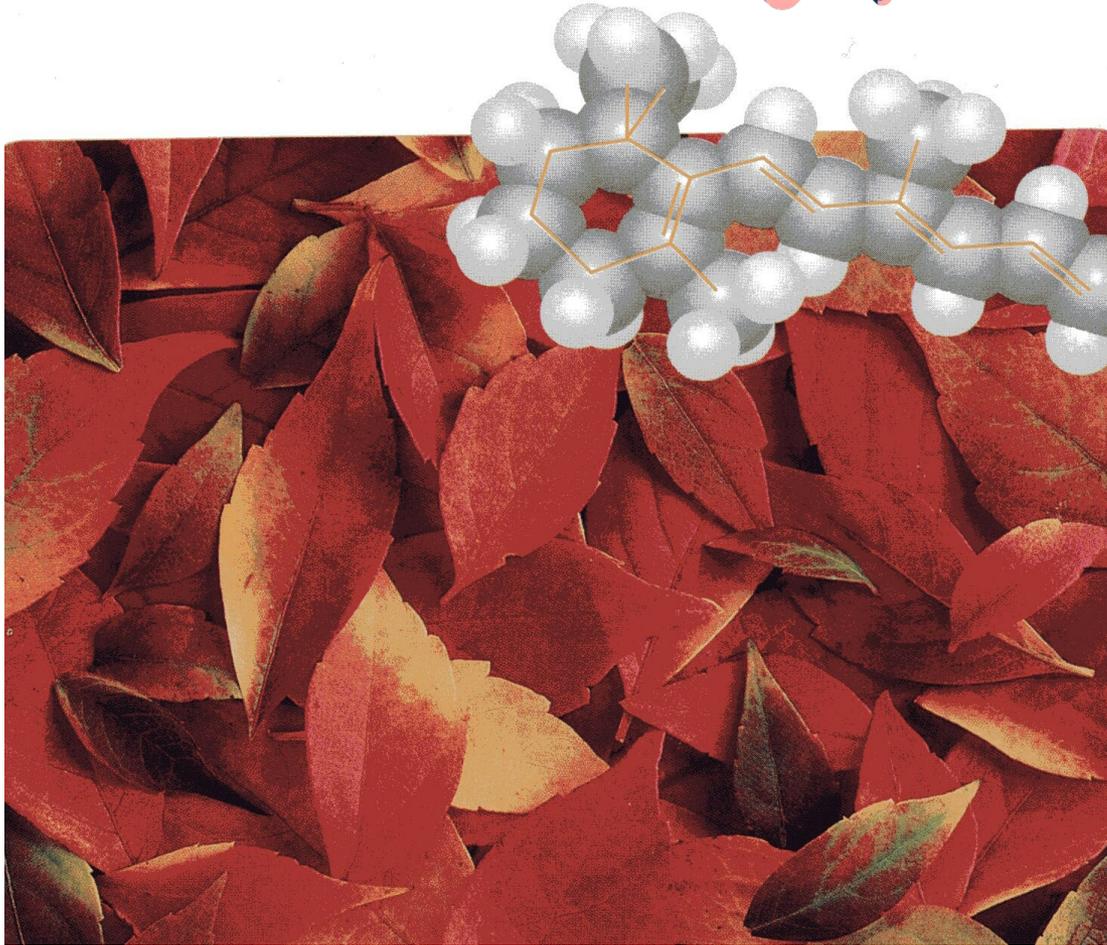


# Estrutura molecular e ligações químicas



# Estrutura de Lewis (elétrons ligantes e pares isolados)

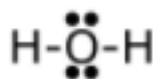
Hidrógeno



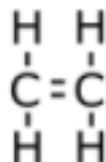
Carbono



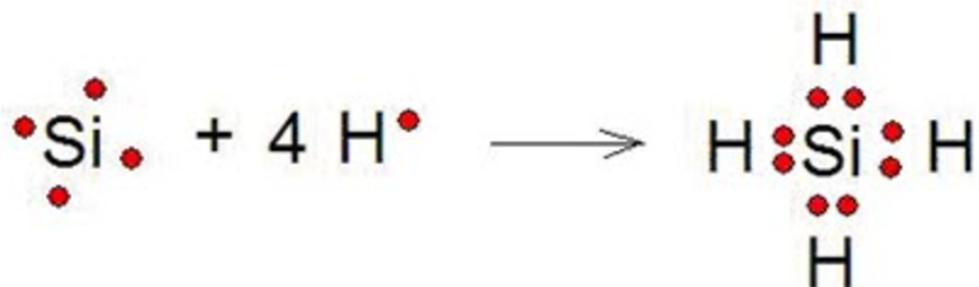
Água



Etileno

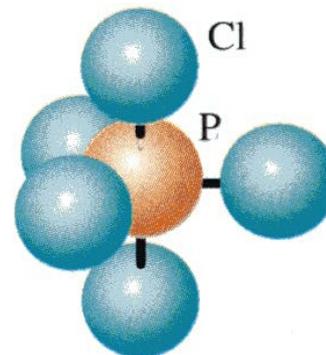
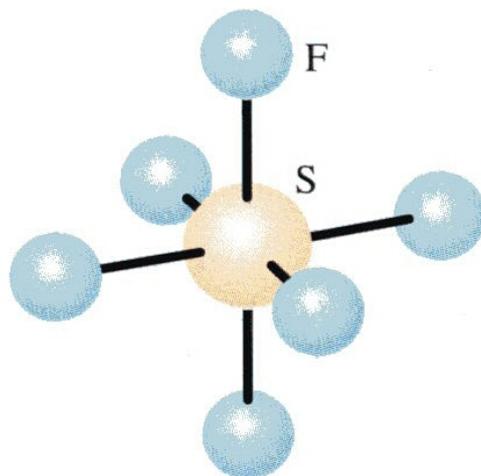
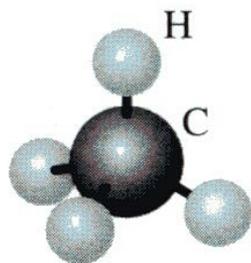


Acetileno



# Estrutura de Lewis (elétrons ligantes e pares isolados) não permitem explicar as formas das moléculas

## Hexafluoreto de enxofre ( $SF_6$ ) octaédrica



Metano ( $CH_4$ )  
tetraédrica

Pentacloroeto de fósforo ( $PCl_5$ )  
Bipirâmide trigonal

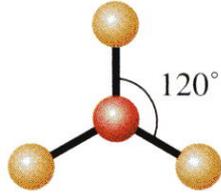
# Diferentes formas das moléculas



Linear



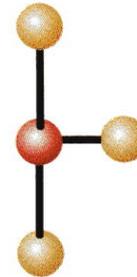
Angular



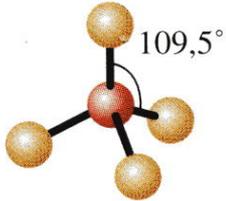
Trigonal planar



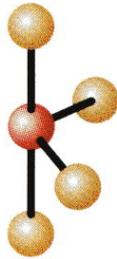
Pirâmide trigonal



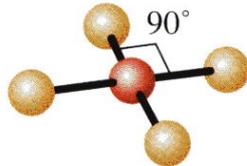
Forma T



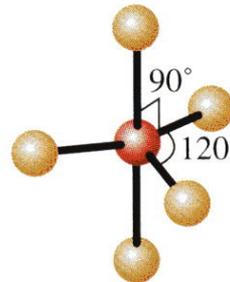
Tetraédrica



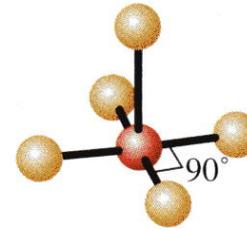
Gangorra



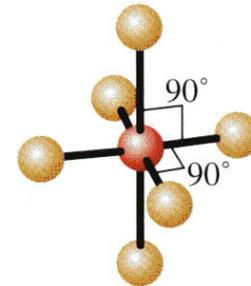
Quadrado planar



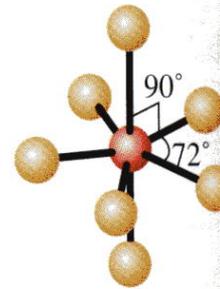
Bipirâmide trigonal



Pirâmide quadrada



Octaédrica



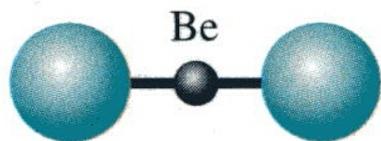
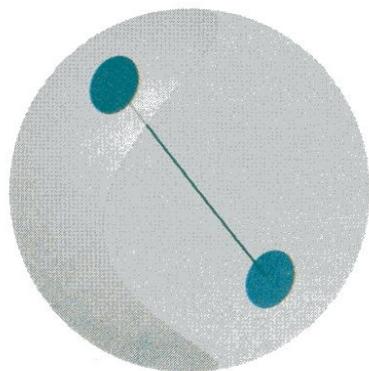
Bipirâmide pentagonal

Equação de Schrödinger

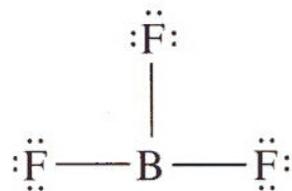
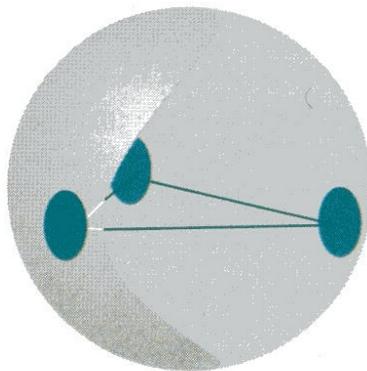
Métodos semi-empíricos

Métodos ab-initio

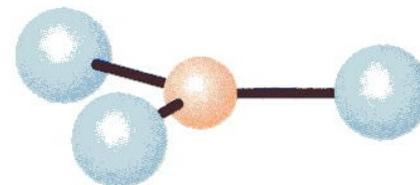
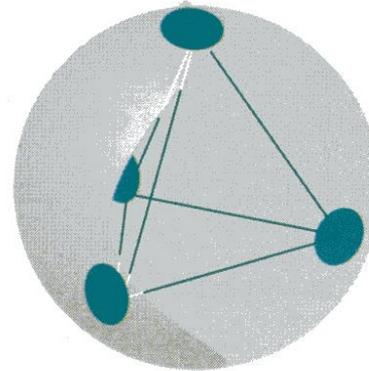
Modelo VSPR: modificar o modelo de ligação de Lewis considerando que regiões de alta concentração eletrônica se repelem. (valence-shell electron-pair repulsion model)



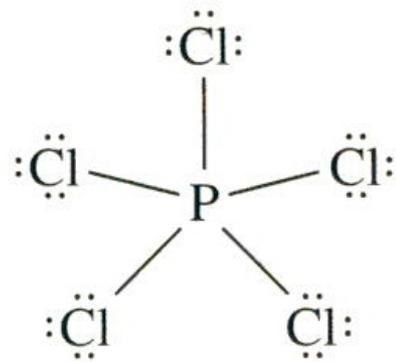
Cloreto de berílio, BeCl<sub>2</sub>



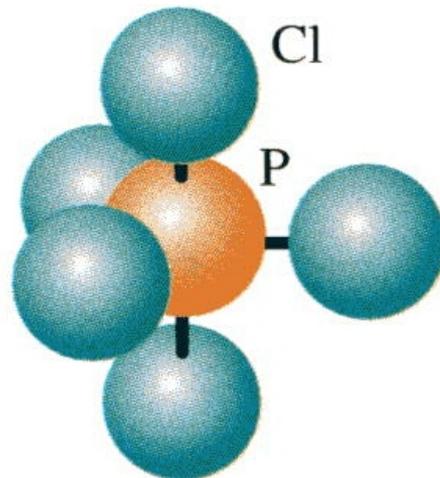
Trifluoreto de boro, BF<sub>3</sub>



Trifluoreto de boro, BF<sub>3</sub>



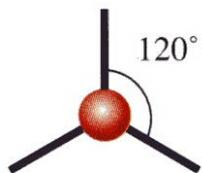
Pentacloreto de fósforo, PCl<sub>5</sub>



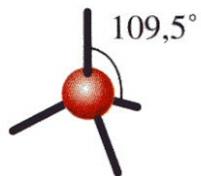
Pentacloreto de fósforo, PCl<sub>5</sub>



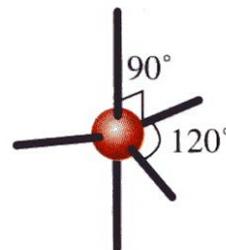
Linear



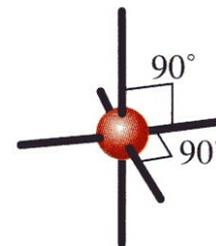
Trigonal planar



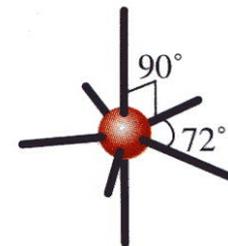
Tetraédrica



Bipirâmide  
trigonal



Octaédrica

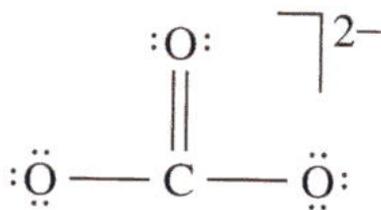


Bipirâmide  
pentagonal

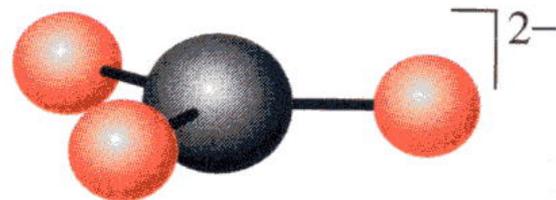
O modelo VSPR não distingue entre ligações simples ou múltiplas, todo é tratado como regiões de alta concentração eletrônica. Os dois pares eletrônicos (ligação dupla) permanecem juntos e repelem outra região de alta concentração eletrônica.



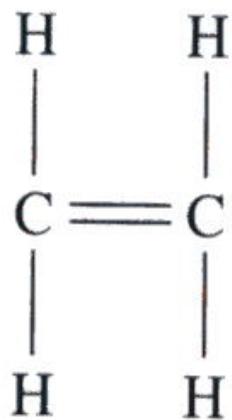
Dióxido de carbono,  $\text{CO}_2$



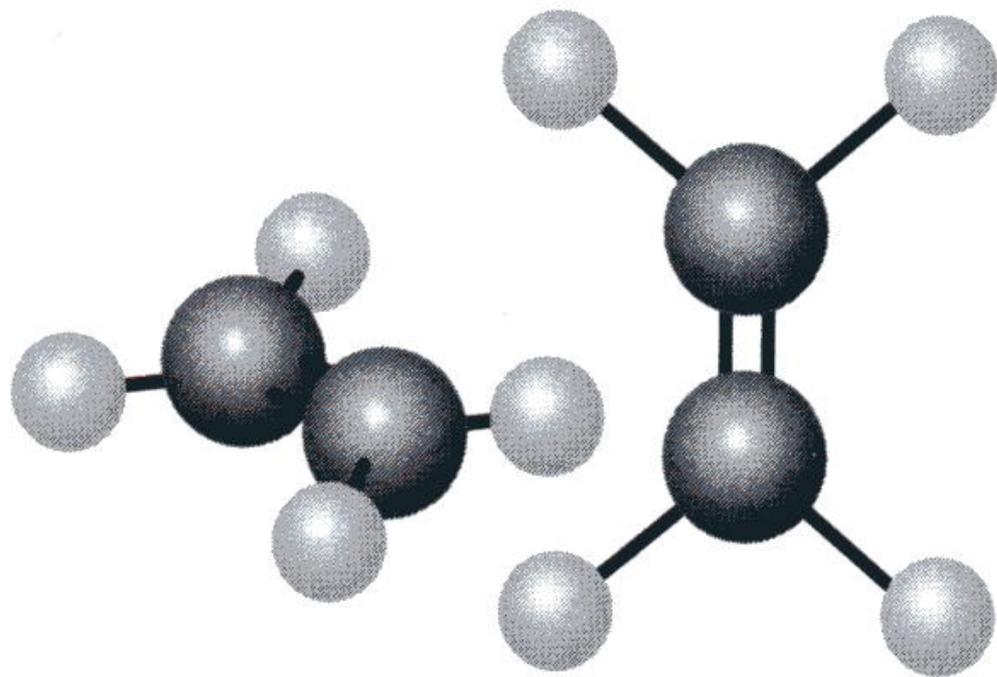
Íon carbonato,  $\text{CO}_3^{2-}$



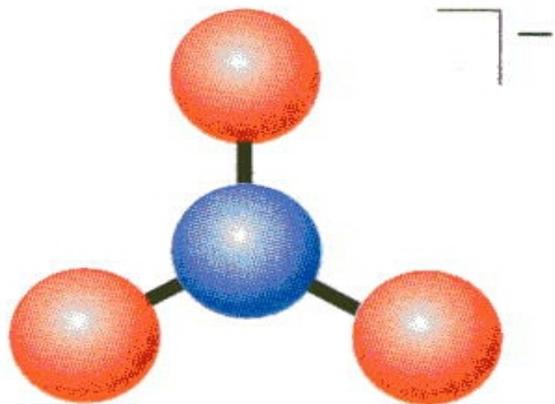
Íon carbonato,  $\text{CO}_3^{2-}$



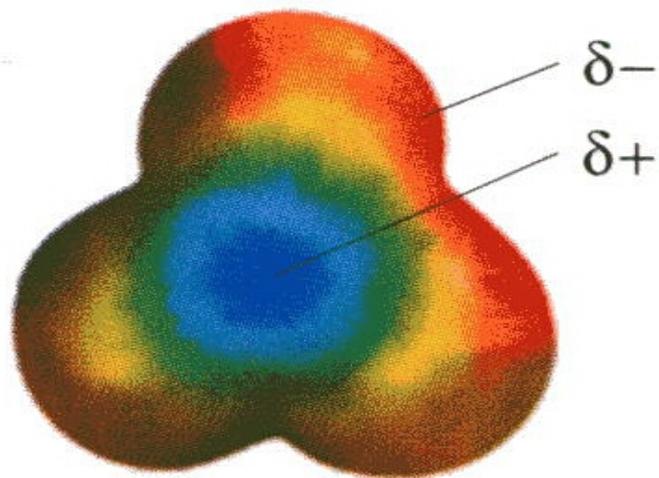
Eteno,  $\text{C}_2\text{H}_4$



Eteno,  $\text{C}_2\text{H}_4$



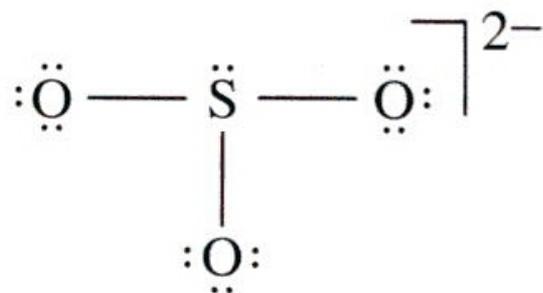
Íon nitrato,  $\text{NO}_3^-$



Íon nitrato

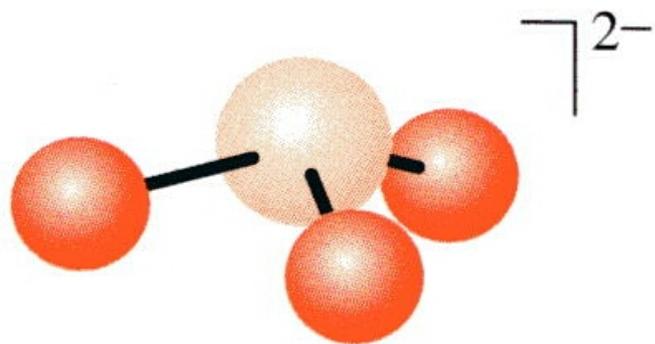
O modelo VSPR não se importa com as diferentes estruturas de Lewis.

Então este modelo considera que pares de elétrons ligantes, pares isolados, se posicionarão de forma de maximizar a distância entre eles. Ligações múltiplas são consideradas como uma unidade simples equivalente a um par de elétrons.

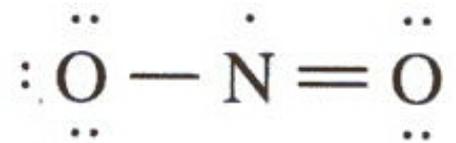


Íon sulfito,  $\text{SO}_3^{2-}$

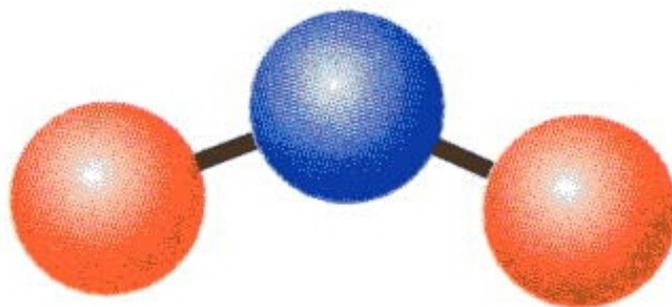
Os pares de elétrons isolados ou elétrons desemparelhados no átomo central são considerados para definir a geometria, mas não aparecem na fórmula química.



Íon sulfito,  $\text{SO}_3^{2-}$

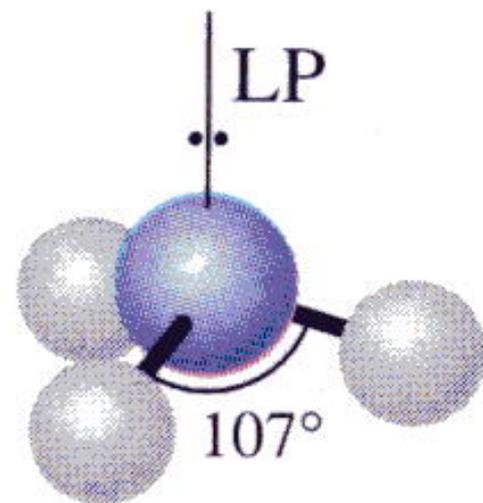
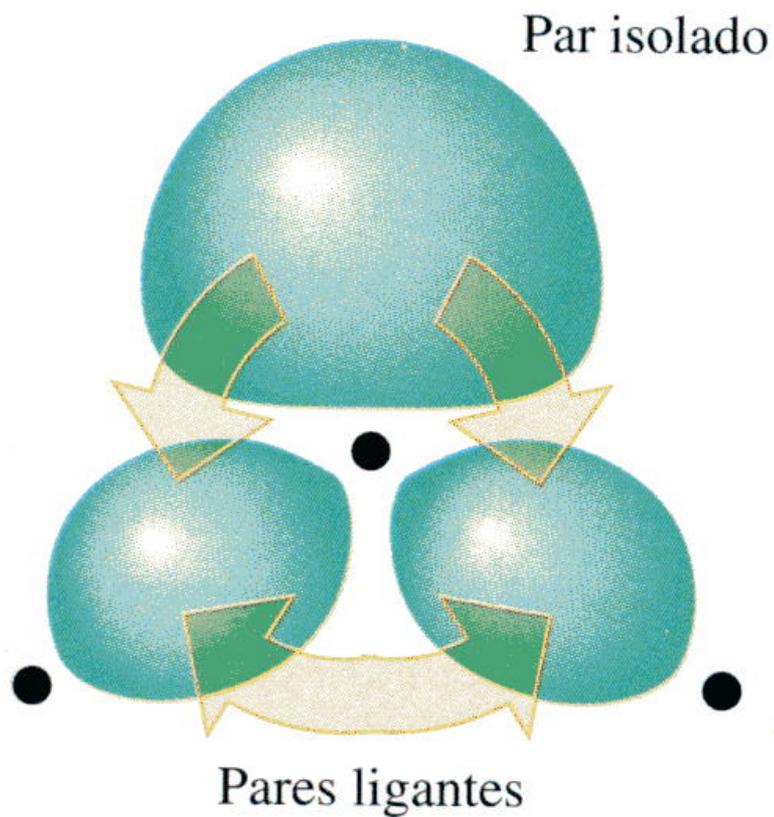


Dióxido de nitrogênio,  $\text{NO}_2$

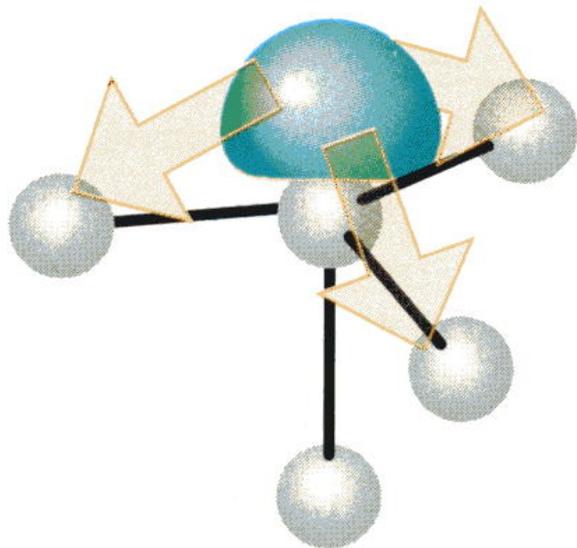


Dióxido de nitrogênio,  $\text{NO}_2$

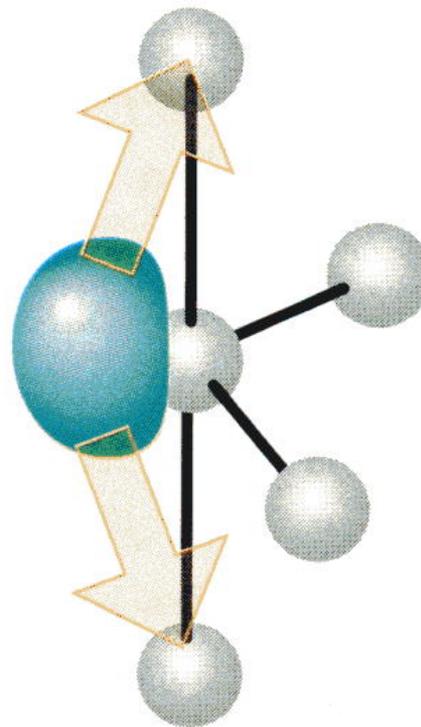
Par isolado-par isolado > par isolado-par ligante > par ligante-par ligante



Amônia,  $\text{NH}_3$

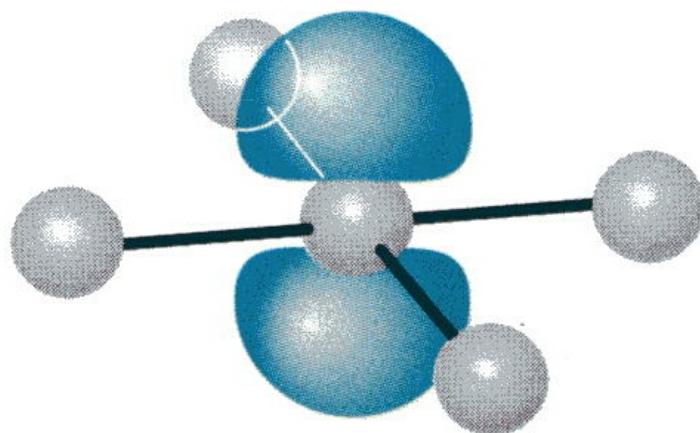


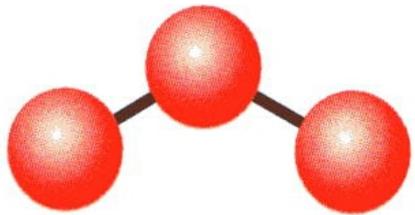
(a)



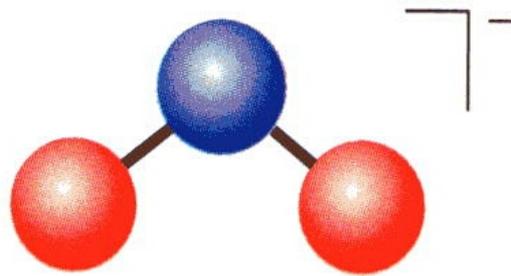
(b)

Os pares de elétrons isolados em uma molécula ou íon tipo  $AX_4E$  poderia ser axial (a) ou equatorial (b), mas nesta posição a molécula é mais estável porque somente está perto de dois átomos.

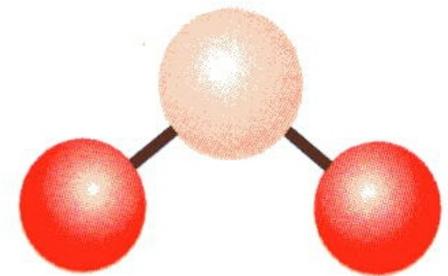




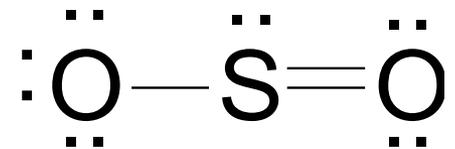
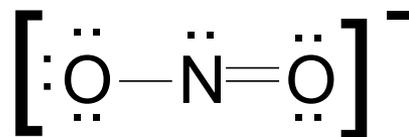
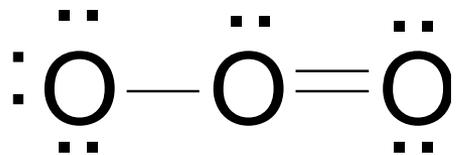
Ozônio,  $O_3$



Íon nitrito,  $NO_2^-$

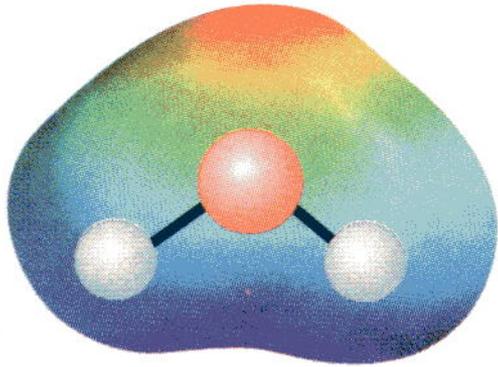


Dióxido de enxofre,  $SO_2$



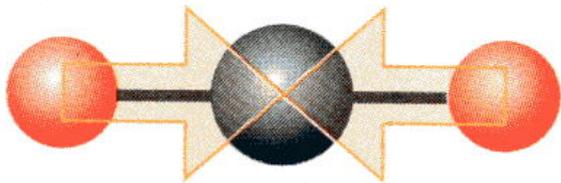
Os pares de elétrons isolados distorcem a forma da molécula

Moléculas polares: momento de dipolo diferente de zero

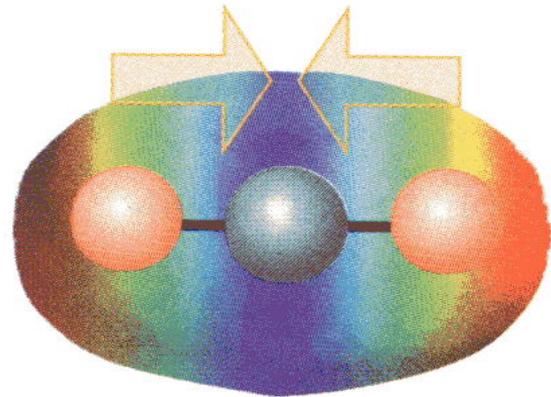


Água, H<sub>2</sub>O

Moléculas não polares: momento de dipolo igual a zero. Moléculas homonucleares (O<sub>2</sub>, Cl<sub>2</sub>, etc.)



Dióxido de carbono, CO<sub>2</sub>



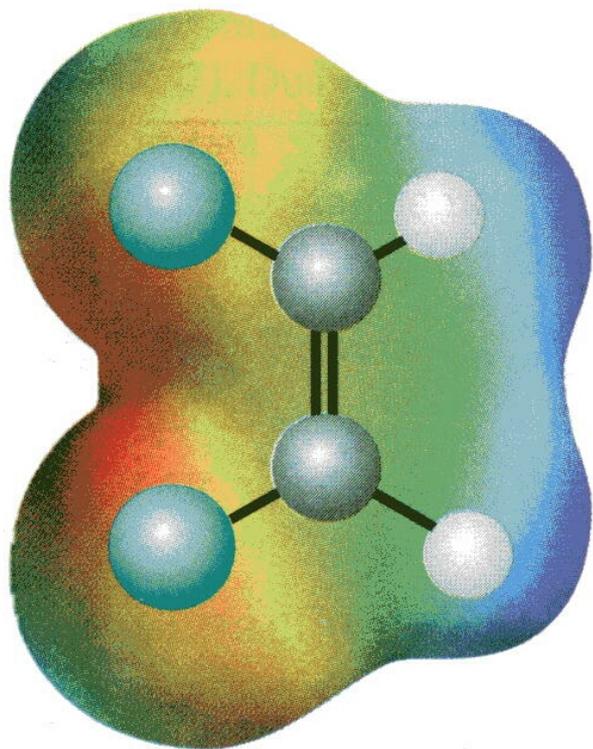
Dióxido de carbono, CO<sub>2</sub>

**TABELA 3.1**

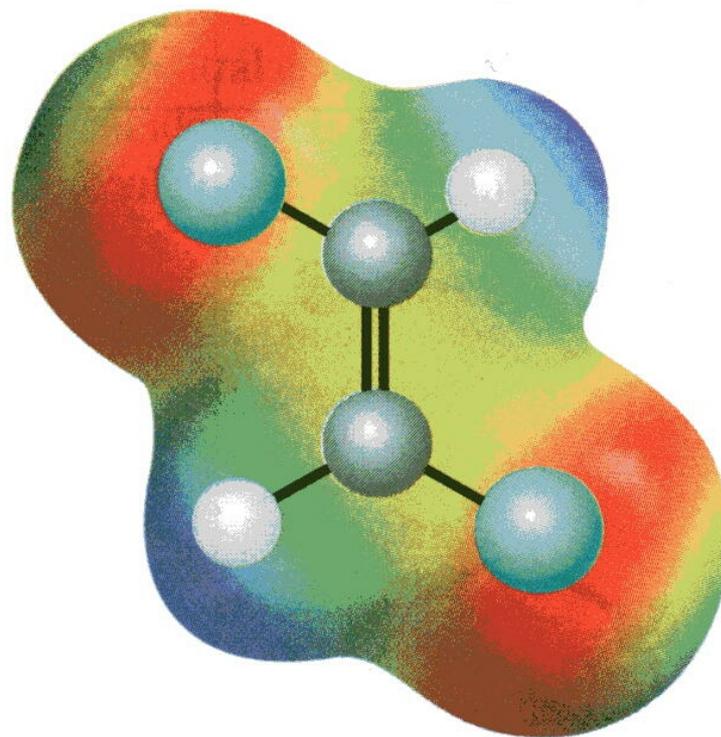
Momentos de dipolo de algumas moléculas

Molécula	Momento de dipolo, D	Molécula	Momento de dipolo, D
HF	1,91	PH <sub>3</sub>	0,58
HCl	1,08	AsH <sub>3</sub>	0,20
HBr	0,80	SbH <sub>3</sub>	0,12
HI	0,42	O <sub>3</sub>	0,53
CO	0,12	CO <sub>2</sub>	0
ClF	0,88	BF <sub>3</sub>	0
NaCl*	9,00	CH <sub>4</sub>	0
CsCl*	10,42	<i>cis</i> -CHCl=CHCl	1,90
H <sub>2</sub> O	1,85	<i>trans</i> -CHCl=CHCl	0
NH <sub>3</sub>	1,47		

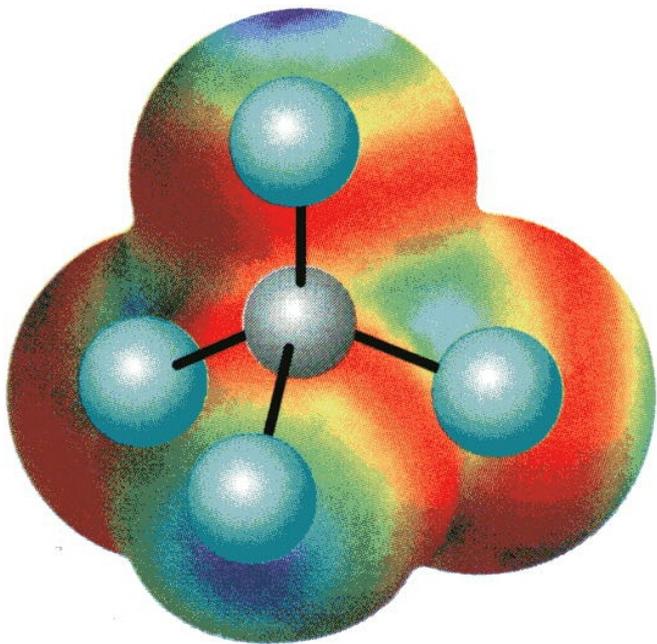
\*Pares iônicos na fase gasosa.



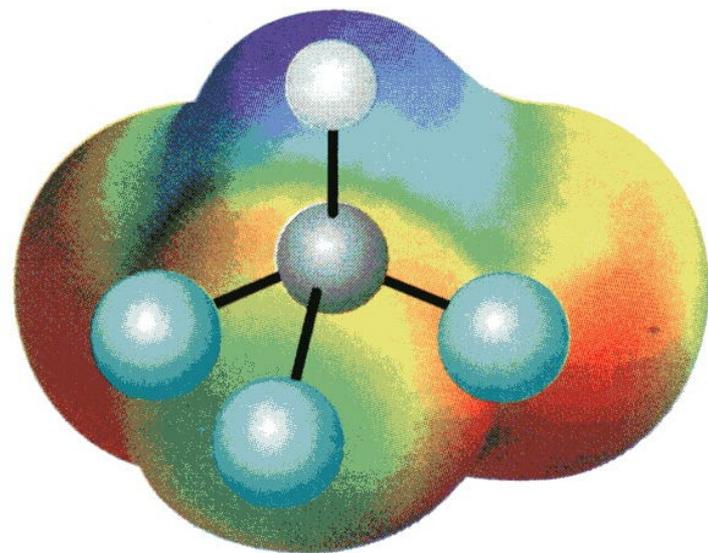
33 *cis*-Dicloroeteno, C<sub>2</sub>H<sub>2</sub>Cl<sub>2</sub>



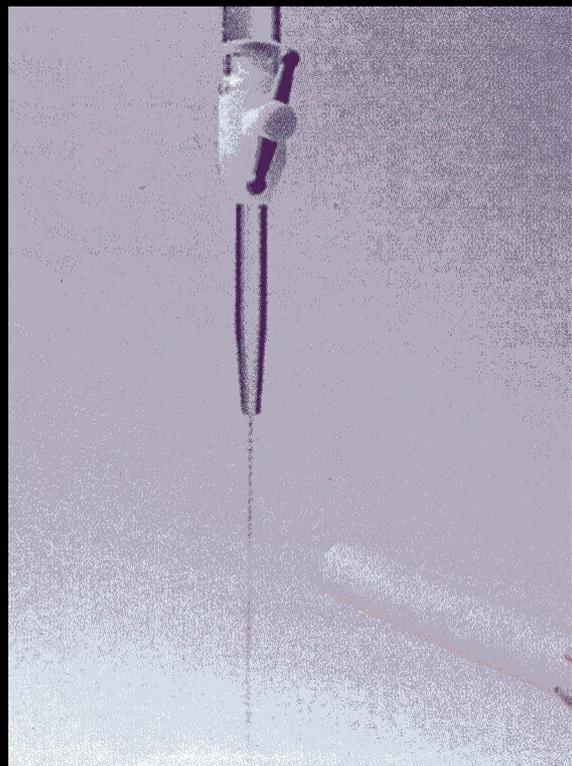
34 *trans*-Dicloroeteno, C<sub>2</sub>H<sub>2</sub>Cl<sub>2</sub>

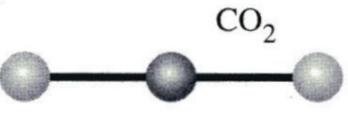
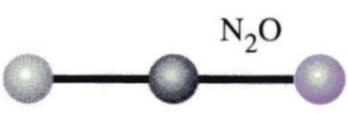
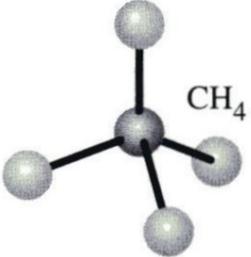
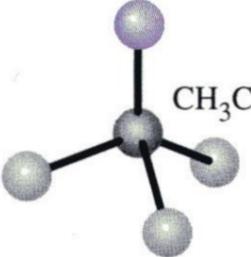
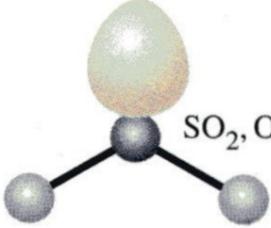
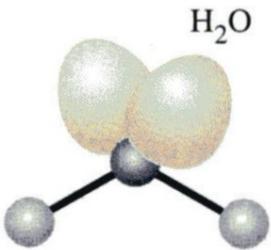
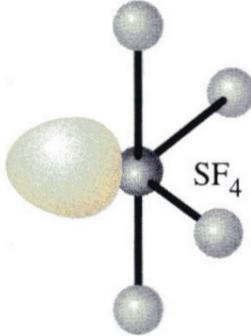
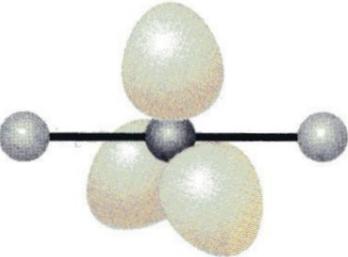
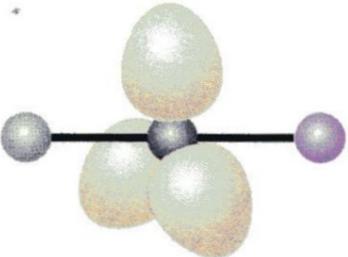
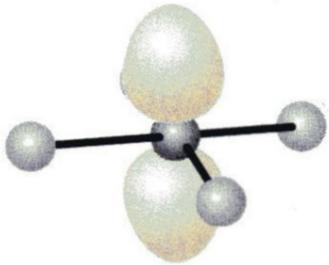
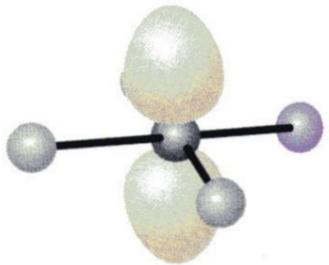


35 Tetraclorometano, CCl<sub>4</sub>



36 Triclorometano, CHCl<sub>3</sub>



Tipo VSEPR	Não-polar	Polar	Tipo VSEPR	Não-polar	Polar
$AX_2$	 <p><math>CO_2</math></p>	 <p><math>N_2O</math></p>	$AX_4$	 <p><math>CH_4</math></p>	 <p><math>CH_3Cl</math></p>
$AX_2E$		 <p><math>SO_2, O_3</math></p>			
$AX_2E_2$		 <p><math>H_2O</math></p>	$AX_4E$		 <p><math>SF_4</math></p>
$AX_2E_3$	 <p><math>I_3^-, XeF_2</math></p>	 <p><math>BrIF^-</math></p>	$AX_4E_2$	 <p><math>XeF_4</math></p>	

Tipo  
VSEPR

Não-polar

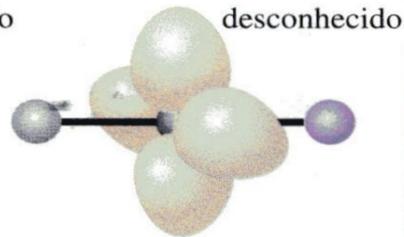
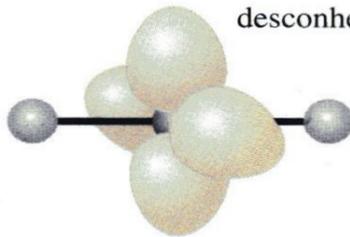
Polar

Tipo  
VSEPR

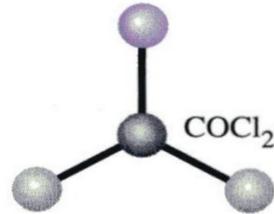
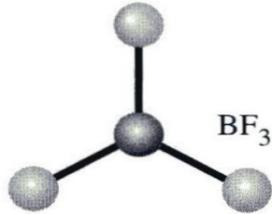
Não-polar

Polar

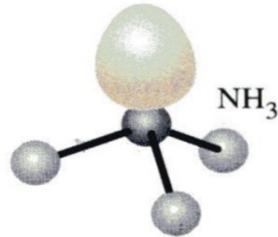
$AX_2E_4$



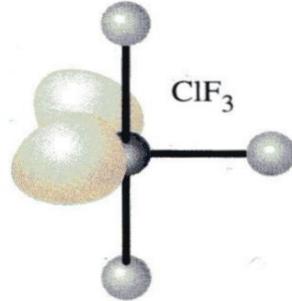
$AX_3$



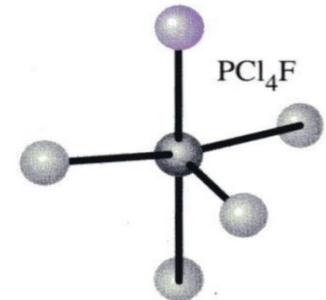
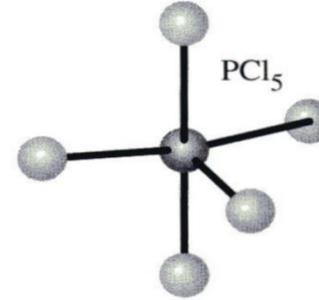
$AX_3E$



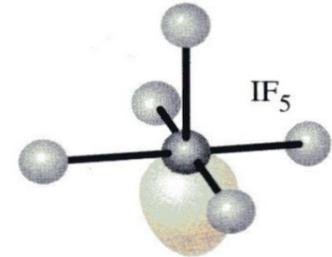
$AX_3E_2$



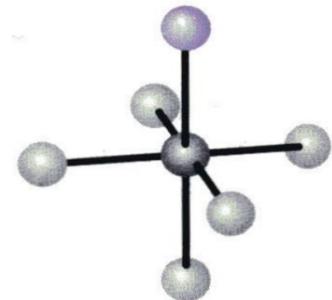
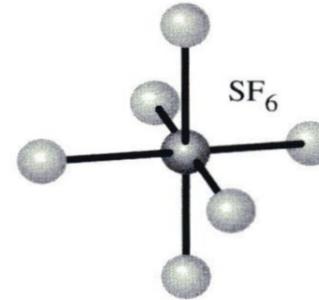
$AX_5$



$AX_5E$



$AX_6$

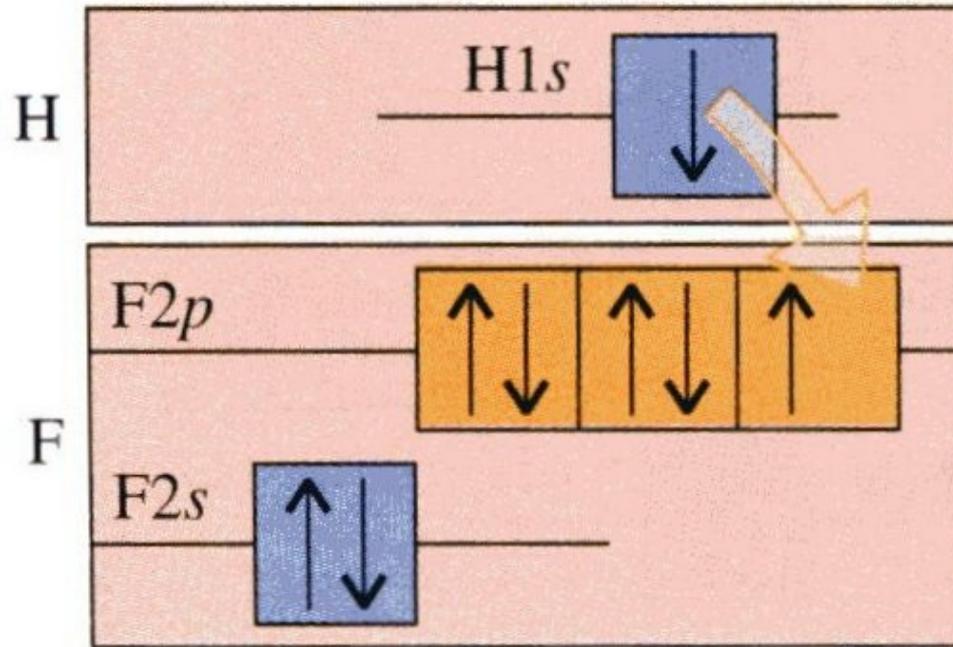


## Teoria da ligação de valência

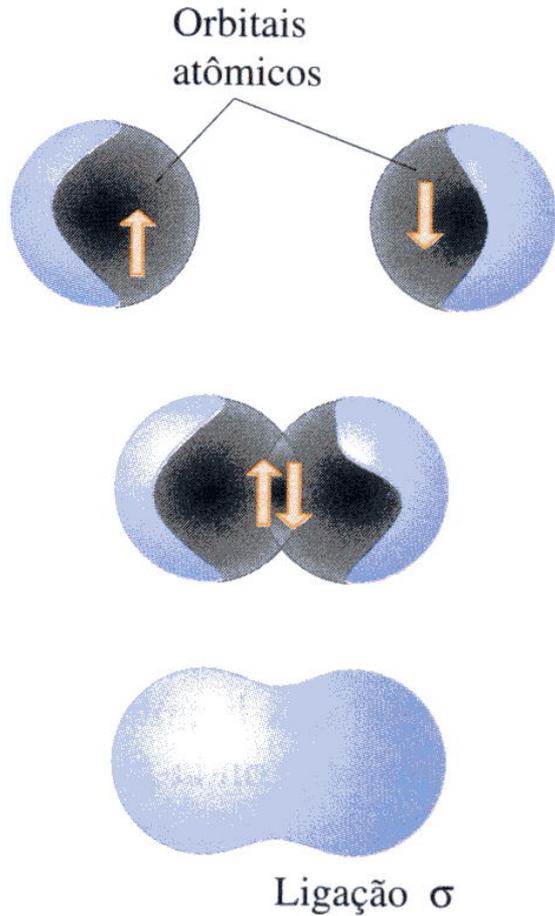
Modelo mecânico-quântico da distribuição dos elétrons nas ligações que vai além da teoria de Lewis e do modelo VSPR, pode se calcular numericamente os ângulos e distâncias das ligações químicas

## As ligações sigma e pi

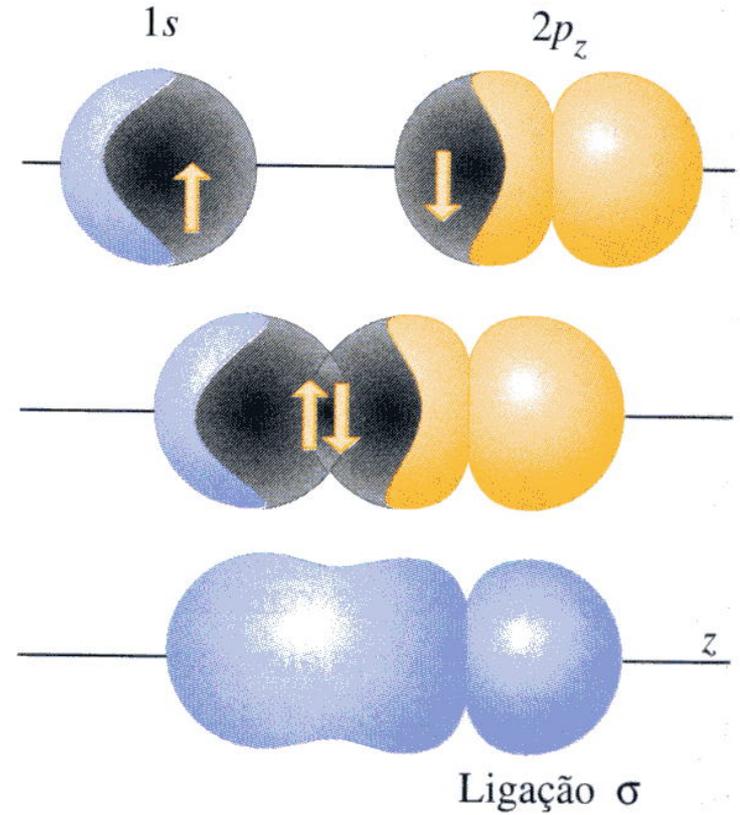
A fusão de dois orbitais atômicos é chamada sobreposição de orbitais. No caso do H<sub>2</sub>, temos a fusão de dois orbitais 1s, formando uma ligação  $\sigma$



Fluoreto de hidrogênio, HF

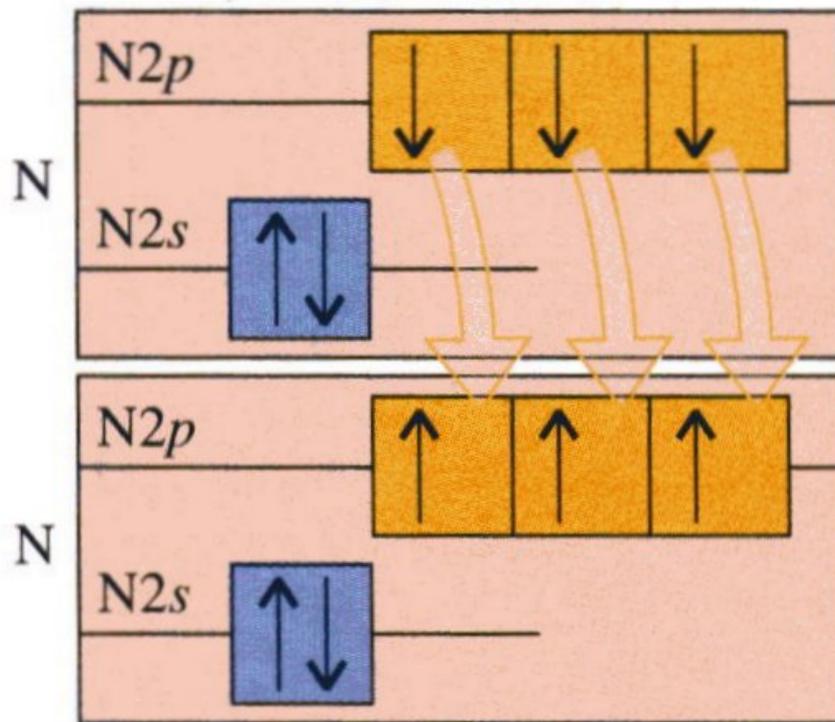


Hidrogênio,  $H_2$

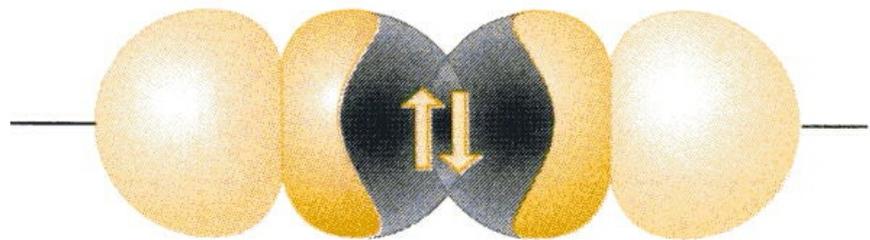
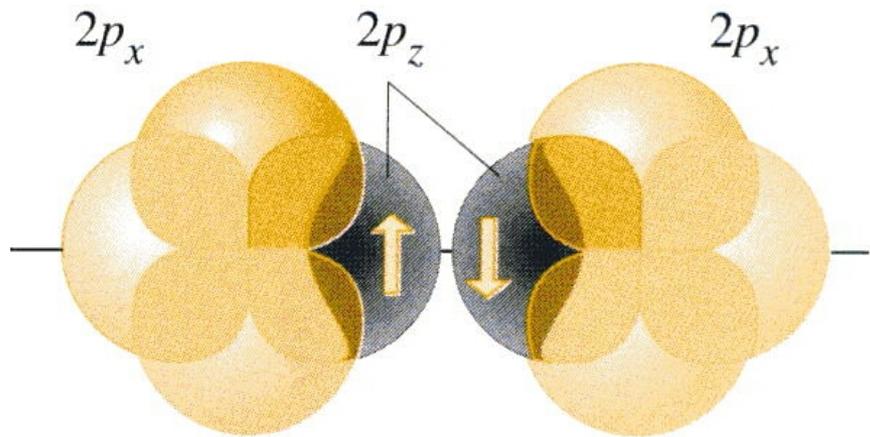


Fluoreto de hidrogênio, HF

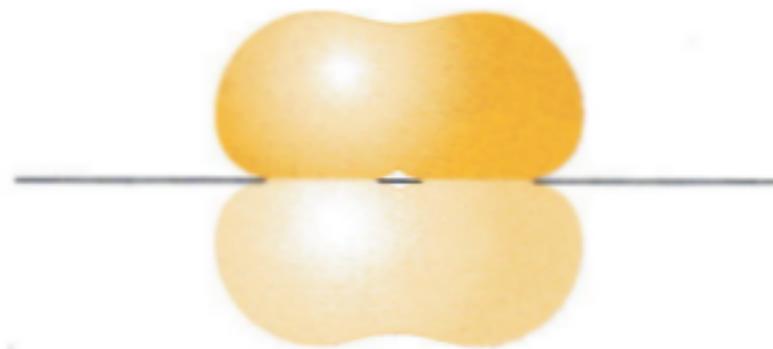
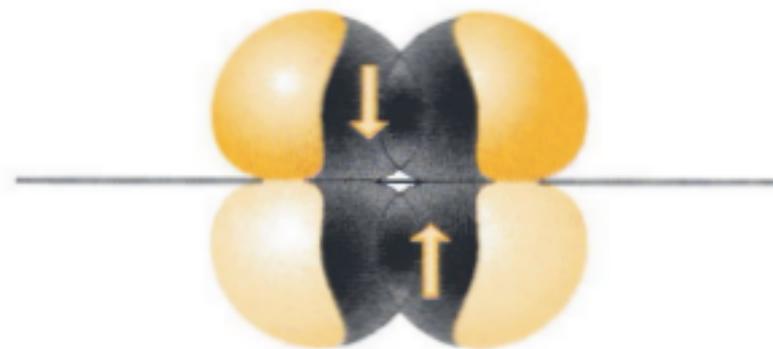
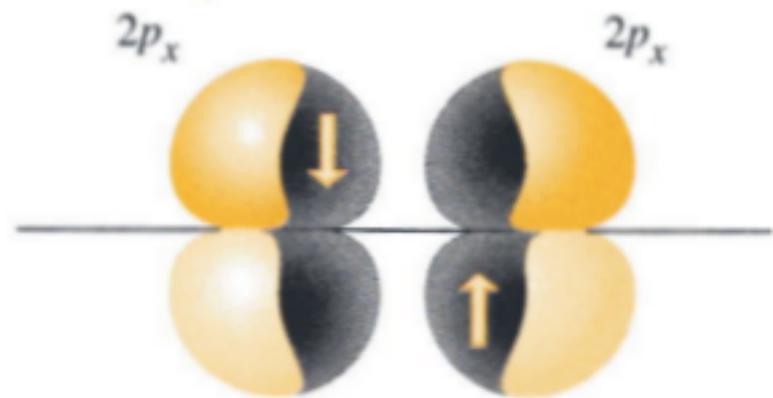
Diferente tipo de ligação: N<sub>2</sub>. Superposição de orbitais atômicos p: formação de uma ligação  $\pi$



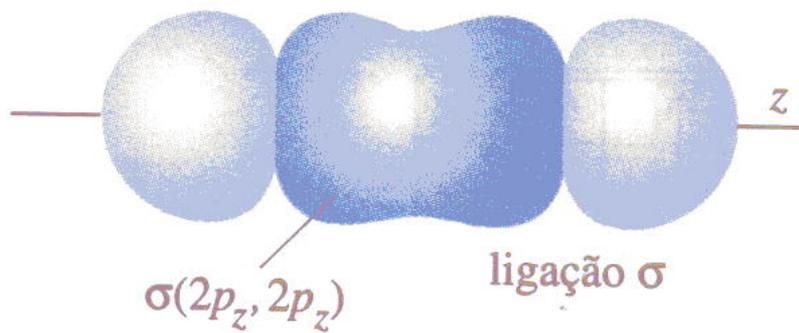
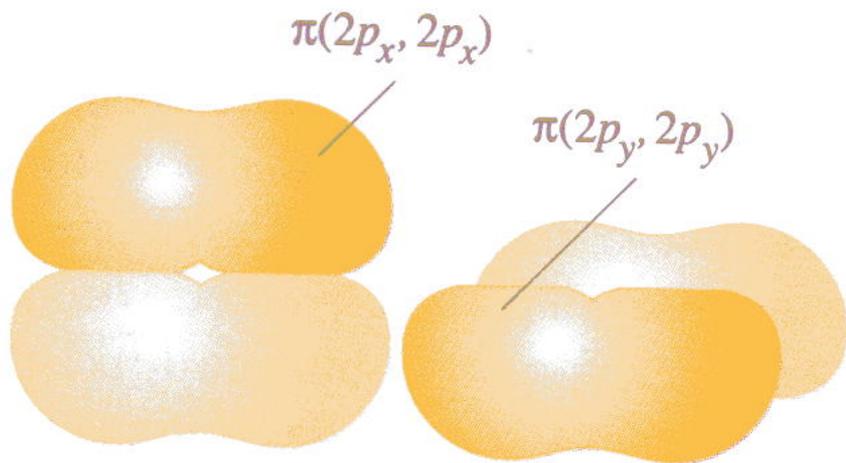
Nitrogênio, N<sub>2</sub>



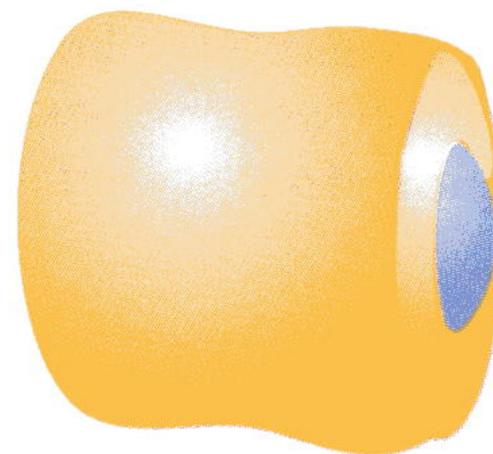
Ligação  $\sigma$



Ligação  $\pi$



(a)



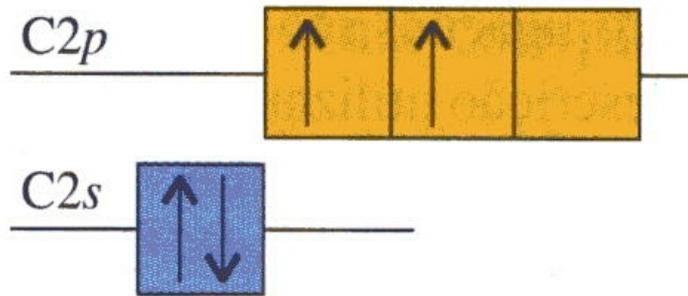
(b)

Ligação simples: é uma ligação  $\sigma$

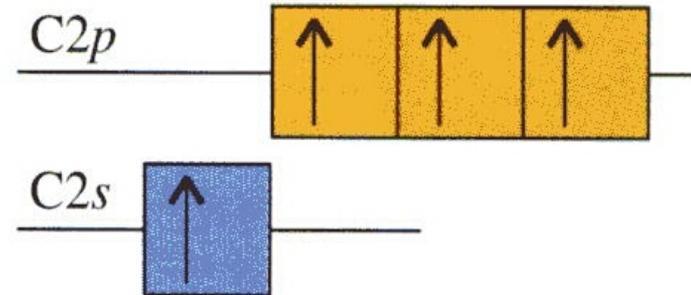
Ligação dupla: é uma ligação  $\sigma$  e uma ligação  $\pi$

Ligação tripla: é uma ligação  $\sigma$  e duas ligações  $\pi$

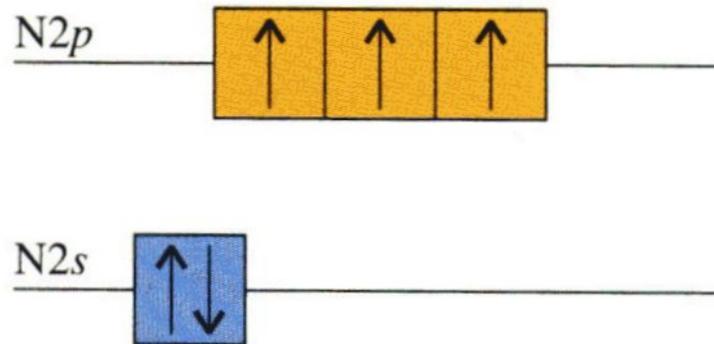
# A hibridização dos orbitais



Carbono,  $[\text{He}]2s^2 2p_x^1 2p_y^1$

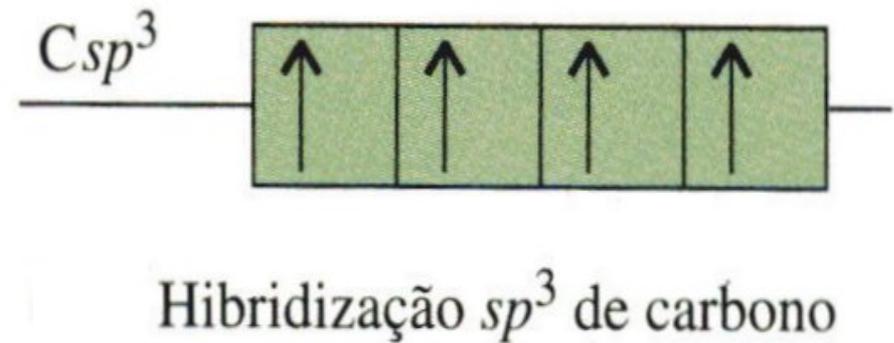
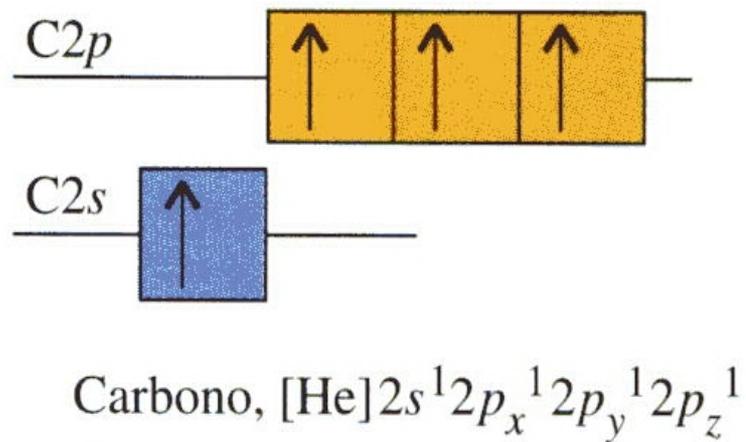


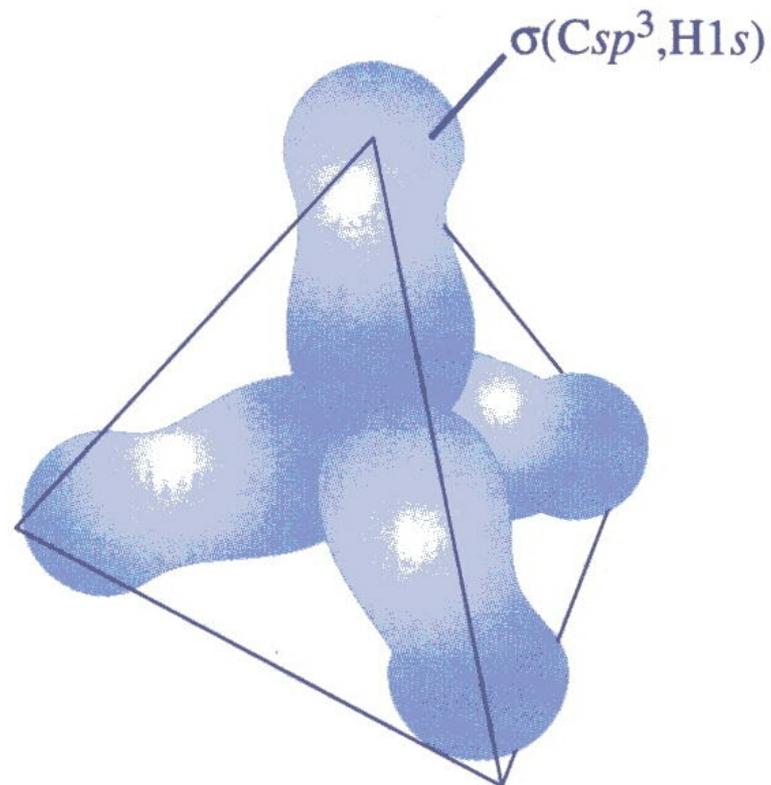
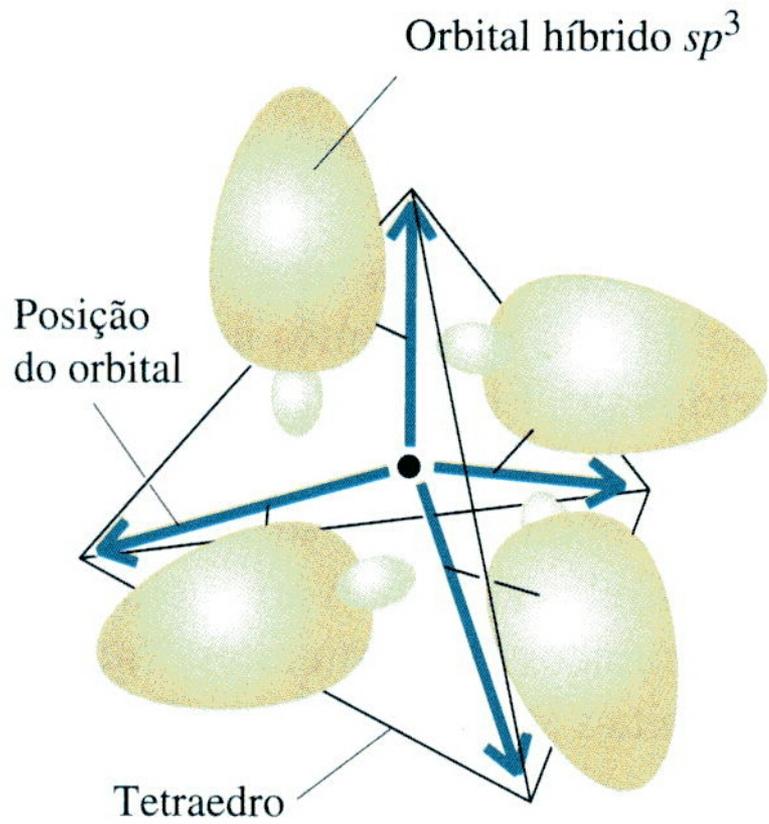
Carbono,  $[\text{He}]2s^1 2p_x^1 2p_y^1 2p_z^1$



Nitrogênio,  $[\text{He}]2s^2 2p_x^1 2p_y^1 2p_z^1$

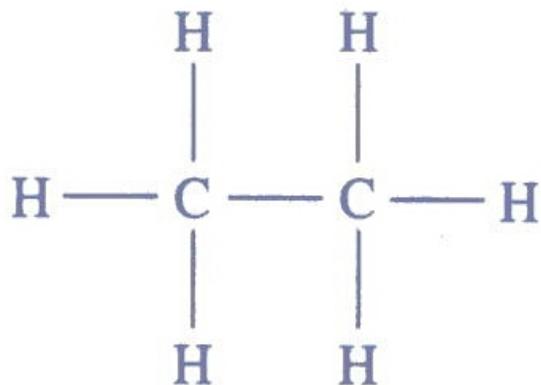
O arranjo dois orbitais s e p produz os orbitais híbridos  $sp^3$  porque são formados pelo orbital s e os três orbitais p. A sobreposição destes orbitais forma ligações  $\sigma$ .



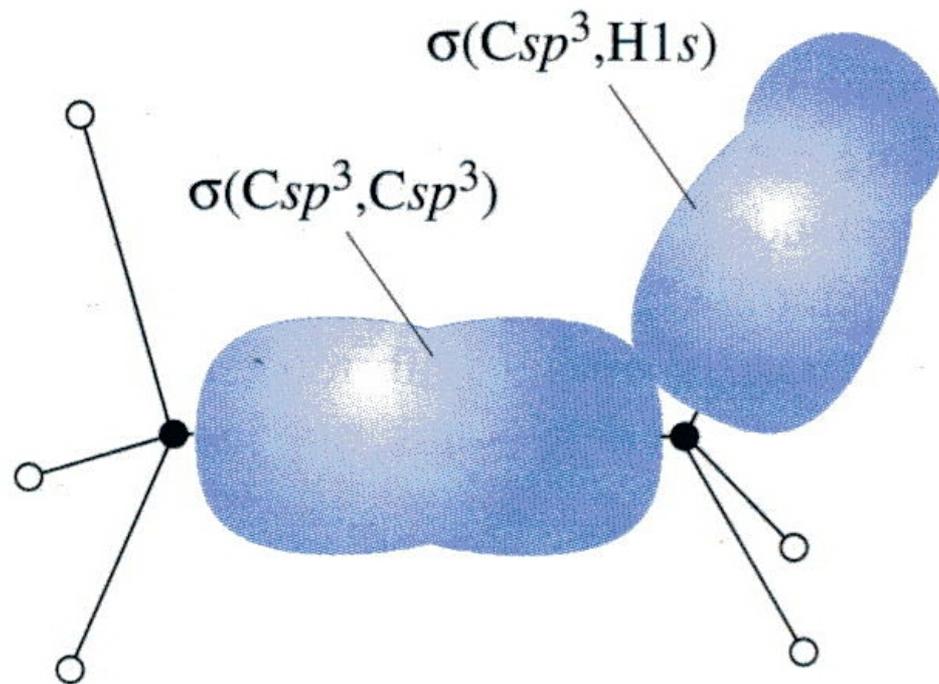


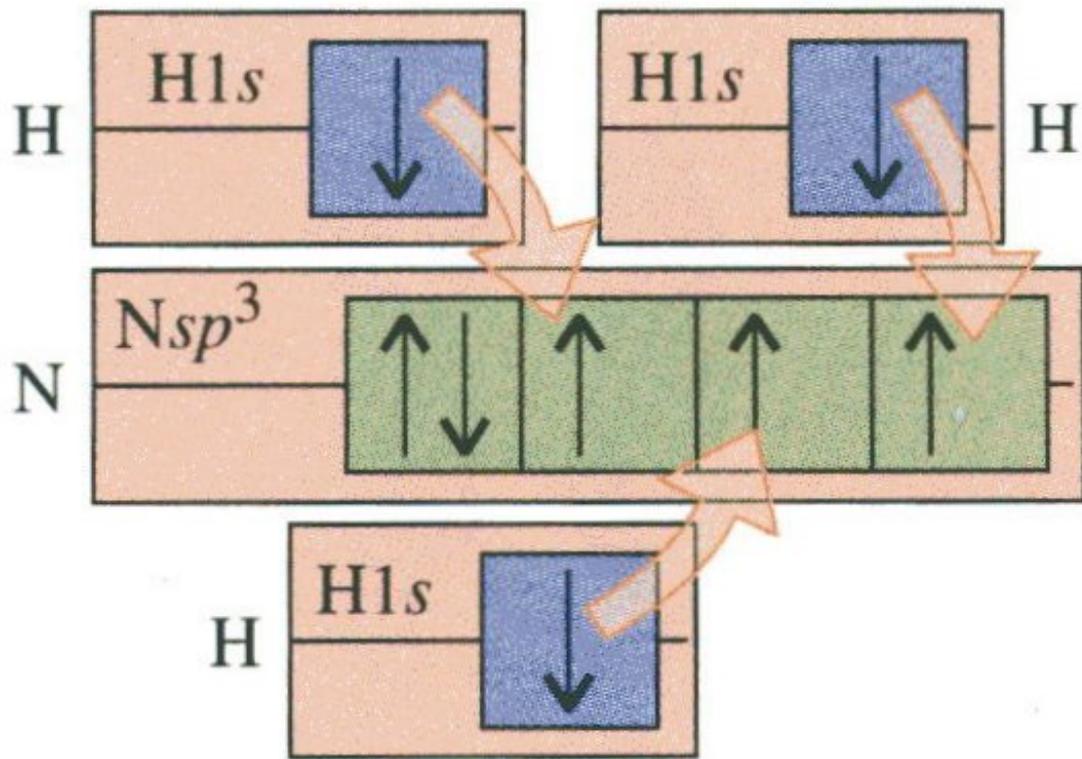
A hibridização é um modelo que permite descrever as ligações que são necessárias para uma dada estrutura molecular.

# A hibridização em moléculas mais complexas

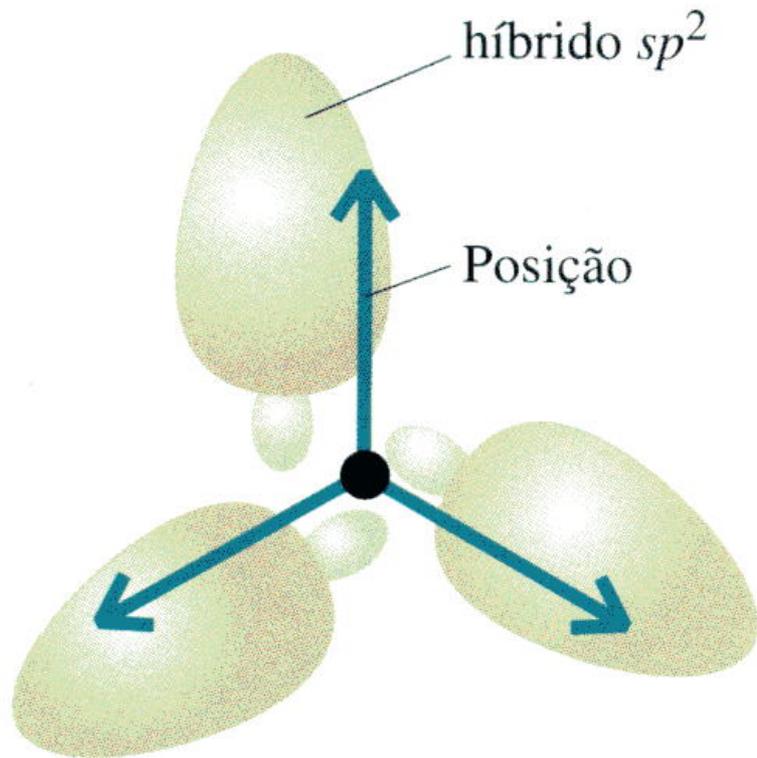


Etano,  $\text{CH}_3\text{CH}_3$

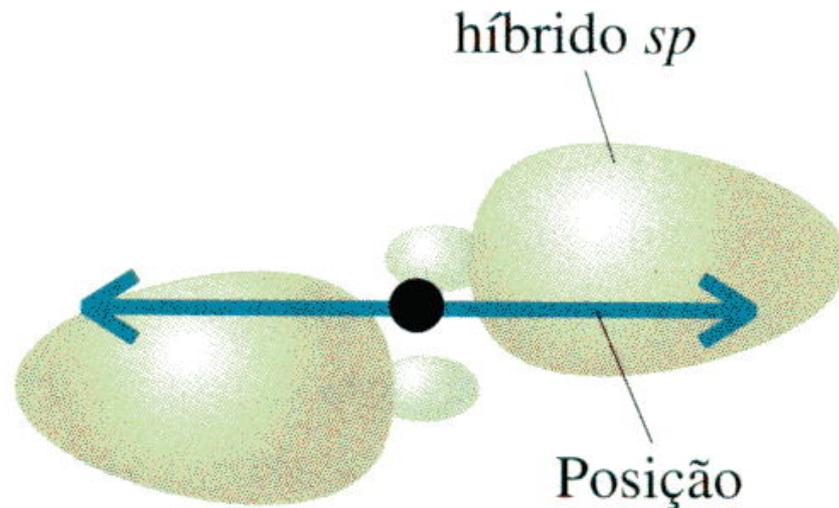




Amônia, NH<sub>3</sub>



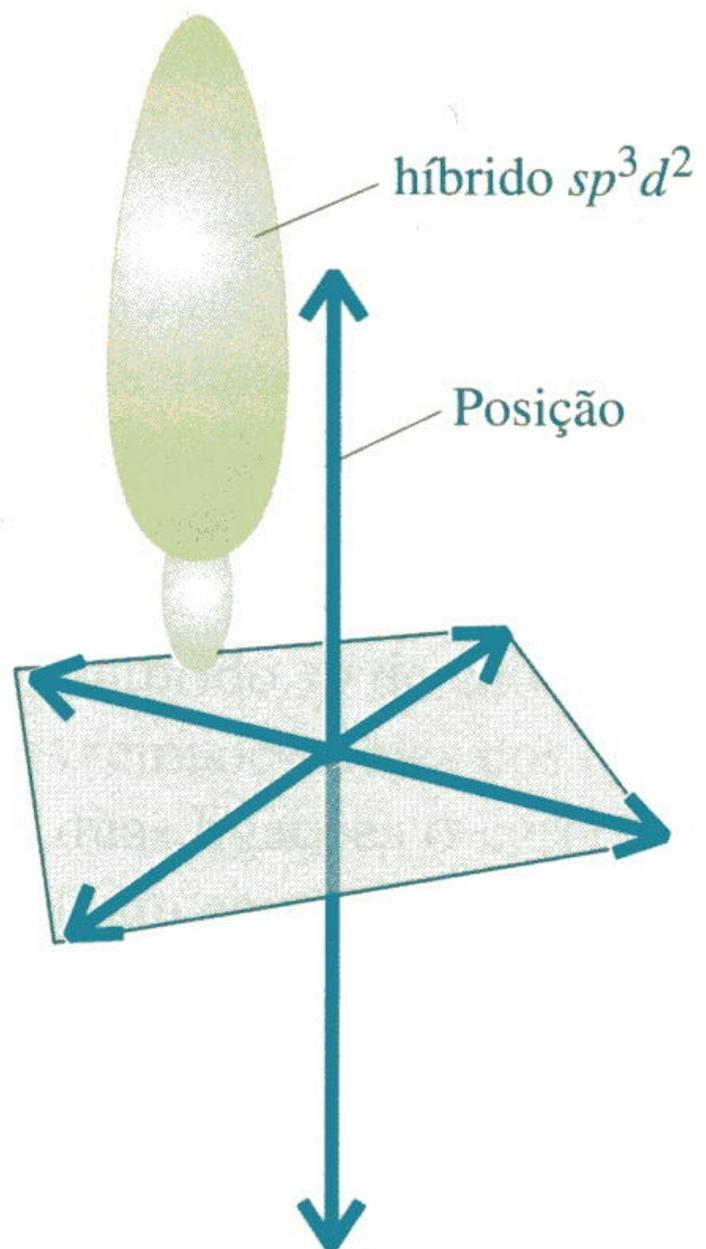
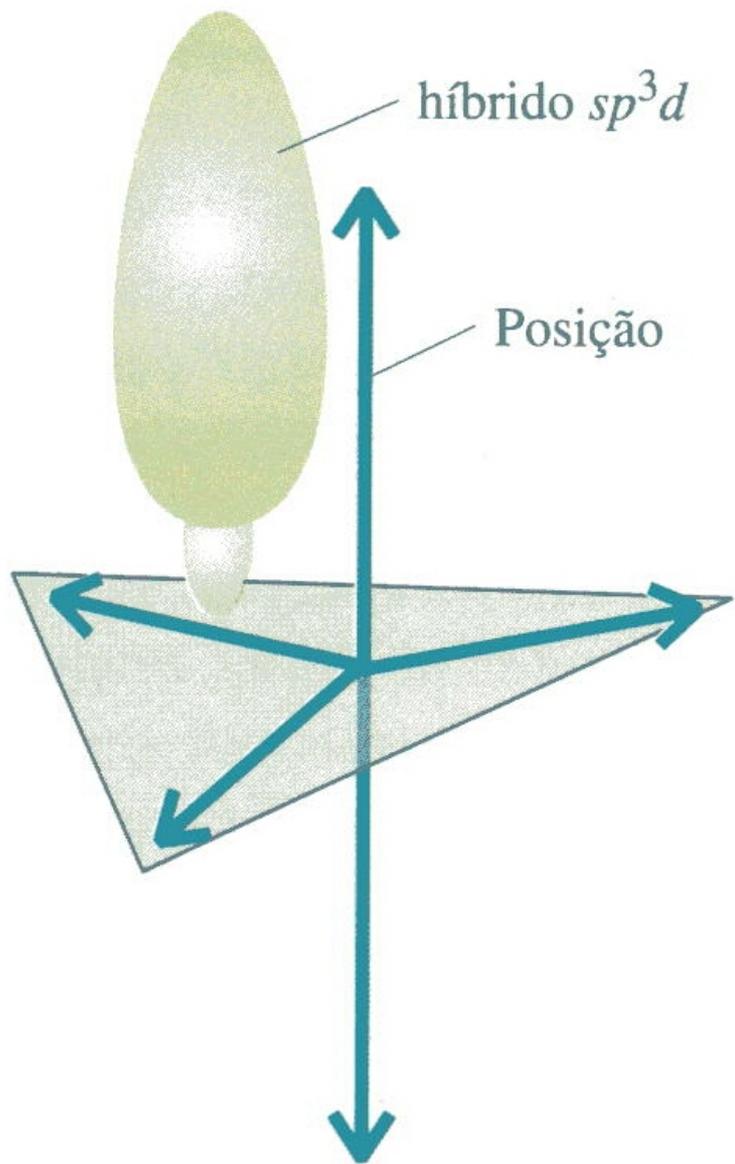
Um orbital s + dois orbitais p =  $sp^2$



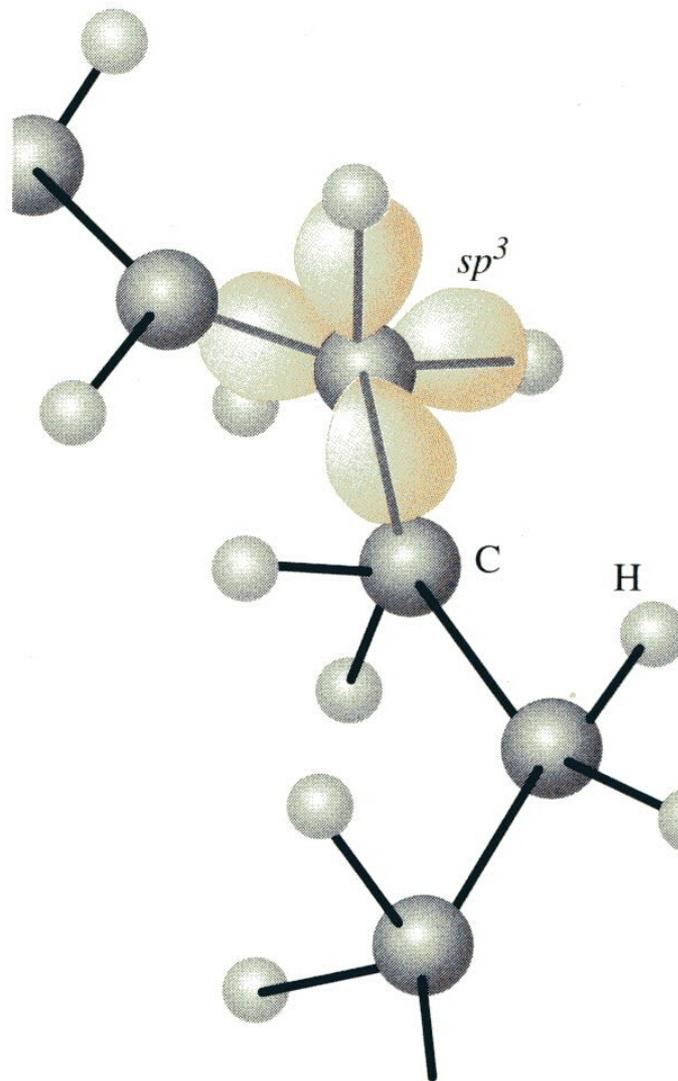
Um orbital s + um orbital p =  $sp$

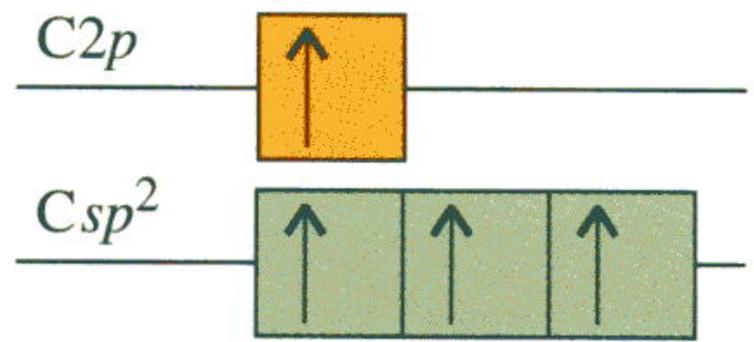
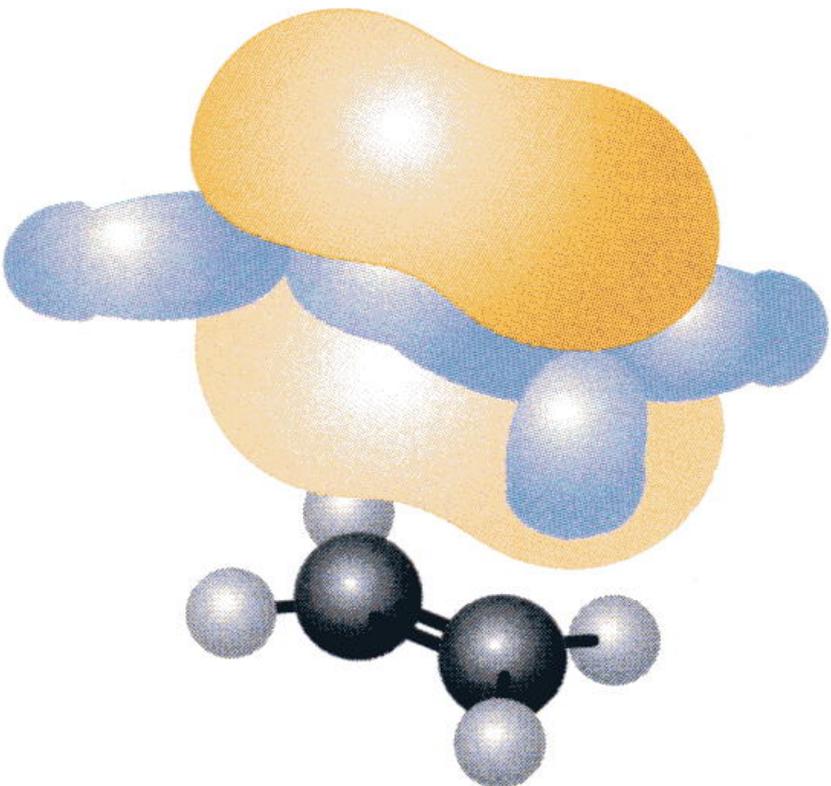
**TABELA 3.2** Esquemas comuns de hibridização

Número de orbitais atômicos combinados	Arranjo eletrônico	Tipo de hibridização	Número de orbitais híbridos ao redor do átomo central
2	linear	$sp$	2
3	trigonal planar	$sp^2$	3
4	tetraédrica	$sp^3$	4
5	bipirâmide trigonal	$sp^3d$	5
6	octaédrica	$sp^3d^2$	6

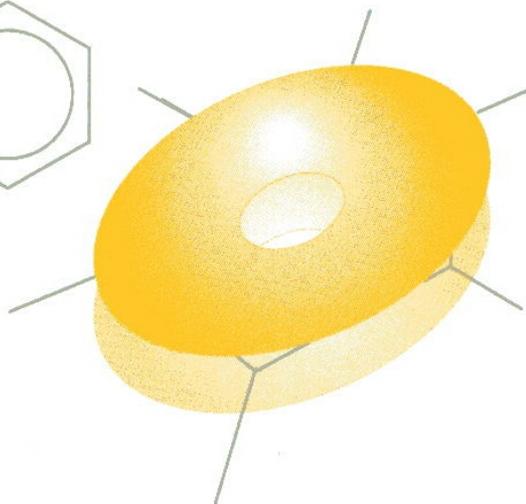
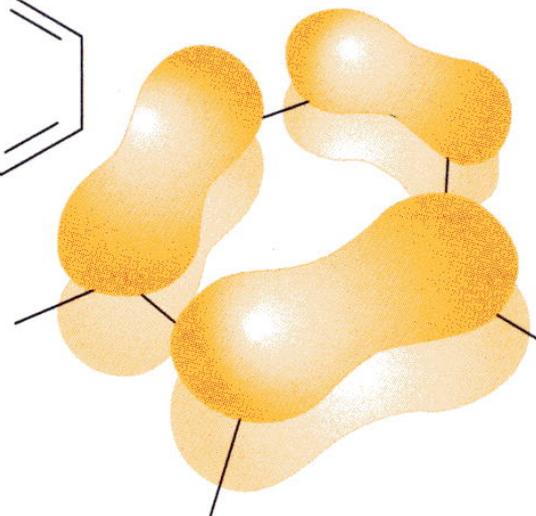
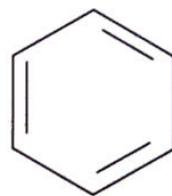
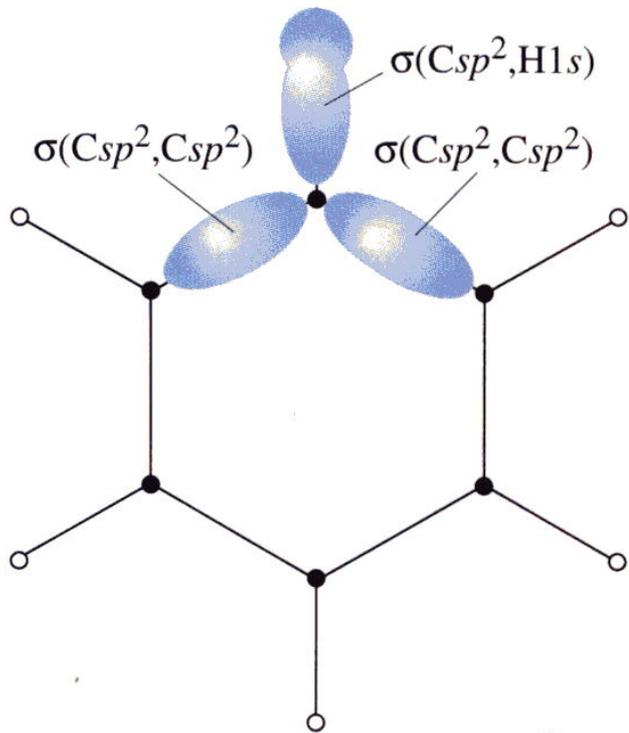


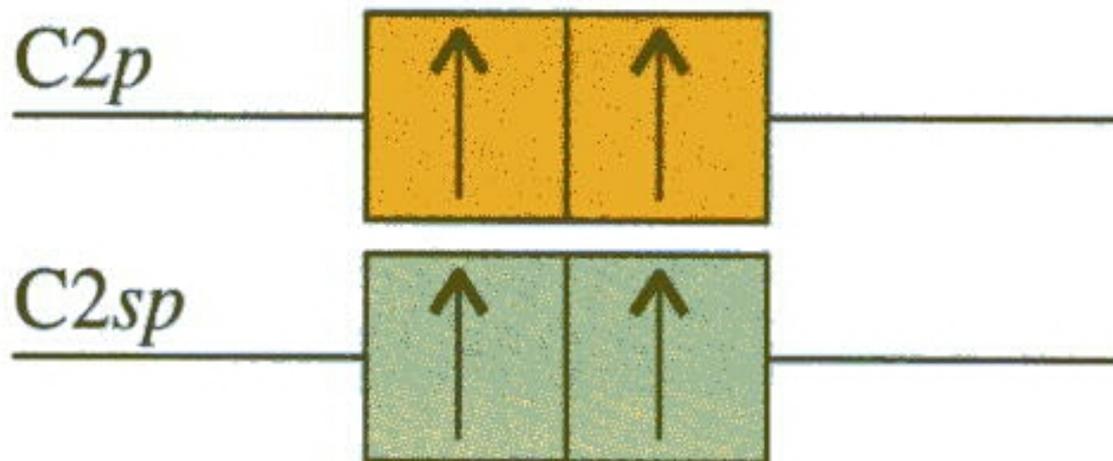
# Ligações em hidrocarbonetos



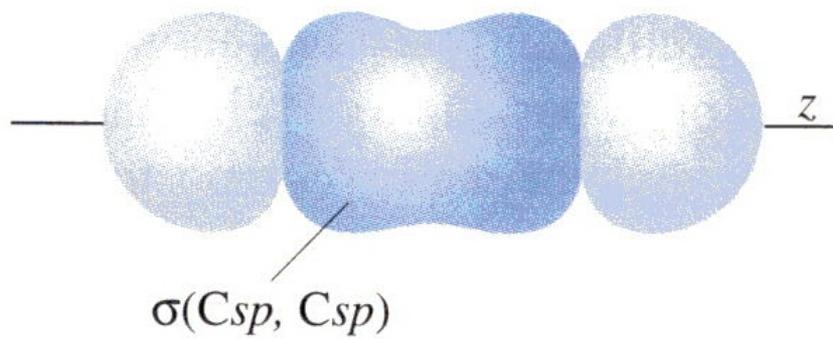
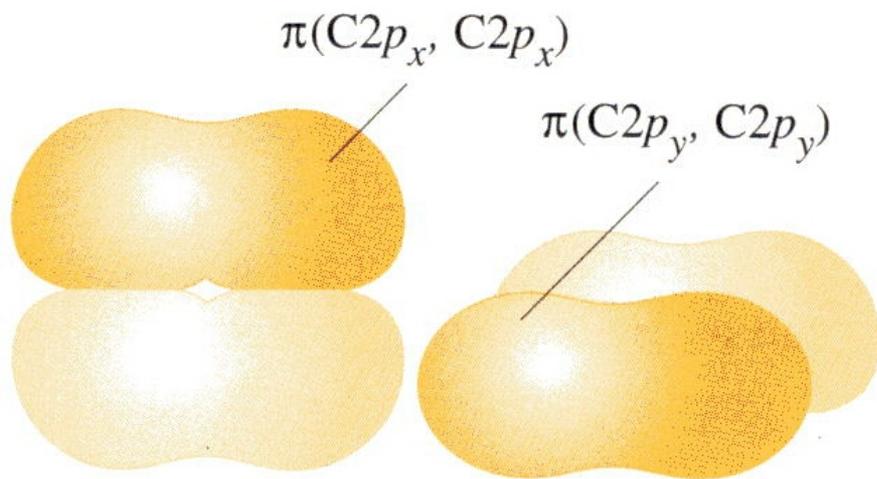


Carbono com hibridização  $sp^2$

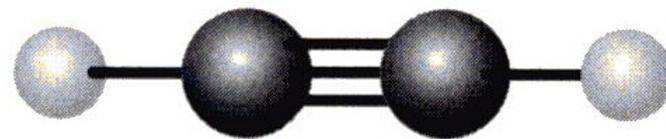
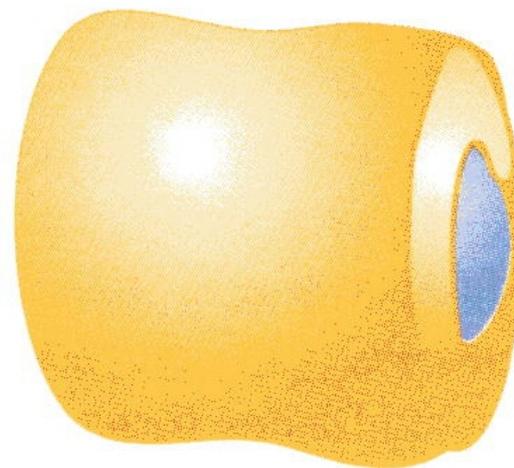




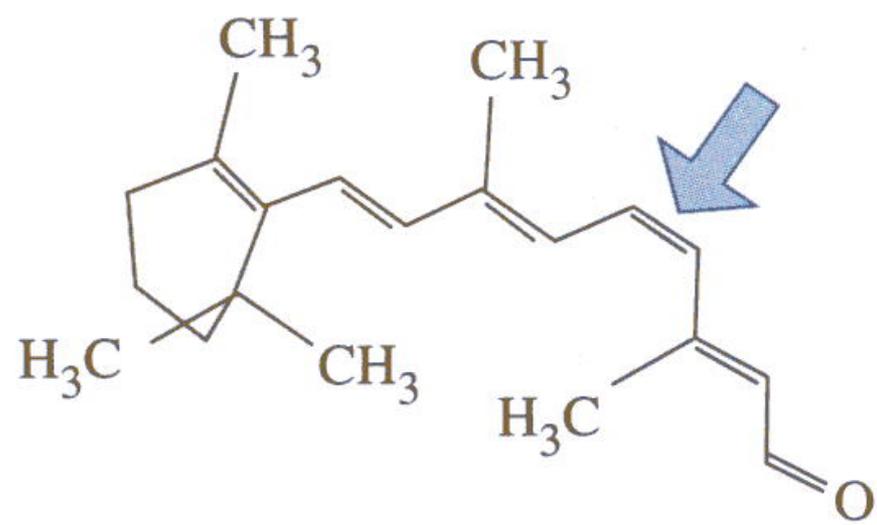
Carbono com hibridização  $sp$



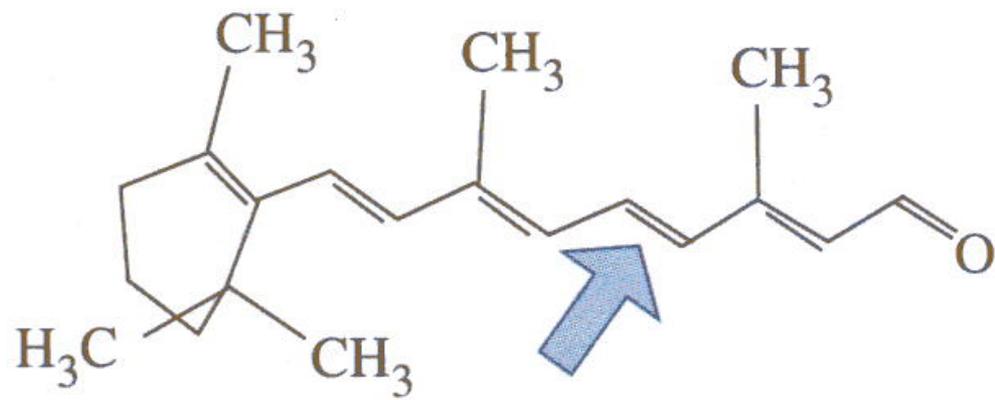
(a)



(b)



*cis*-Retinal

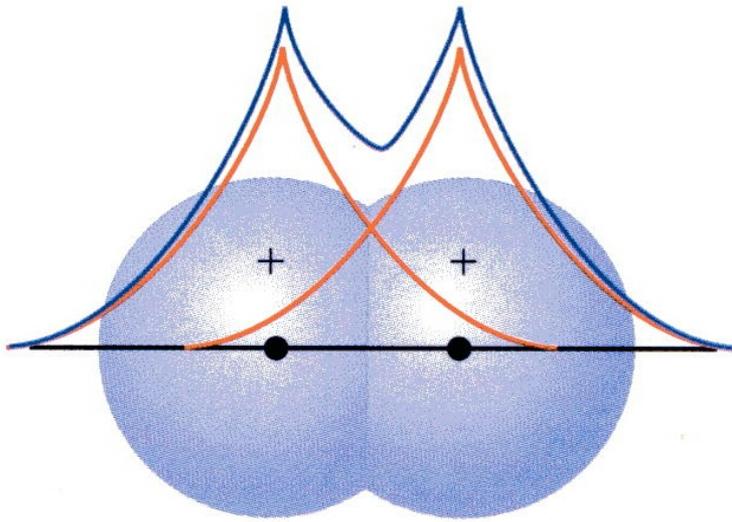


*trans*-Retinal

# Teoria do orbital molecular



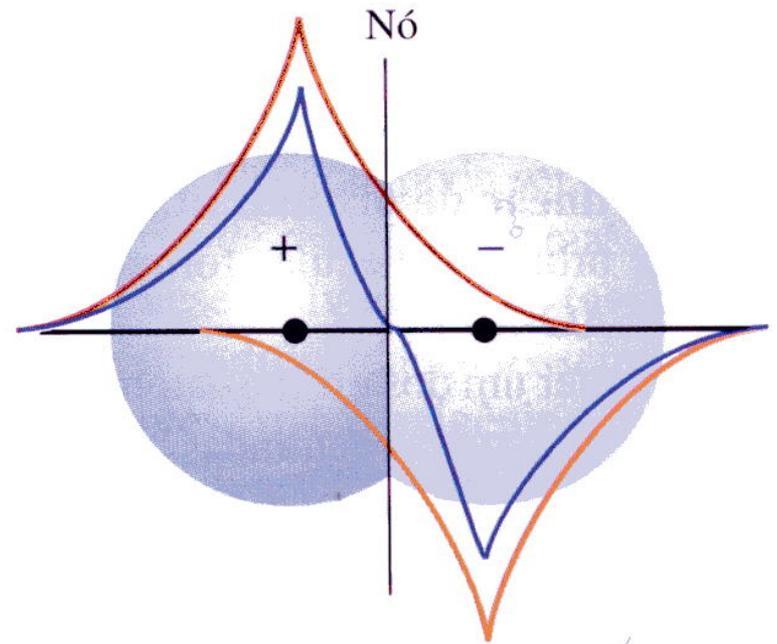
$O_2$  líquido



$$\Psi = \Psi_{A1s} + \Psi_{B1s}$$

Interferência construtiva

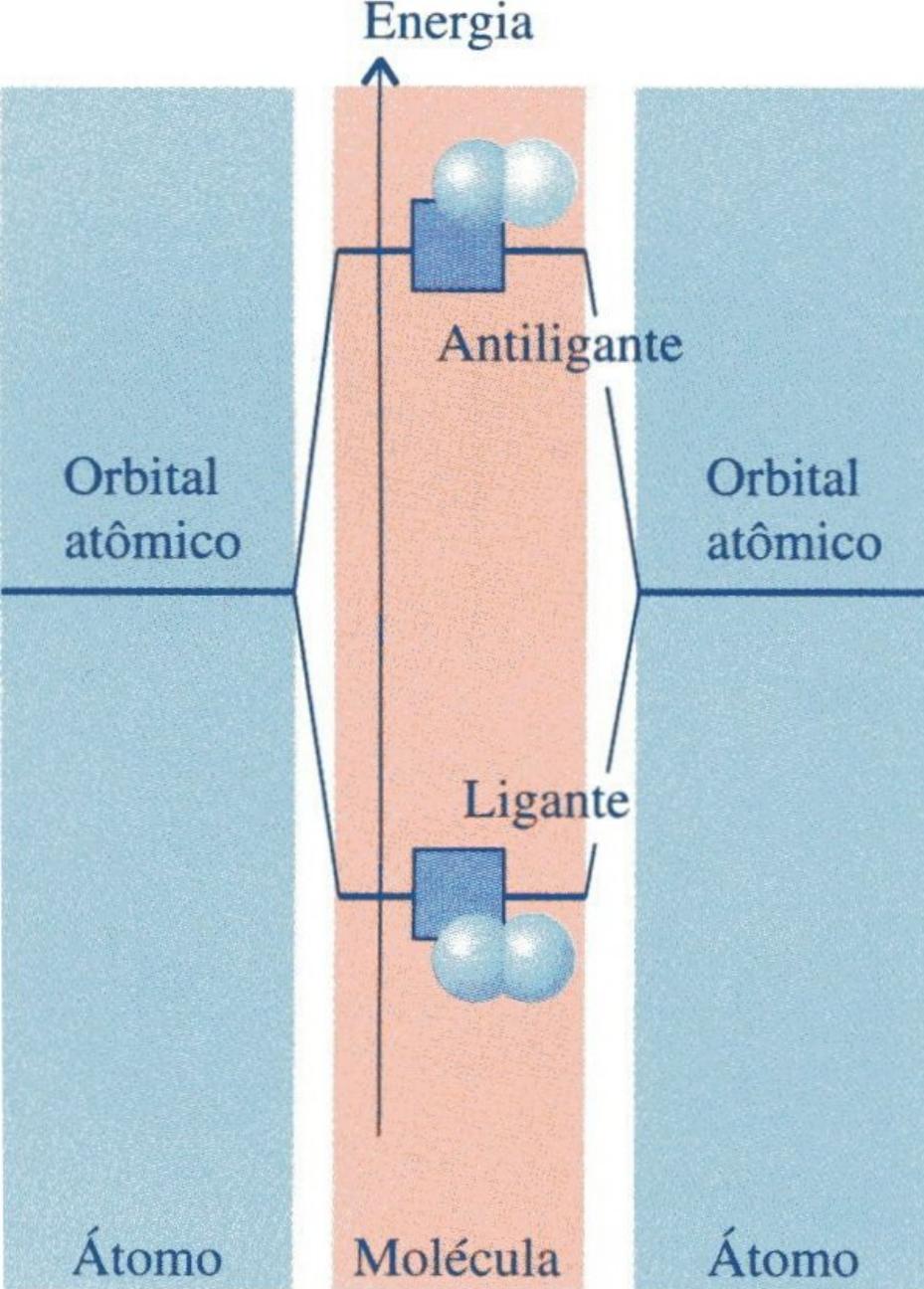
Orbital ligante



$$\Psi = \Psi_{A1s} - \Psi_{B1s}$$

Interferência destrutiva

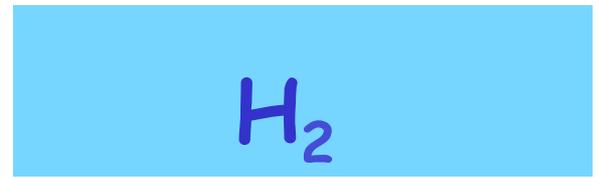
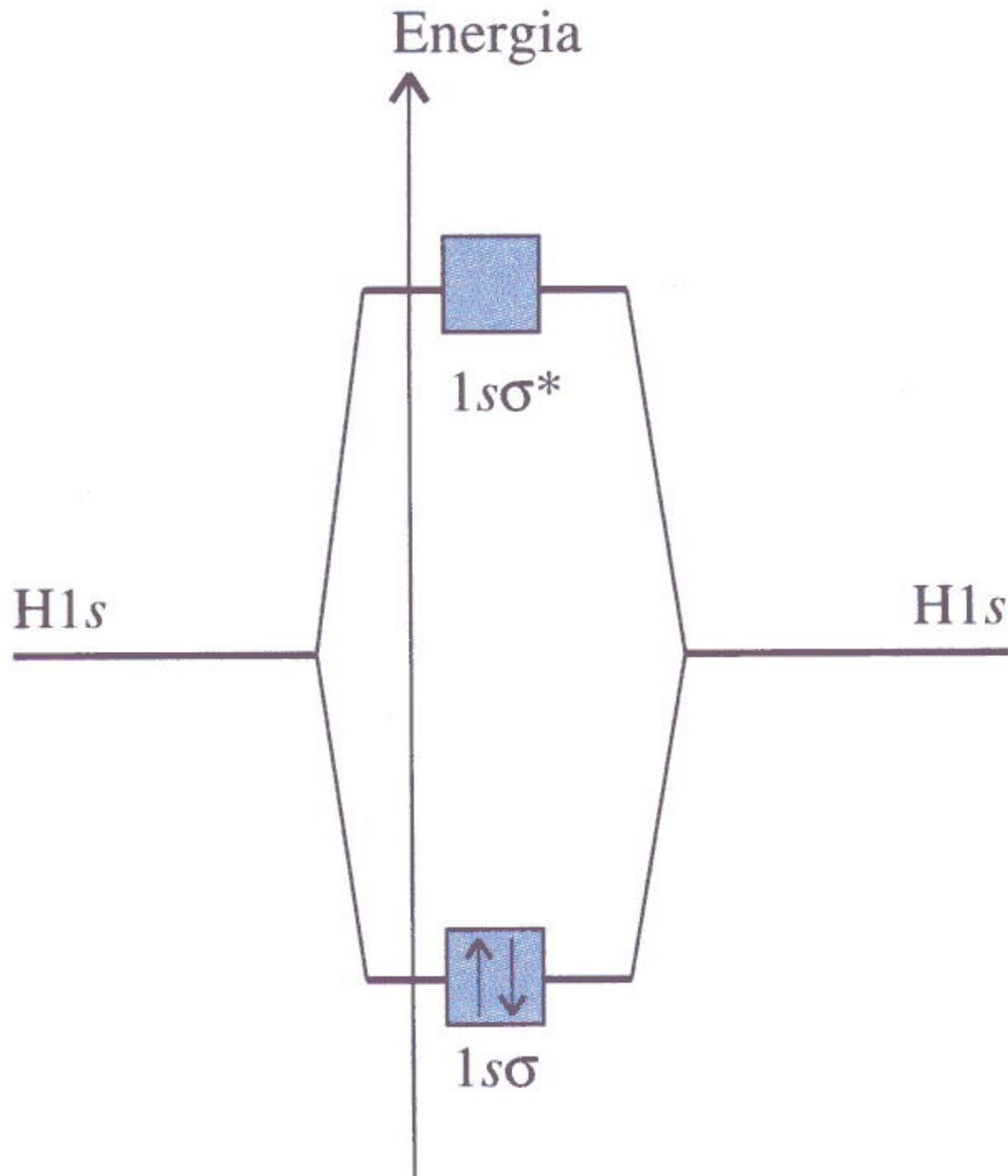
Orbital antiligante

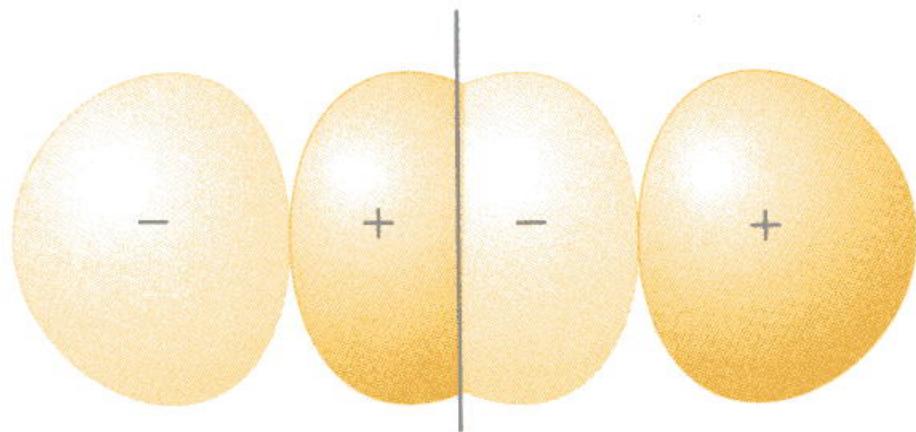


Passo 1: Acomodar os elétrons no orbital de menor energia.

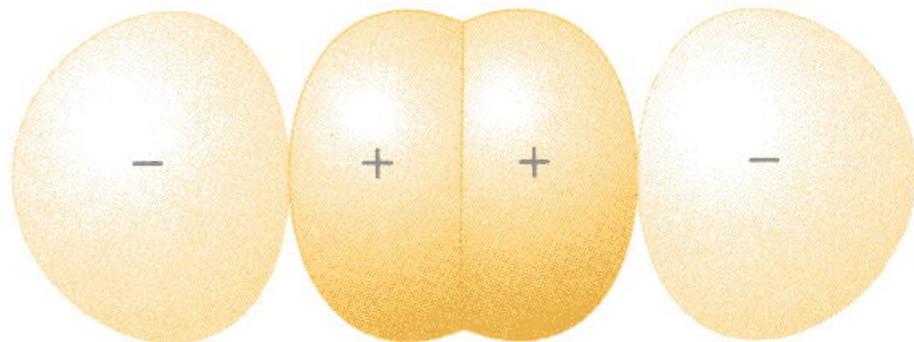
Passo 2: Princípio de exclusão de Pauli. Máximo dois elétrons por orbital.

Passo 3: Se mais de um orbital da mesma energia estiver disponível, são ocupados um a um (Regra de Hund).





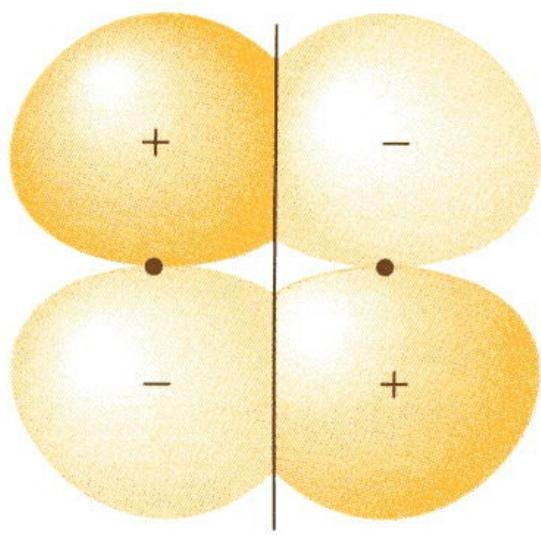
$2p\sigma^*$



$2p\sigma$

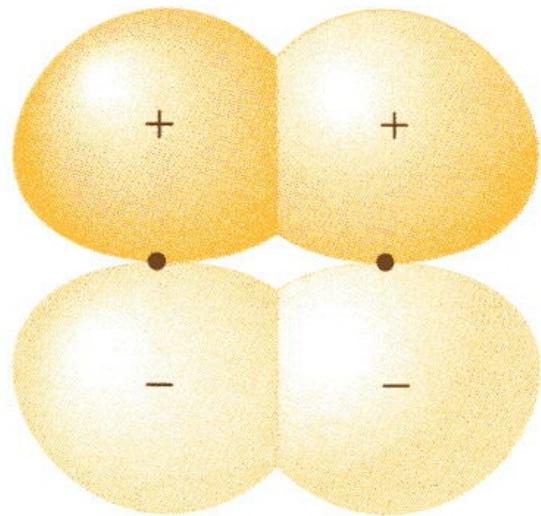
**Orbitais moleculares formados pelos átomos do grupo 2, ou seja, elétrons de valência no 2s 2p**

**Orbitais p direcionados ao longo do eixo nuclear formam orbitais moleculares  $\sigma$**

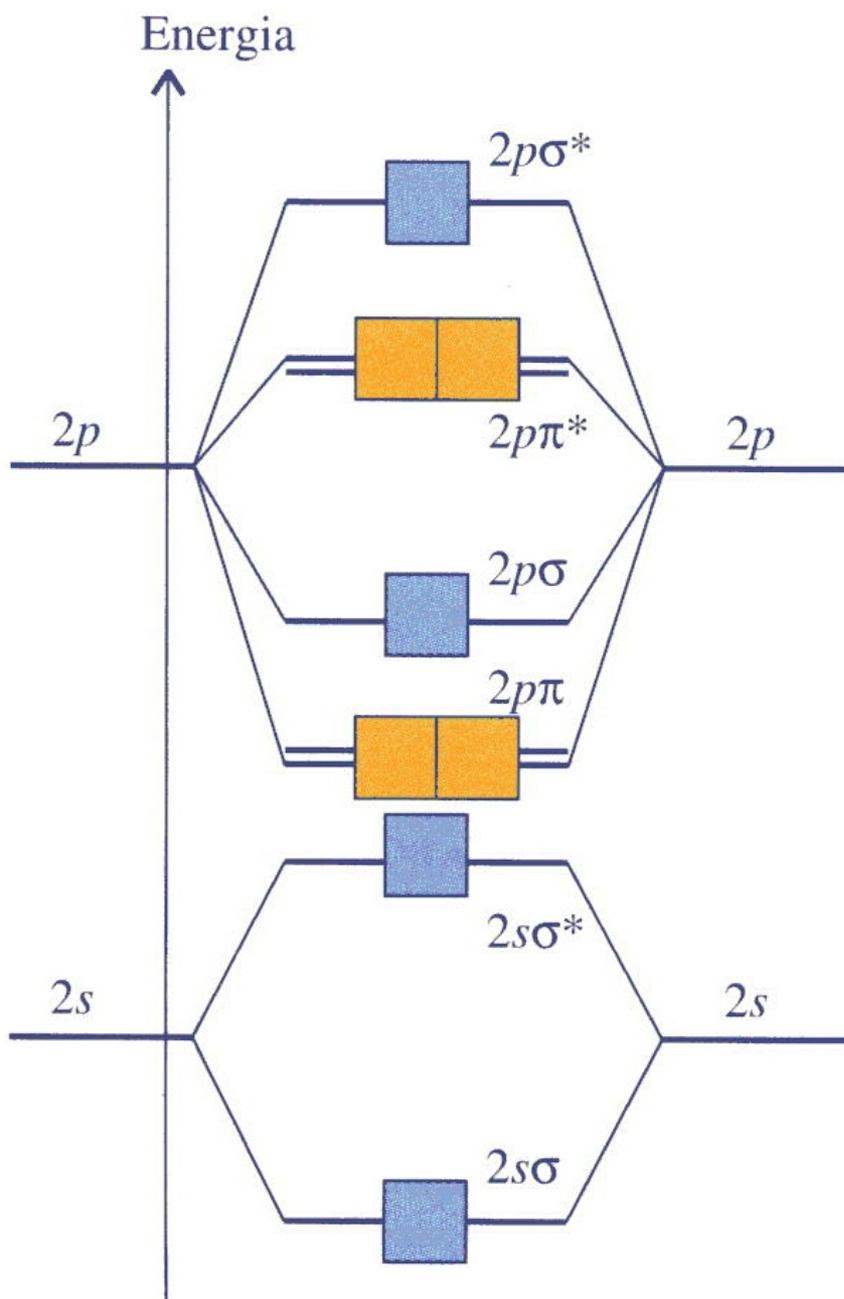


$2p\pi^*$

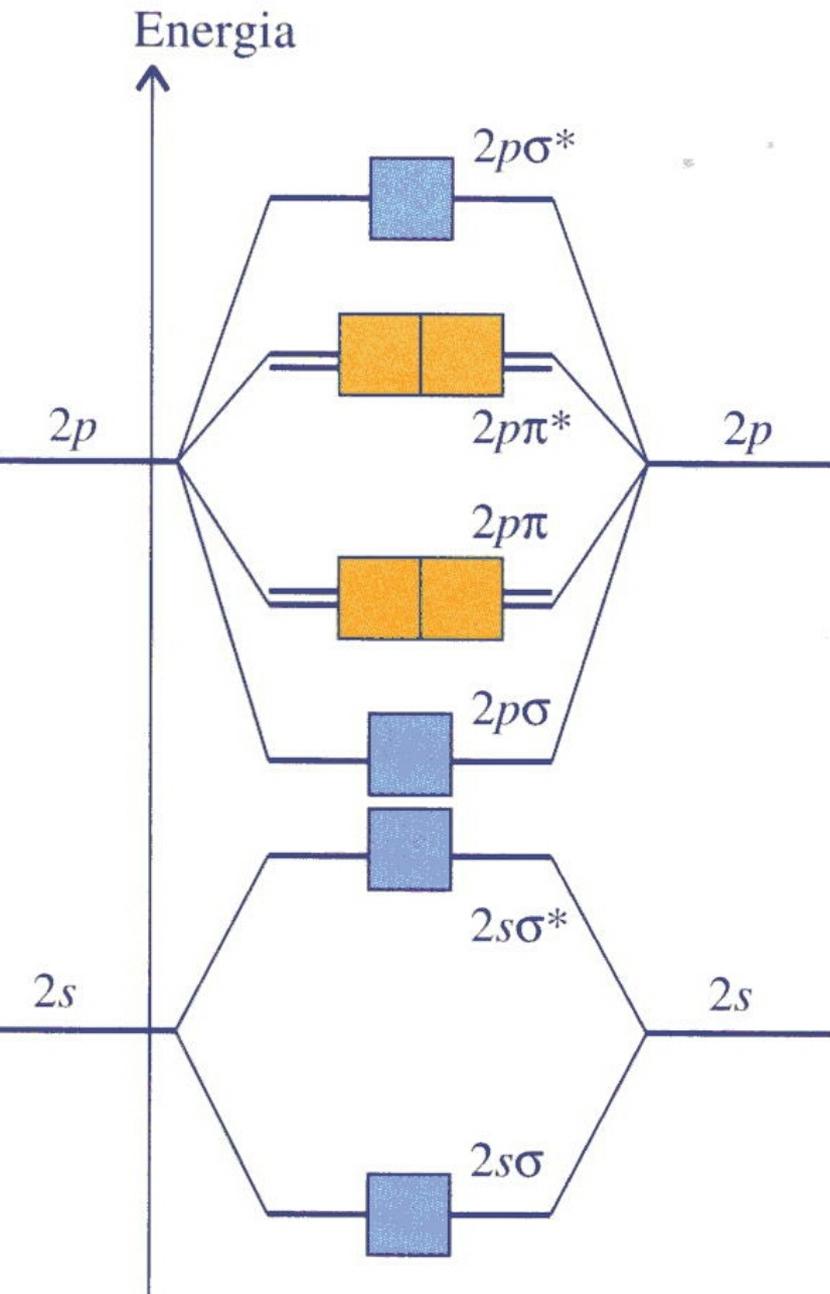
Orbitais p direcionados em  
forma perpendicular ao eixo  
nuclear formam orbitais  
moleculares  $\pi$



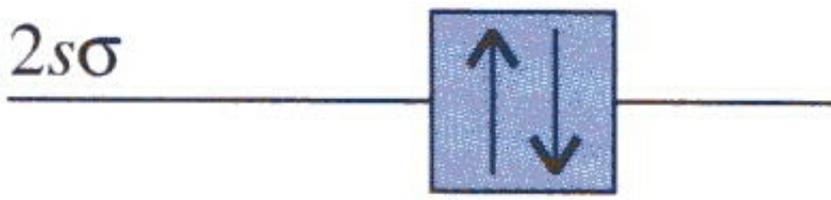
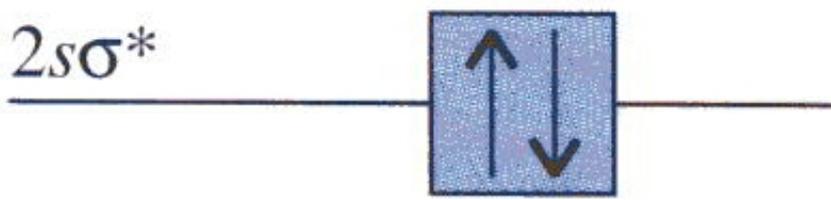
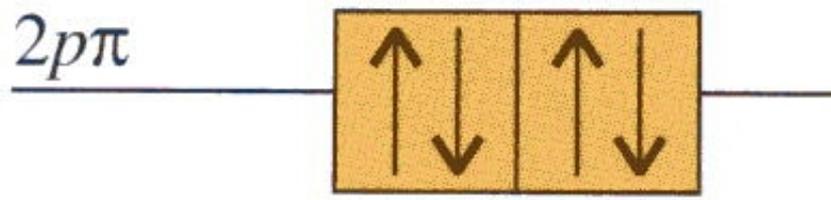
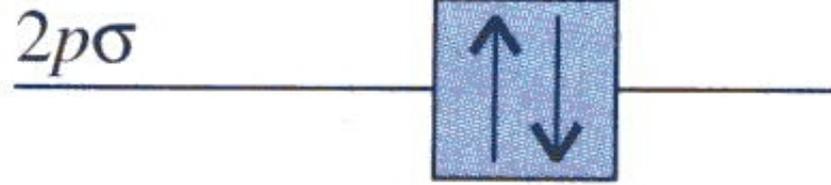
$2p\pi$



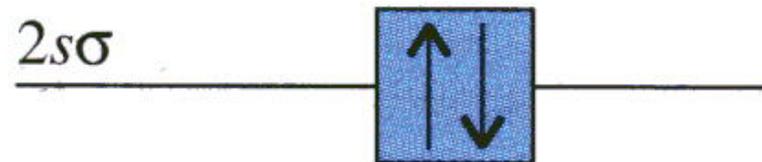
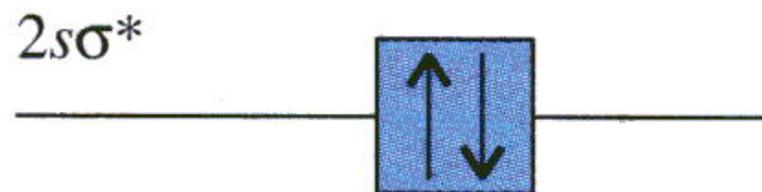
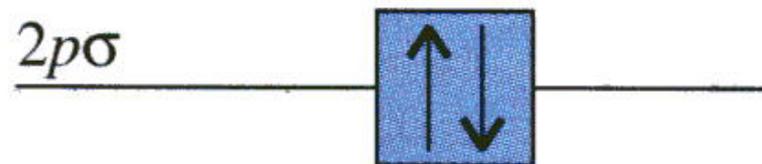
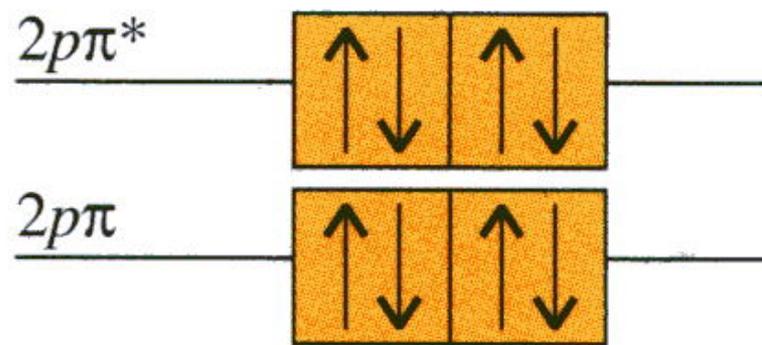
Li<sub>2</sub> até o N<sub>2</sub>



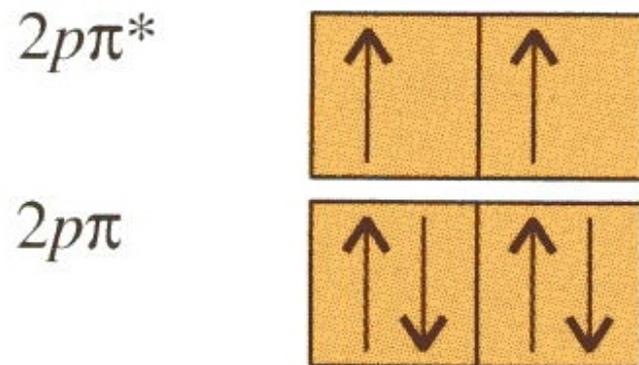
$O_2$  e  $F_2$



$N_2$

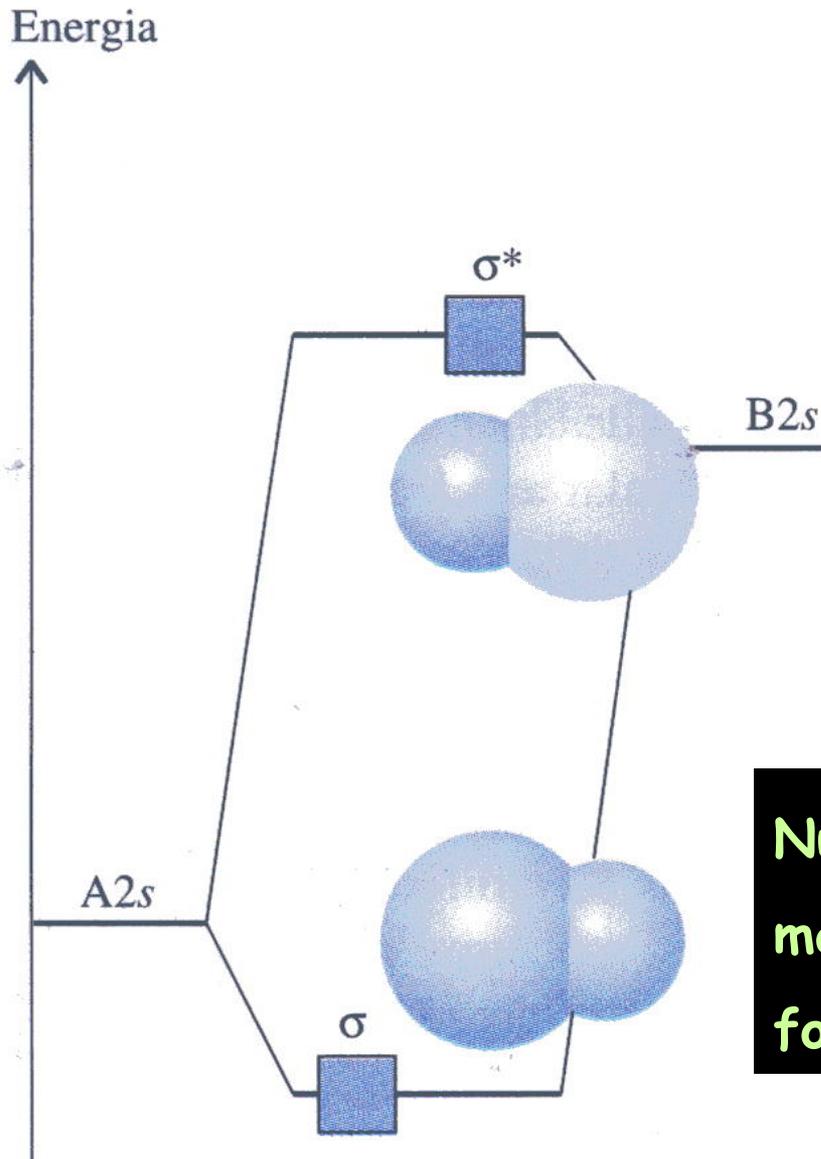


Flúor,  $F_2$



Oxigênio,  $O_2$

# Moléculas diatômicas heteronucleares



$$\Psi = c_A \Psi_A + c_B \Psi_B$$

Relação entre a eletronegatividade dos diferentes átomos. Em uma ligação iônica um dos coeficientes é zero.

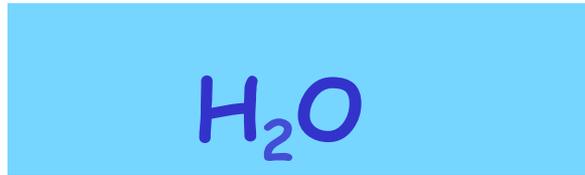
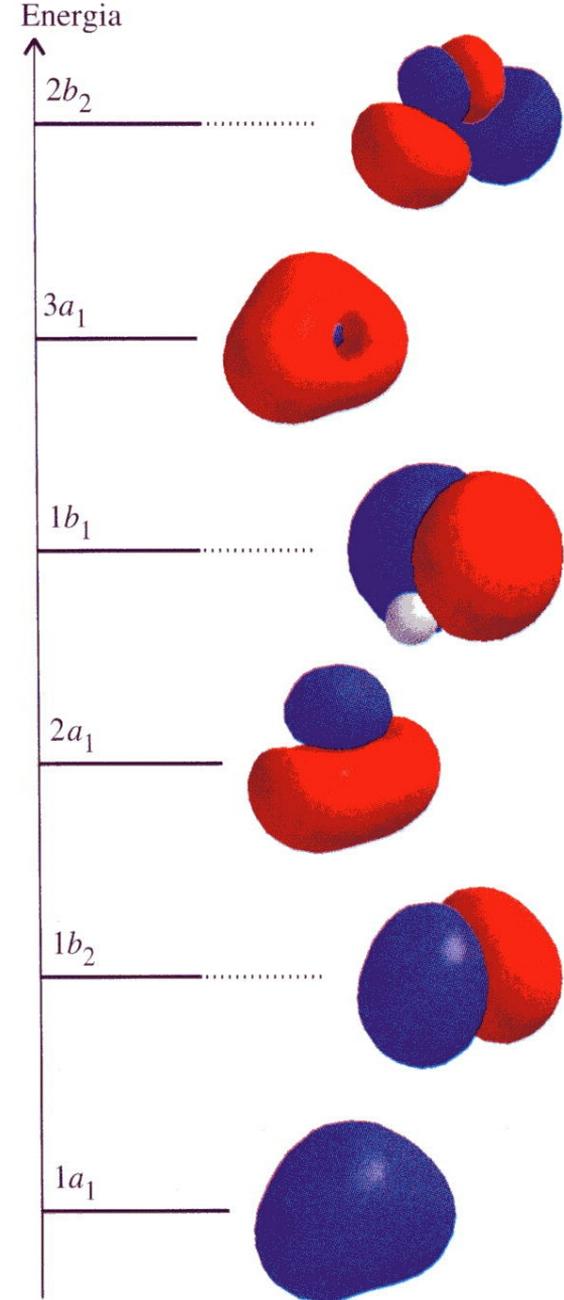
Numa ligação covalente polar o elemento mais eletronegativo contribui mais fortemente com o orbital ligante.

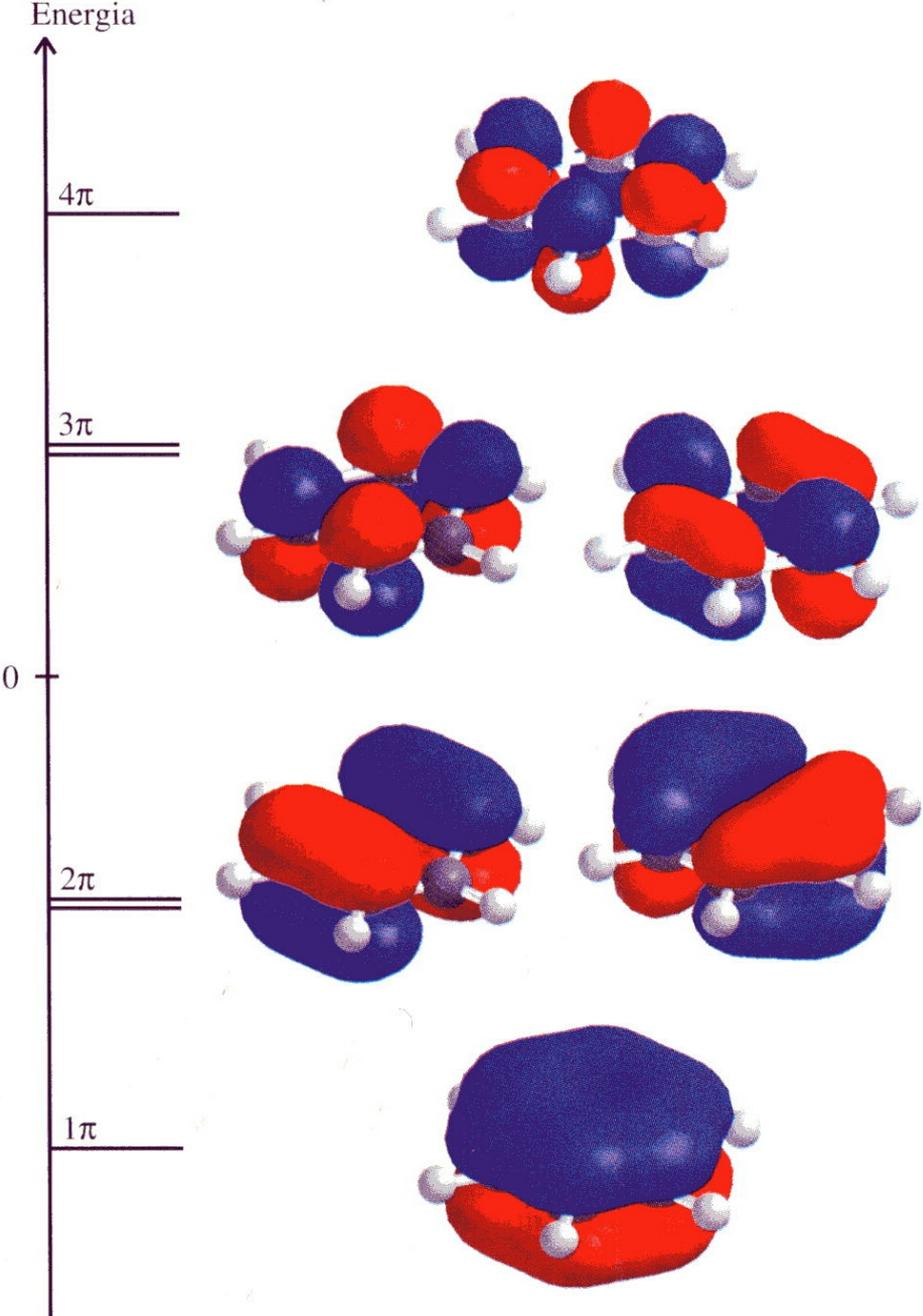
# Moléculas poliatômicas

Orbitais ligantes

Orbitais anti ligantes

Orbitais não ligantes





Benzeno

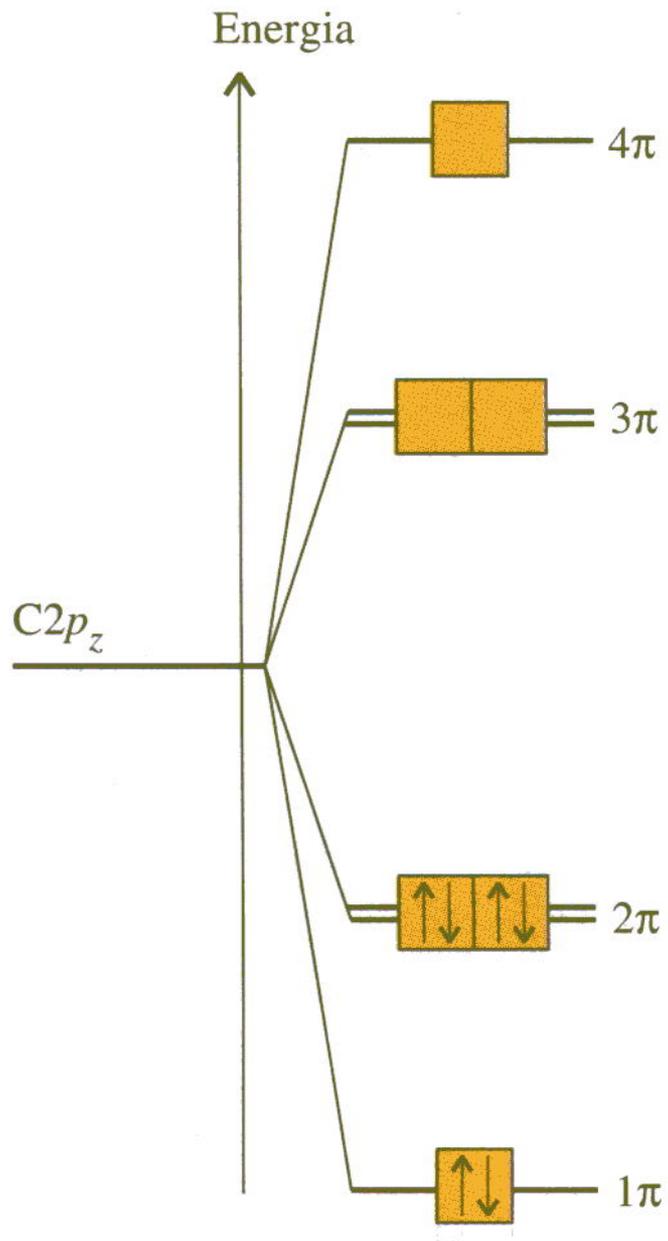
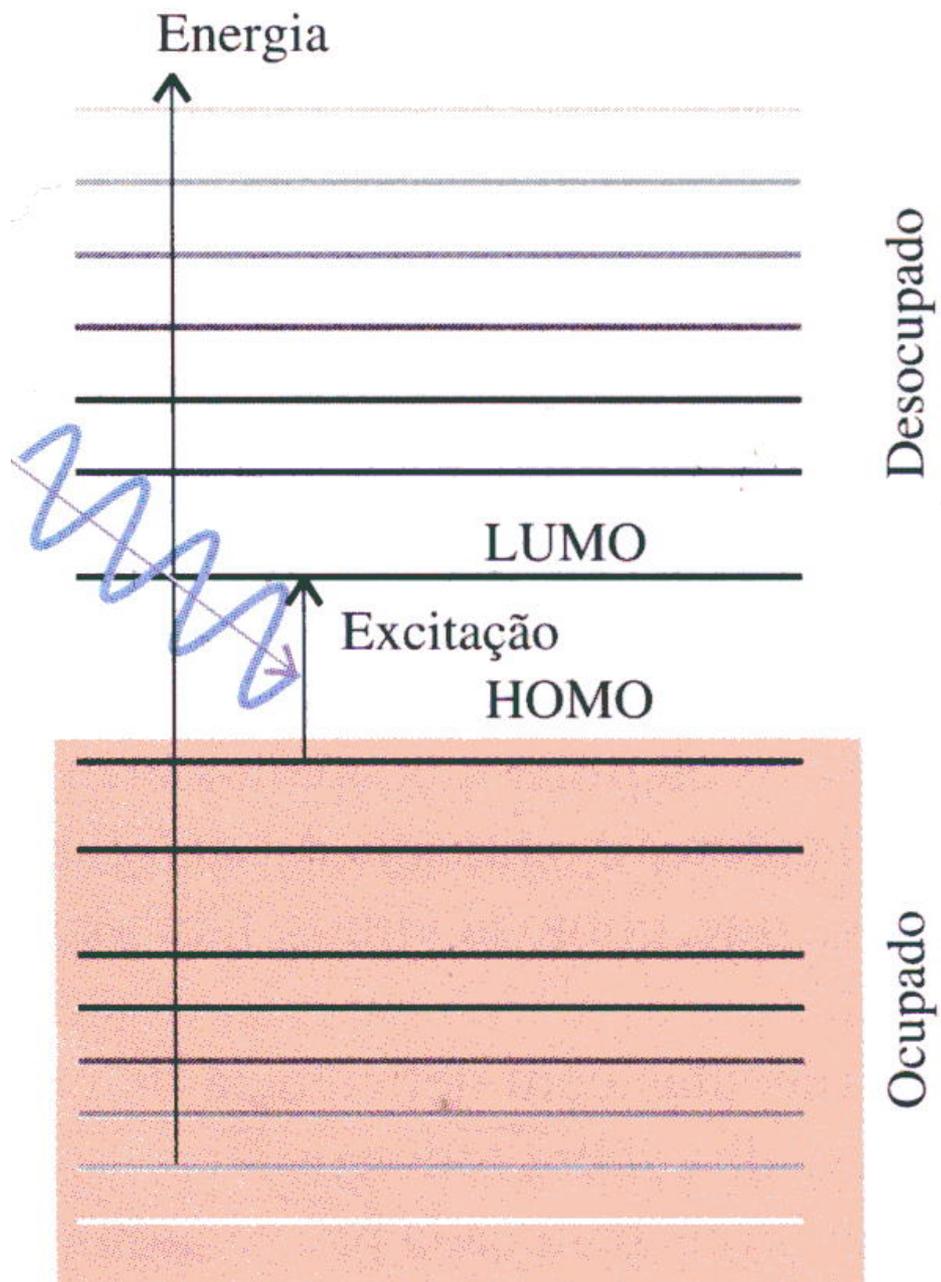
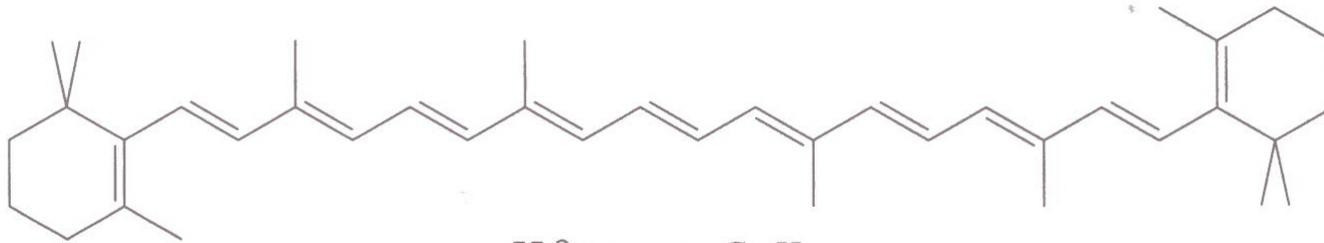


Diagrama de níveis de energia dos orbitais  $\pi$  do benzeno

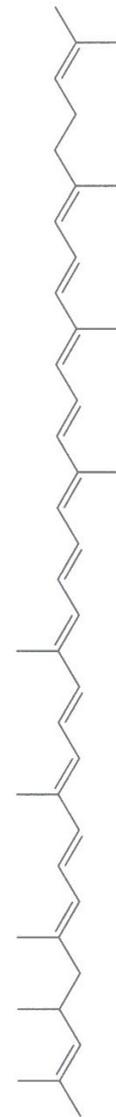
Em grandes moléculas, o **orbital molecular mais alto ocupado (HOMO)** - highest occupied molecular orbital), é muito próximo em termos de energia do **orbital molecular mais baixo não ocupado (LUMO - lowest unoccupied molecular orbital)**.





55  $\beta$ -caroteno,  $C_{40}H_{56}$

Algumas moléculas também podem absorver no visível e por isso são utilizadas como protetores solares



56 Licopeno,  $C_{40}H_{58}$

# A teoria de bandas no sólidos

Condutores

Semicondutores

Isolantes

Supercondutores

