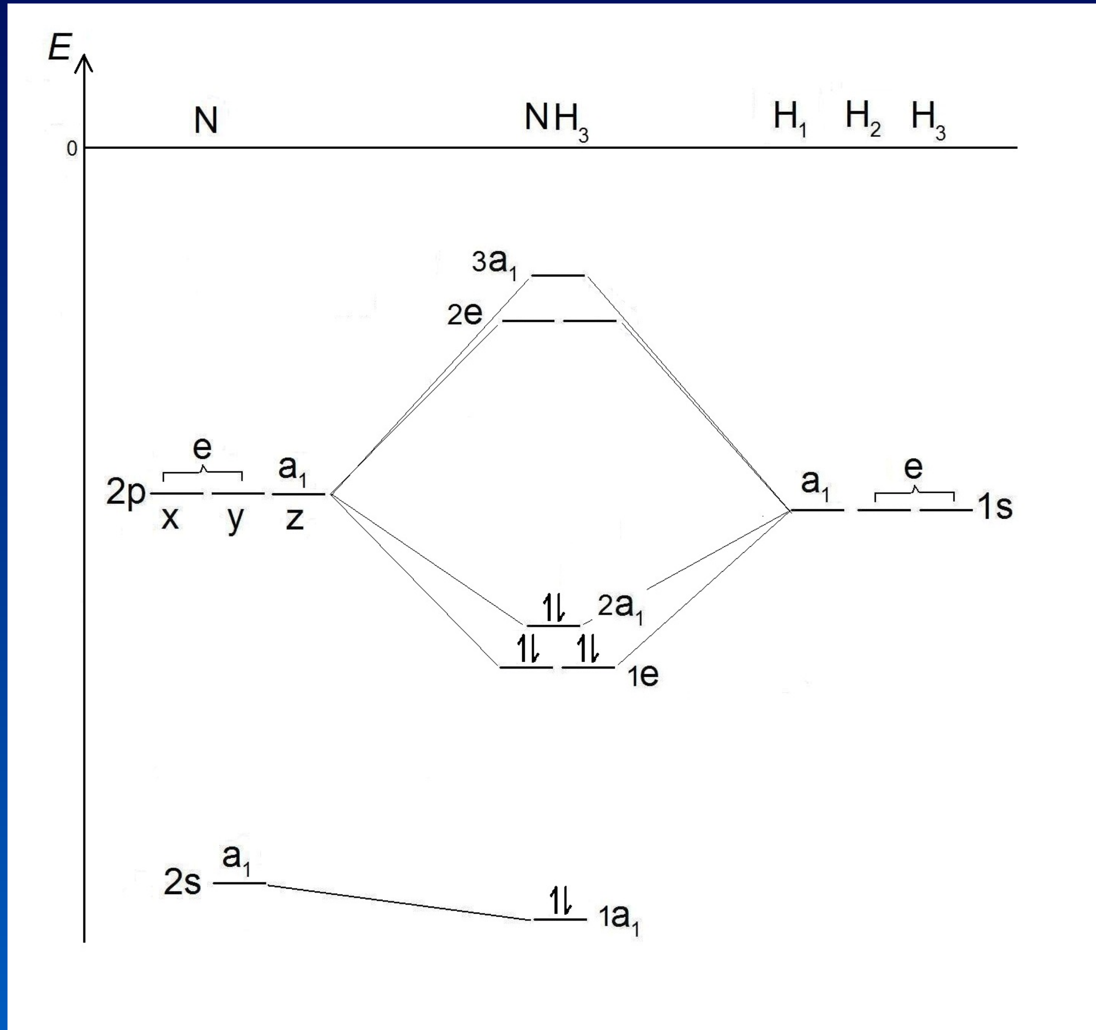
		A_1
E	φ_1	1
C_3	φ_2	1
$C_3^{\ 2}$	φ_3	1
$\sigma_v^{(1)}$	φ_1	1
$\sigma_v^{(2)}$	φ_3	1
$\sigma_v^{(3)}$	φ_2	1

C_{3v}	E	$2C_3$	$3\sigma_v$
A_1	1	1	1
A_2	1	1	-1
E	2	-1	0

$$\hat{P}_{A_1}(\varphi_1) = \varphi_1 + \varphi_2 + \varphi_3$$

Amônia, NH_3 - C_{3v}

Diagrama de energia dos orbitais moleculares



Amônia, NH_3 - C_{3v}

E	φ_1
C_3	φ_2
C_3^2	φ_3
$\sigma_v^{(1)}$	φ_1
$\sigma_v^{(2)}$	φ_3
$\sigma_v^{(3)}$	φ_2

C_{3v}	E	$2C_3$	$3\sigma_v$
A_1	1	1	1
A_2	1	1	-1
E	2	-1	0

$$\hat{P}_E(\varphi_1) = ?$$

Amônia, NH_3 - C_{3v}

E	φ_1
C_3	φ_2
$C_3^{\,2}$	φ_3
$\sigma_v^{(1)}$	φ_1
$\sigma_v^{(2)}$	φ_3
$\sigma_v^{(3)}$	φ_2

$$E = \begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix}$$

$$C_3 = \begin{bmatrix} -1/2 & \sqrt{3}/2 \\ -\sqrt{3}/2 & -1/2 \end{bmatrix}$$

$$C_3^2 = \begin{bmatrix} -1/2 & -\sqrt{3}/2 \\ \sqrt{3}/2 & -1/2 \end{bmatrix}$$

$${}^{(x)}\sigma_v = \begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix}$$

$${}^{(\bar{x}y)}\sigma_v = \begin{bmatrix} -1/2 & -\sqrt{3}/2 \\ -\sqrt{3}/2 & 1/2 \end{bmatrix}$$

$${}^{(\overline{xy})}\sigma_v = \begin{bmatrix} -1/2 & \sqrt{3}/2 \\ \sqrt{3}/2 & 1/2 \end{bmatrix}$$

$\hat{P}_{E_{11}}(\varphi_1) =$

$\hat{P}_{E_{12}}(\varphi_1) =$

$\hat{P}_{E_{21}}(\varphi_1) =$

$\hat{P}_{E_{22}}(\varphi_1) =$

Amônia, NH_3 - C_{3v}

		E_{11}
E	φ_1	1
C_3	φ_2	-1/2
C_3^2	φ_3	-1/2
$\sigma_v^{(1)}$	φ_1	1
$\sigma_v^{(2)}$	φ_3	-1/2
$\sigma_v^{(3)}$	φ_2	-1/2

$$E = \begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix}$$

$$C_3 = \begin{bmatrix} -1/2 & \sqrt{3}/2 \\ -\sqrt{3}/2 & -1/2 \end{bmatrix}$$

$$C_3^2 = \begin{bmatrix} -1/2 & -\sqrt{3}/2 \\ \sqrt{3}/2 & -1/2 \end{bmatrix}$$

$$^{(x)}\sigma_v = \begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix}$$

$$^{(\bar{x}y)}\sigma_v = \begin{bmatrix} -1/2 & -\sqrt{3}/2 \\ -\sqrt{3}/2 & 1/2 \end{bmatrix}$$

$$^{(\overline{xy})}\sigma_v = \begin{bmatrix} -1/2 & \sqrt{3}/2 \\ \sqrt{3}/2 & 1/2 \end{bmatrix}$$

$$\hat{P}_{E_{11}}(\varphi_1) = 1\times\varphi_1 - \tfrac{1}{2}\times\varphi_2 - \tfrac{1}{2}\times\varphi_3 + 1\times\varphi_1 - \tfrac{1}{2}\times\varphi_3 - \tfrac{1}{2}\times\varphi_2$$

Amônia, NH_3 - C_{3v}

		E_{11}
E	φ_1	1
C_3	φ_2	-1/2
C_3^2	φ_3	-1/2
$\sigma_v^{(1)}$	φ_1	1
$\sigma_v^{(2)}$	φ_3	-1/2
$\sigma_v^{(3)}$	φ_2	-1/2

$$E = \begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix}$$

$$C_3 = \begin{bmatrix} -1/2 & \sqrt{3}/2 \\ -\sqrt{3}/2 & -1/2 \end{bmatrix}$$

$$C_3^2 = \begin{bmatrix} -1/2 & -\sqrt{3}/2 \\ \sqrt{3}/2 & -1/2 \end{bmatrix}$$

$$^{(x)}\sigma_v = \begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix}$$

$$^{(\bar{x}y)}\sigma_v = \begin{bmatrix} -1/2 & -\sqrt{3}/2 \\ -\sqrt{3}/2 & 1/2 \end{bmatrix}$$

$$^{(\overline{xy})}\sigma_v = \begin{bmatrix} -1/2 & \sqrt{3}/2 \\ \sqrt{3}/2 & 1/2 \end{bmatrix}$$

$$\hat{P}_{E_{11}}(\varphi_1) = 2\varphi_1 - \varphi_2 - \varphi_3$$

Amônia, NH_3 - C_{3v}

		E_{12}
E	φ_1	0
C_3	φ_2	$\sqrt{3}/2$
$C_3^{\ 2}$	φ_3	$-\sqrt{3}/2$
$\sigma_v^{(1)}$	φ_1	0
$\sigma_v^{(2)}$	φ_3	$-\sqrt{3}/2$
$\sigma_v^{(3)}$	φ_2	$\sqrt{3}/2$

$$E = \begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix}$$

$$C_3 = \begin{bmatrix} -1/2 & \sqrt{3}/2 \\ -\sqrt{3}/2 & -1/2 \end{bmatrix}$$

$$C_3^2 = \begin{bmatrix} -1/2 & -\sqrt{3}/2 \\ \sqrt{3}/2 & -1/2 \end{bmatrix}$$

$$^{(x)}\sigma_v = \begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix}$$

$$^{(\bar{x}y)}\sigma_v = \begin{bmatrix} -1/2 & -\sqrt{3}/2 \\ -\sqrt{3}/2 & 1/2 \end{bmatrix}$$

$$^{(\overline{xy})}\sigma_v = \begin{bmatrix} -1/2 & \sqrt{3}/2 \\ \sqrt{3}/2 & 1/2 \end{bmatrix}$$

$$\hat{P}_{E_{12}}(\varphi_1) = 0\times\varphi_1 + (\sqrt{3}/2)\times\varphi_2 - (\sqrt{3}/2)\times\varphi_3 + 0\times\varphi_1 - (\sqrt{3}/2)\times\varphi_3 + (\sqrt{3}/2)\times\varphi_2$$

Amônia, NH_3 - C_{3v}

		E_{12}
E	φ_1	0
C_3	φ_2	$\sqrt{3}/2$
C_3^2	φ_3	$-\sqrt{3}/2$
$\sigma_v^{(1)}$	φ_1	0
$\sigma_v^{(2)}$	φ_3	$-\sqrt{3}/2$
$\sigma_v^{(3)}$	φ_2	$\sqrt{3}/2$

$$E = \begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix}$$

$$C_3 = \begin{bmatrix} -1/2 & \sqrt{3}/2 \\ -\sqrt{3}/2 & -1/2 \end{bmatrix}$$

$$C_3^2 = \begin{bmatrix} -1/2 & -\sqrt{3}/2 \\ \sqrt{3}/2 & -1/2 \end{bmatrix}$$

$${}^{(x)}\sigma_v = \begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix}$$

$${}^{(\bar{x}y)}\sigma_v = \begin{bmatrix} -1/2 & -\sqrt{3}/2 \\ -\sqrt{3}/2 & 1/2 \end{bmatrix}$$

$${}^{(\overline{xy})}\sigma_v = \begin{bmatrix} -1/2 & \sqrt{3}/2 \\ \sqrt{3}/2 & 1/2 \end{bmatrix}$$

$$\hat{P}_{E_{12}}(\varphi_1) = \sqrt{3}\varphi_2 - \sqrt{3}\varphi_3$$

Amônia, NH_3 - C_{3v}

		E_{12}
E	φ_1	0
C_3	φ_2	$\sqrt{3}/2$
C_3^2	φ_3	$-\sqrt{3}/2$
$\sigma_v^{(1)}$	φ_1	0
$\sigma_v^{(2)}$	φ_3	$-\sqrt{3}/2$
$\sigma_v^{(3)}$	φ_2	$\sqrt{3}/2$

$$E = \begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix}$$

$$C_3 = \begin{bmatrix} -1/2 & \sqrt{3}/2 \\ -\sqrt{3}/2 & -1/2 \end{bmatrix}$$

$$C_3^2 = \begin{bmatrix} -1/2 & -\sqrt{3}/2 \\ \sqrt{3}/2 & -1/2 \end{bmatrix}$$

$$^{(x)}\sigma_v = \begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix}$$

$$^{(\bar{x}y)}\sigma_v = \begin{bmatrix} -1/2 & -\sqrt{3}/2 \\ -\sqrt{3}/2 & 1/2 \end{bmatrix}$$

$$^{(\overline{xy})}\sigma_v = \begin{bmatrix} -1/2 & \sqrt{3}/2 \\ \sqrt{3}/2 & 1/2 \end{bmatrix}$$

$$\hat{P}_{E_{12}}(\varphi_1) = \varphi_2 - \varphi_3$$

Amônia, NH_3 - C_{3v}

		E_{21}
E	φ_1	0
C_3	φ_2	$-\sqrt{3}/2$
C_3^2	φ_3	$\sqrt{3}/2$
$\sigma_v^{(1)}$	φ_1	0
$\sigma_v^{(2)}$	φ_3	$-\sqrt{3}/2$
$\sigma_v^{(3)}$	φ_2	$\sqrt{3}/2$

$$E = \begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix}$$

$$C_3 = \begin{bmatrix} -1/2 & \sqrt{3}/2 \\ -\sqrt{3}/2 & -1/2 \end{bmatrix}$$

$$C_3^2 = \begin{bmatrix} -1/2 & -\sqrt{3}/2 \\ \sqrt{3}/2 & -1/2 \end{bmatrix}$$

$$^{(x)}\sigma_v = \begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix}$$

$$^{(\bar{x}y)}\sigma_v = \begin{bmatrix} -1/2 & -\sqrt{3}/2 \\ -\sqrt{3}/2 & 1/2 \end{bmatrix}$$

$$^{(\overline{xy})}\sigma_v = \begin{bmatrix} -1/2 & \sqrt{3}/2 \\ \sqrt{3}/2 & 1/2 \end{bmatrix}$$

$$\hat{P}_{E_{21}}(\varphi_1) = 0\times\varphi_1 - (\sqrt{3}/2)\times\varphi_2 + (\sqrt{3}/2)\times\varphi_3 + 0\times\varphi_1 - (\sqrt{3}/2)\times\varphi_3 + (\sqrt{3}/2)\times\varphi_2 = 0$$

Amônia, NH_3 - C_{3v}

		E_{22}
E	φ_1	1
C_3	φ_2	-1/2
C_3^2	φ_3	-1/2
$\sigma_v^{(1)}$	φ_1	-1
$\sigma_v^{(2)}$	φ_3	1/2
$\sigma_v^{(3)}$	φ_2	1/2

$$E = \begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix}$$

$$C_3 = \begin{bmatrix} -1/2 & \sqrt{3}/2 \\ -\sqrt{3}/2 & -1/2 \end{bmatrix}$$

$$C_3^2 = \begin{bmatrix} -1/2 & -\sqrt{3}/2 \\ \sqrt{3}/2 & -1/2 \end{bmatrix}$$

$$^{(x)}\sigma_v = \begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix}$$

$$^{(\bar{x}y)}\sigma_v = \begin{bmatrix} -1/2 & -\sqrt{3}/2 \\ -\sqrt{3}/2 & 1/2 \end{bmatrix}$$

$$^{(\overline{xy})}\sigma_v = \begin{bmatrix} -1/2 & \sqrt{3}/2 \\ \sqrt{3}/2 & 1/2 \end{bmatrix}$$

$$\hat{P}_{E_{22}}(\varphi_1) = 1\times\varphi_1 - \tfrac{1}{2}\times\varphi_2 - \tfrac{1}{2}\times\varphi_3 - 1\times\varphi_1 + \tfrac{1}{2}\times\varphi_3 + \tfrac{1}{2}\times\varphi_2 = 0$$

Amônia, NH_3 - C_{3v}

E	φ_1
C_3	φ_2
$C_3^{\,2}$	φ_3
$\sigma_v^{(1)}$	φ_1
$\sigma_v^{(2)}$	φ_3
$\sigma_v^{(3)}$	φ_2

$$E = \begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix}$$

$$C_3 = \begin{bmatrix} -1/2 & \sqrt{3}/2 \\ -\sqrt{3}/2 & -1/2 \end{bmatrix}$$

$$C_3^2 = \begin{bmatrix} -1/2 & -\sqrt{3}/2 \\ \sqrt{3}/2 & -1/2 \end{bmatrix}$$

$$^{(x)}\sigma_v = \begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix}$$

$$^{(\bar{x}y)}\sigma_v = \begin{bmatrix} -1/2 & -\sqrt{3}/2 \\ -\sqrt{3}/2 & 1/2 \end{bmatrix}$$

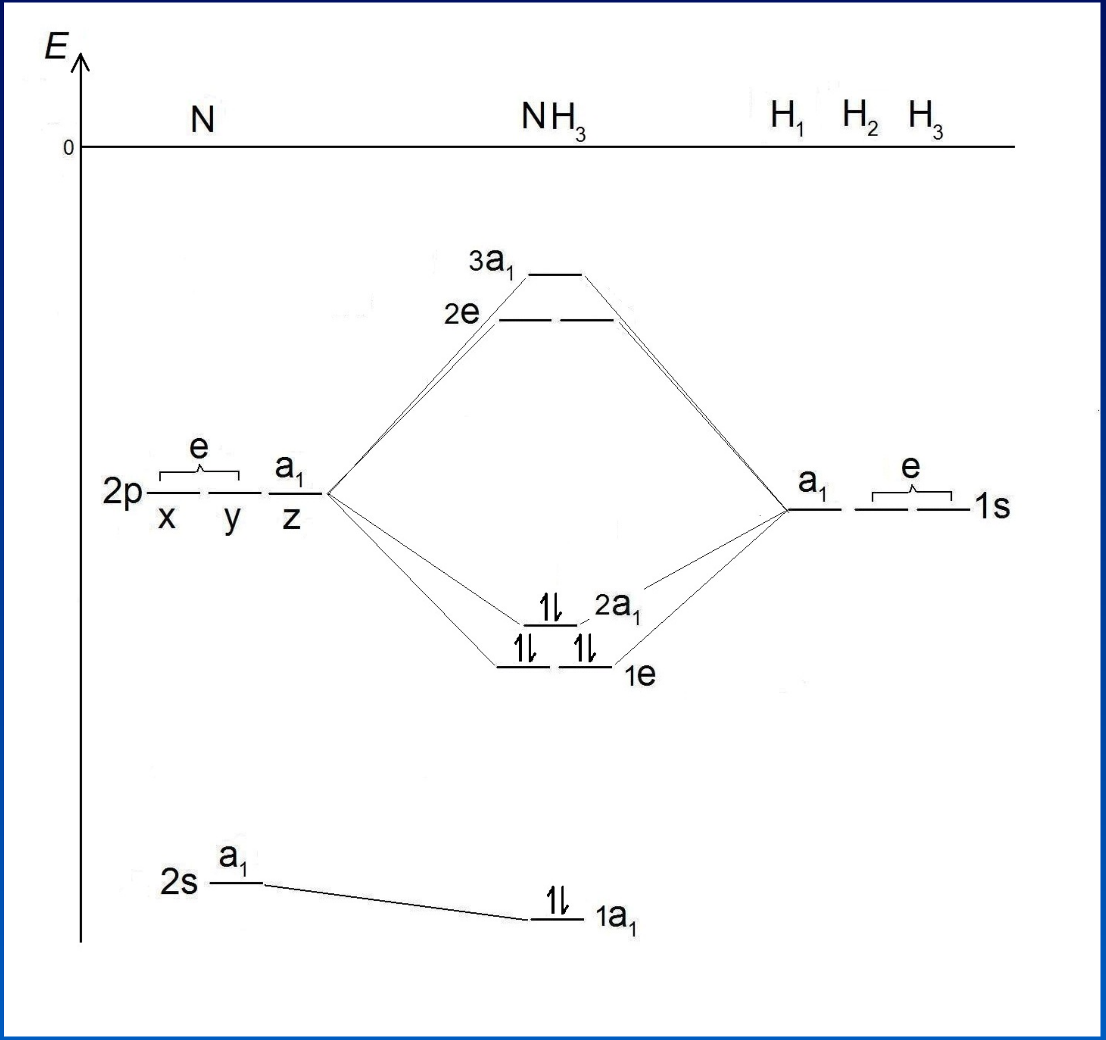
$$^{(\overline{xy})}\sigma_v = \begin{bmatrix} -1/2 & \sqrt{3}/2 \\ \sqrt{3}/2 & 1/2 \end{bmatrix}$$

$$\hat{P}_{E_{11}}(\varphi_1) = 2\varphi_1 - \varphi_2 - \varphi_3$$

$$\hat{P}_{E_{12}}(\varphi_1) = \varphi_2 - \varphi_3$$

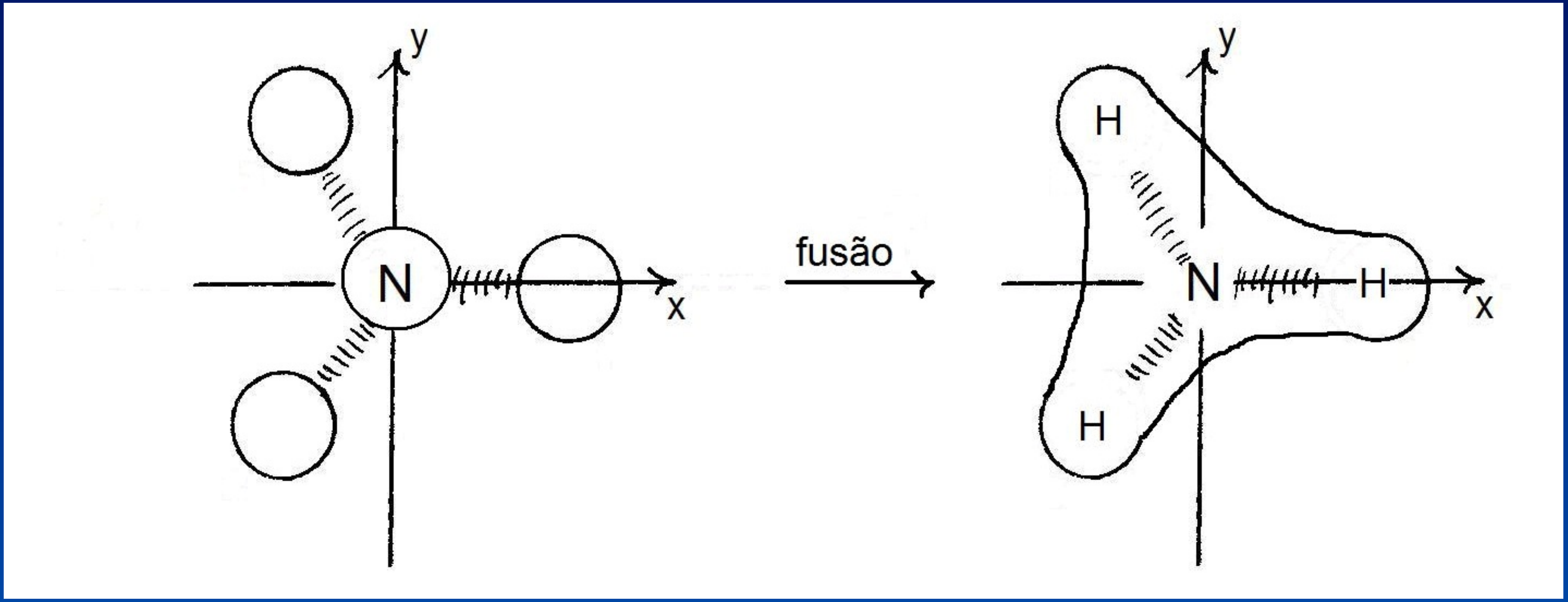
Amônia, NH_3 - C_{3v}

Diagrama de energia dos orbitais moleculares



Amônia, NH_3 - C_{3v}

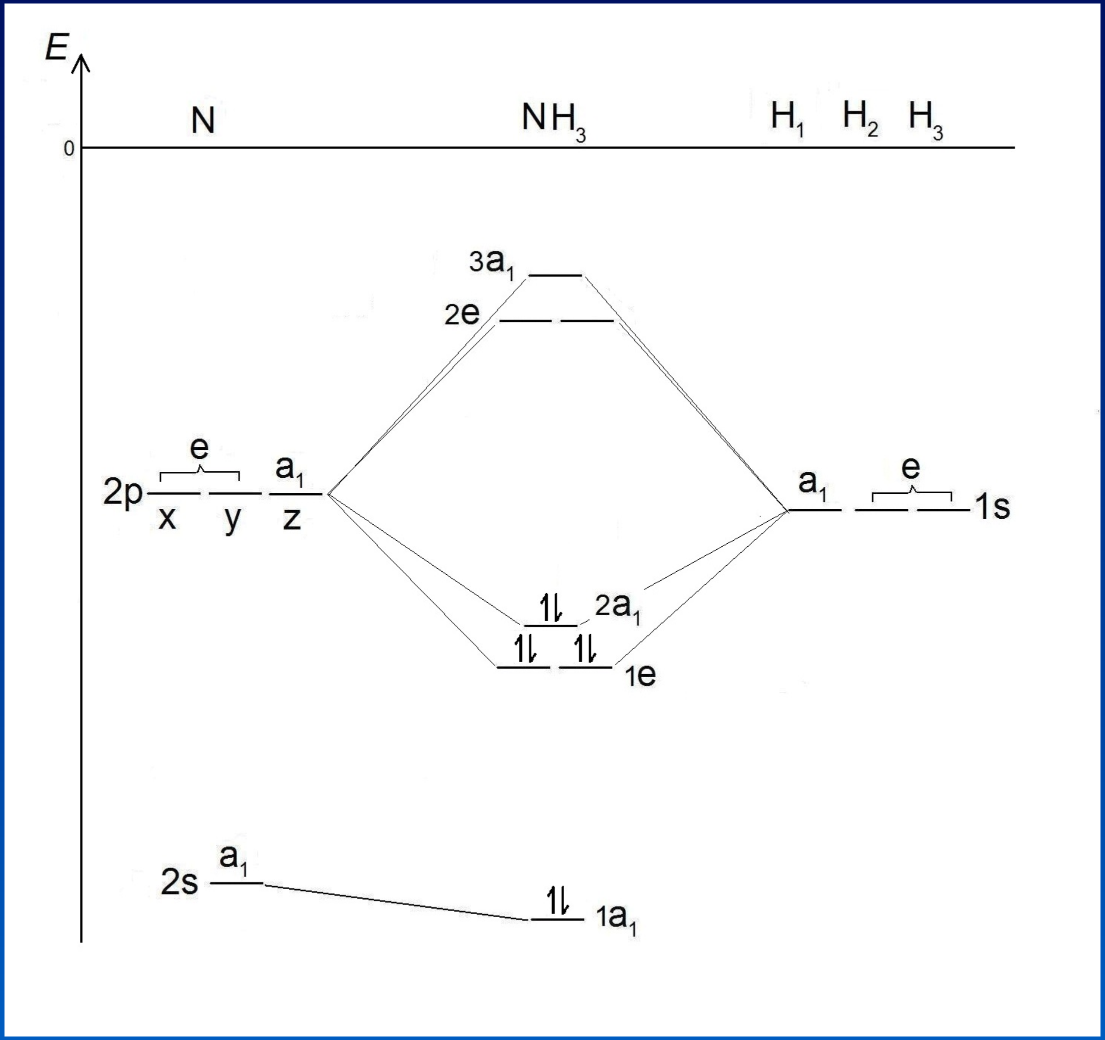
Orbital $1a_1$, ligante



$$\hat{P}_{A_1}(\varphi_1) = \varphi_1 + \varphi_2 + \varphi_3$$

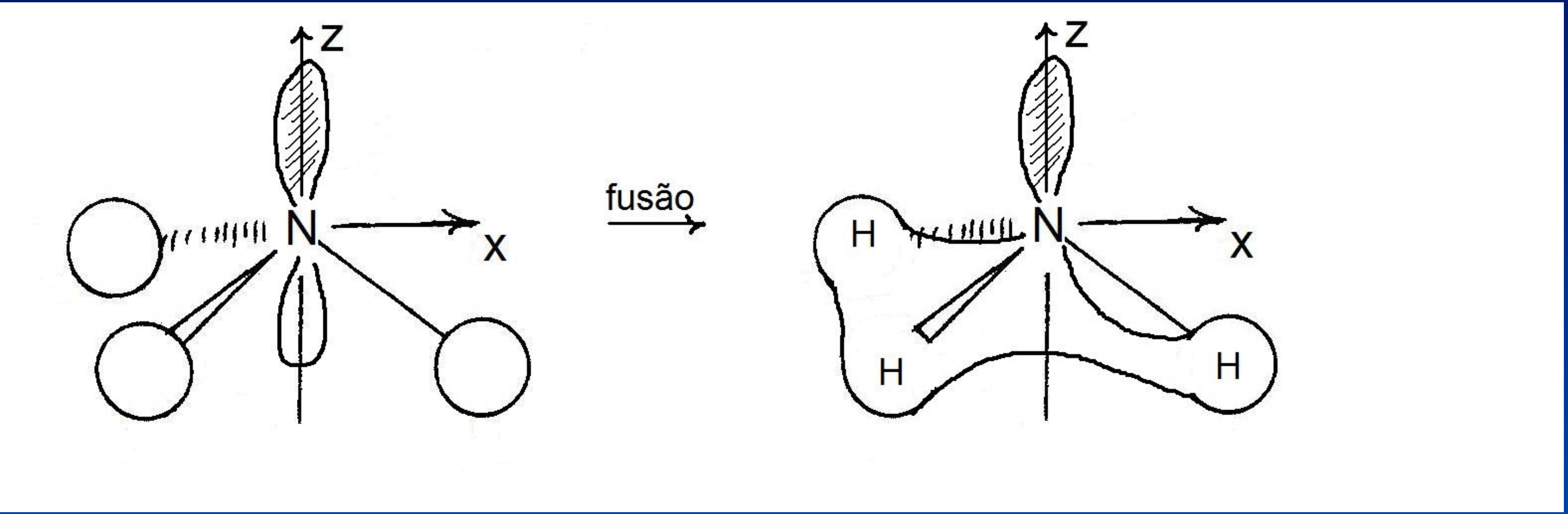
Amônia, NH_3 - C_{3v}

Diagrama de energia dos orbitais moleculares



Amônia, NH_3 - C_{3v}

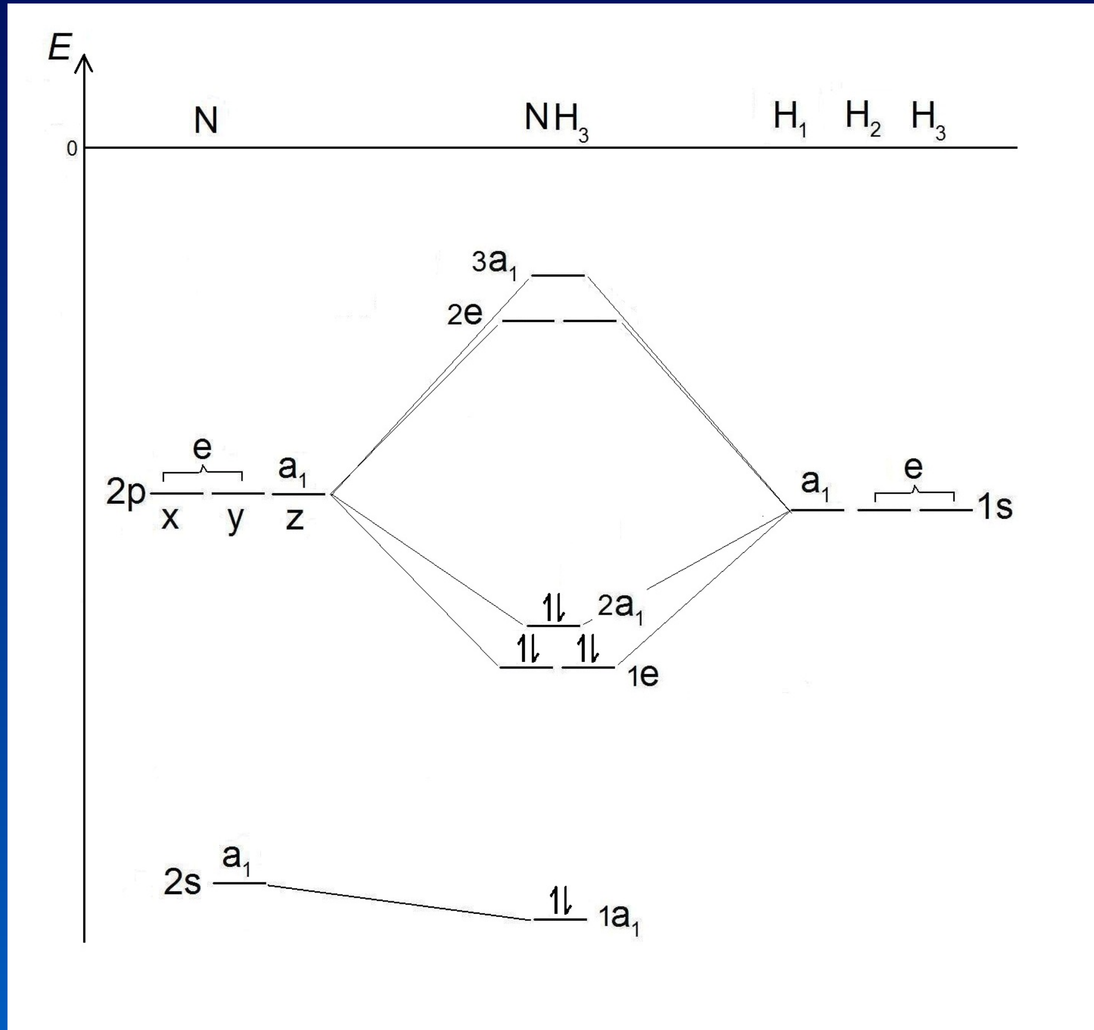
Orbital $2a_1$, ligante



$$\hat{P}_{A_1}(\varphi_1) = \varphi_1 + \varphi_2 + \varphi_3$$

Amônia, NH_3 - C_{3v}

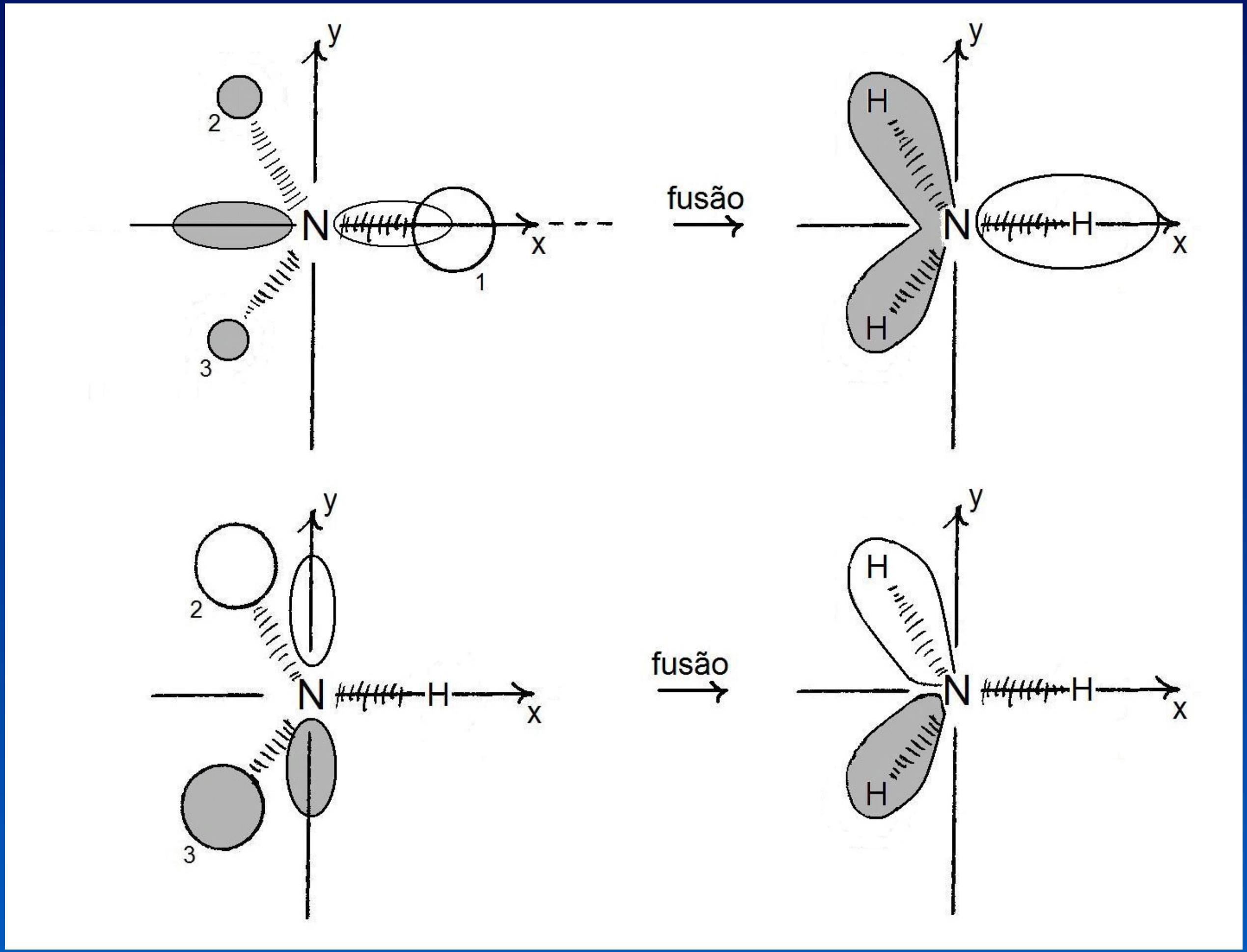
Diagrama de energia dos orbitais moleculares



Amônia, NH_3 - C_{3v}

Par degenerado de orbitais E, ligantes

$$\hat{P}_{E_{11}}(\varphi_1) = 2\varphi_1 - \varphi_2 - \varphi_3$$

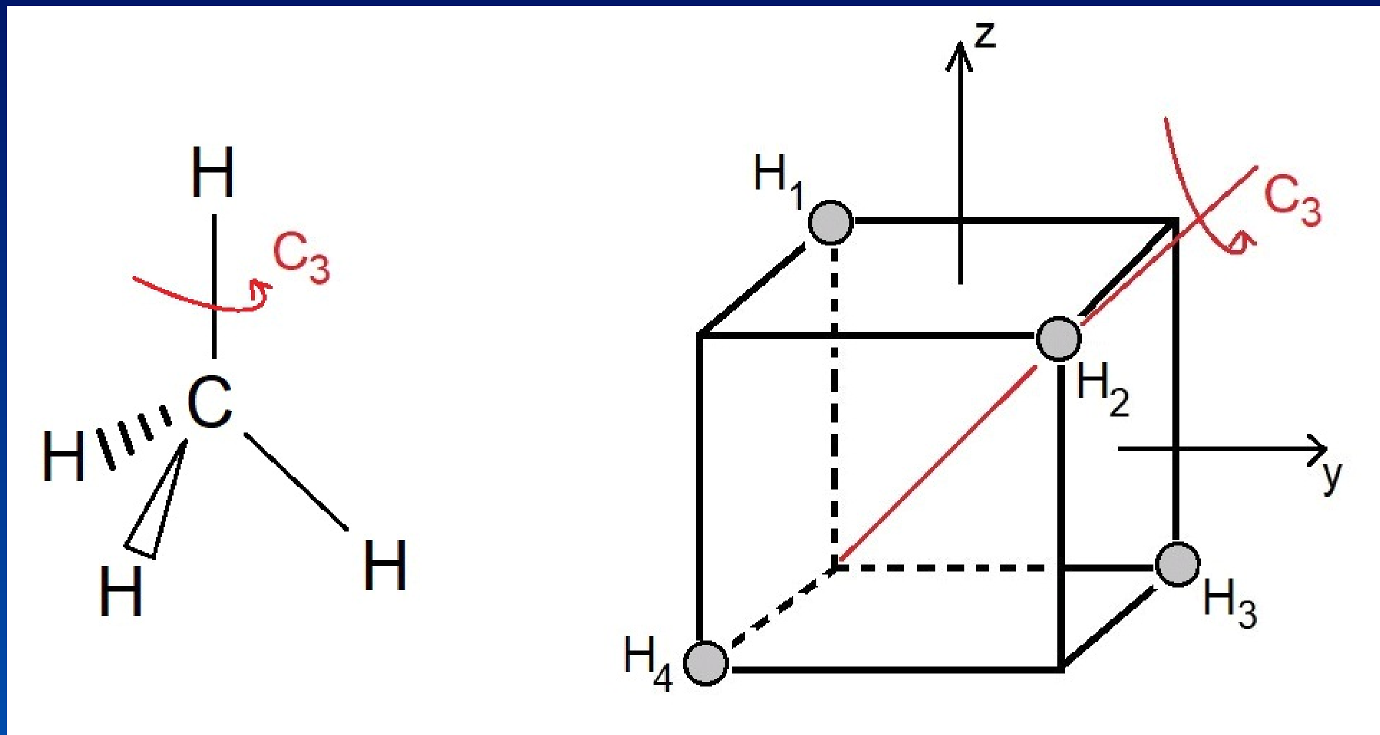


$$\hat{P}_{E_{12}}(\varphi_1) = \varphi_2 - \varphi_3$$

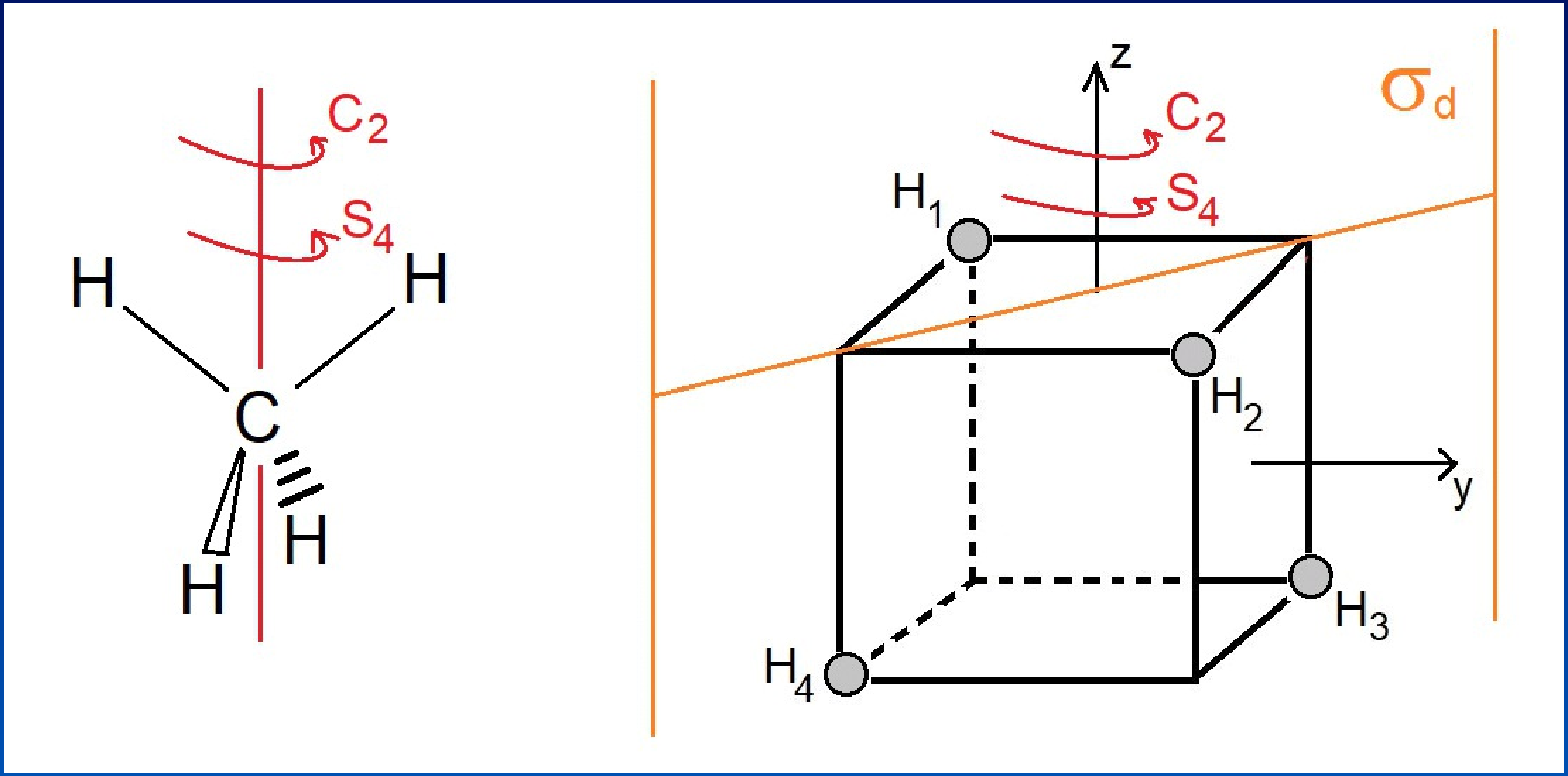
Metano, CH_4 - T_d

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

Metano, CH_4 - T_d



Metano, CH_4 - T_d



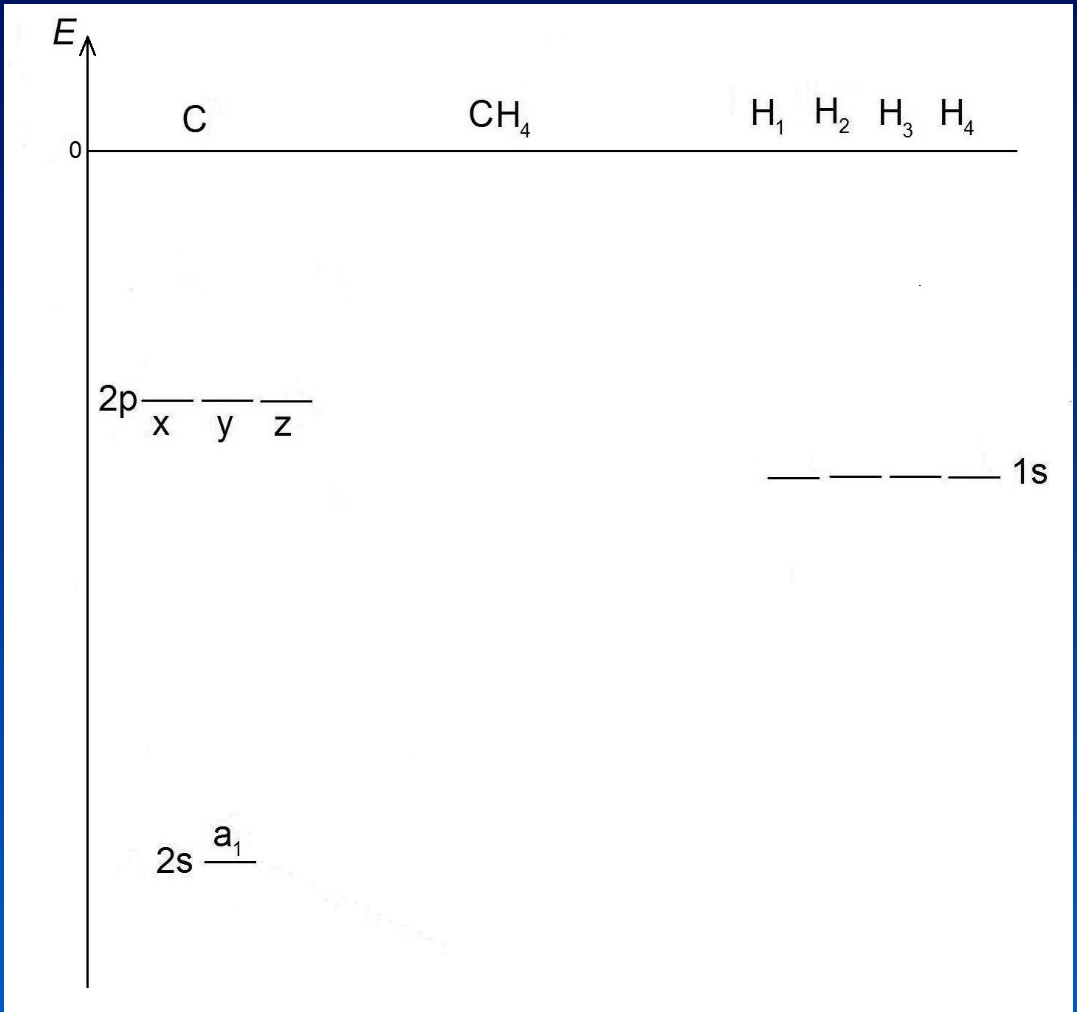
Metano, CH_4 - T_d

Classificando o orbital 2s do C

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	
2s	1	1	1	1	1	A_1

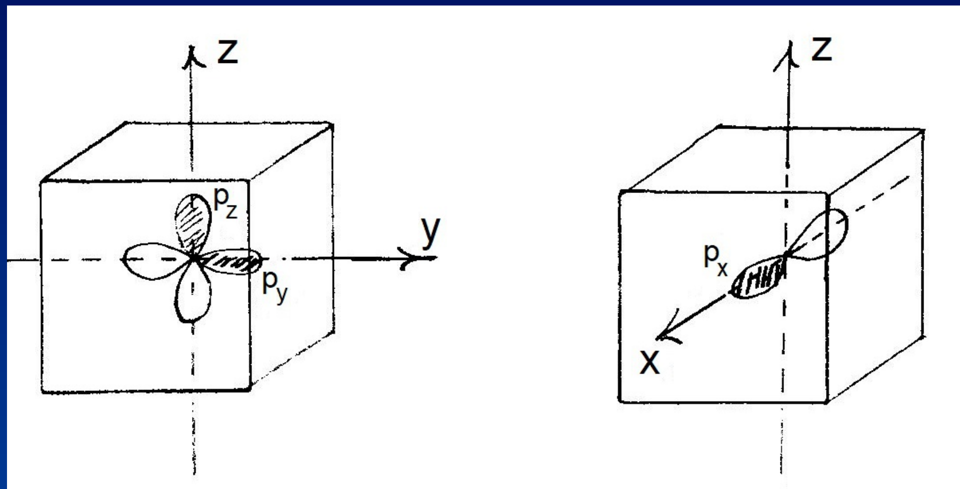
Metano, CH_4 - T_d

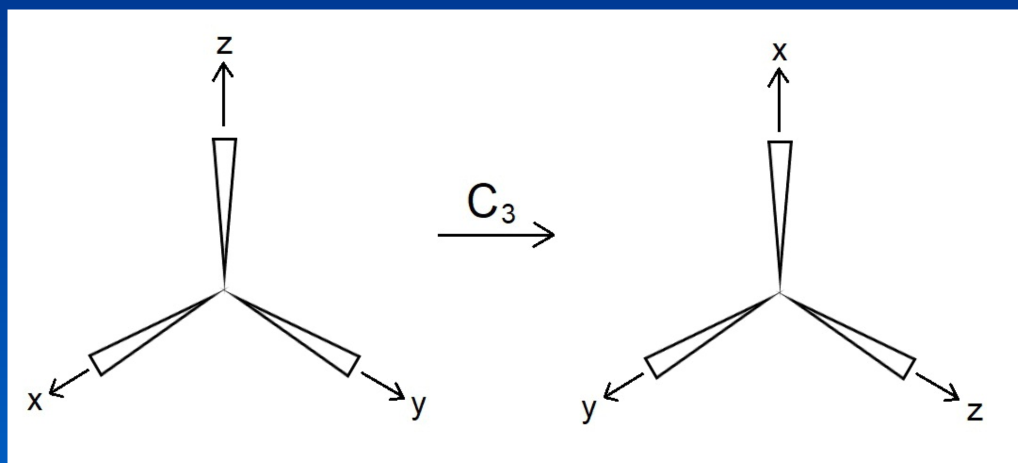
Construindo o diagrama de energia dos orbitais moleculares



Metano, CH_4 - T_d

Classificando os orbitais 2p do C - INSEPARÁVEIS





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

Metano, CH_4 - T_d

Classificando os orbitais 2p do C - INSEPARÁVEIS

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

$\xrightarrow{C_3}$

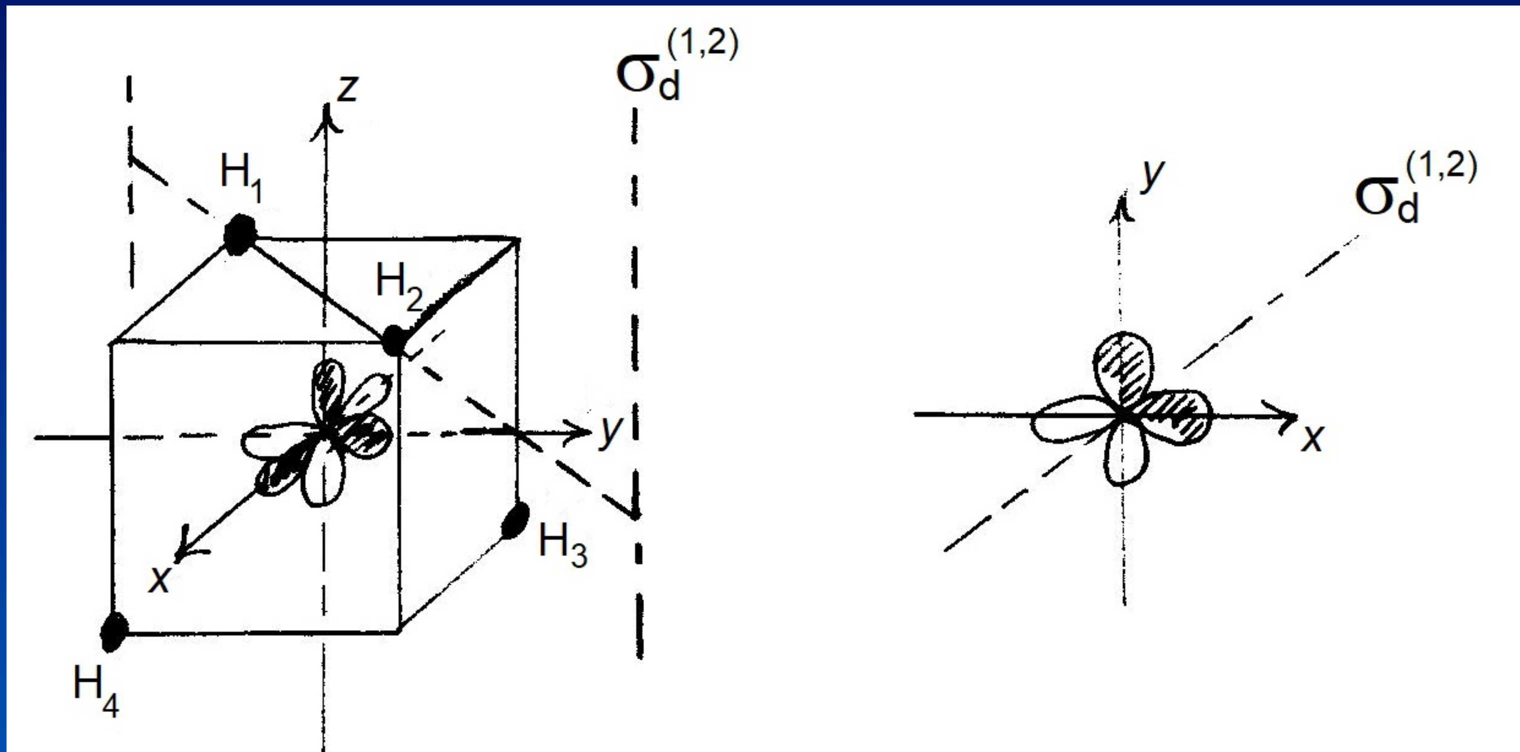
	$2p_x$	$2p_y$	$2p_z$
$2p_x$	0	1	0
$2p_y$	0	0	1
$2p_z$	1	0	0

$\chi = 0$

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_x,p_y,p_z)	3	0			

Metano, CH_4 - T_d

Classificando os orbitais 2p do C - INSEPARÁVEIS



Metano, CH_4 - T_d

Classificando os orbitais 2p do C - INSEPARÁVEIS

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

$\sigma_d \rightarrow$

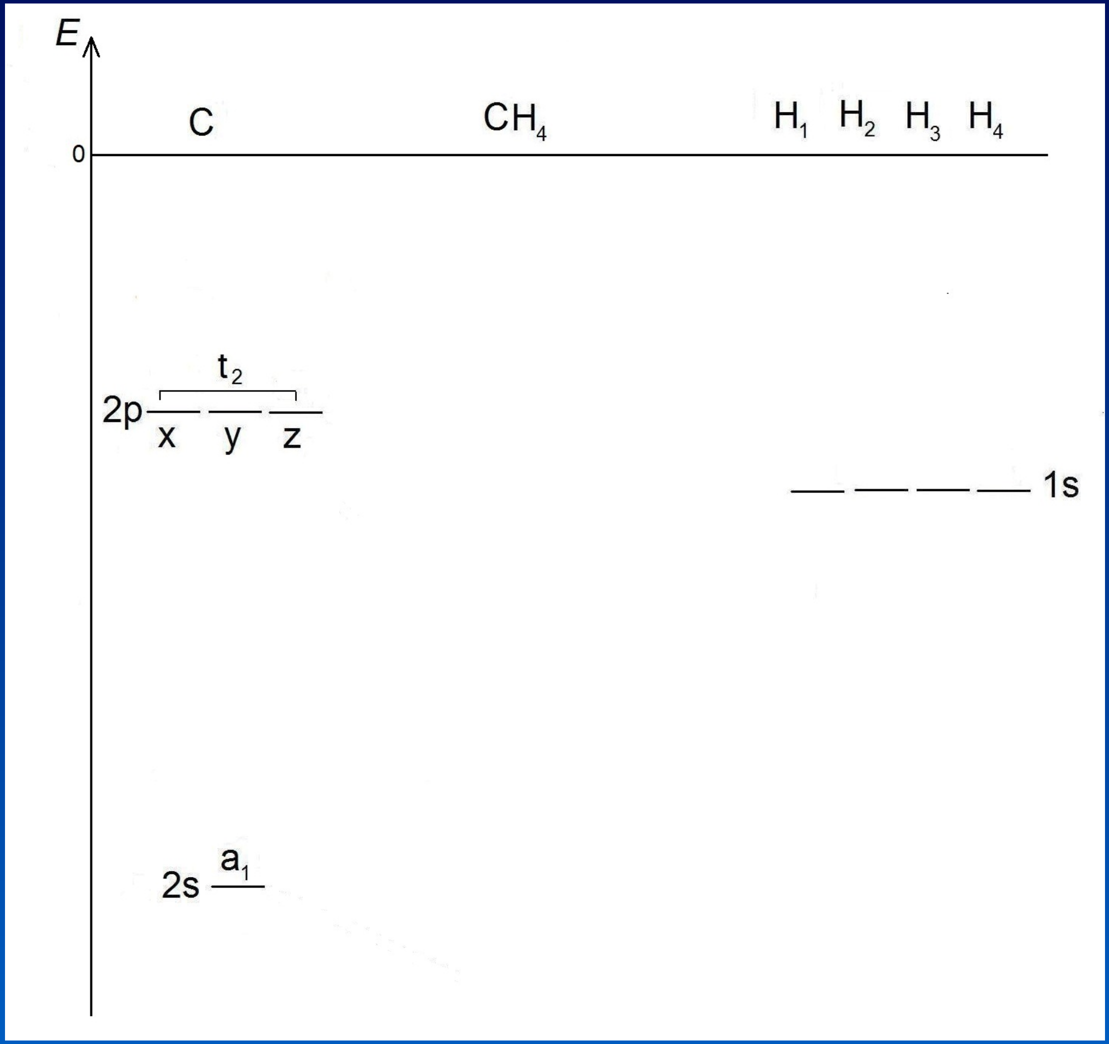
	$2p_x$	$2p_y$	$2p_z$
$2p_x$	0	1	0
$2p_y$	1	0	0
$2p_z$	0	0	1

$\chi = 1$

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_x,p_y,p_z)	3	0				1 T_2

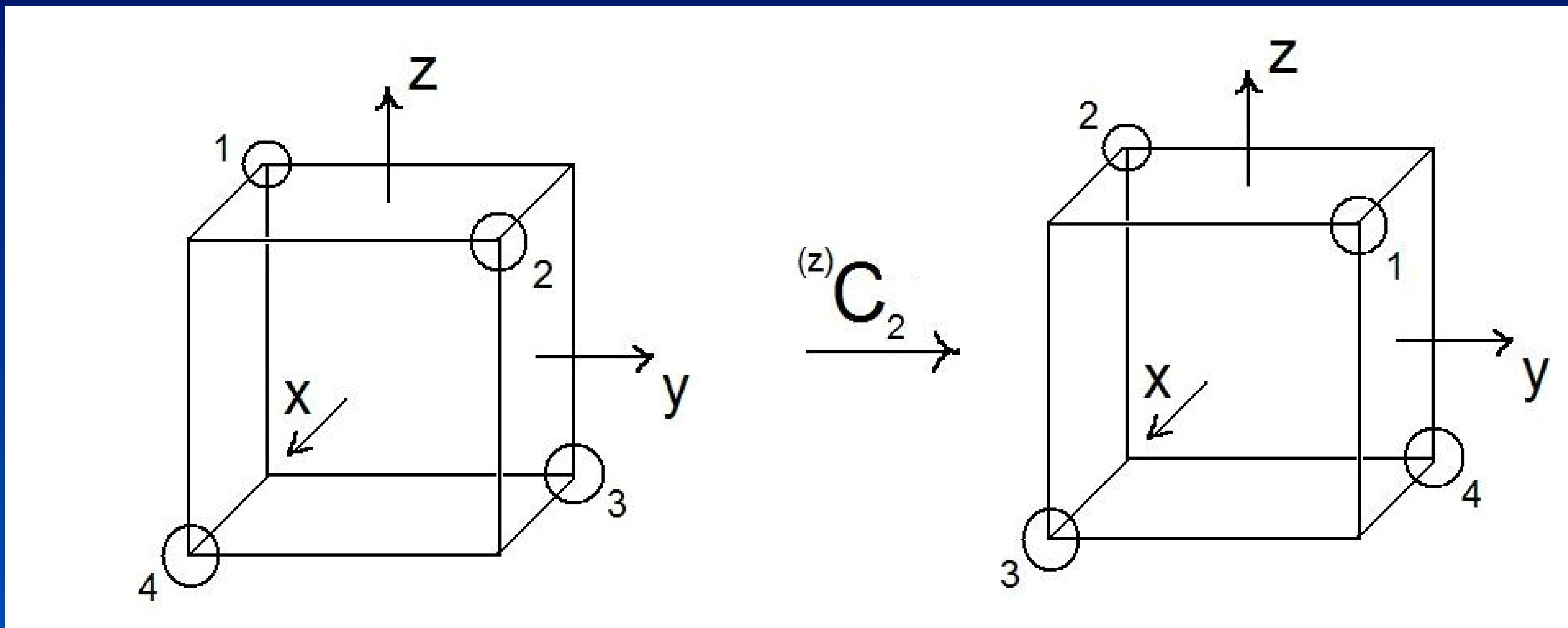
Metano, CH_4 - T_d

Construindo o diagrama de energia dos orbitais moleculares



Metano, CH_4 - T_d

Classificando os orbitais 1s dos H - INSEPARÁVEIS



Metano, CH_4 - T_d

Classificando os orbitais 1s dos H - INSEPARÁVEIS

	$1sH_1$	$1sH_2$	$1sH_3$	$1sH_4$
$1sH_1$	1	0	0	0
$1sH_2$	0	1	0	0
$1sH_3$	0	0	1	0
$1sH_4$	0	0	0	1

C_2 →

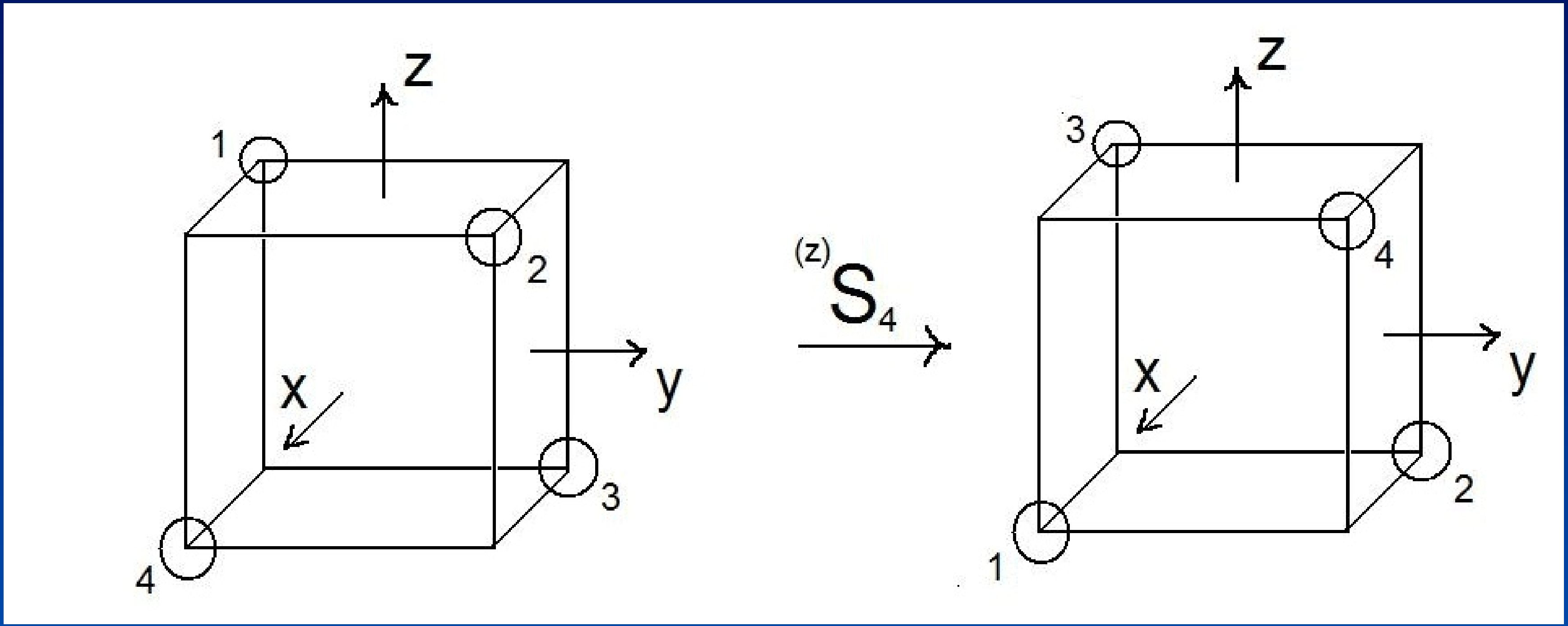
	$1sH_1$	$1sH_2$	$1sH_3$	$1sH_4$
$1sH_1$	0	1	0	0
$1sH_2$	1	0	0	0
$1sH_3$	0	0	0	1
$1sH_4$	0	0	1	0

$\chi = 0$

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
(H_1,H_2,H_3,H_4)	4		0		

Metano, CH_4 - T_d

Classificando os orbitais 1s dos H - INSEPARÁVEIS



Metano, CH_4 - T_d

Classificando os orbitais 1s dos H - INSEPARÁVEIS

	$1sH_1$	$1sH_2$	$1sH_3$	$1sH_4$
$1sH_1$	1	0	0	0
$1sH_2$	0	1	0	0
$1sH_3$	0	0	1	0
$1sH_4$	0	0	0	1

$\xrightarrow{S_4}$

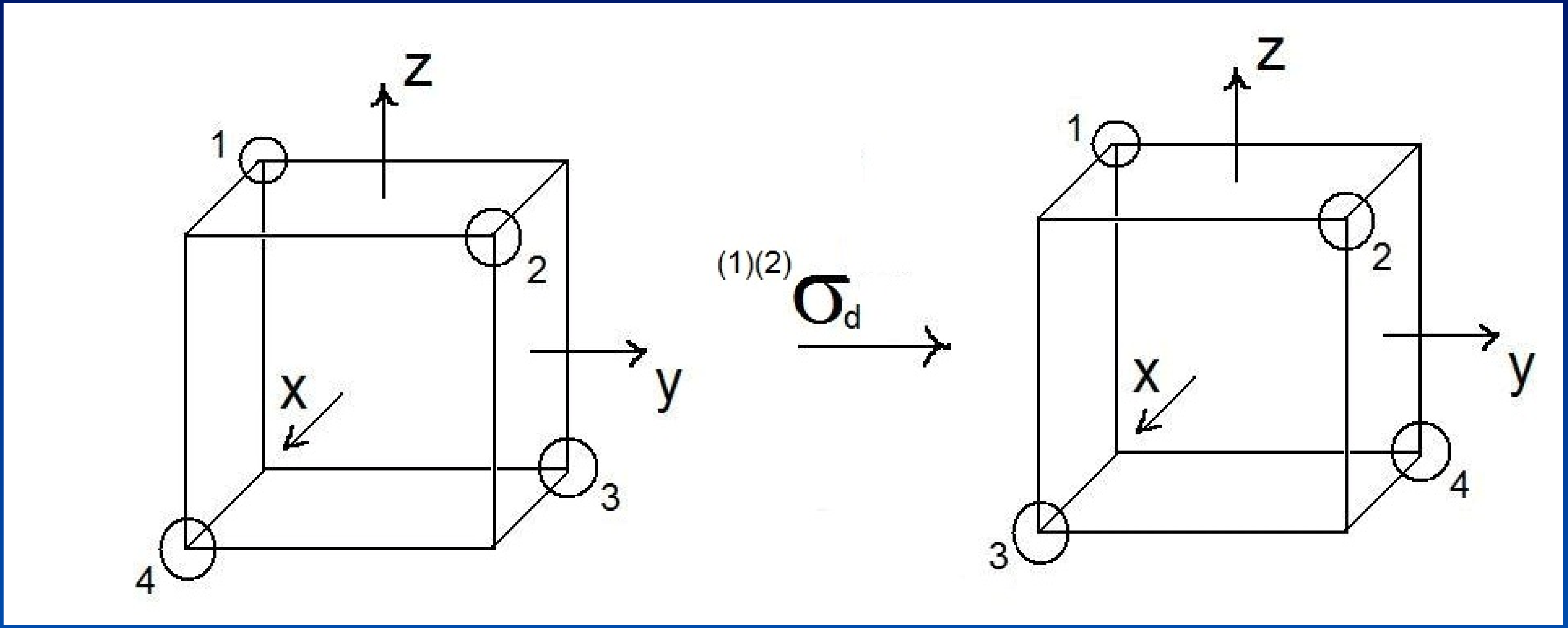
	$1sH_1$	$1sH_2$	$1sH_3$	$1sH_4$
$1sH_1$	0	0	0	1
$1sH_2$	0	0	1	0
$1sH_3$	1	0	0	0
$1sH_4$	0	1	0	0

$\chi = 0$

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
(H_1,H_2,H_3,H_4)	4		0	0	

Metano, CH_4 - T_d

Classificando os orbitais 1s dos H - INSEPARÁVEIS



Metano, CH_4 - T_d

Classificando os orbitais 1s dos H - INSEPARÁVEIS

	$1sH_1$	$1sH_2$	$1sH_3$	$1sH_4$
$1sH_1$	1	0	0	0
$1sH_2$	0	1	0	0
$1sH_3$	0	0	1	0
$1sH_4$	0	0	0	1

$\sigma_d \rightarrow$

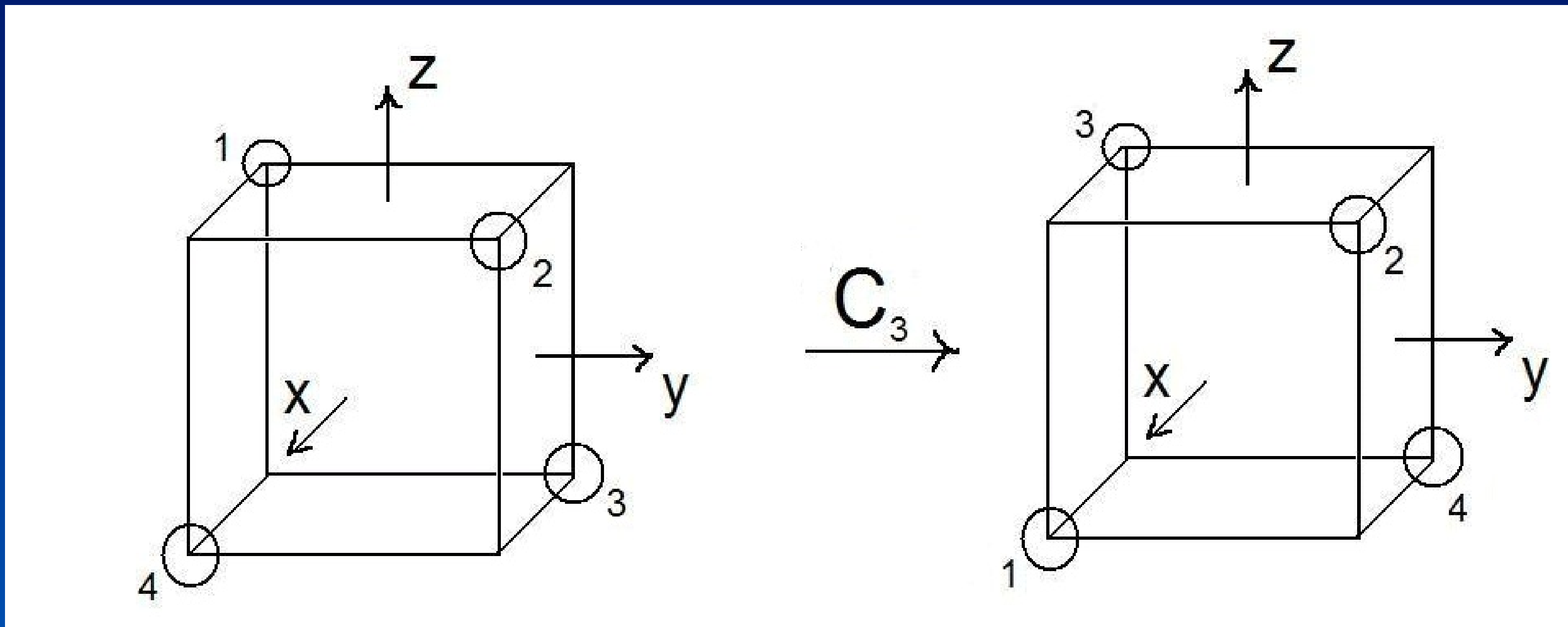
	$1sH_1$	$1sH_2$	$1sH_3$	$1sH_4$
$1sH_1$	1	0	0	0
$1sH_2$	0	1	0	0
$1sH_3$	0	0	0	1
$1sH_4$	0	0	1	0

$\chi = 2$

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
(H_1,H_2,H_3,H_4)	4		0	0	2

Metano, CH_4 - T_d

Classificando os orbitais 1s dos H - INSEPARÁVEIS



Metano, CH_4 - T_d

Classificando os orbitais 1s dos H - INSEPARÁVEIS

	$1sH_1$	$1sH_2$	$1sH_3$	$1sH_4$
$1sH_1$	1	0	0	0
$1sH_2$	0	1	0	0
$1sH_3$	0	0	1	0
$1sH_4$	0	0	0	1

C_3 $\rightarrow$

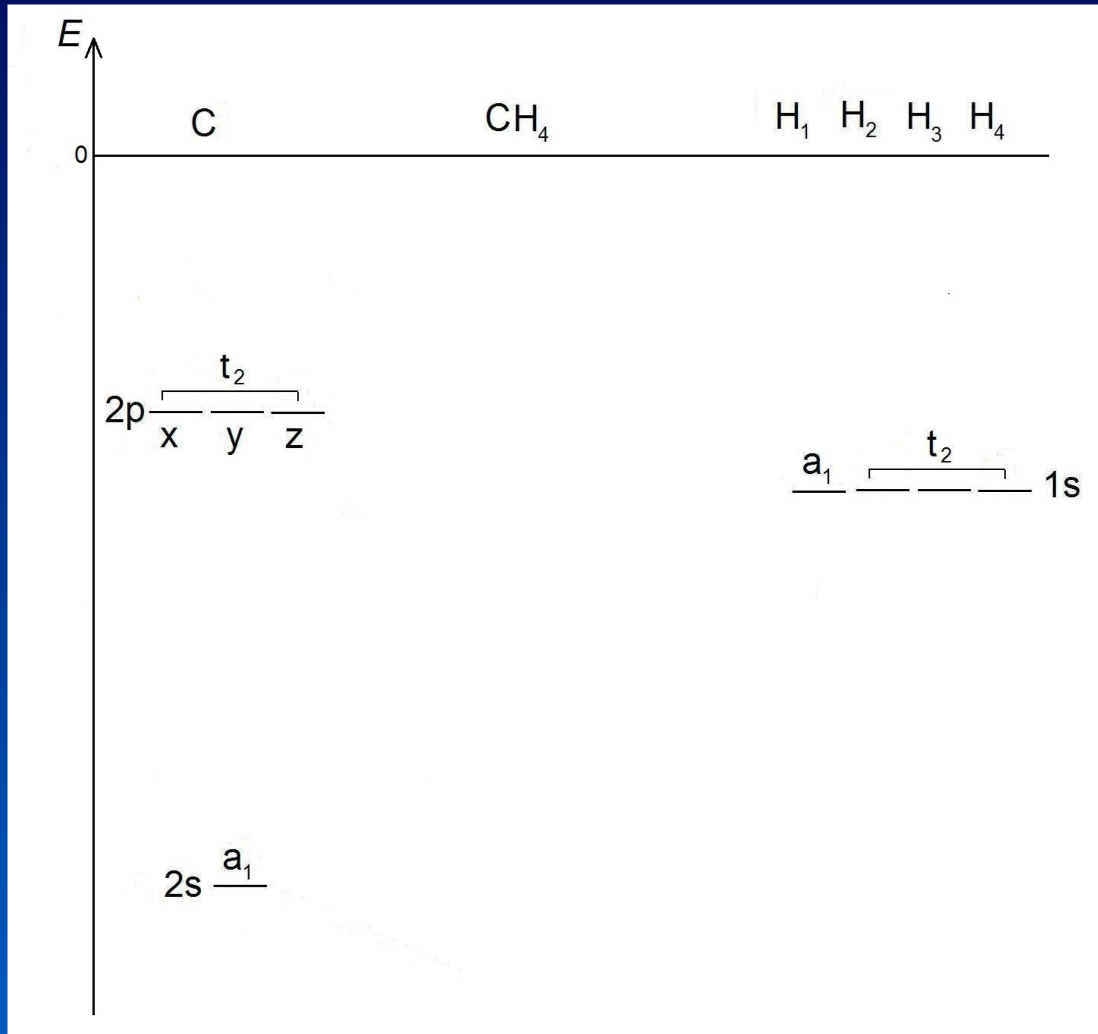
	$1sH_1$	$1sH_2$	$1sH_3$	$1sH_4$
$1sH_1$	0	0	0	1
$1sH_2$	0	1	0	0
$1sH_3$	1	0	0	0
$1sH_4$	0	0	1	0

$\chi = 1$

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	
(H_1,H_2,H_3,H_4)	4	1	0	0	2	$T_2 + A_1$

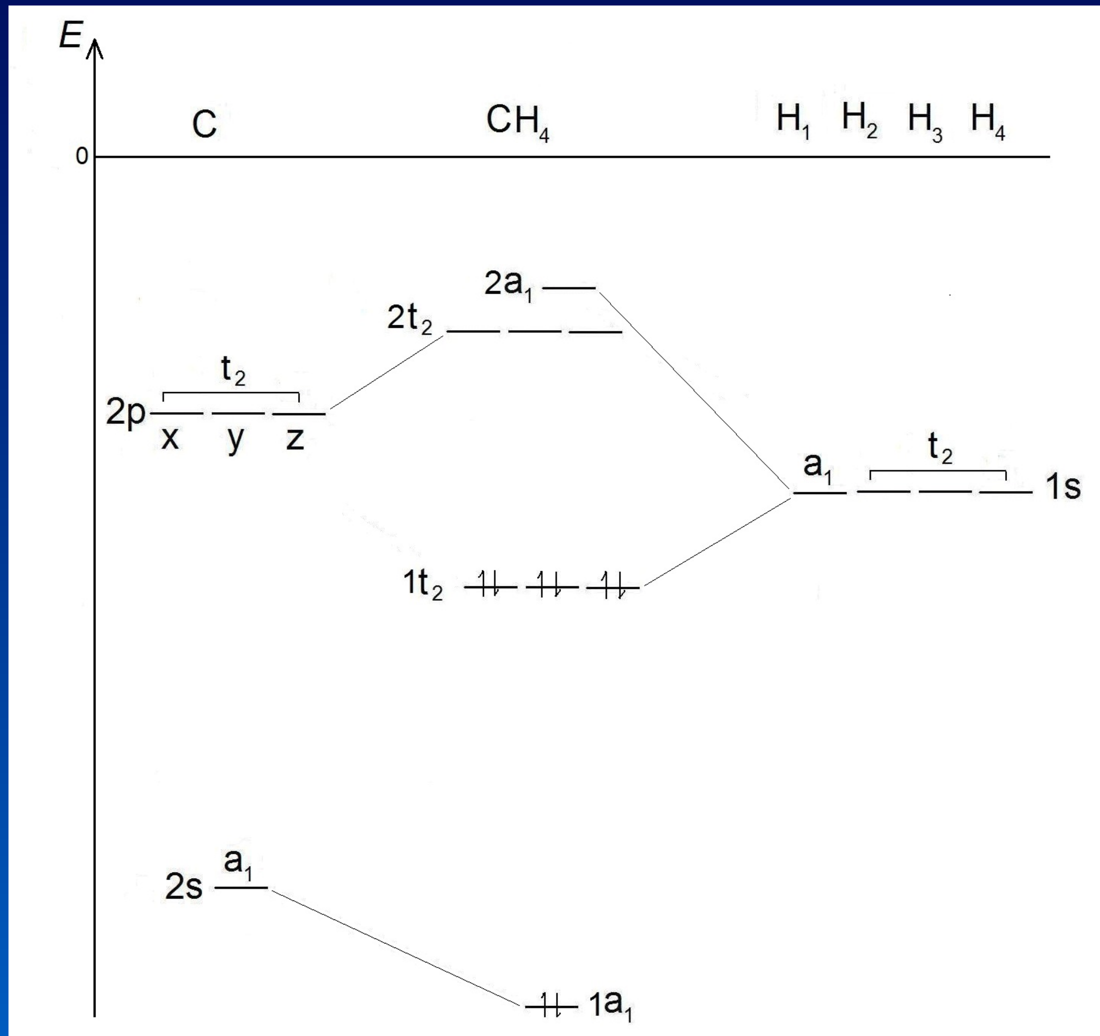
Metano, CH_4 - T_d

Construindo o diagrama de energia dos orbitais moleculares

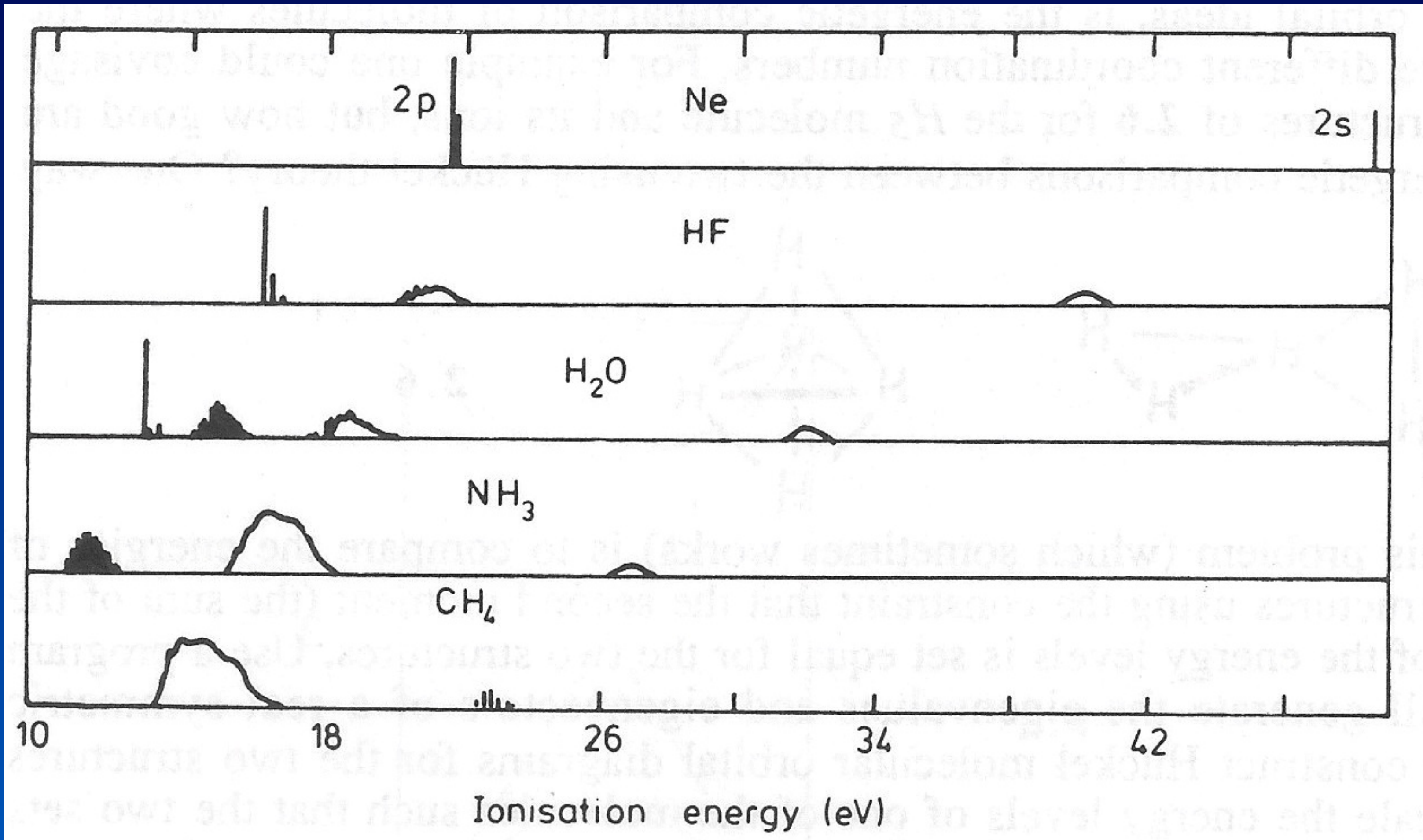


Metano, CH_4 - T_d

Construindo o diagrama de energia dos orbitais moleculares

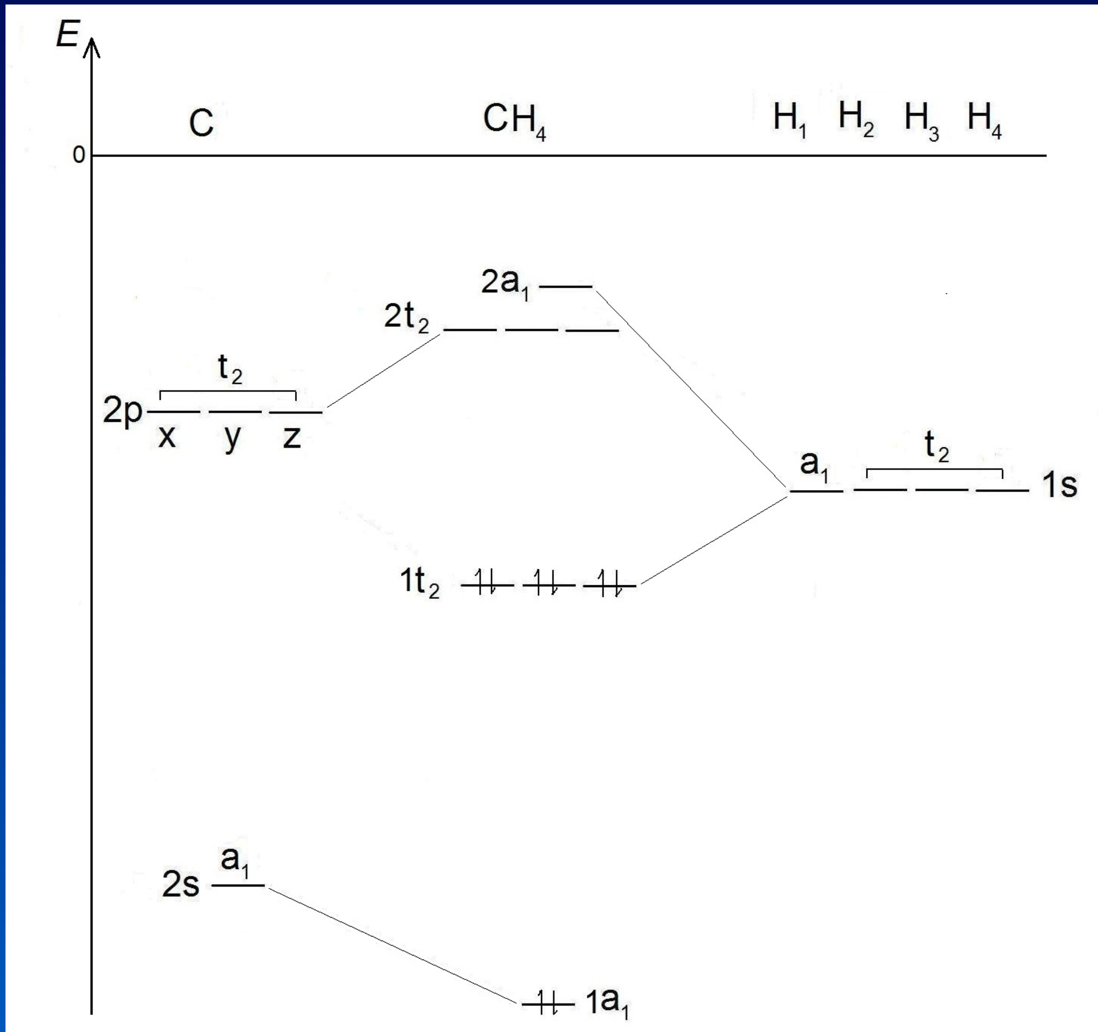


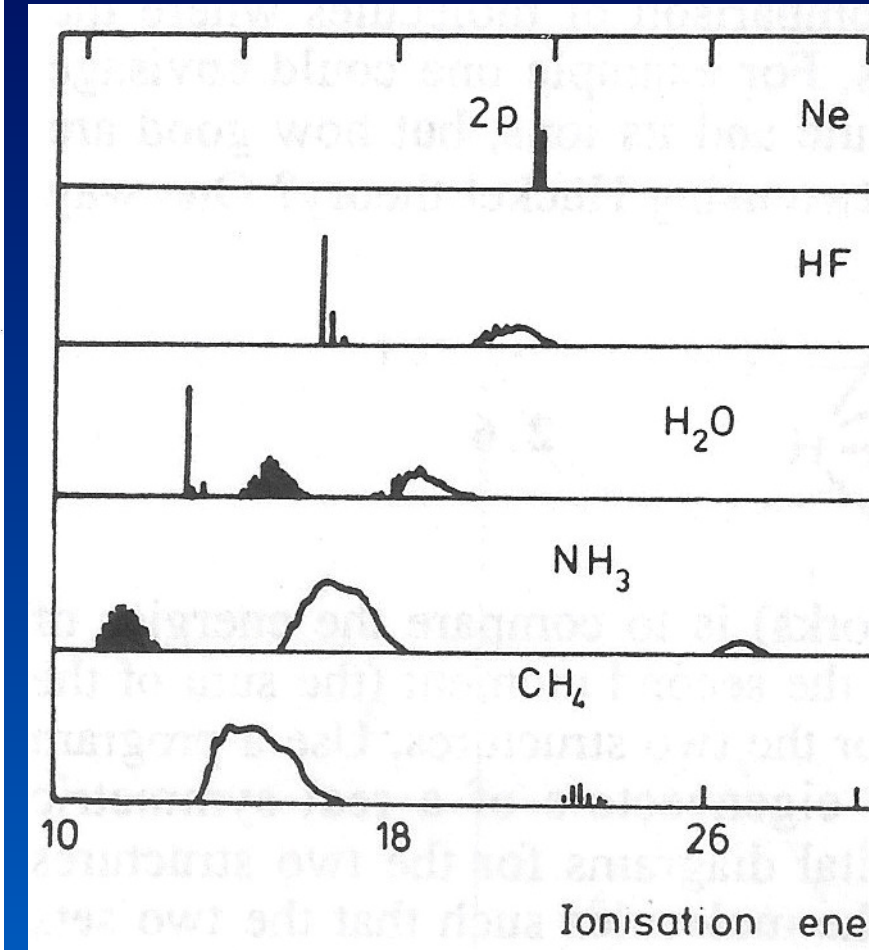
Espectros de fotoelétron



Albright, T. A.; Burdett, J. K. *Problems in Molecular Orbital Theory*, Oxford University Press, 1992. pg. 32

Espectros de fotoelétron





Albright, T. A.; Burdett, J. K. *Problems in Molecular Orbital T*

Metano, CH_4 - T_d

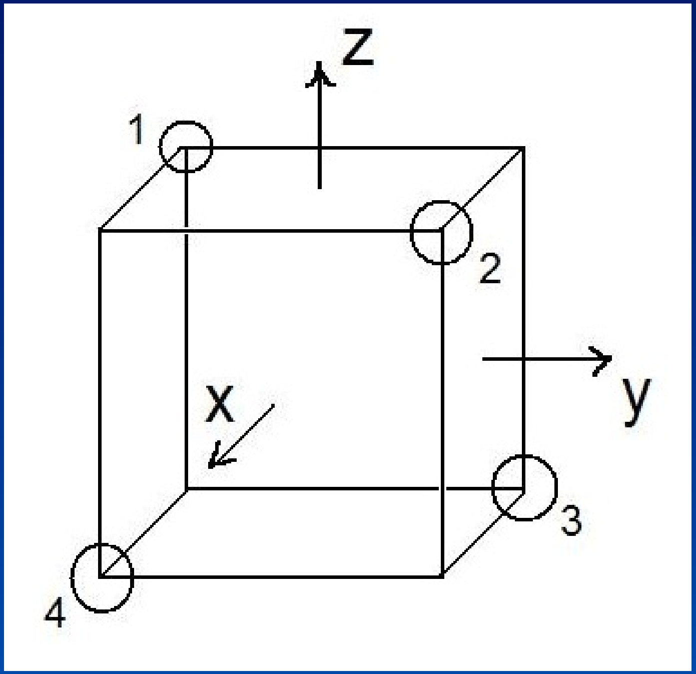
Desenhando os orbitais moleculares

Aplicando o Método do Operador Projeção

Construindo uma lista de projeções

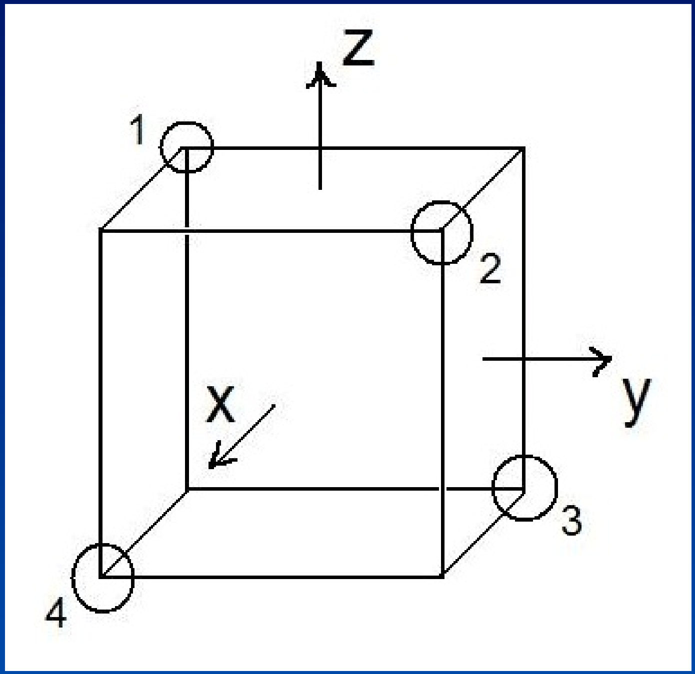
Metano, CH_4 - T_d

E	φ_1
$^{(1)}C_3$	φ_1
$^{(1)}C_3^{\;2}$	φ_1
$^{(2)}C_3$	φ_4
$^{(2)}C_3^{\;2}$	φ_3
$^{(3)}C_3$	φ_2
$^{(3)}C_3^{\;2}$	φ_4
$^{(4)}C_3$	φ_3
$^{(4)}C_3^{\;2}$	φ_2



Metano, CH_4 - T_d

$^{(x)}C_2$	φ_3
$^{(y)}C_2$	φ_4
$^{(z)}C_2$	φ_2
$^{(x)}S_4$	φ_4
$^{(x)}S_4^{\ 3}$	φ_2
$^{(y)}S_4$	φ_2
$^{(y)}S_4^{\ 3}$	φ_3
$^{(z)}S_4$	φ_4
$^{(z)}S_4^{\ 3}$	φ_3



Metano, CH_4 - T_d

$^{(1)(2)}\sigma_d \quad \varphi_1$

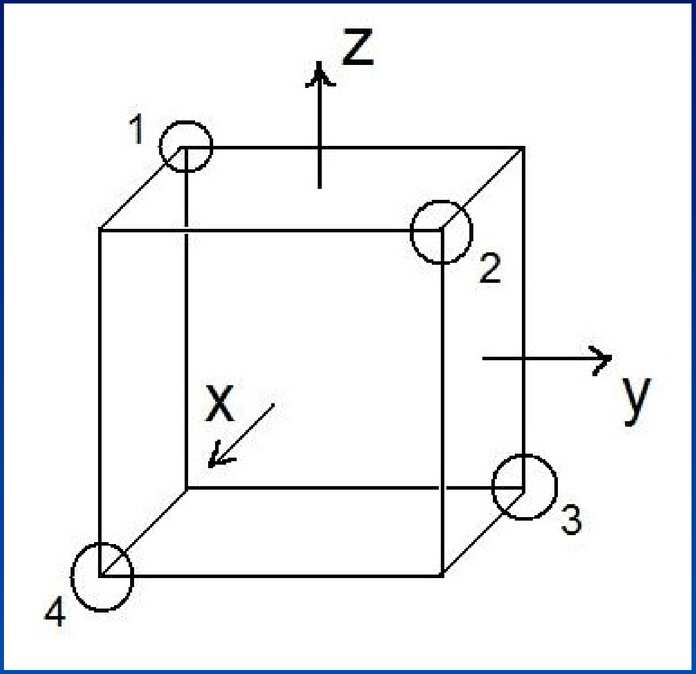
$^{(3)(4)}\sigma_d \quad \varphi_2$

$^{(2)(3)}\sigma_d \quad \varphi_4$

$^{(1)(4)}\sigma_d \quad \varphi_1$

$^{(2)(4)}\sigma_d \quad \varphi_3$

$^{(1)(3)}\sigma_d \quad \varphi_1$



Metano, CH_4 - T_d

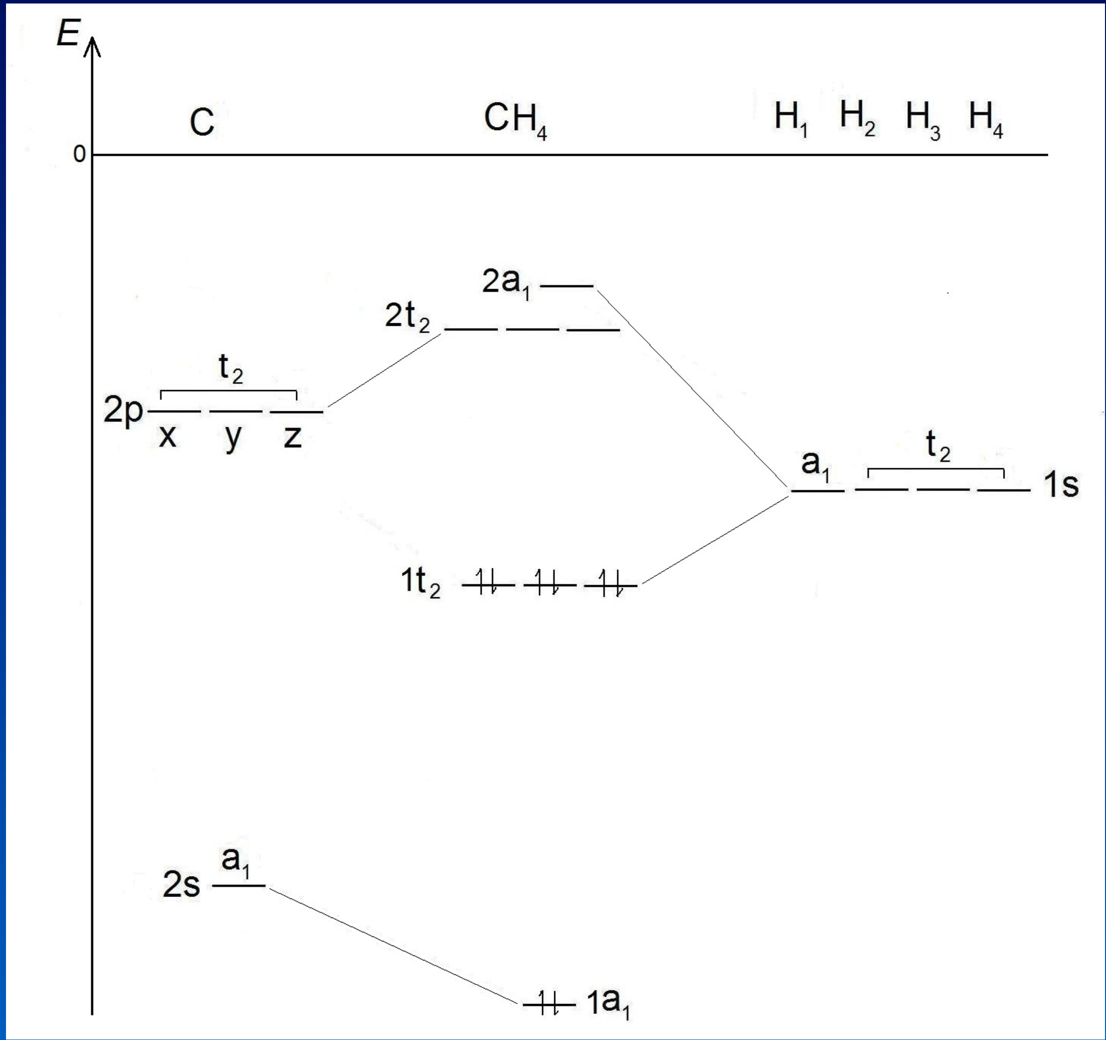
T_d	E	$8C_3$	$3C_2$	$6S_4$	$6\sigma_d$
A_1	1	1	1	1	1
A_2	1	1	1	-1	-1
E	2	-1	2	0	0
T_1	3	0	-1	1	-1
T_2	3	0	-1	-1	1

$$\hat{P}_{A_1}(\varphi_1) = 6\varphi_1 + 6\varphi_2 + 6\varphi_3 + 6\varphi_4$$

$$\hat{P}_{A_1}(\varphi_1) = \varphi_1 + \varphi_2 + \varphi_3 + \varphi_4$$

Metano, CH_4 - T_d

Diagrama de energia dos orbitais moleculares



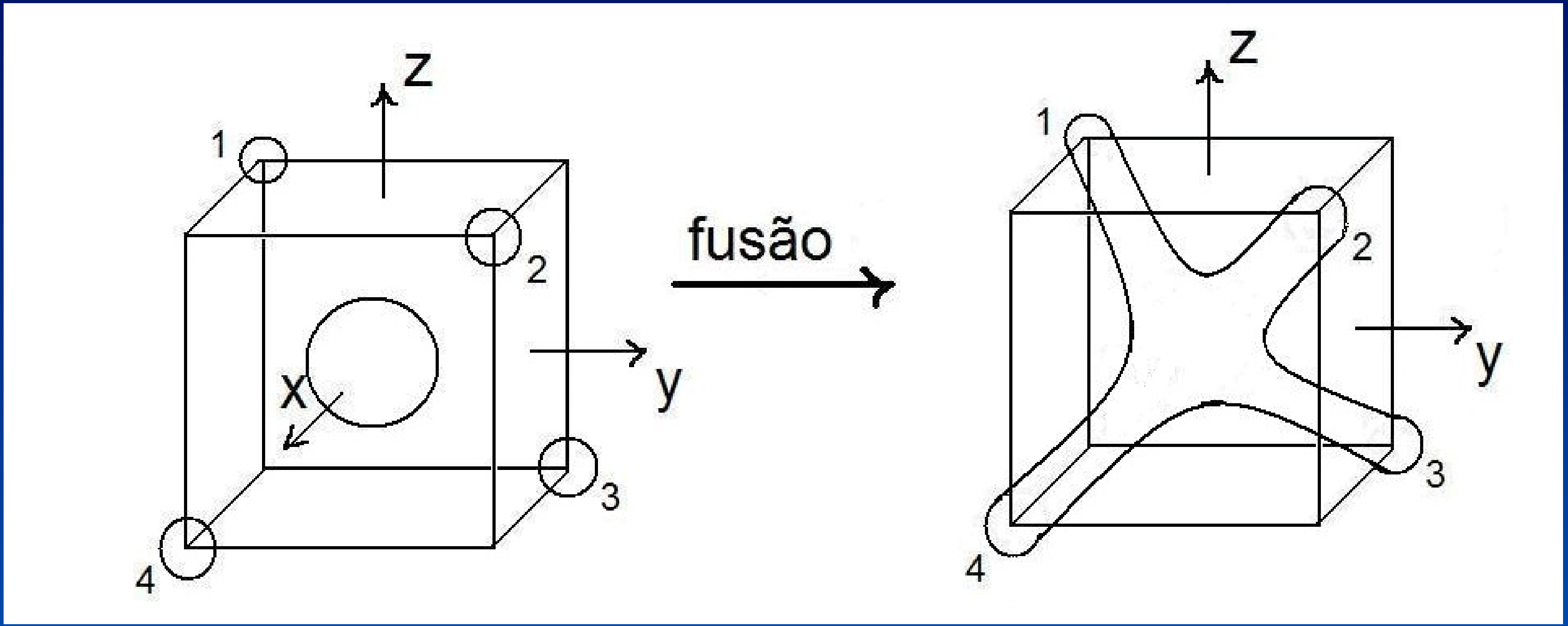
Metano, CH_4 - T_d

Desenhando o orbital molecular $1a_1$

Juntando as regiões de mesma fase matemática

Metano, CH_4 - T_d

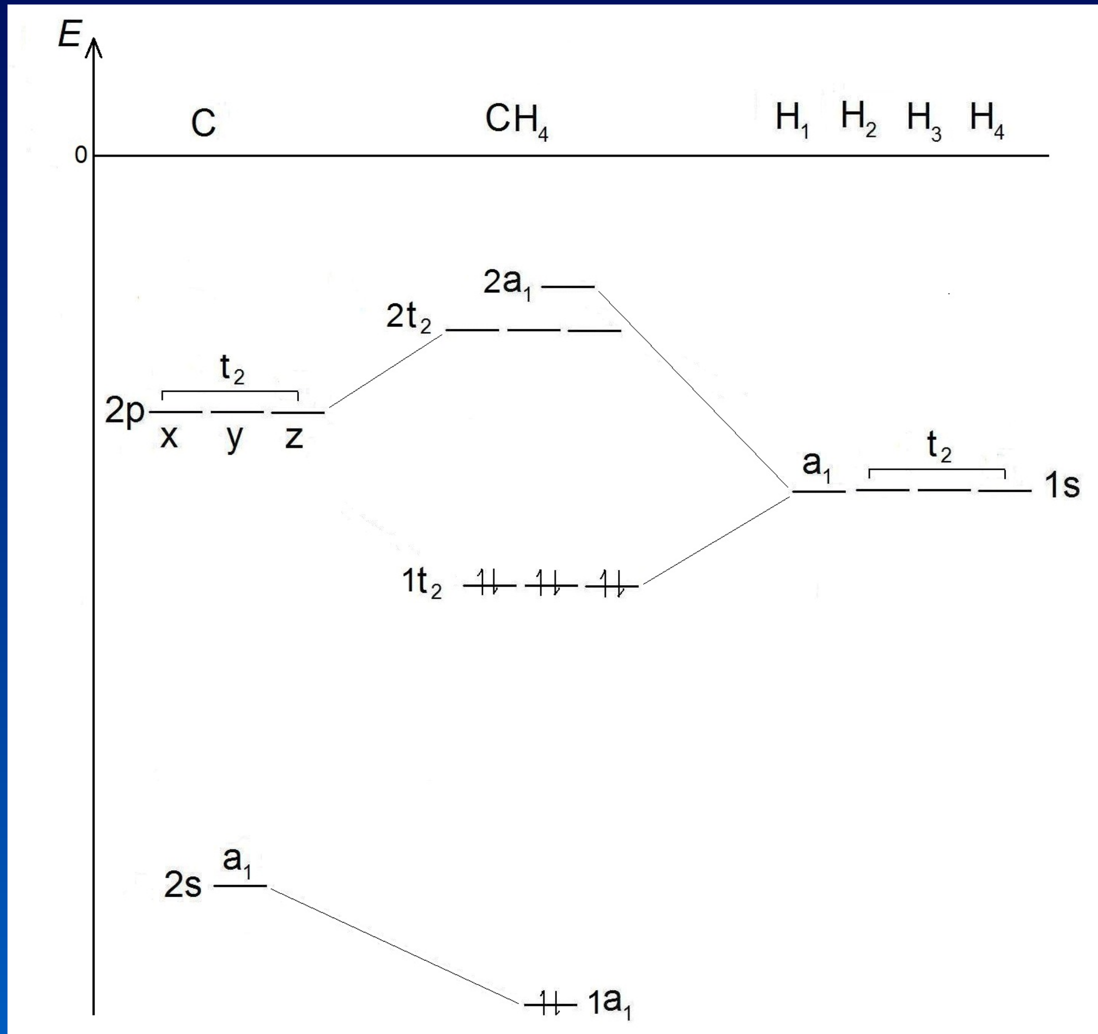
Orbital $1a_1$, ligante



$$\hat{P}_{A_1}(\varphi_1) = \varphi_1 + \varphi_2 + \varphi_3 + \varphi_4$$

Metano, CH_4 - T_d

Diagrama de energia dos orbitais moleculares



Metano, CH_4 - 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

$$\hat{P}_{T_2}(\varphi_1) = ?$$

Metano, CH_4 - T_d

Representação irredutível T_2

		$T_2^{(11)}$
E	φ_1	1
$^{(1)}C_3$	φ_1	0
$^{(1)}C_3^{\,2}$	φ_1	0
$^{(2)}C_3$	φ_4	0
$^{(2)}C_3^{\,2}$	φ_3	0
$^{(3)}C_3$	φ_2	0
$^{(3)}C_3^{\,2}$	φ_4	0
$^{(4)}C_3$	φ_3	0
$^{(4)}C_3^{\,2}$	φ_2	0

$$E = \begin{bmatrix} 1 & & \\ & 1 & \\ & & 1 \end{bmatrix}$$

$$C_3 = \begin{bmatrix} 0 & & \\ & 0 & \\ & & 0 \end{bmatrix}$$

$$\hat{P}_{T_{2(11)}}(\varphi_1) = \varphi_1 + \ldots$$

Metano, CH_4 - T_d

Representação irredutível T_2

		$T_2^{(11)}$
$^{(x)}C_2$	φ_3	-1
$^{(y)}C_2$	φ_4	-1
$^{(z)}C_2$	φ_2	1
$^{(x)}S_4$	φ_4	0
$^{(x)}S_4^3$	φ_2	0
$^{(y)}S_4$	φ_2	0
$^{(y)}S_4^3$	φ_3	0
$^{(z)}S_4$	φ_4	-1
$^{(z)}S_4^3$	φ_3	-1

$$^{x}C_2 = \begin{bmatrix} -1 & & \\ & -1 & \\ & & 1 \end{bmatrix} \qquad ^{x}S_4 = {}^{x}S_4^3 = \begin{bmatrix} 0 & & \\ & 0 & \\ & & -1 \end{bmatrix}$$

$$^{y}C_2 = \begin{bmatrix} -1 & & \\ & 1 & \\ & & -1 \end{bmatrix} \qquad ^{y}S_4 = {}^{y}S_4^3 = \begin{bmatrix} 0 & & \\ & -1 & \\ & & 0 \end{bmatrix}$$

$$^{z}C_2 = \begin{bmatrix} 1 & & \\ & -1 & \\ & & -1 \end{bmatrix} \qquad ^{z}S_4 = {}^{z}S_4^3 = \begin{bmatrix} -1 & & \\ & 0 & \\ & & 0 \end{bmatrix}$$

$$\hat{P}_{T_{2(11)}}(\varphi_1) = \varphi_1 + \varphi_2 - 2\varphi_3 - 2\varphi_4 + \dots$$

Metano, CH_4 - T_d

Representação irredutível T_2

		$T_2^{(11)}$
${}^{(4)(2)}\sigma_d$	φ_3	0
${}^{(1)(3)}\sigma_d$	φ_1	0
${}^{(2)(3)}\sigma_d$	φ_4	0
${}^{(1)(4)}\sigma_d$	φ_1	0
${}^{(1)(2)}\sigma_d$	φ_1	1
${}^{(3)(4)}\sigma_d$	φ_2	1

$$^{x-42}\sigma_d = {}^{x-13}\sigma_d = \begin{bmatrix} 0 & & \\ & 0 & \\ & & 1 \end{bmatrix}$$

$$^{y-23}\sigma_d = {}^{y-14}\sigma_d = \begin{bmatrix} 0 & & \\ & 1 & \\ & & 0 \end{bmatrix}$$

$$^{z-12}\sigma_d = {}^{z-34}\sigma_d = \begin{bmatrix} 1 & & \\ & 0 & \\ & & 0 \end{bmatrix}$$

$$\hat{P}_{T_{2_{(11)}}}(\varphi_1) = 2\varphi_1 + 2\varphi_2 - 2\varphi_3 - 2\varphi_4$$

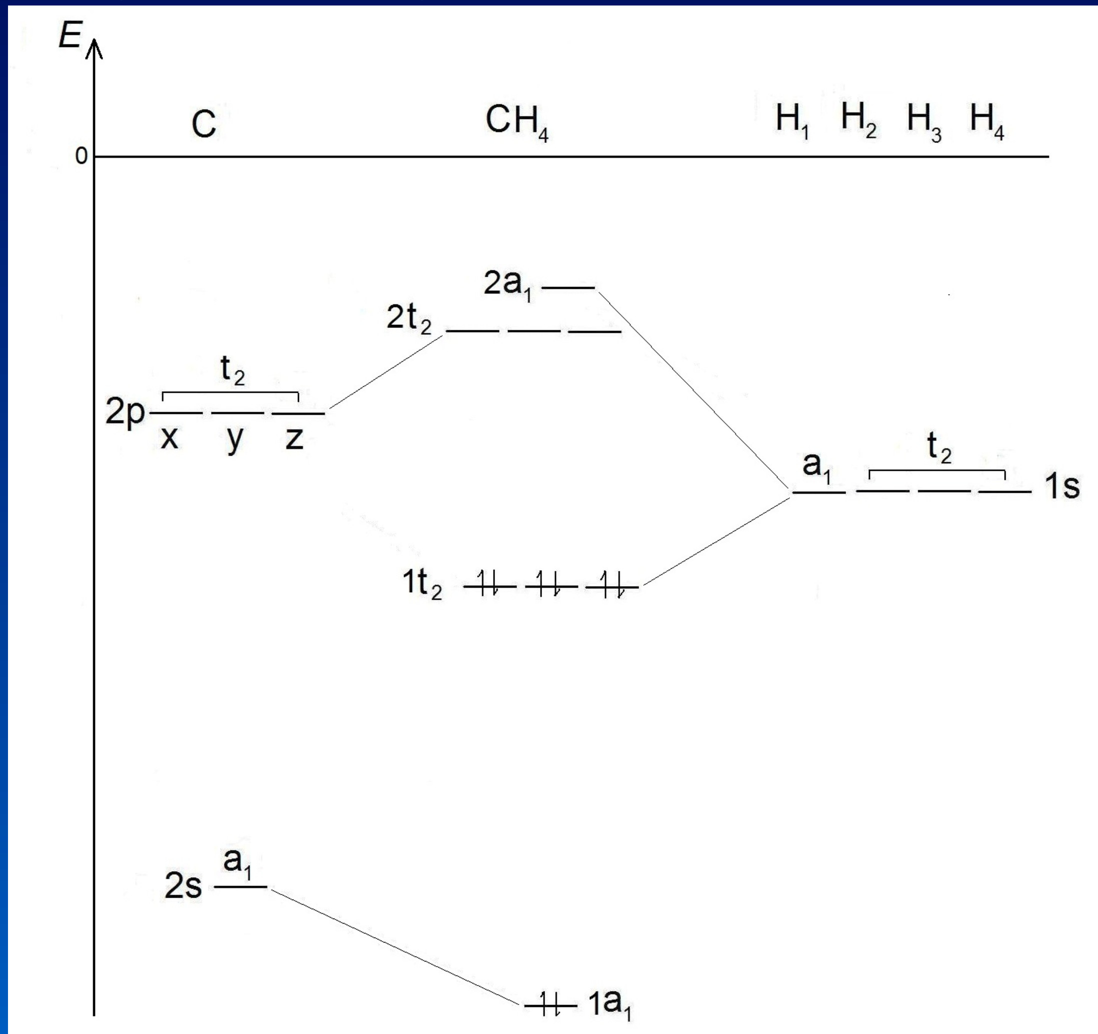
Metano, CH_4 - T_d

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

$$\hat{P}_{T_{2(11)}}(\varphi_1) = \varphi_1 + \varphi_2 - \varphi_3 - \varphi_4$$

Metano, CH_4 - T_d

Diagrama de energia dos orbitais moleculares



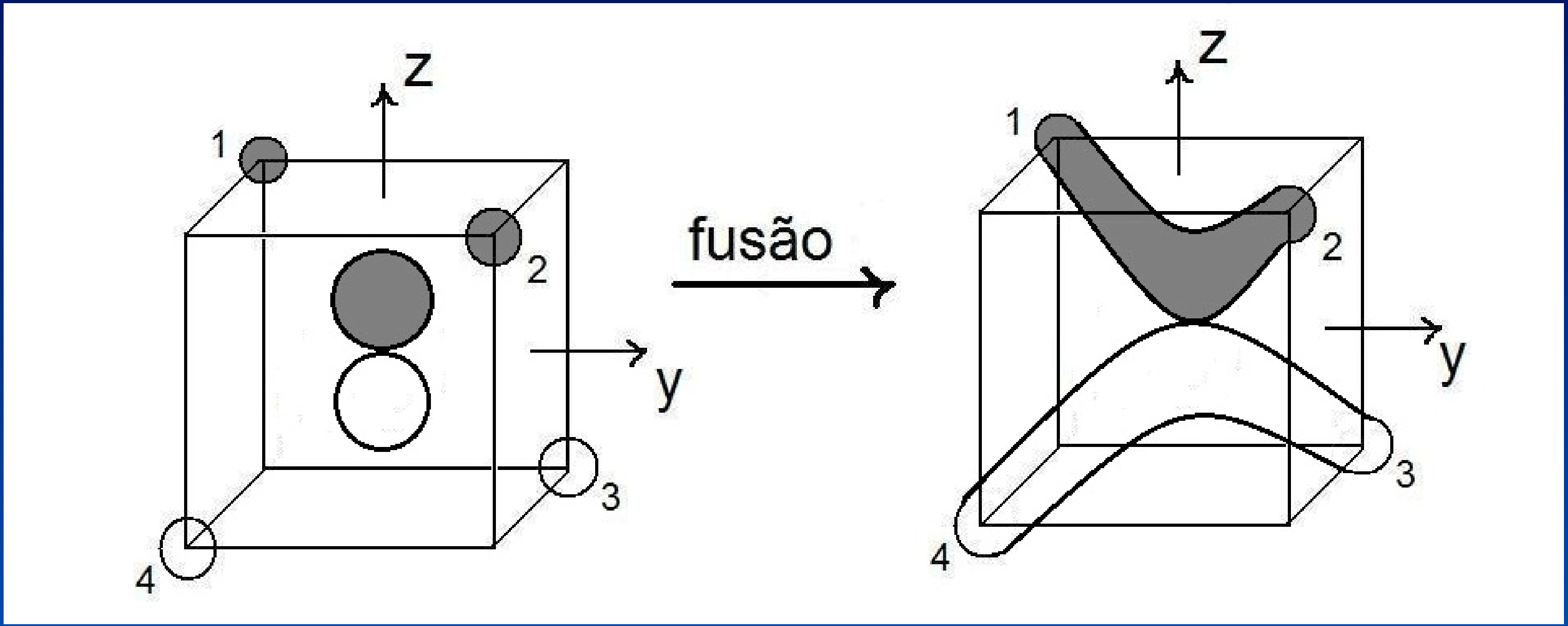
Metano, CH_4 - T_d

Desenhando um dos orbitais moleculares $1T_2$

Juntando as regiões de mesma fase matemática

Metano, CH_4 - T_d

Um dos orbitais T_2, ligante



$$\hat{P}_{T_{2(11)}}(\varphi_1) = \varphi_1 + \varphi_2 - \varphi_3 - \varphi_4$$

Metano, CH_4 - T_d

Representação irredutível T_2

		$T_2^{(22)}$
E	φ_1	1
$^{(1)}C_3$	φ_1	0
$^{(1)}C_3^2$	φ_1	0
$^{(2)}C_3$	φ_4	0
$^{(2)}C_3^2$	φ_3	0
$^{(3)}C_3$	φ_2	0
$^{(3)}C_3^2$	φ_4	0
$^{(4)}C_3$	φ_3	0
$^{(4)}C_3^2$	φ_2	0

$$E = \begin{bmatrix} 1 & & \\ & 1 & \\ & & 1 \end{bmatrix}$$

$$C_3 = \begin{bmatrix} 0 & & \\ & 0 & \\ & & 0 \end{bmatrix}$$

$$\hat{P}_{T_{2_{(22)}}}(\varphi_1) = \varphi_1 + \ldots$$

Metano, CH_4 - T_d

Representação irredutível T_2

		$T_2^{(22)}$
$^{(x)}C_2$	φ_3	-1
$^{(y)}C_2$	φ_4	1
$^{(z)}C_2$	φ_2	-1
$^{(x)}S_4$	φ_4	0
$^{(x)}S_4^3$	φ_2	0
$^{(y)}S_4$	φ_2	-1
$^{(y)}S_4^3$	φ_3	-1
$^{(z)}S_4$	φ_4	0
$^{(z)}S_4^3$	φ_3	0

$$^{x}C_2 = \begin{bmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

$$^{y}C_2 = \begin{bmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{bmatrix}$$

$$^{z}C_2 = \begin{bmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{bmatrix}$$

$$^{x}S_4 = {}^{x}S_4^3 = \begin{bmatrix} 0 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & -1 \end{bmatrix}$$

$$^{y}S_4 = {}^{y}S_4^3 = \begin{bmatrix} 0 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 0 \end{bmatrix}$$

$$^{z}S_4 = {}^{z}S_4^3 = \begin{bmatrix} -1 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix}$$

$$\hat{P}_{T_{2_{(22)}}}(\varphi_1) = \varphi_1 - 2\varphi_2 - 2\varphi_3 + \varphi_4 + \ldots$$

Metano, CH_4 - T_d

Representação irredutível T_2

		$T_2^{(22)}$
$^{(4)(2)}\sigma_d$	φ_3	0
$^{(1)(3)}\sigma_d$	φ_1	0
$^{(2)(3)}\sigma_d$	φ_4	1
$^{(1)(4)}\sigma_d$	φ_1	1
$^{(1)(2)}\sigma_d$	φ_1	0
$^{(3)(4)}\sigma_d$	φ_2	0

$$^{x-42}\sigma_d = {}^{x-13}\sigma_d = \begin{bmatrix} 0 & & \\ & 0 & \\ & & 1 \end{bmatrix}$$

$$^{y-23}\sigma_d = {}^{y-14}\sigma_d = \begin{bmatrix} 0 & & \\ & 1 & \\ & & 0 \end{bmatrix}$$

$$^{z-12}\sigma_d = {}^{z-34}\sigma_d = \begin{bmatrix} 1 & & \\ & 0 & \\ & & 0 \end{bmatrix}$$

$$\hat{P}_{T_{2_{(22)}}}(\varphi_1) = 2\varphi_1 - 2\varphi_2 - 2\varphi_3 + 2\varphi_4$$

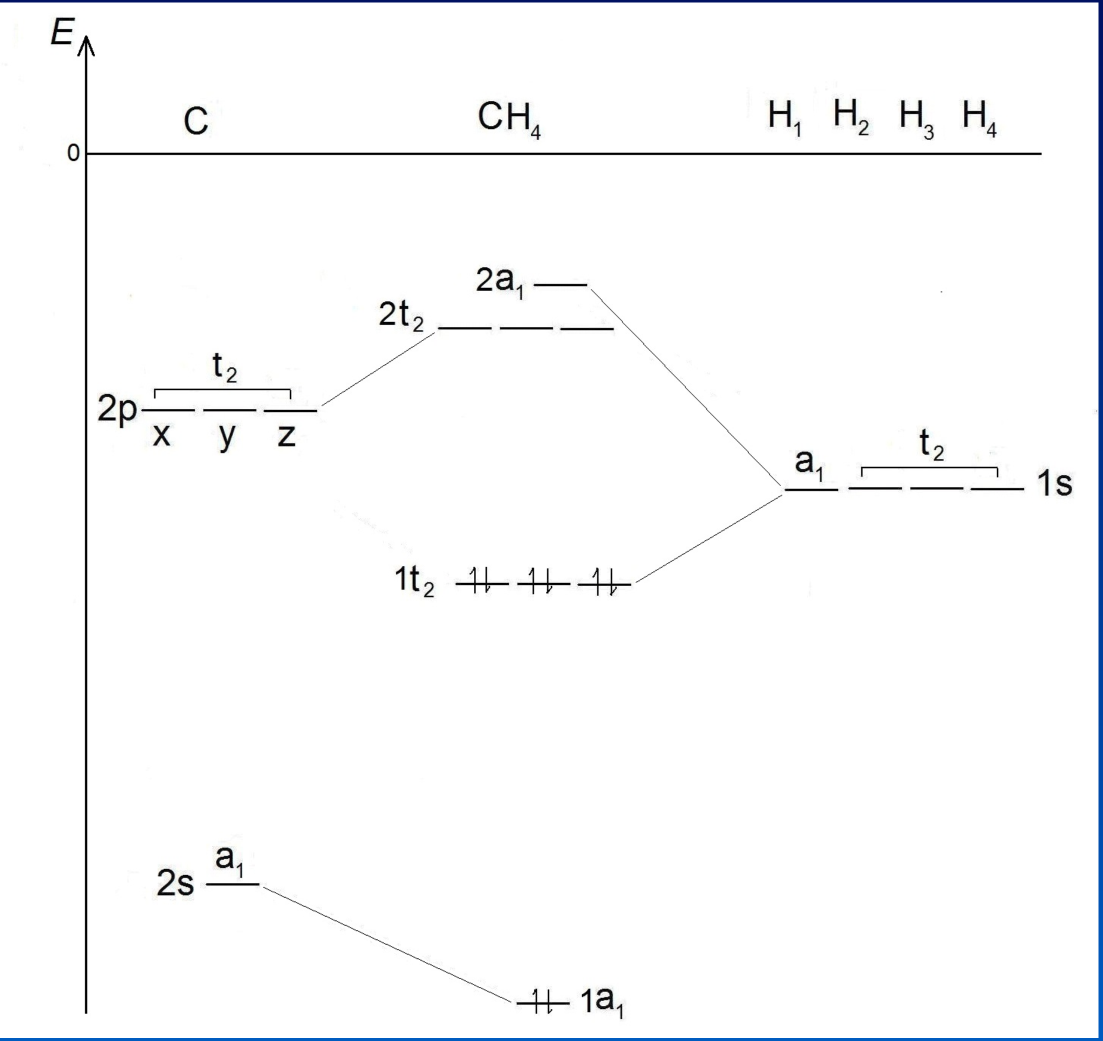
Metano, CH_4 - T_d

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

$$\hat{P}_{T_{2_{(22)}}}(\varphi_1) = \varphi_1 - \varphi_2 - \varphi_3 + \varphi_4$$

Metano, CH_4 - T_d

Diagrama de energia dos orbitais moleculares



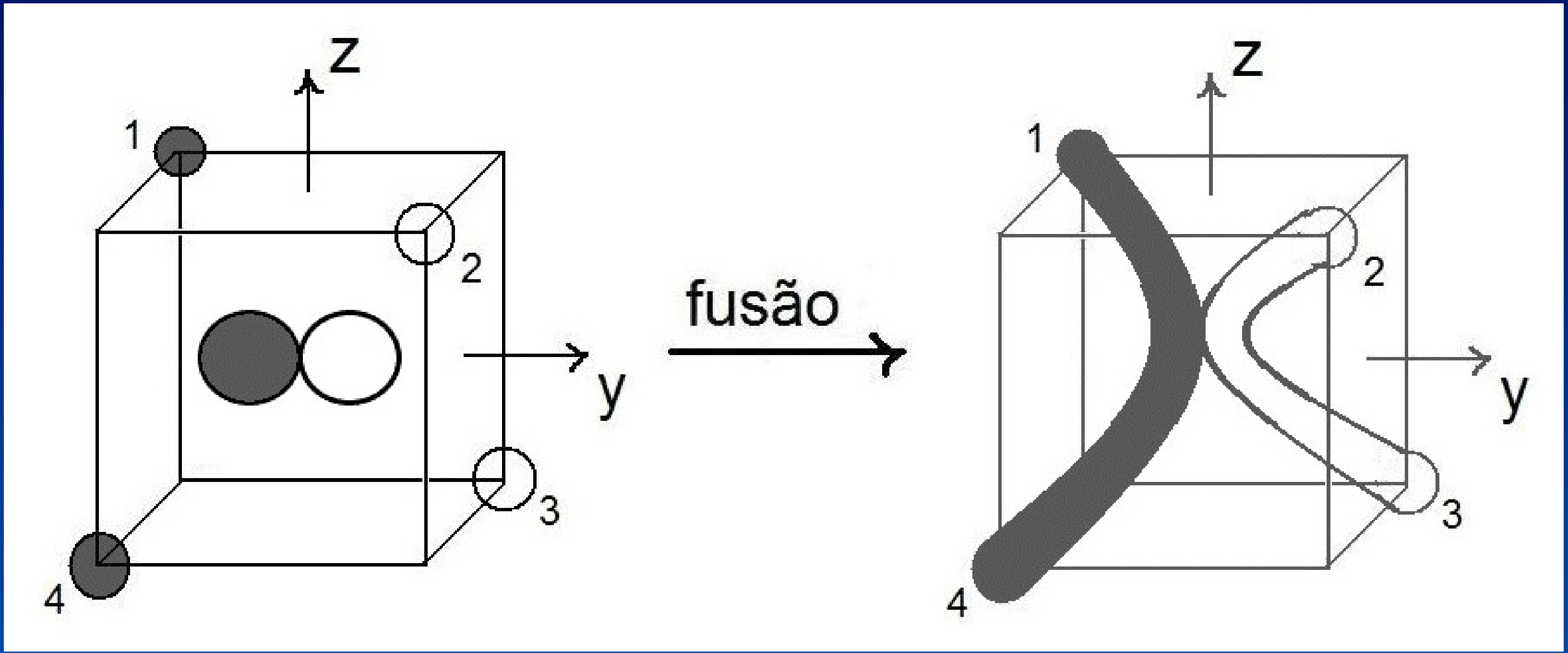
Metano, CH_4 - T_d

Desenhando mais um dos orbitais moleculares $1T_2$

Juntando as regiões de mesma fase matemática

Metano, CH_4 - T_d

Um dos orbitais T_2, ligante



$$\hat{P}_{T_{2_{(22)}}}(\varphi_1) = \varphi_1 - \varphi_2 - \varphi_3 + \varphi_4$$

Metano, CH_4 - T_d

FIM DA AULA 2