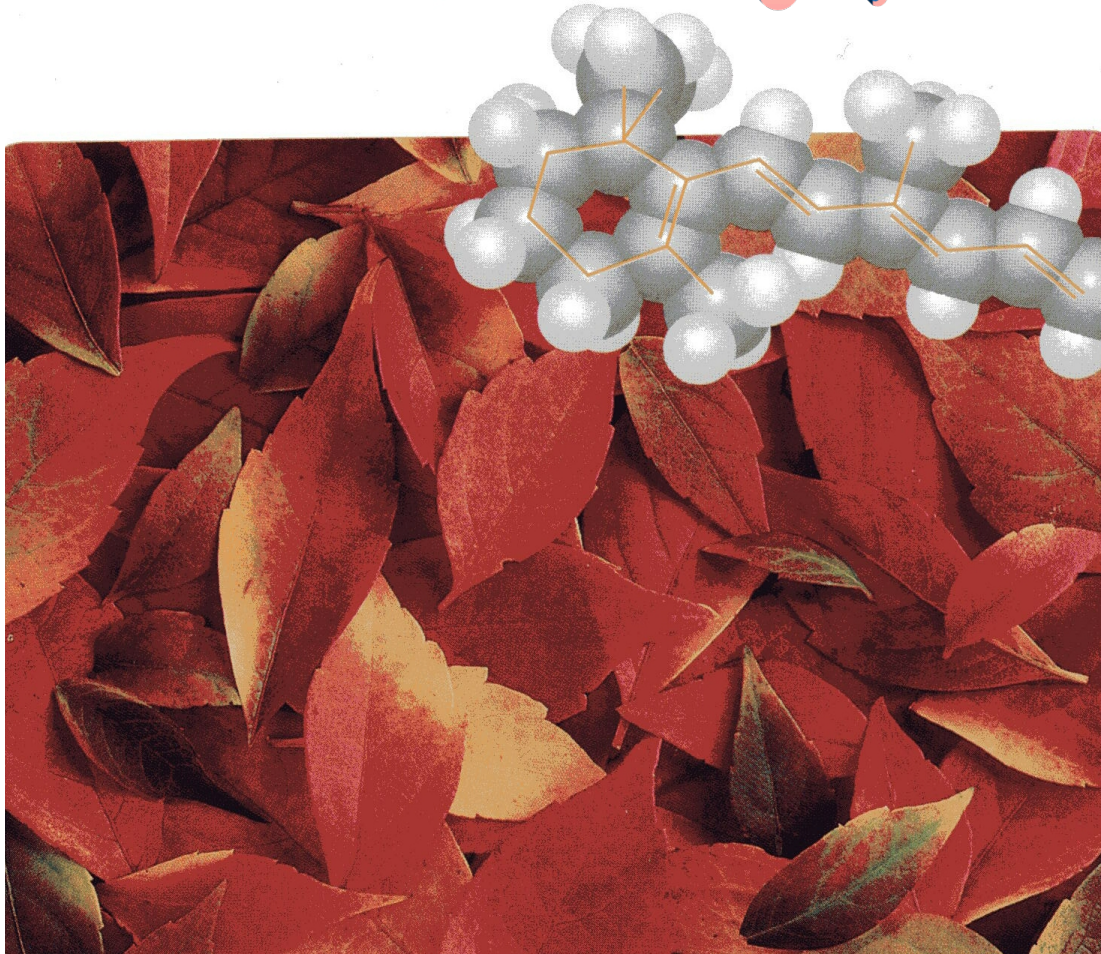


Estrutura molecular e ligações químicas



Estrutura de Lewis (elétrons ligantes e pares isolados)

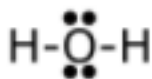
Hidrógeno



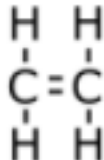
Carbono



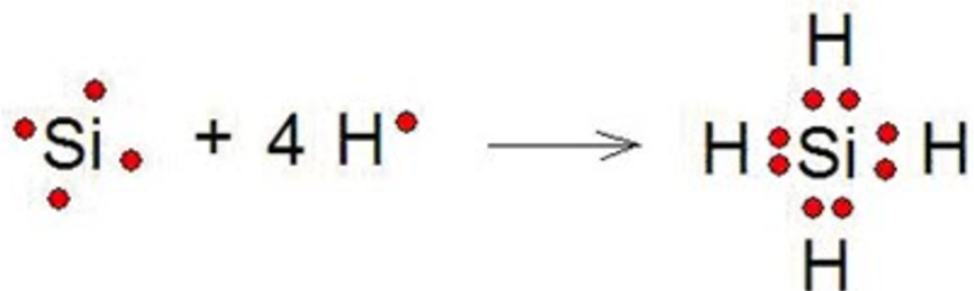
Água



Etileno

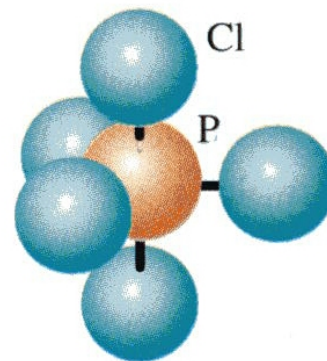
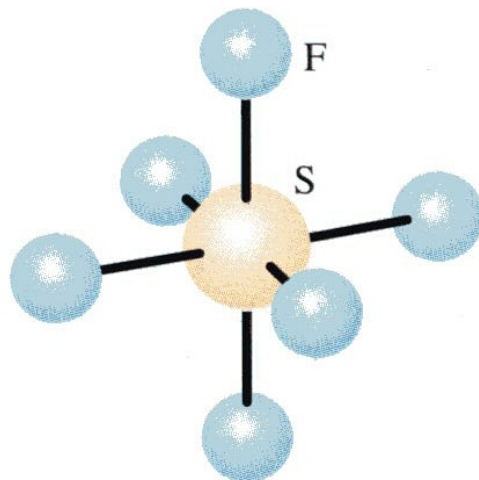
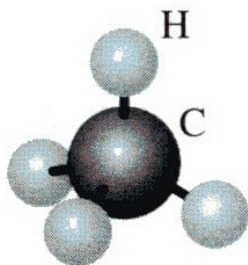


Acetileno



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

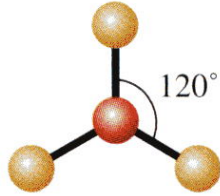
Diferentes formas das moléculas



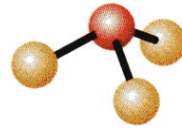
Linear



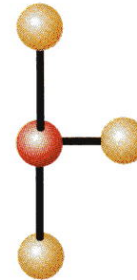
Angular



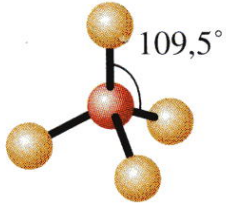
Trigonal planar



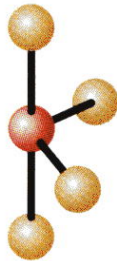
Pirâmide trigonal



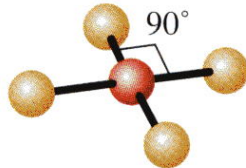
Forma T



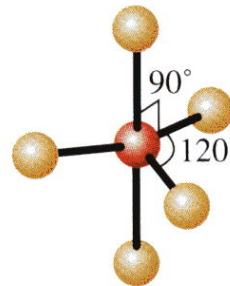
Tetraédrica



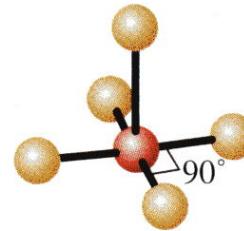
Gangorra



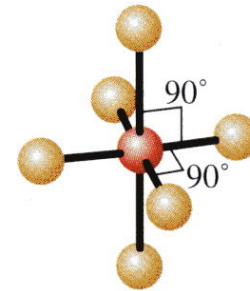
Quadrado planar



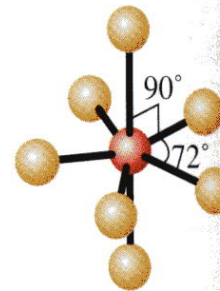
Bipirâmide trigonal



Pirâmide quadrada



Octaédrica



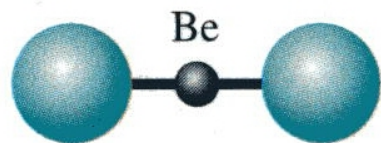
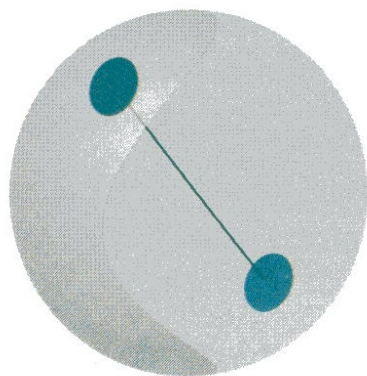
Bipirâmide pentagonal

Equação de Schrödinger

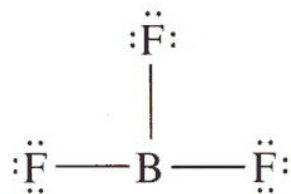
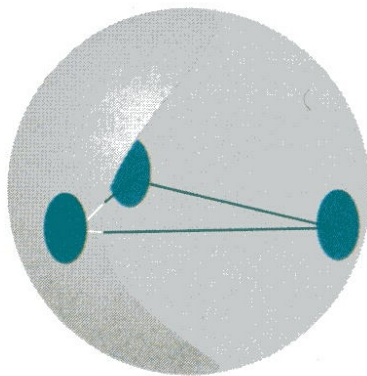
Métodos semi-empíricos

Métodos ab-initio

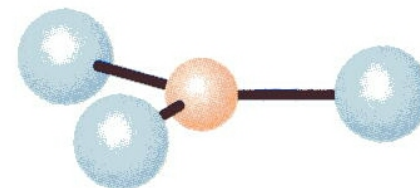
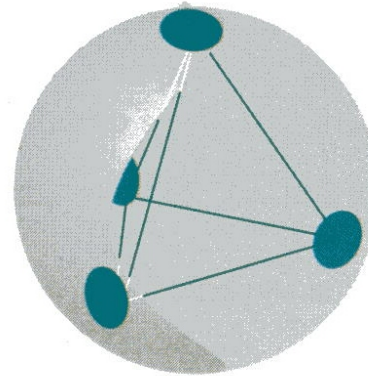
Modelo VSPR: modificar o modelo de ligação de Lewis considerando que regiões de alta concentração eletrônica se repelem. (valence-shell electron-pair repulsion model)



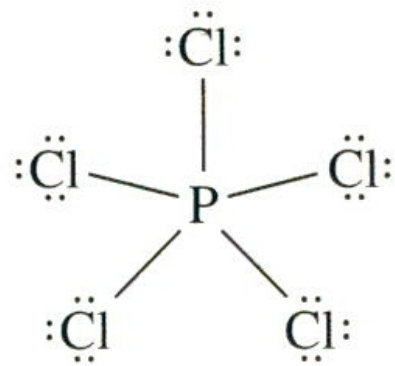
Cloreto de berílio, BeCl₂



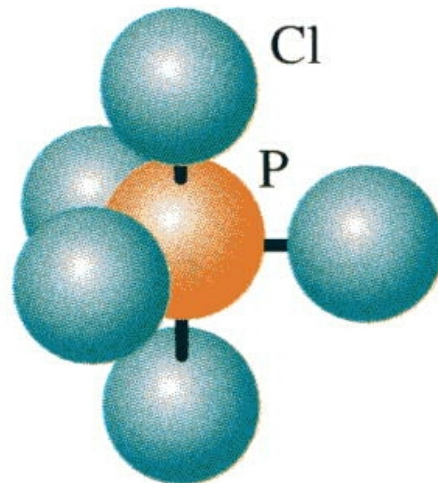
Trifluoreto de boro, BF₃



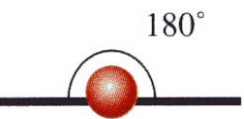
Trifluoreto de boro, BF₃



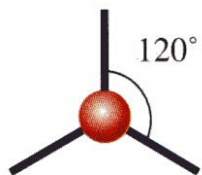
Pentacloruro de fósforo, PCl₅



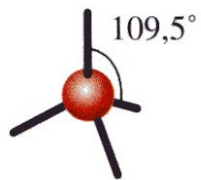
Pentacloruro de fósforo, PCl₅



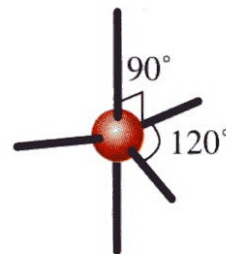
Linear



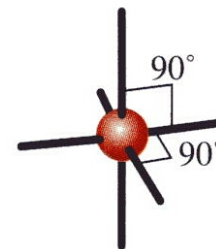
Trigonal planar



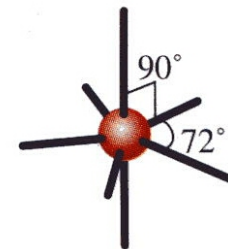
Tetraédrica



Bipirâmide
trigonal



Octaédrica

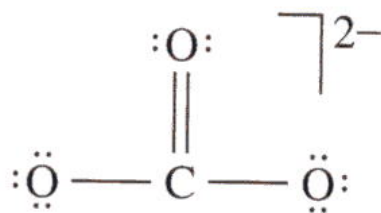


Bipirâmide
pentagonal

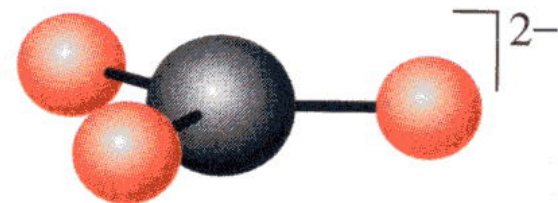
O modelo VSPR não distingue entre ligações simples ou múltiplas, todo é tratado como regiões de alta concentração eletrônica. Os dois pares eletrônicos (ligação dupla) permanecem juntos e repelem outra região de alta concentração eletrônica.



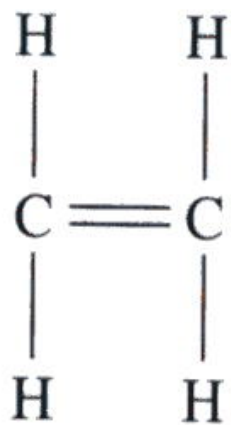
Dióxido de carbono, CO_2



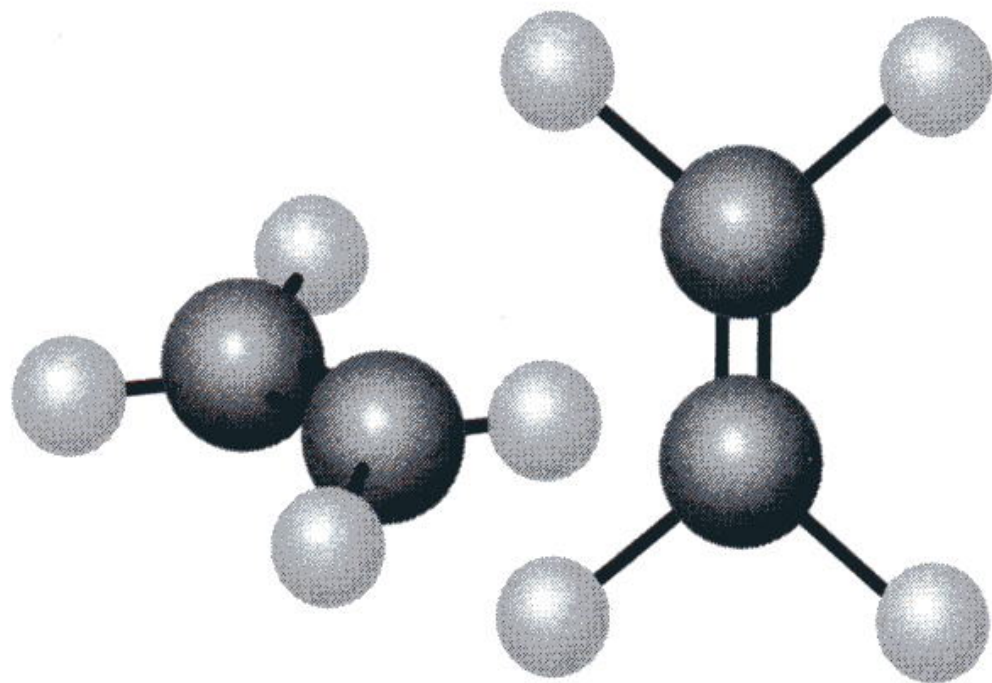
Íon carbonato, CO_3^{2-}



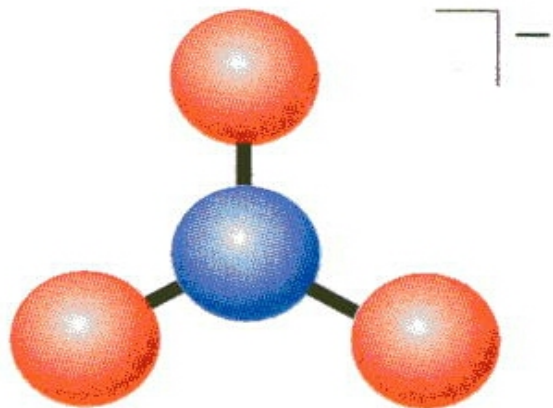
Íon carbonato, CO_3^{2-}



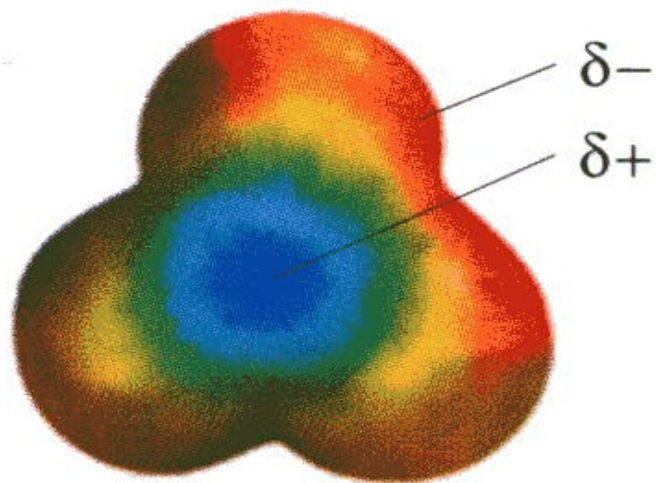
Eteno, C_2H_4



Eteno, C_2H_4



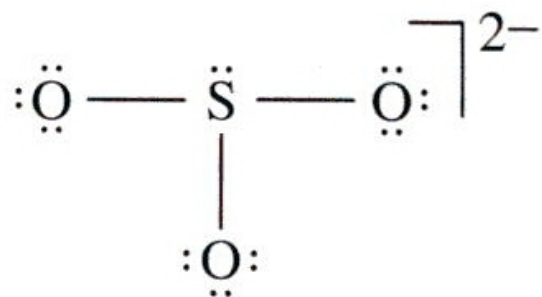
Íon nitrato, NO_3^-



Íon nitrato

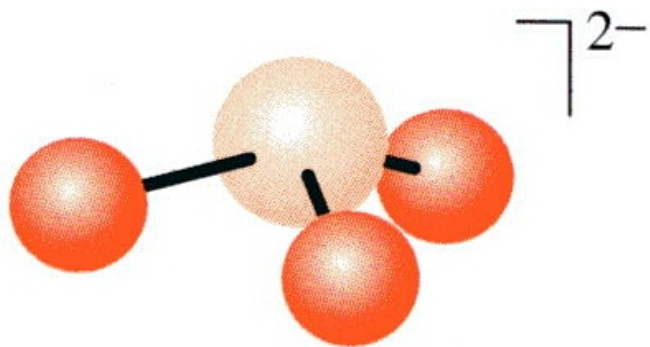
O modelo VSPR não se importa com as diferentes estruturas de Lewis.

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.

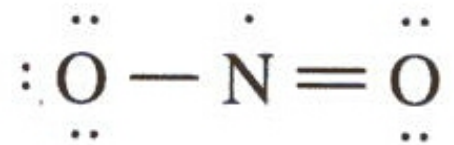


Íon sulfito, SO_3^{2-}

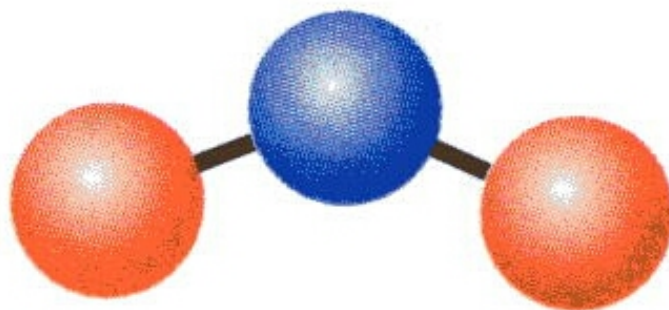
Os pares de elétrons isolados ou elétrons desemparelhados no átomo central são considerados para definir a geometria, mas não aparecem na fórmula química.



Íon sulfito, SO_3^{2-}

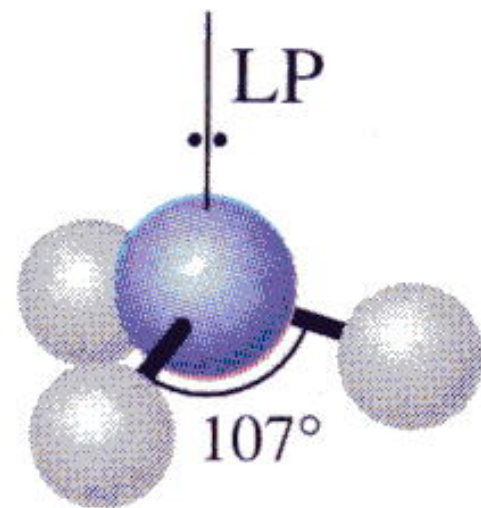
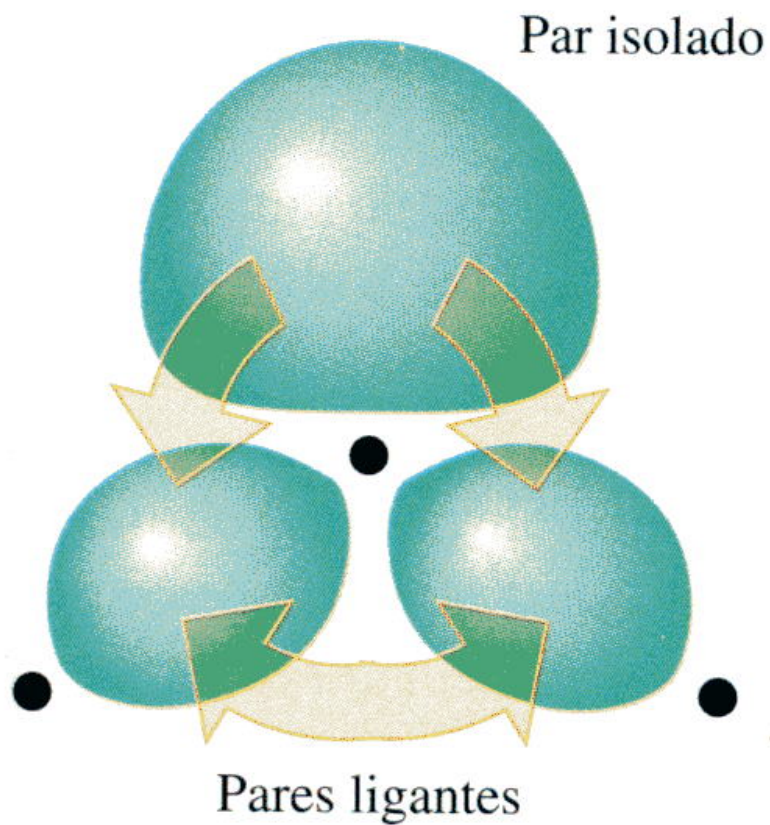


Dióxido de nitrogênio, NO_2

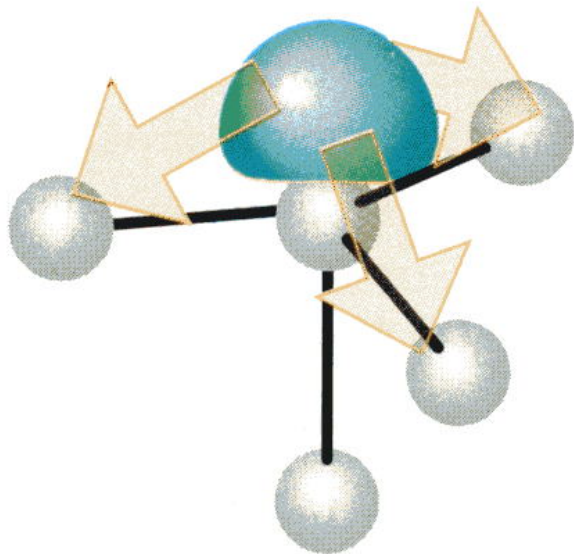


Dióxido de nitrogênio, NO_2

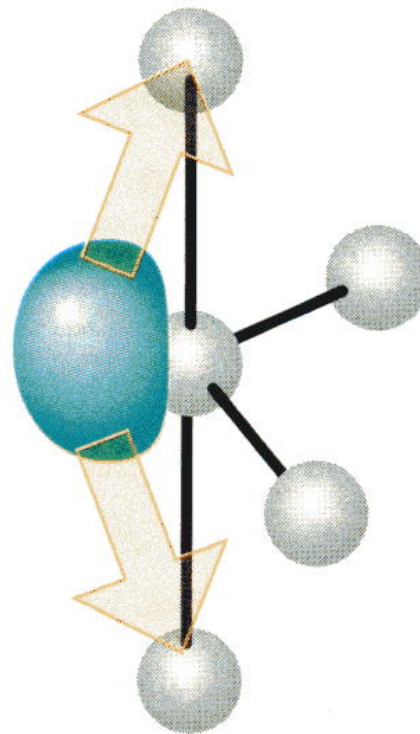
Par isolado-par isolado > par isolado-par ligante > par ligante-par ligante



Amônia, NH_3

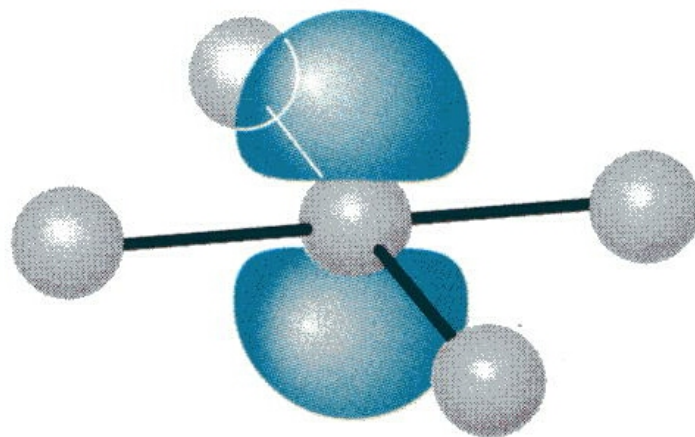


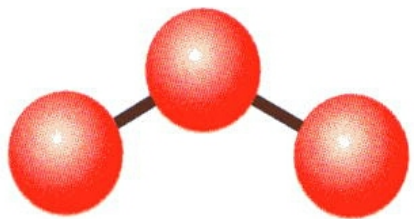
(a)



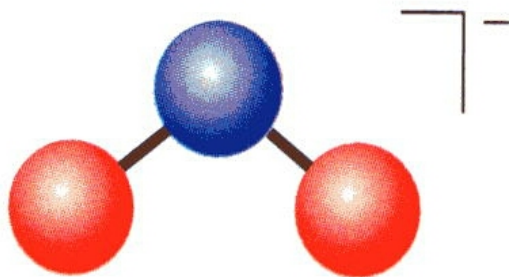
(b)

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.

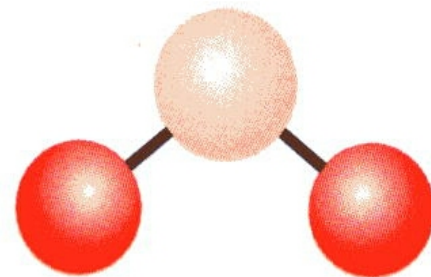




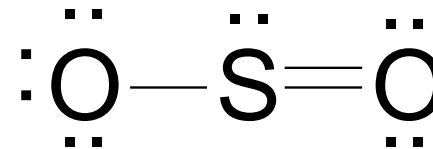
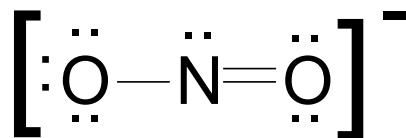
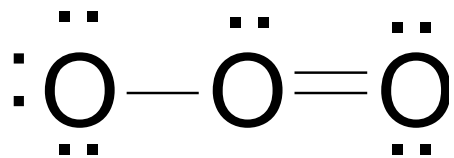
Ozônio, O_3



Íon nitrito, NO_2^-

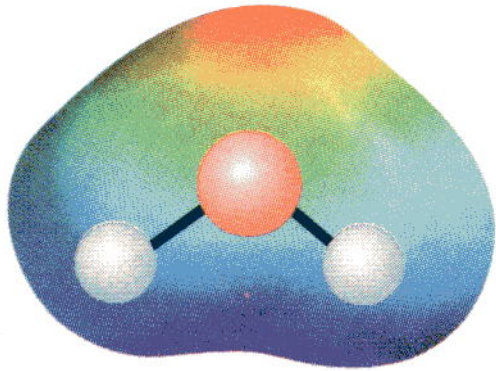


Dióxido de enxofre, SO_2



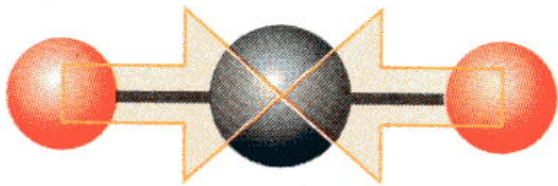
Os pares de elétrons isolados distorcem a forma da molécula

Moléculas polares: momento de dipolo diferente de zero

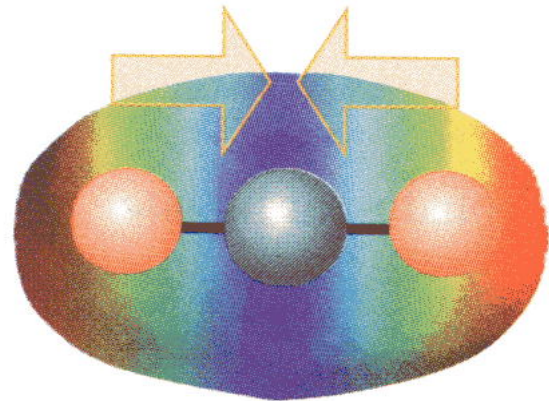


Água, H₂O

Moléculas não polares: momento de dipolo igual a zero. Moléculas homonucleares (O₂, Cl₂, etc.)



Dióxido de carbono, CO₂



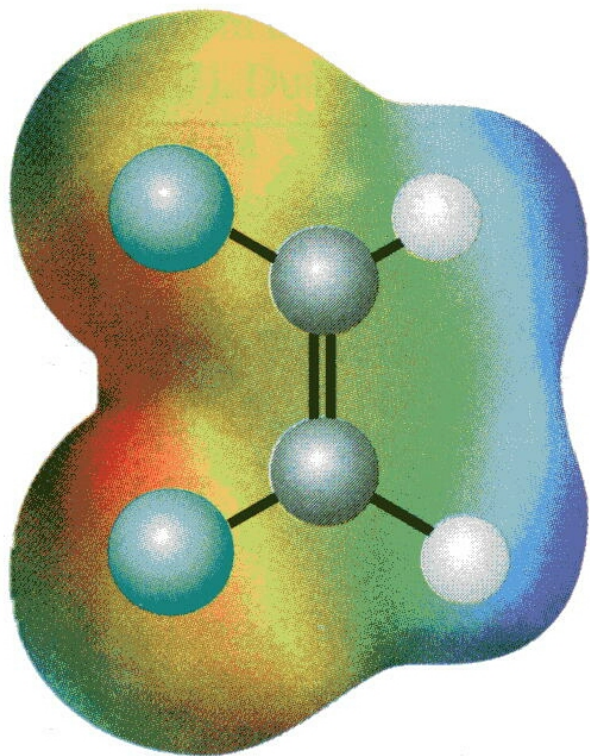
Dióxido de carbono, CO₂

TABELA 3.1

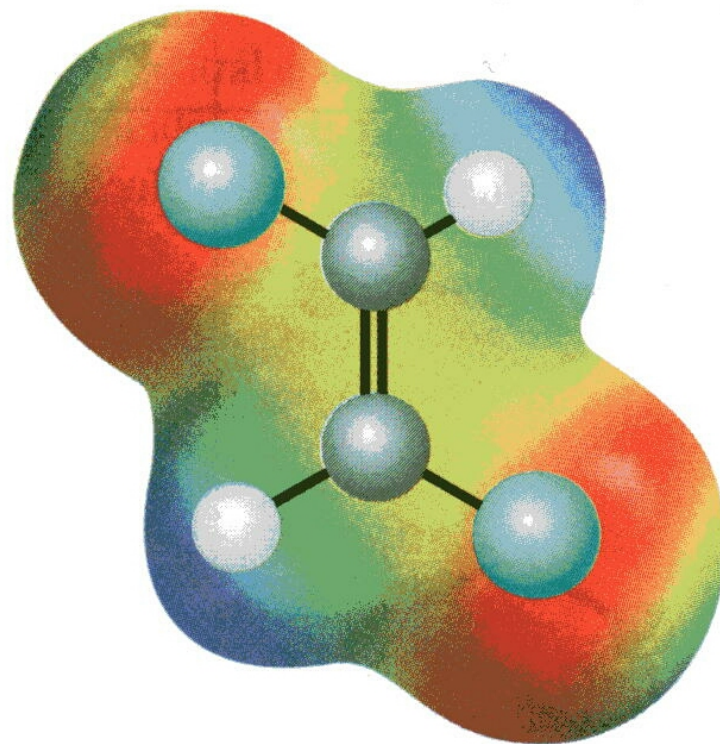
Momentos de dipolo de algumas moléculas

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

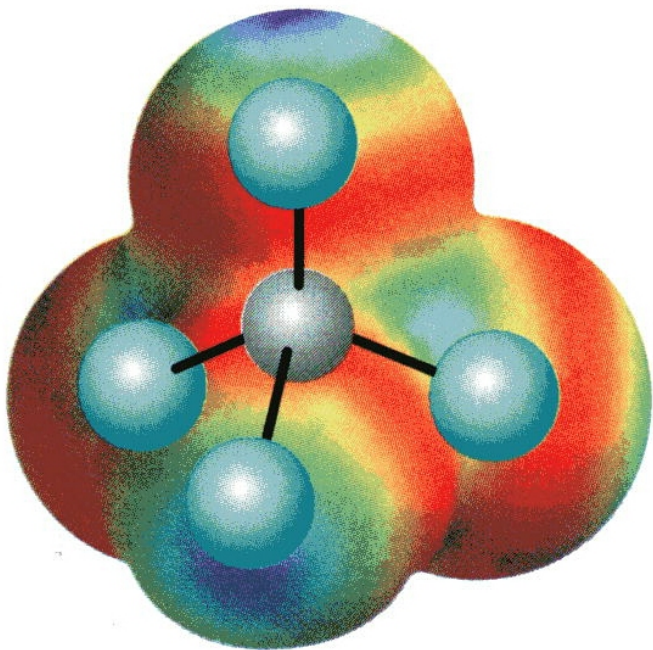
*Pares iônicos na fase gasosa.



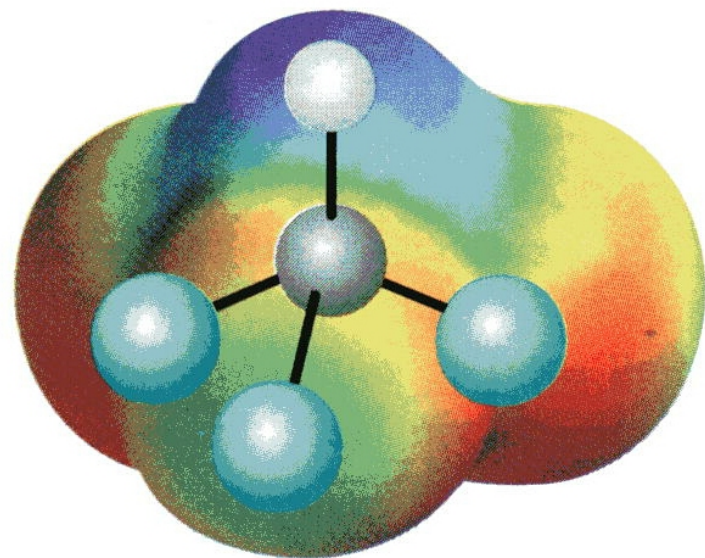
33 *cis*-Dicloroeteno, $C_2H_2Cl_2$



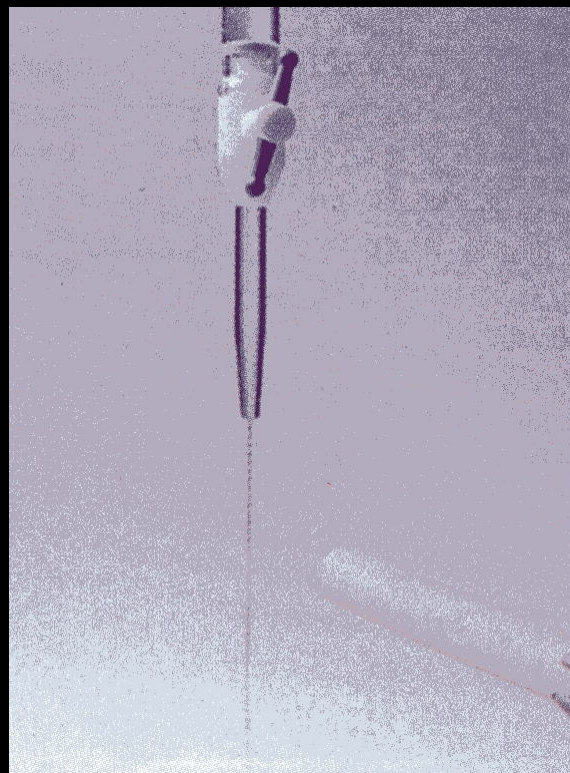
34 *trans*-Dicloroeteno, $C_2H_2Cl_2$

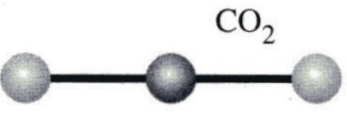
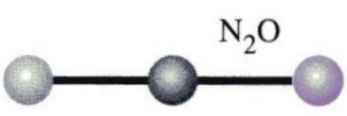
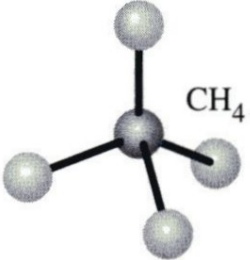
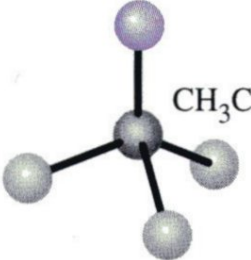
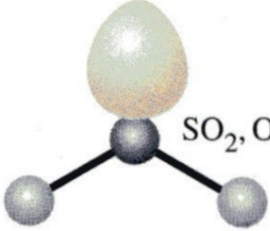
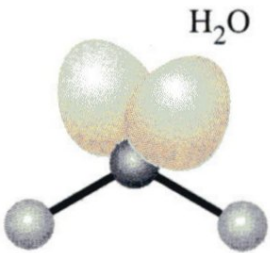
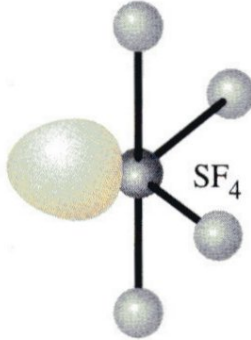
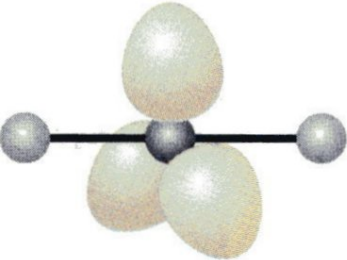
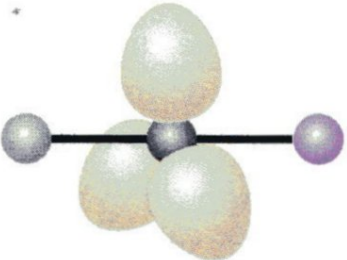
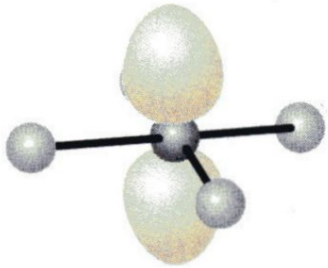
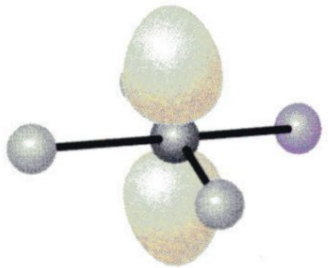


35 Tetraclorometano, CCl₄



36 Triclorometano, CHCl₃



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

Tipo
VSEPR

Não-polar

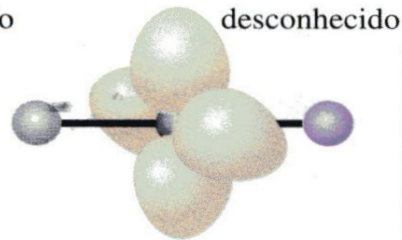
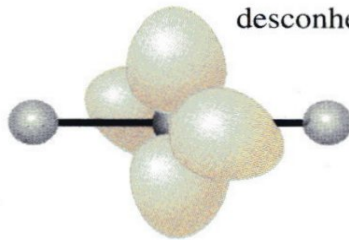
Polar

Tipo
VSEPR

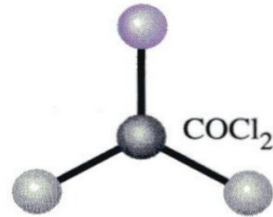
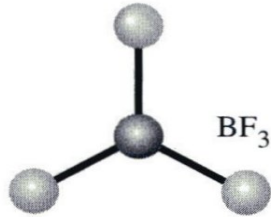
Não-polar

Polar

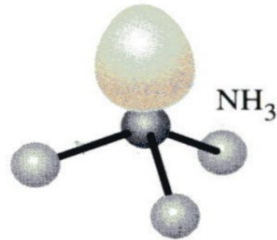
AX_2E_4



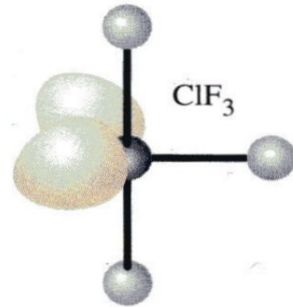
AX_3



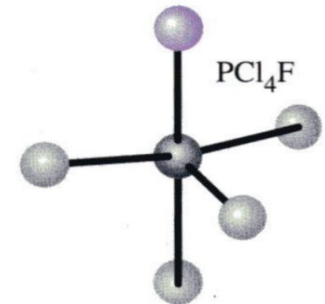
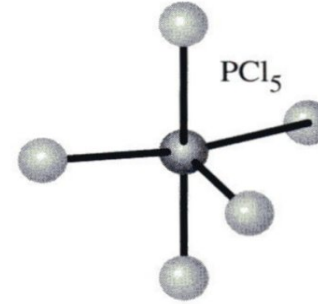
AX_3E



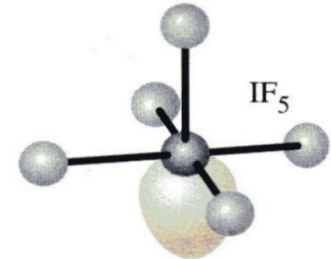
AX_3E_2



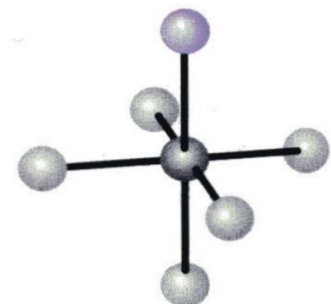
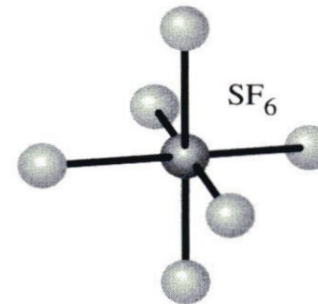
AX_5



AX_5E



AX_6

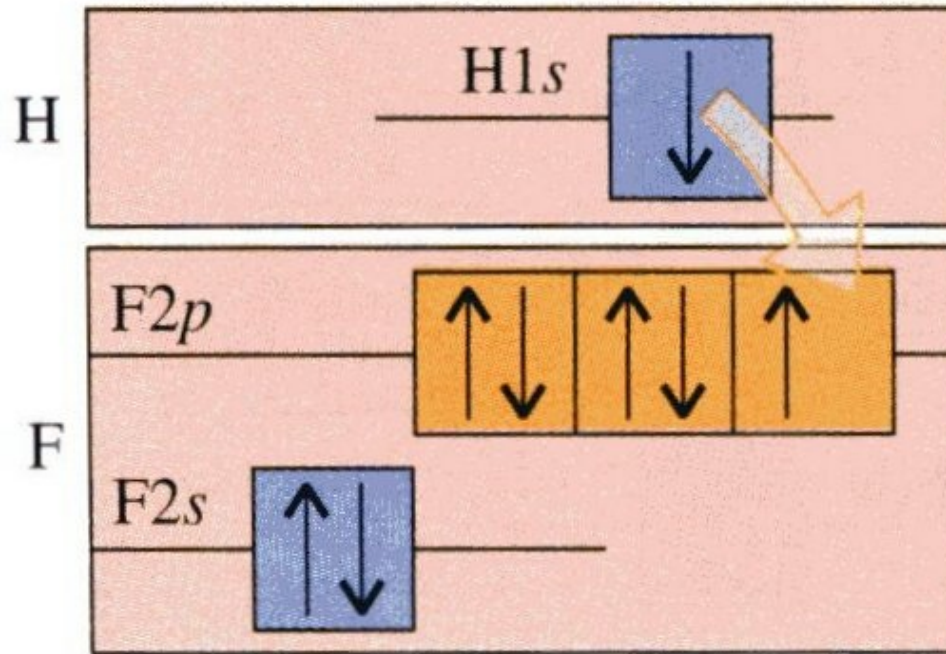


Teoria da ligação de valência

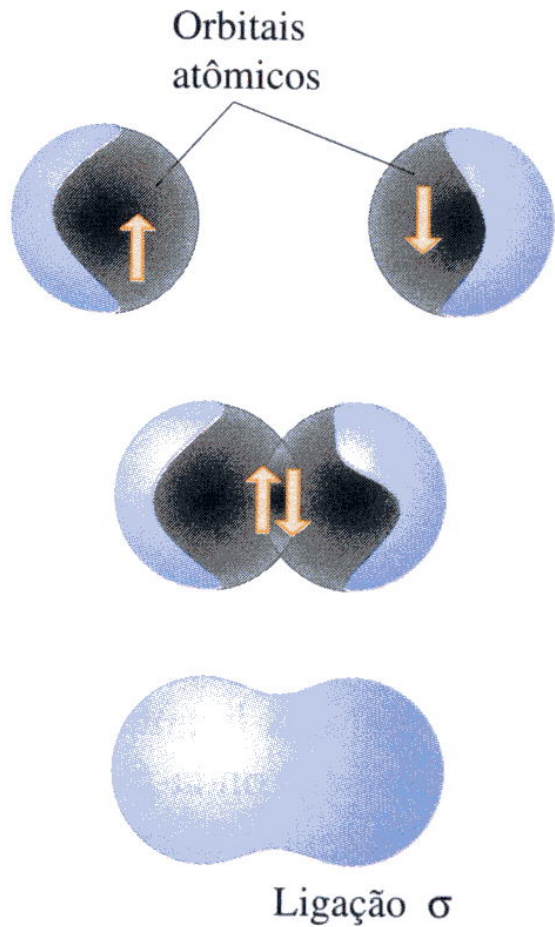
Modelo mecânico-quântico da distribuição dos elétrons nas ligações que vai além da teoria de Lewis e do modelo VSPR, pode se calcular numericamente os ângulos e distancias das ligações químicas

As ligações sigma e pi

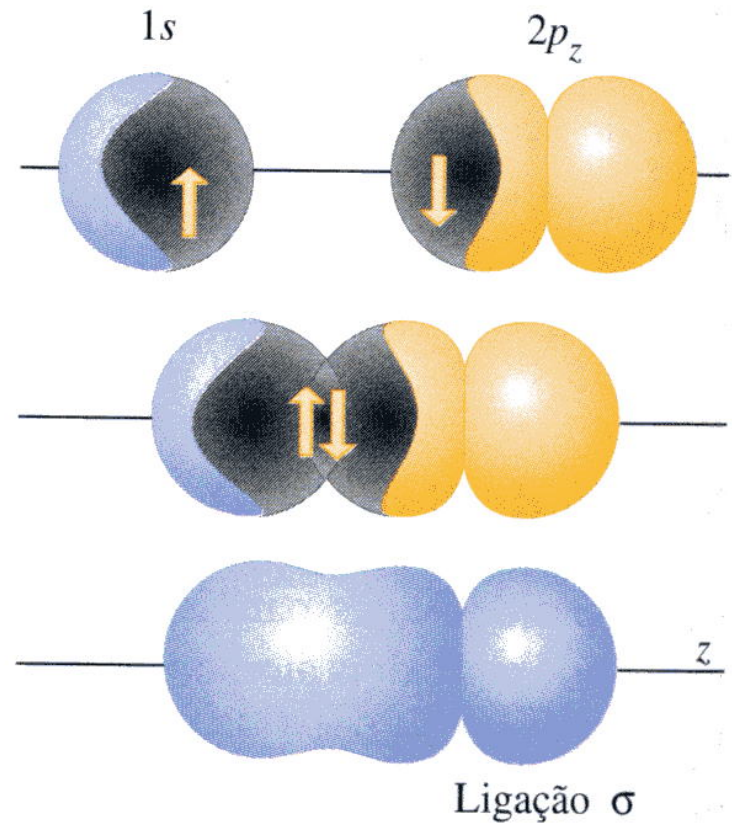
A fusão de dois orbitais atômicos é chamada sobreposição de orbitais. No caso do H_2 , temos a fusão de dois orbitais $1s$, formando uma ligação σ



Fluoreto de hidrogênio, HF

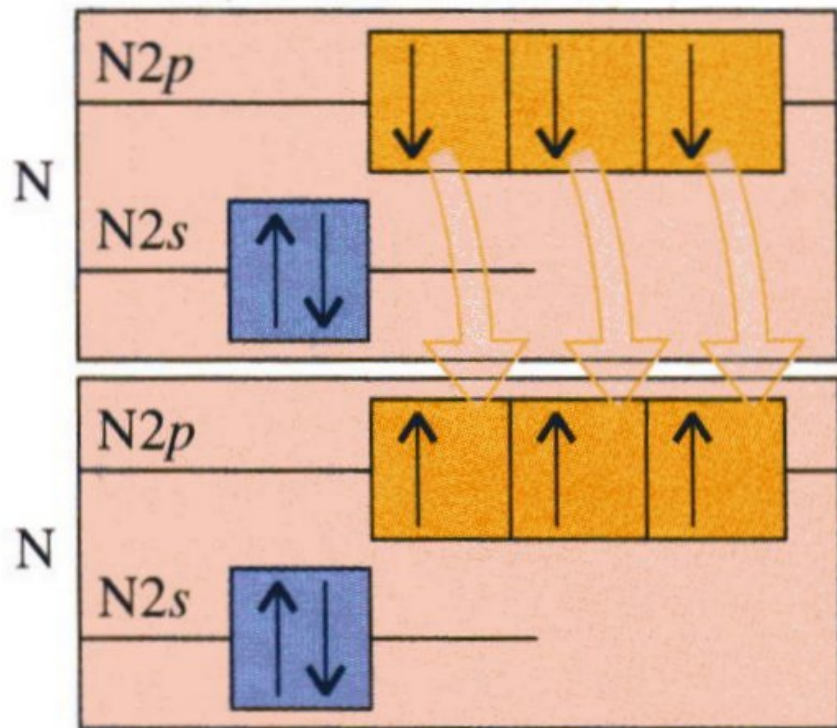


Hidrogênio, H_2

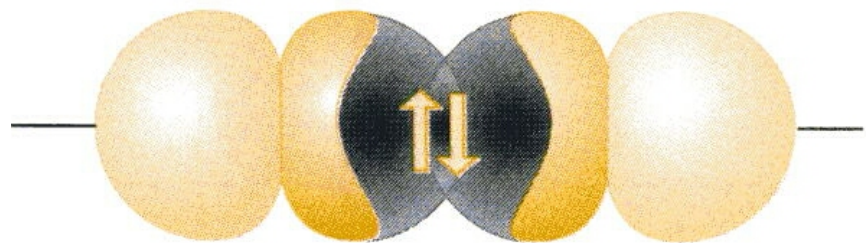
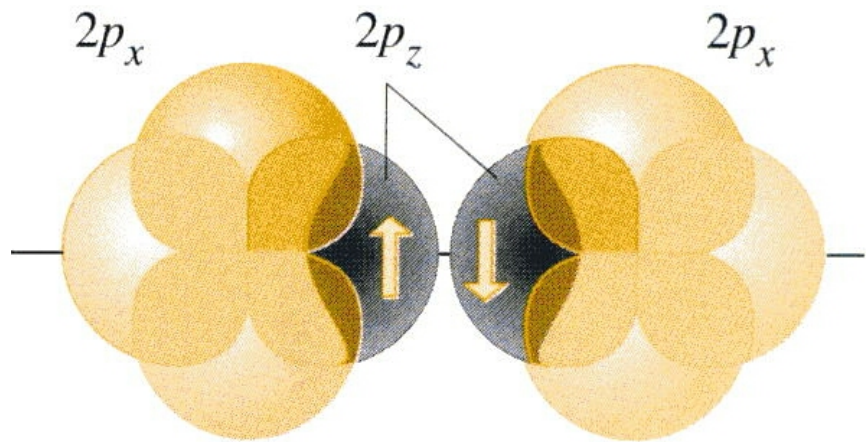


Fluoreto de hidrogênio, HF

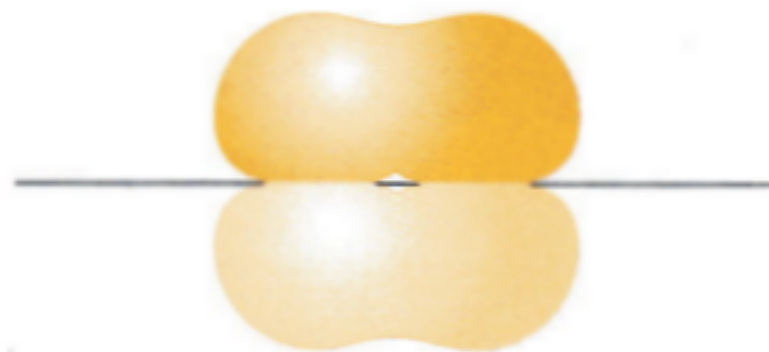
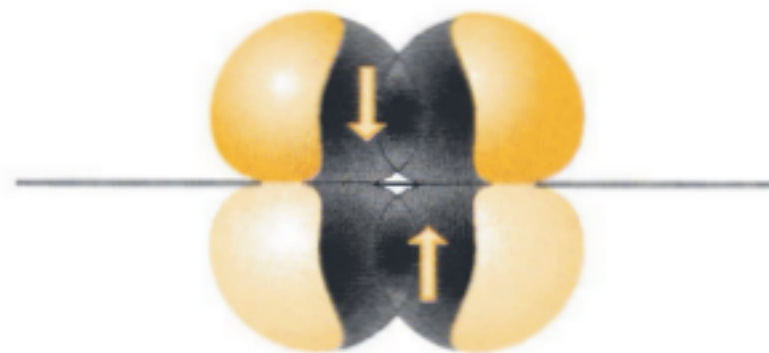
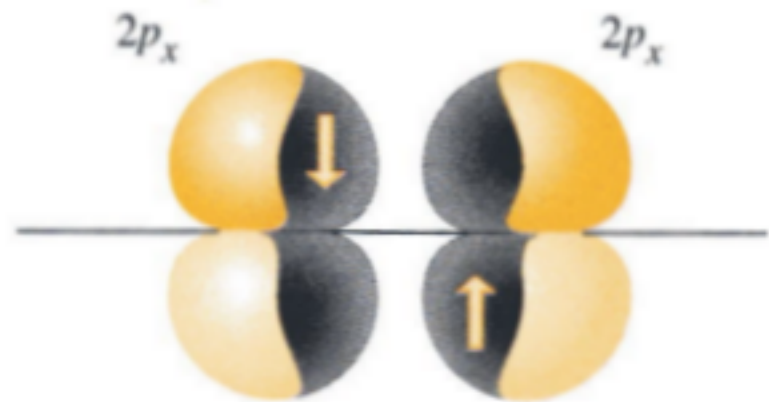
Diferente tipo de ligação: N₂. Superposição de orbitais atômicos p: formação de uma ligação π



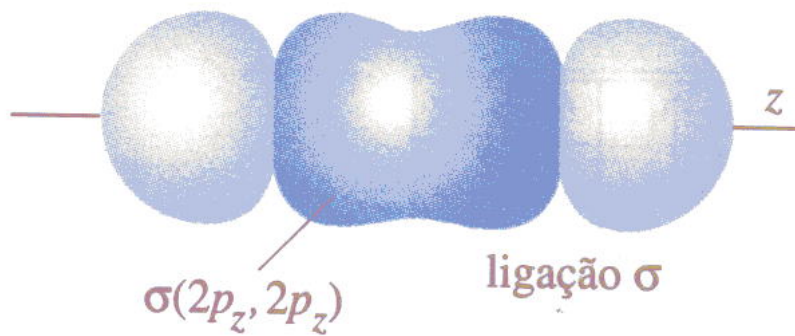
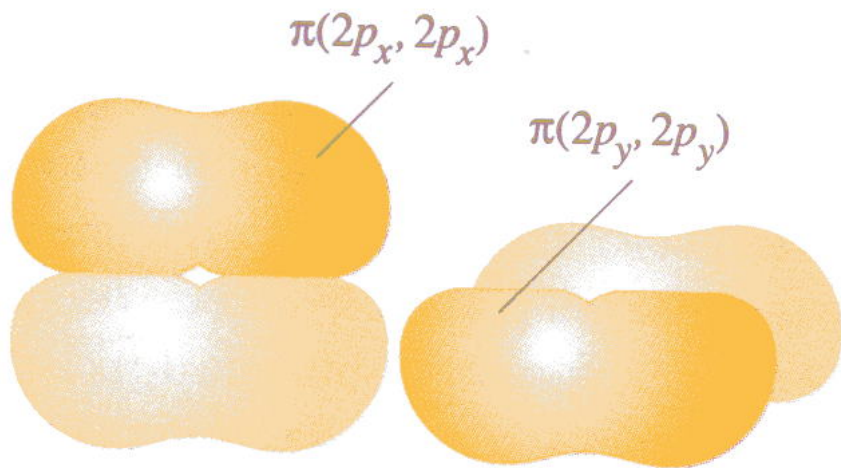
Nitrogênio, N₂



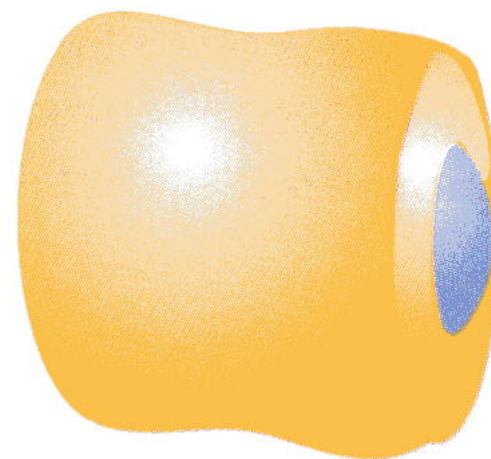
Ligação σ



Ligação π



(a)



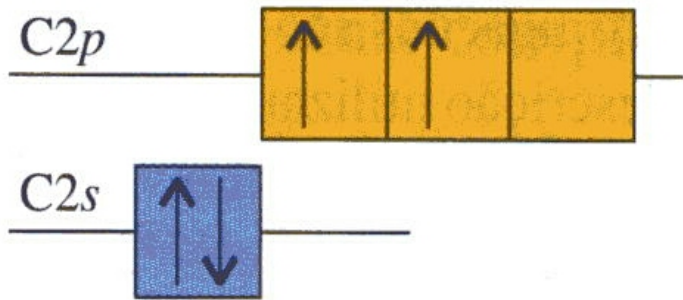
(b)

Ligação simples: é uma ligação σ

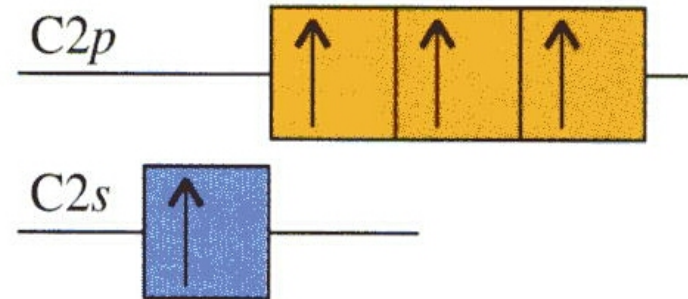
Ligação dupla: é uma ligação σ e uma ligação π

Ligação tripla: é uma ligação σ e duas ligações π

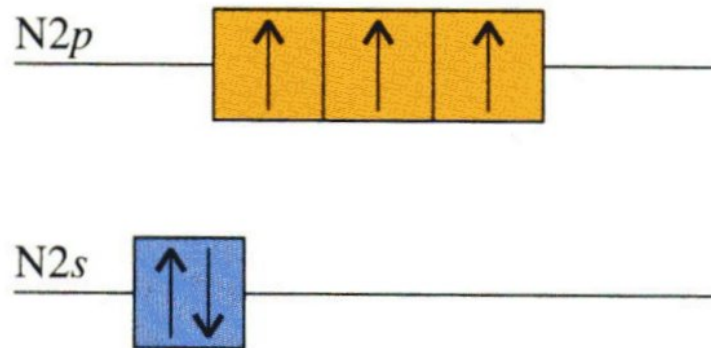
A hibridização dos orbitais



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

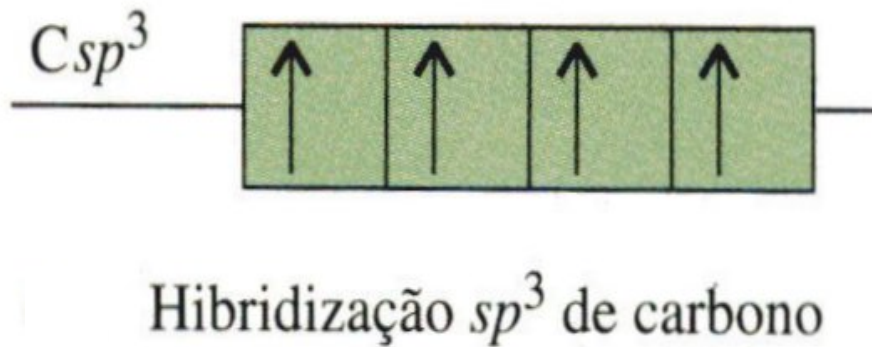
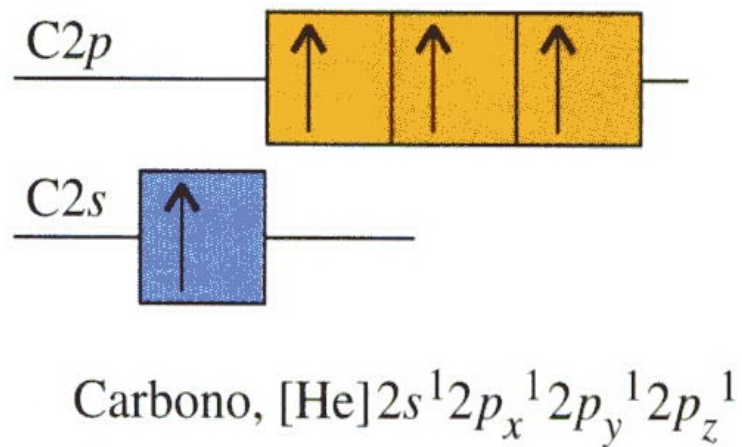


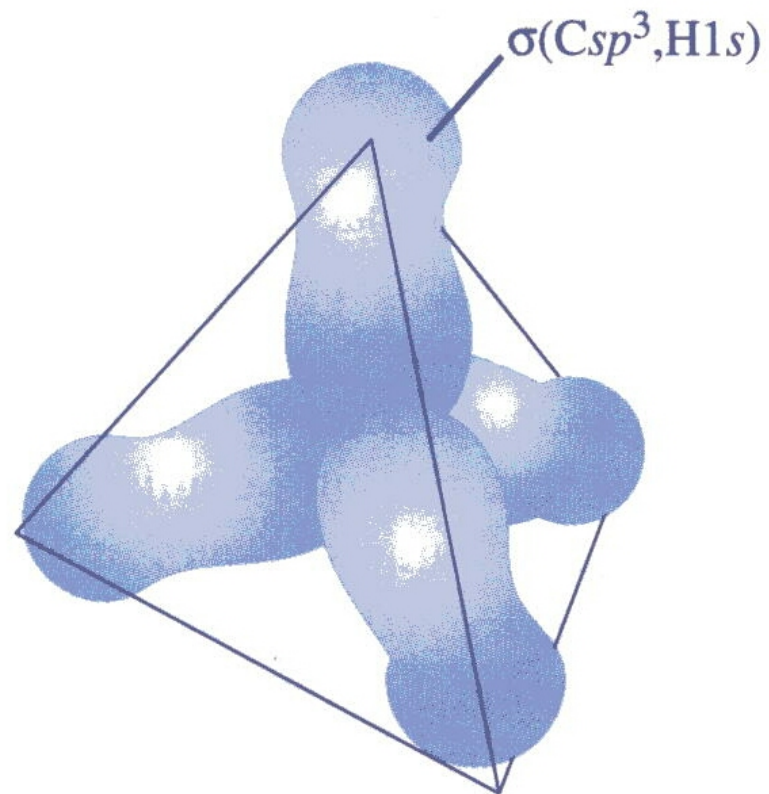
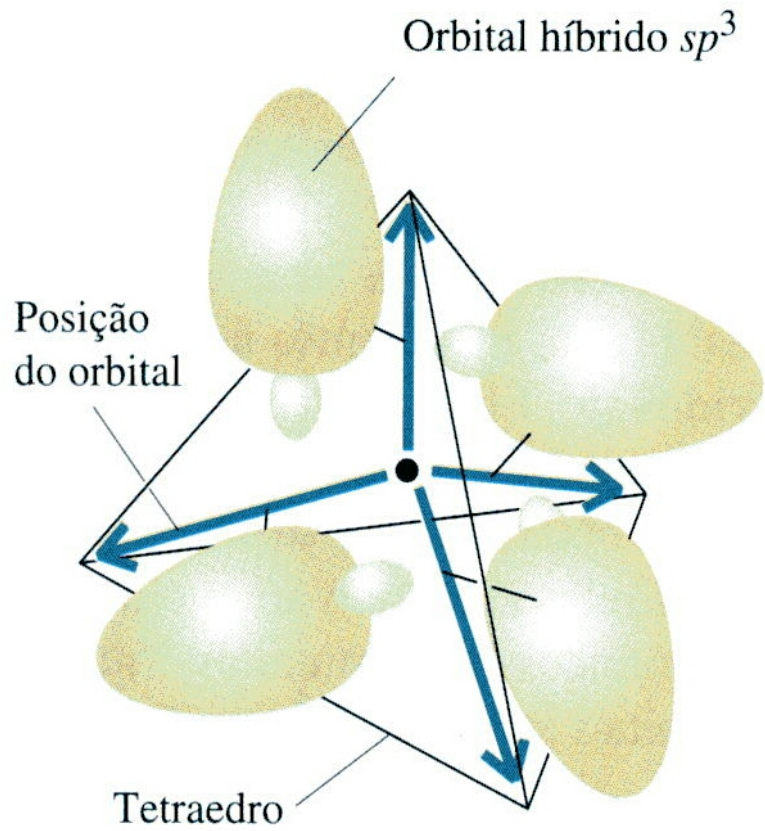
Carbono, $[\text{He}]2s^1 2p_x^1 2p_y^1 2p_z^1$



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

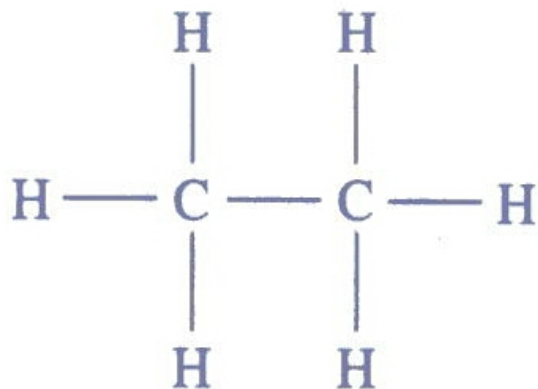
O arranjo dois orbitais s e p produz os orbitais híbridos sp^3 porque são formados pelo orbital s e os três orbitais p. A sobreposição destes orbitais forma ligações σ .



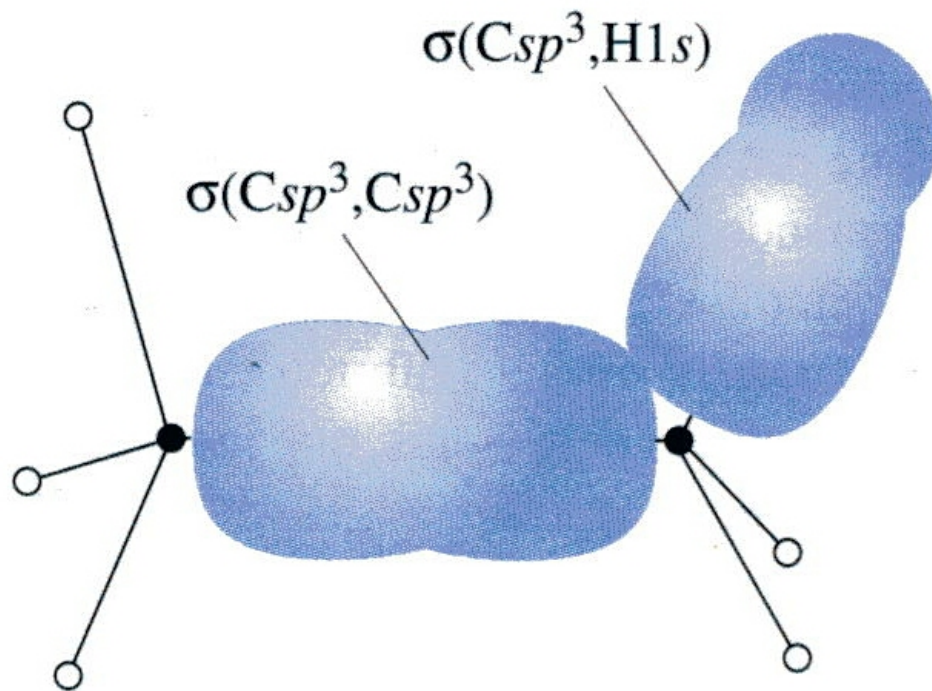


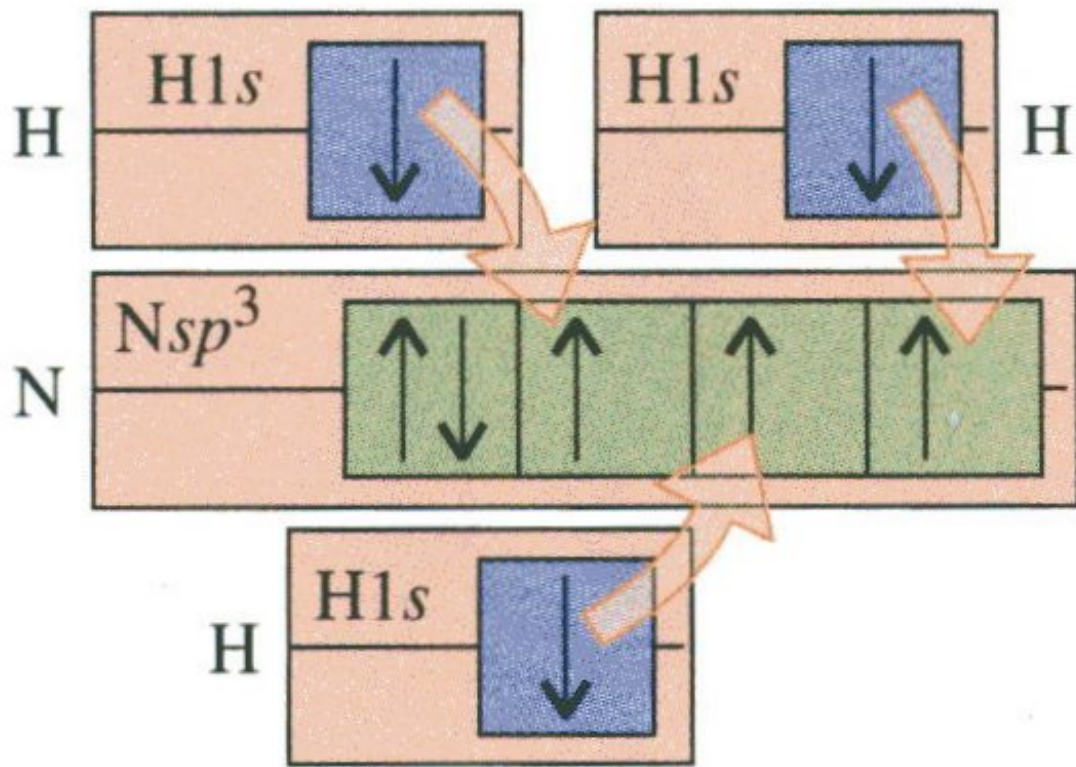
A hibridização é um modelo que permite descrever as ligações que são necessárias para uma dada estrutura molecular.

A hibridização em moléculas mais complexas

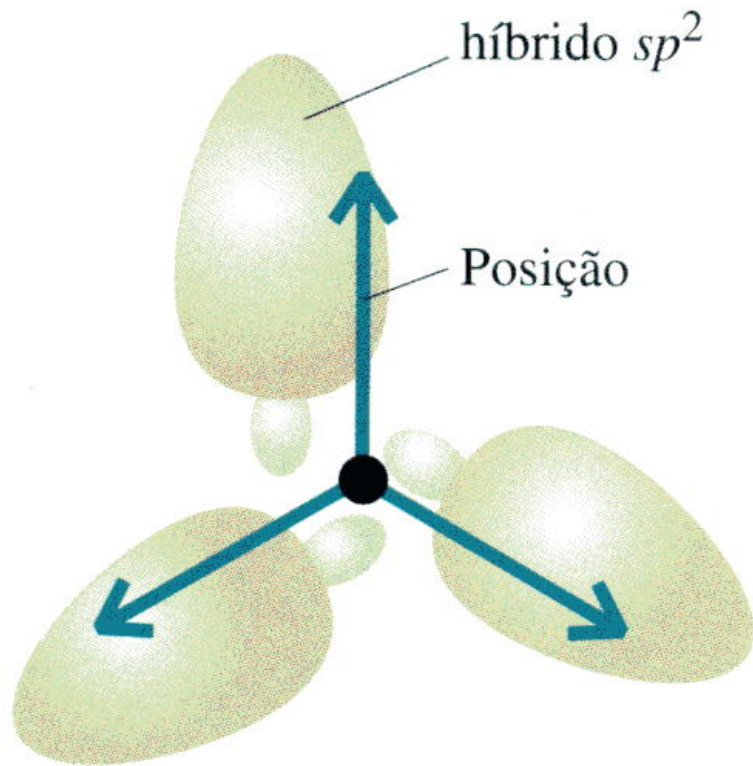


Etano, CH_3CH_3

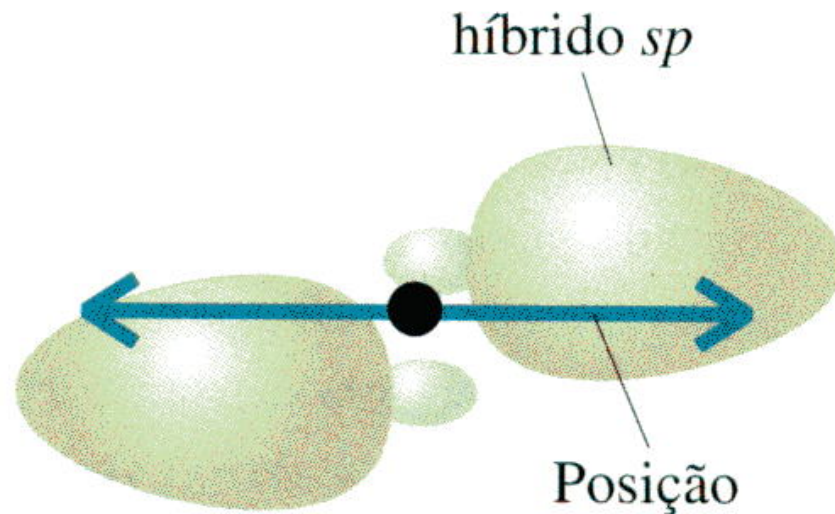




Amônia, NH₃



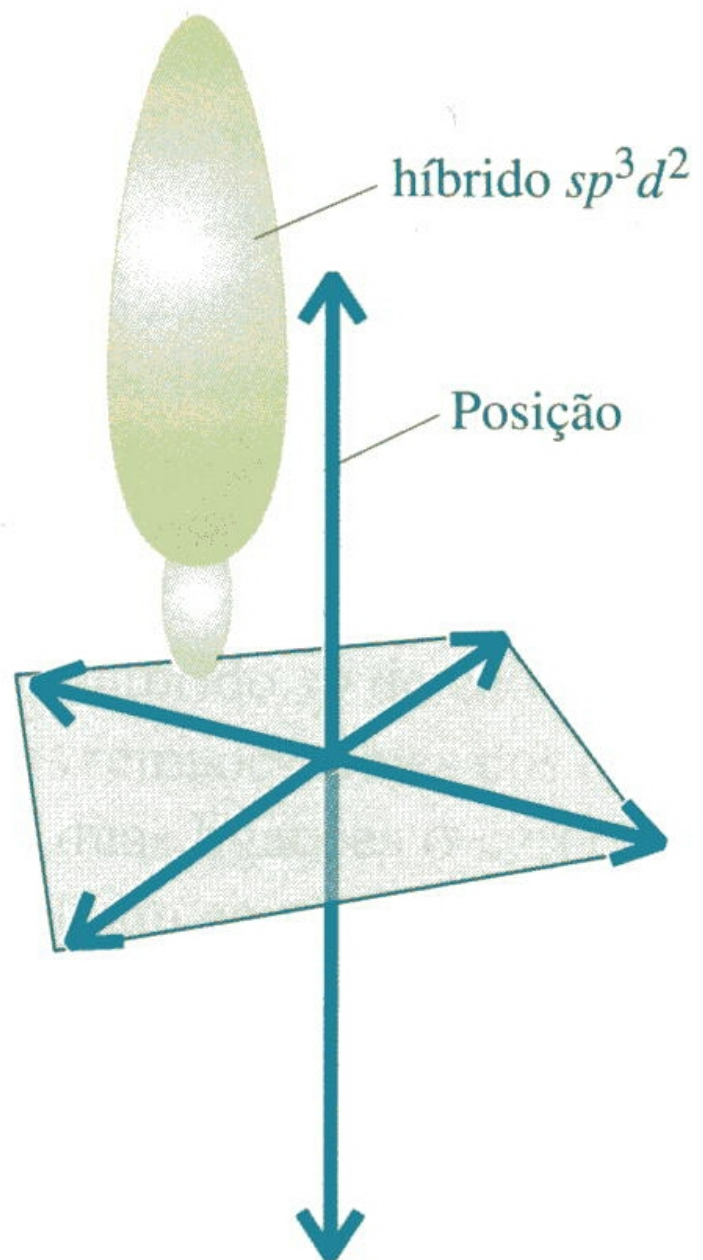
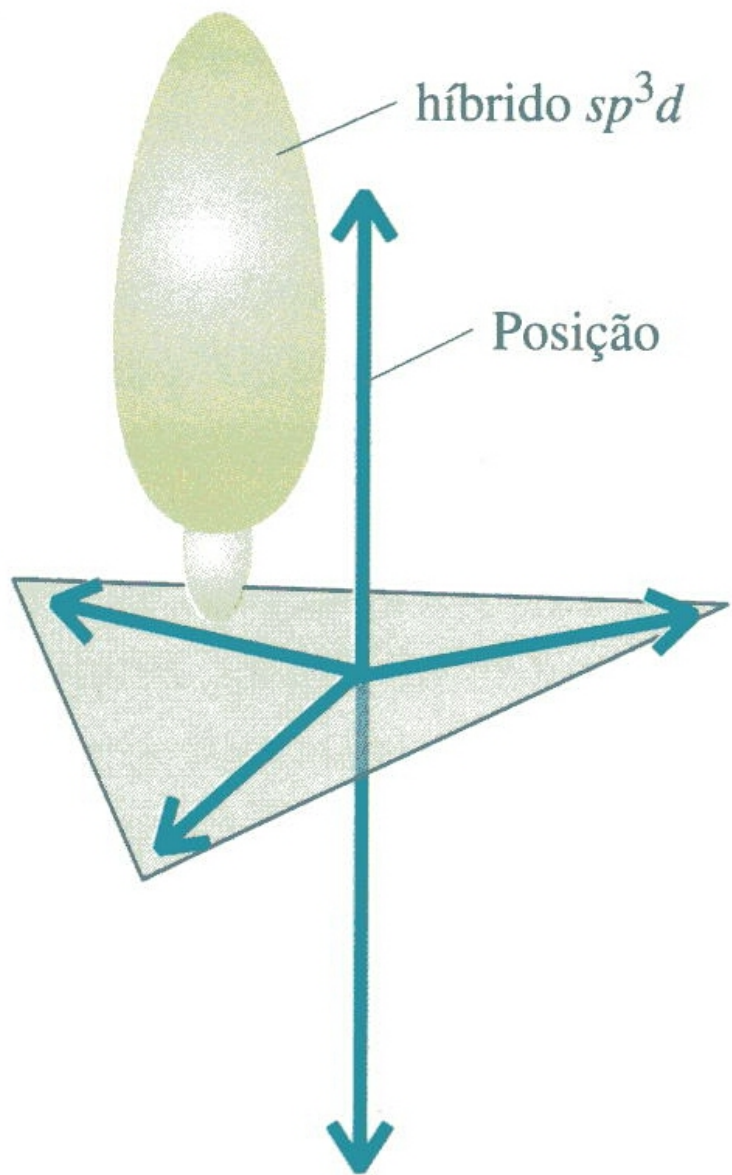
Um orbital s + dois orbitais $p = sp^2$



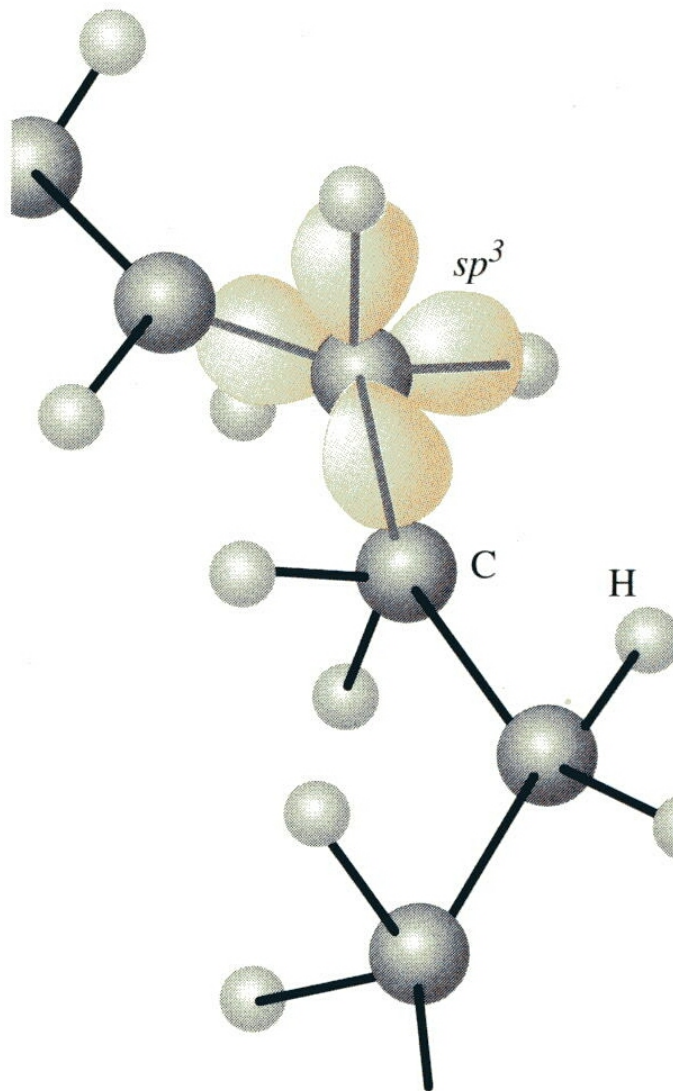
Um orbital s + um orbital $p = sp$

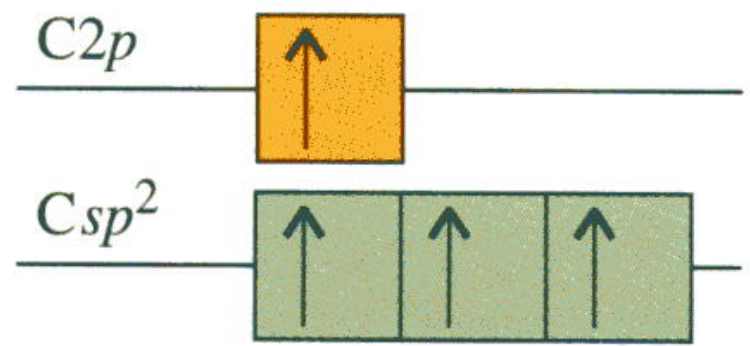
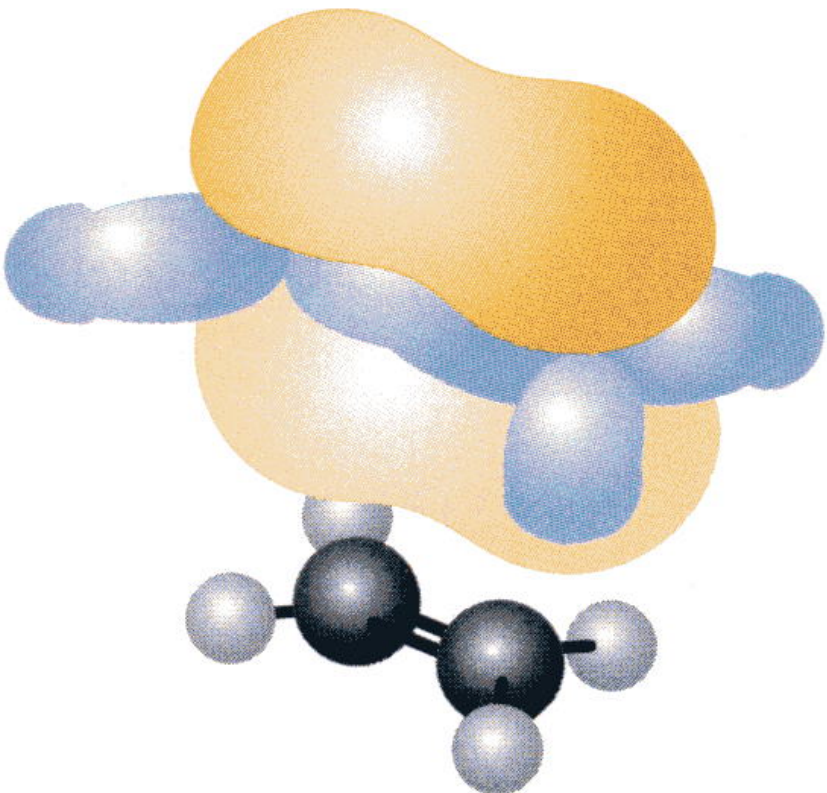
TABELA 3.2 Esquemas comuns de hibridização

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

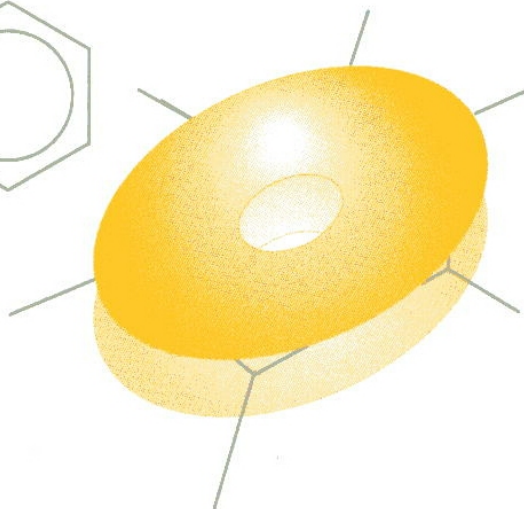
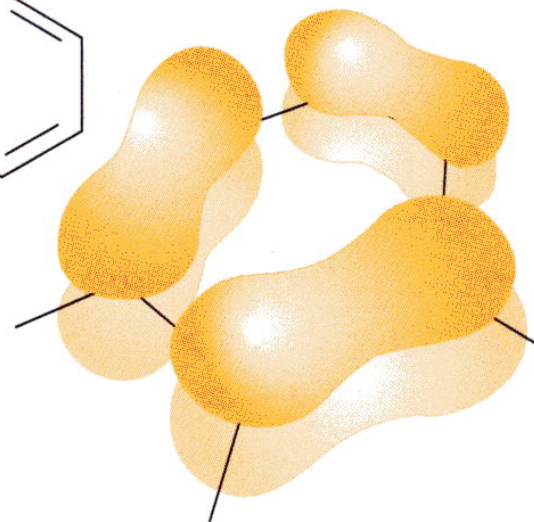
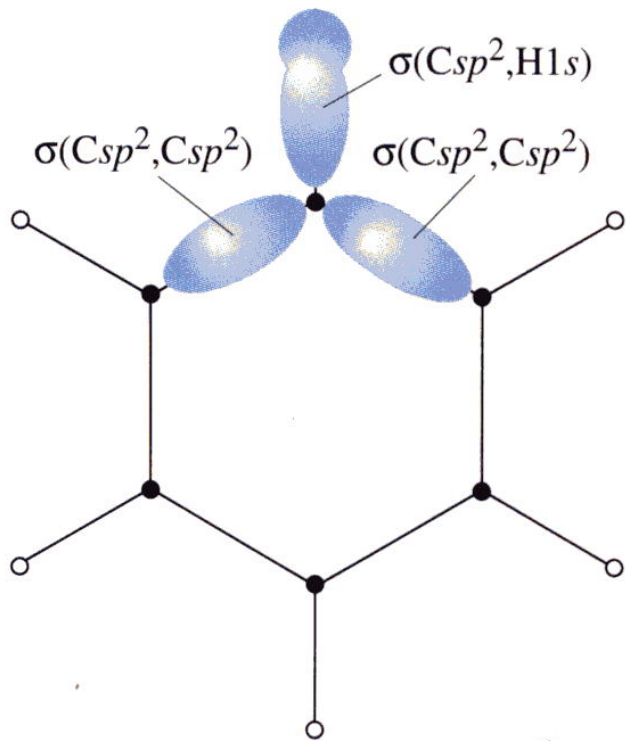


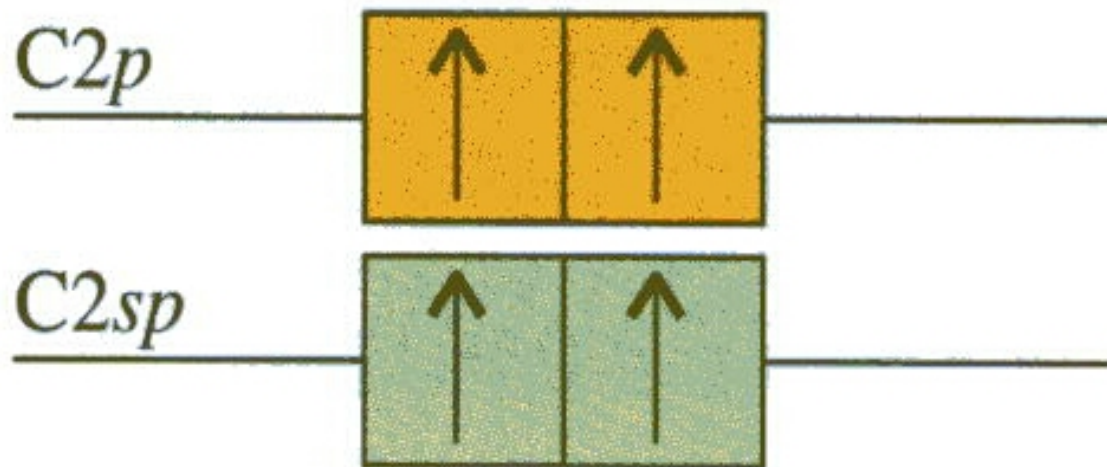
Ligações em hidrocarbonetos



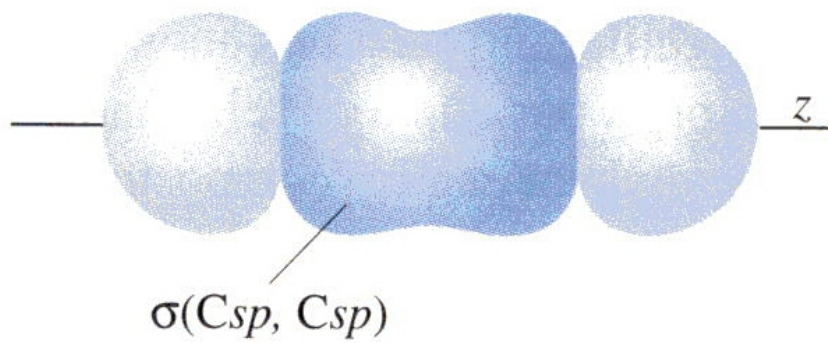
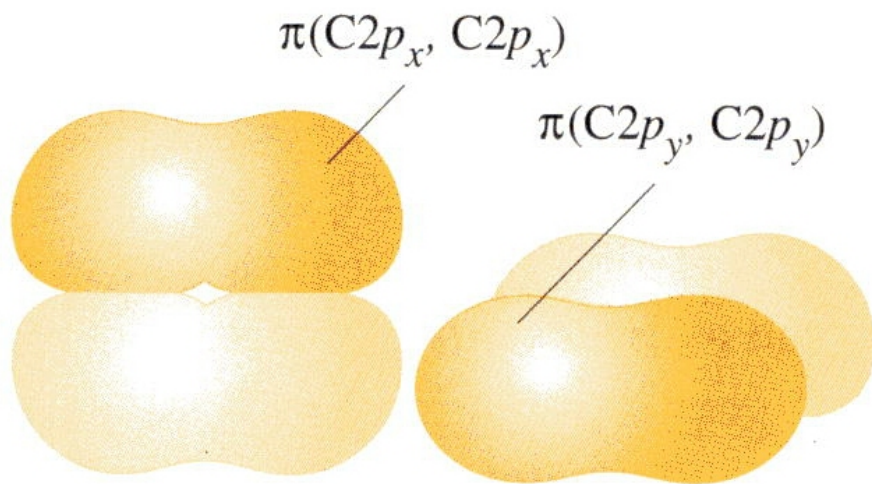


Carbono com hibridização sp^2

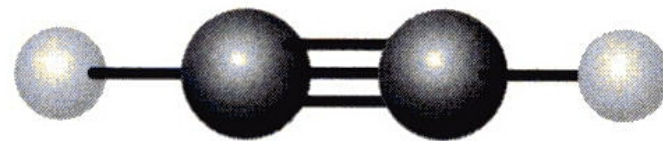
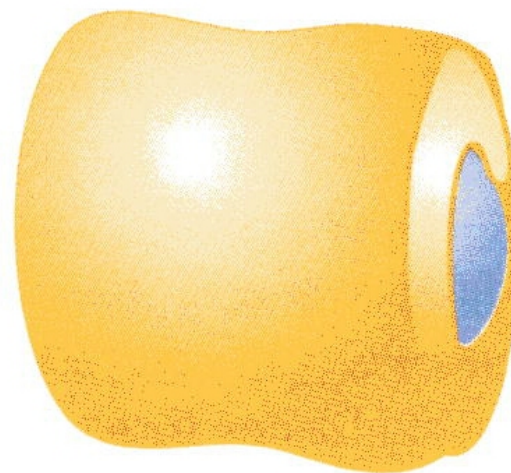




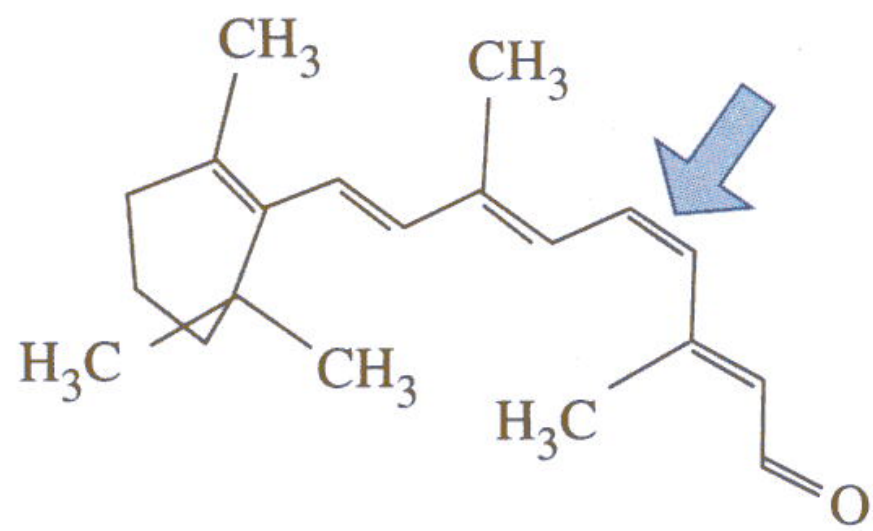
Carbono com hibridização sp



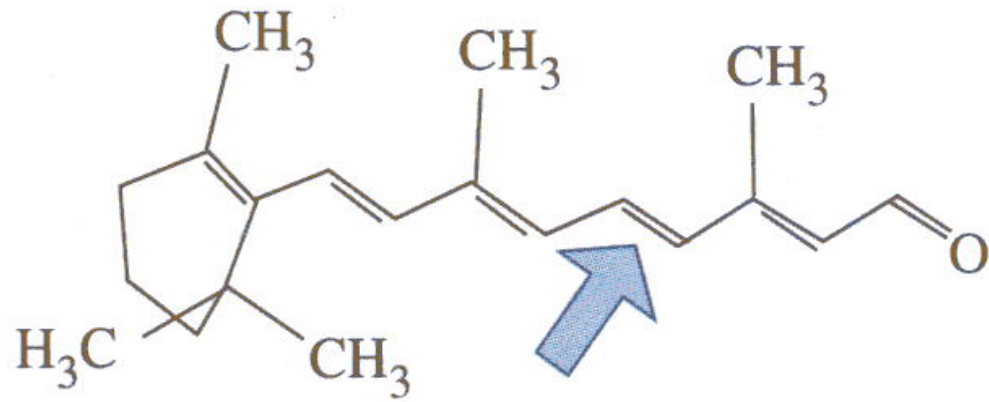
(a)



(b)



cis-Retinal

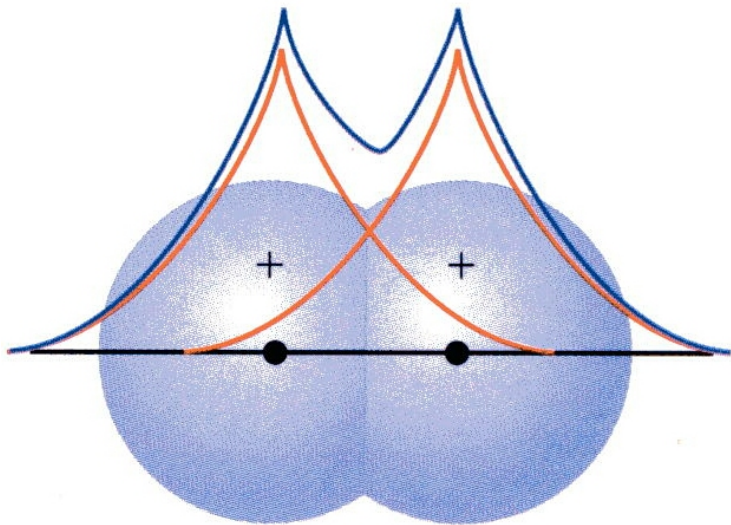


trans-Retinal

Teoria do orbital molecular



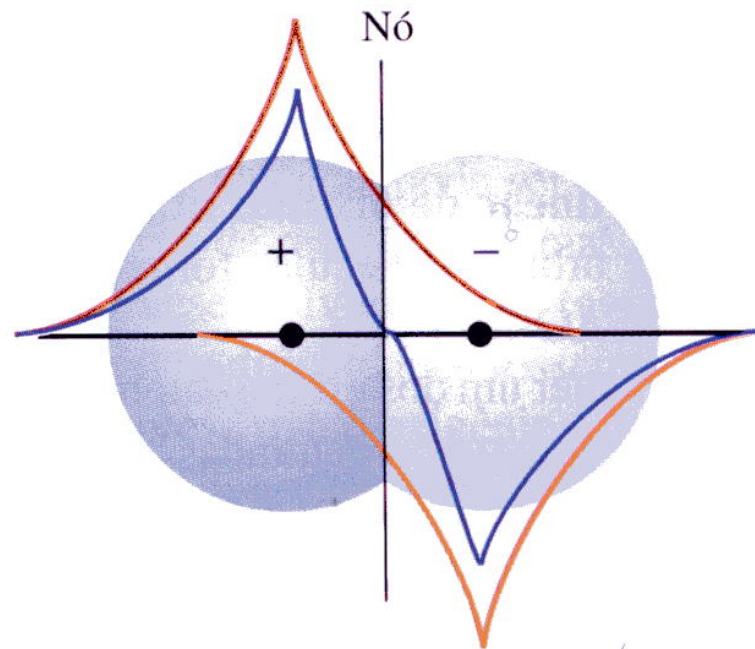
O_2 líquido



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

Interferência construtiva

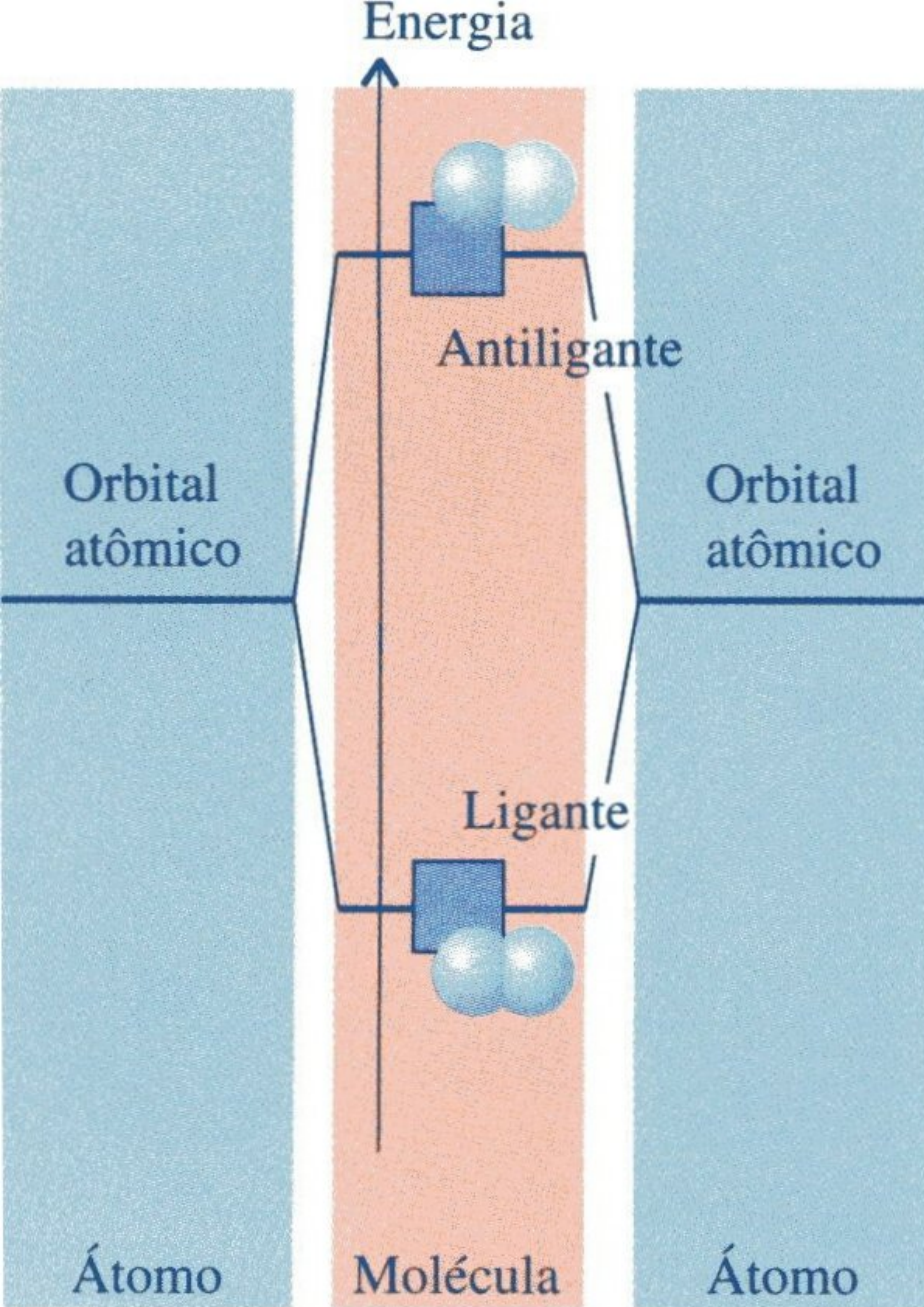
Orbital ligante



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

Interferência destrutiva

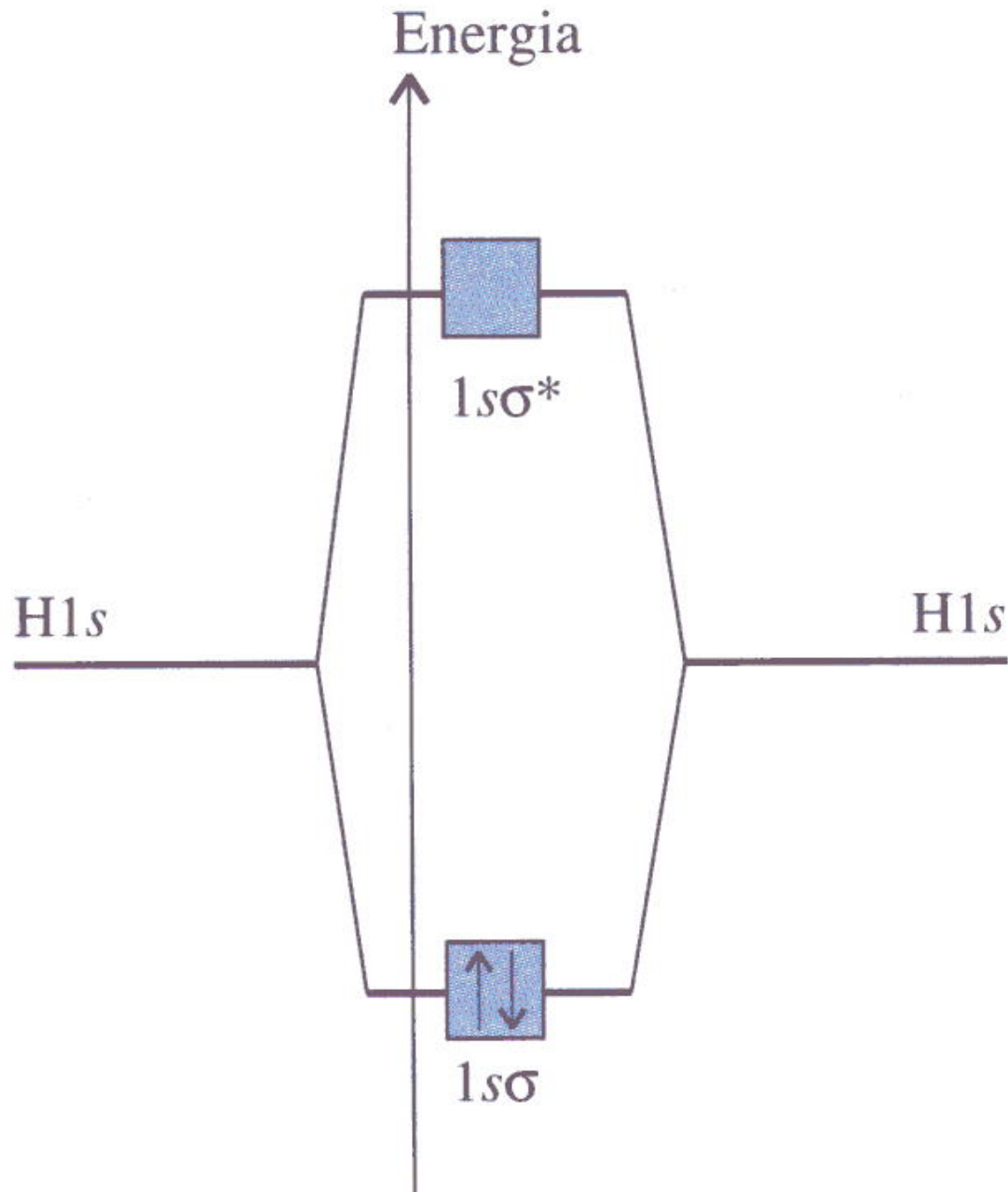
Orbital antiligante



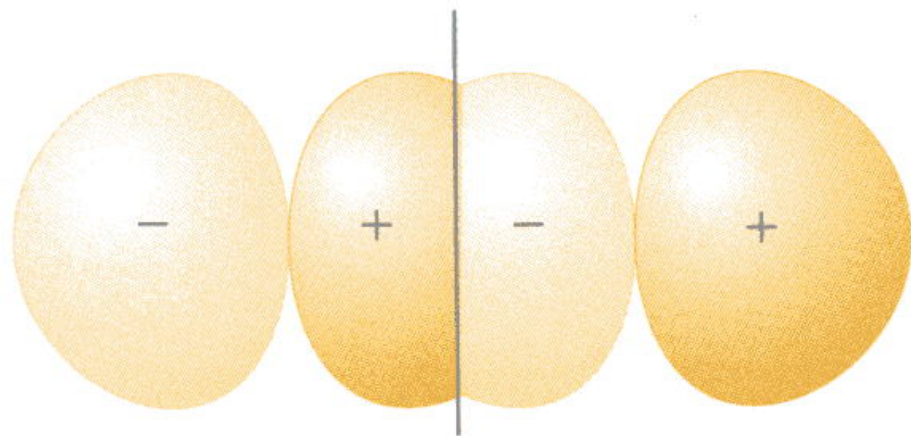
Passo 1: Acomodar os elétrons no orbital de menor energia.

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

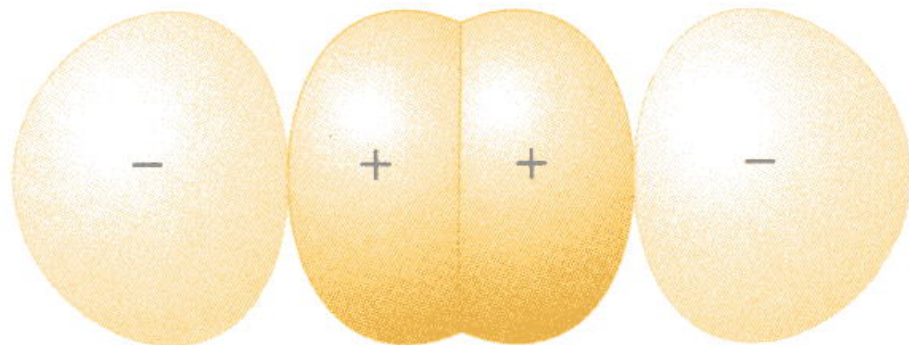
Passo 3: Se mais de um orbital da mesma energia estiver disponível, são ocupados um a um (Regra de Hund).



H_2



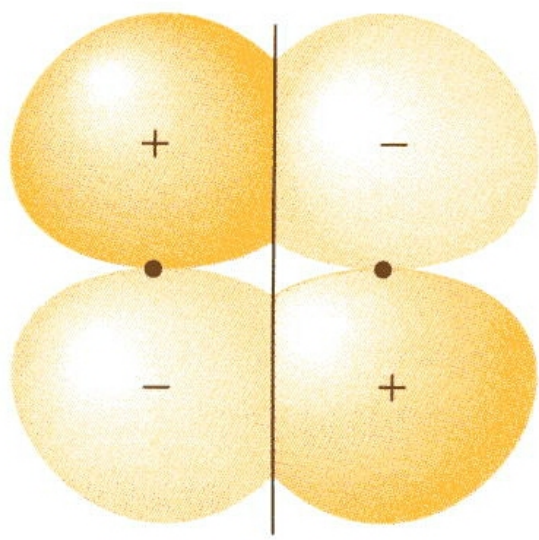
$2p\sigma^*$



$2p\sigma$

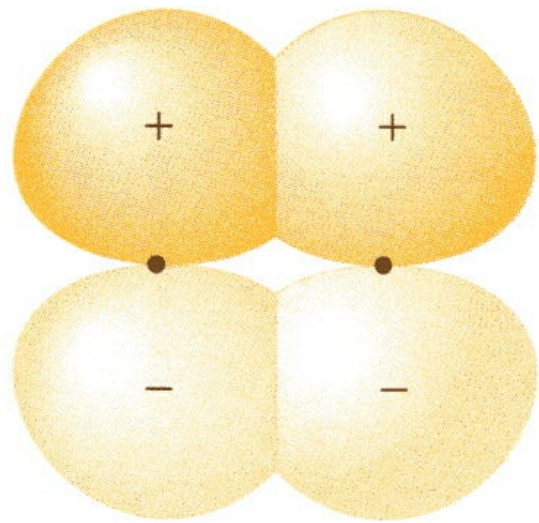
Orbitais moleculares formados pelos átomos do grupo 2, ou seja, elétrons de valência no 2s 2p

Orbitais p direcionados ao longo do eixo nuclear formam orbitais moleculares σ

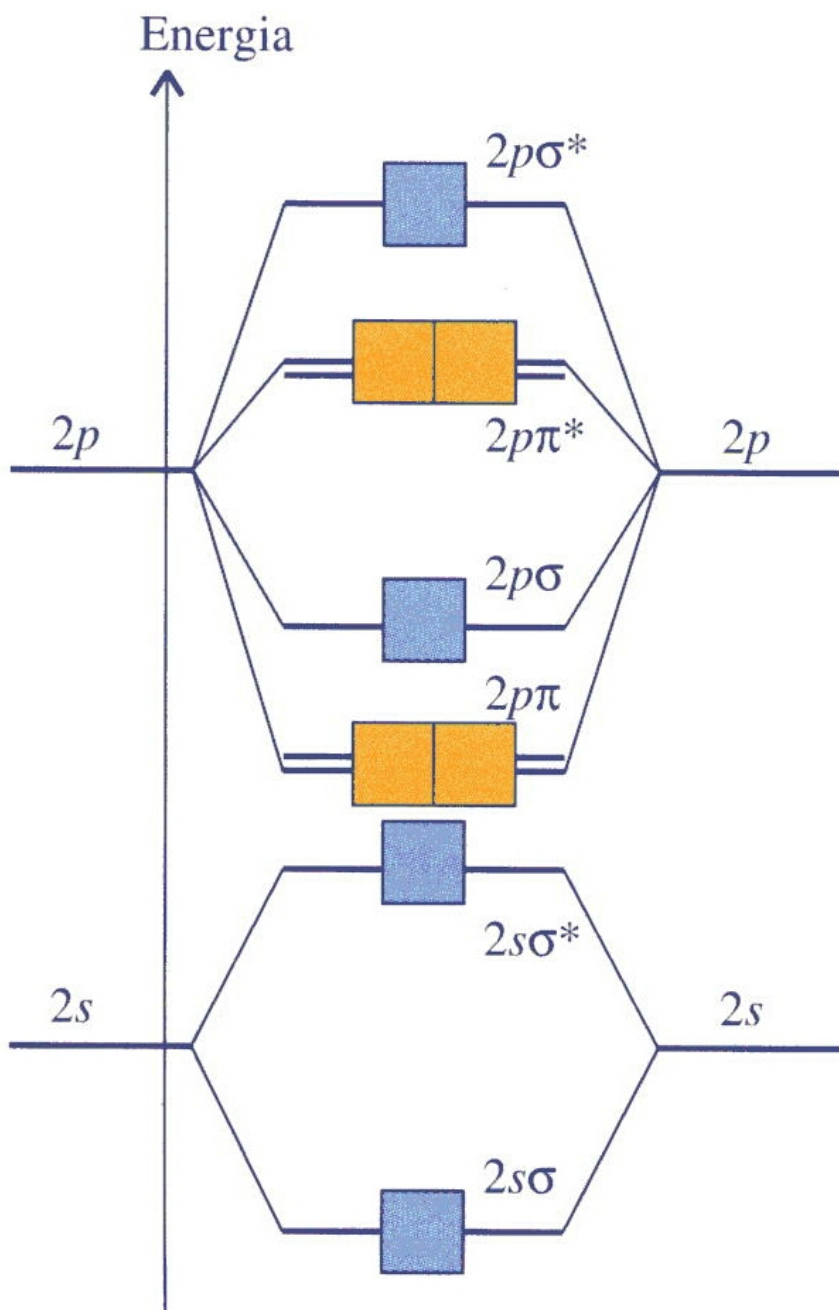


$2p\pi^*$

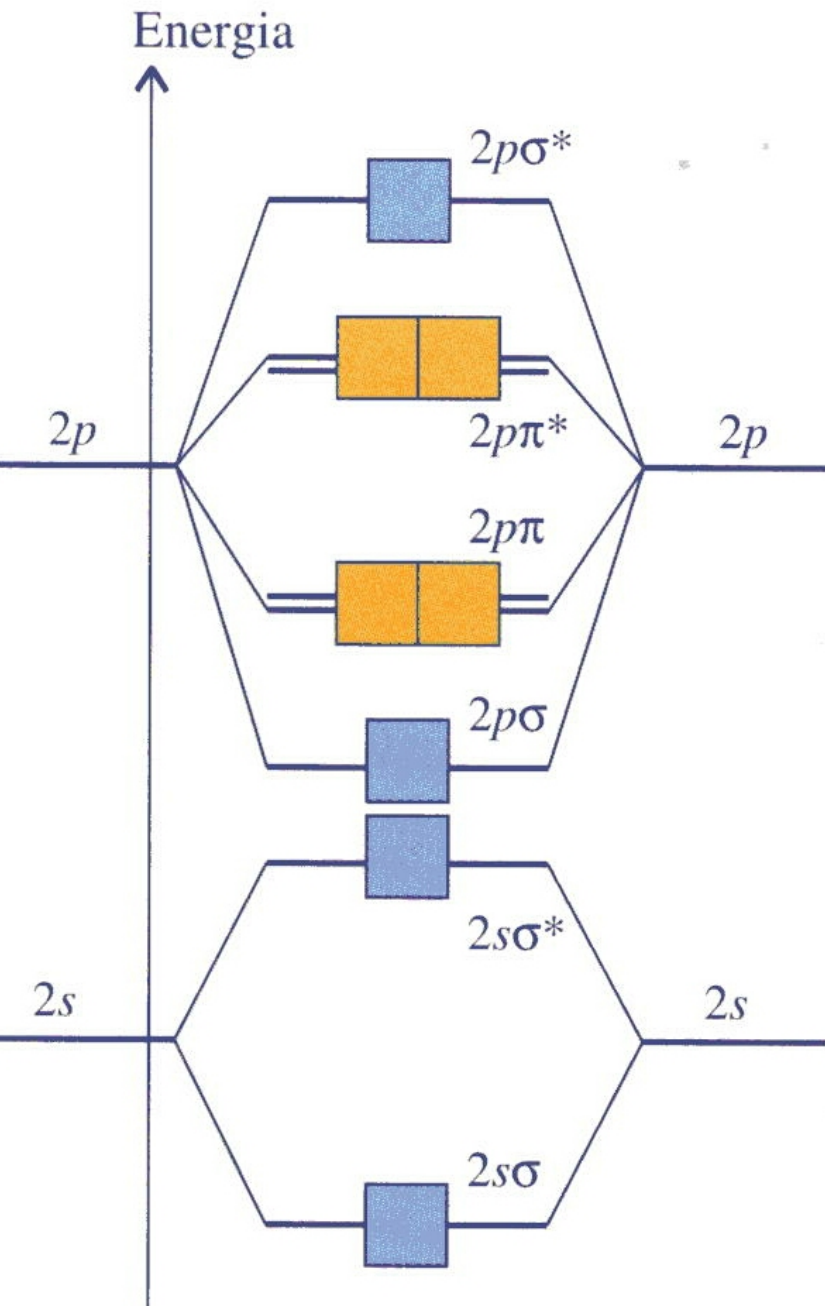
Orbitais p direcionados em forma perpendicular ao eixo nuclear formam orbitais moleculares π



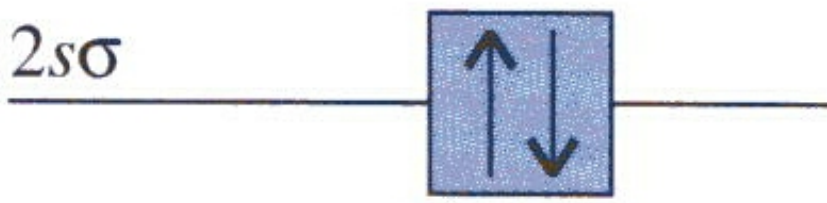
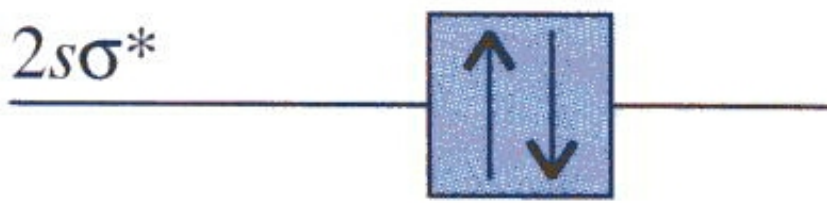
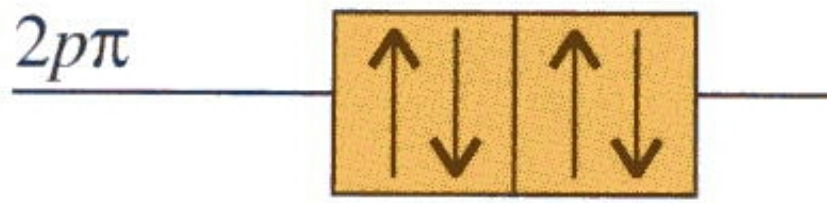
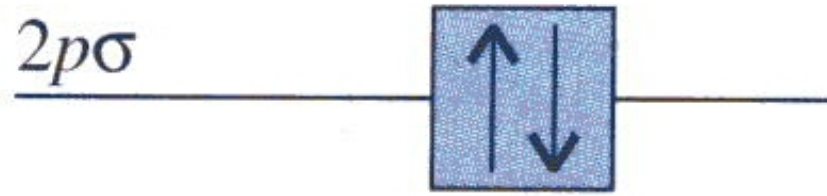
$2p\pi$



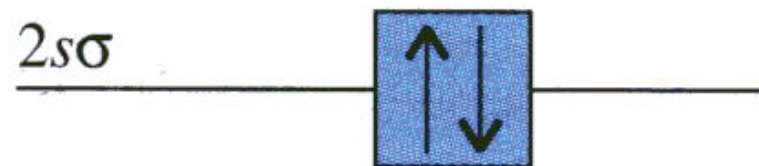
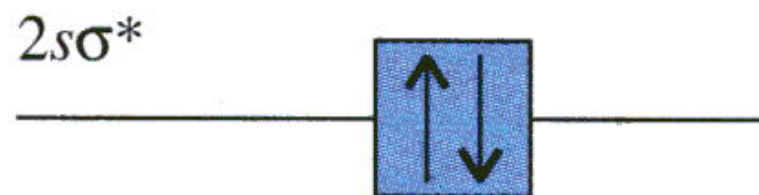
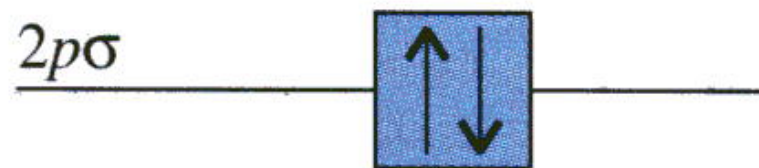
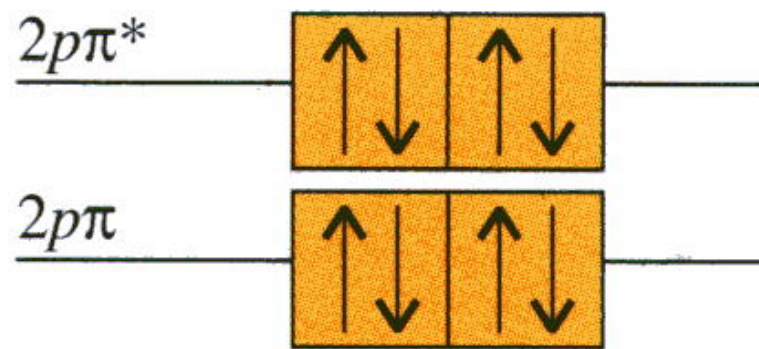
Li_2 até o N_2



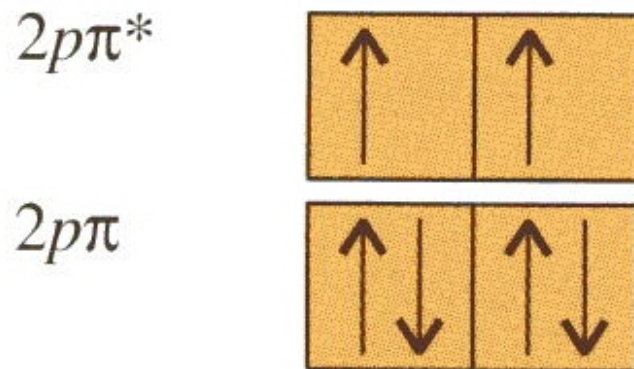
O_2 e F_2



N_2

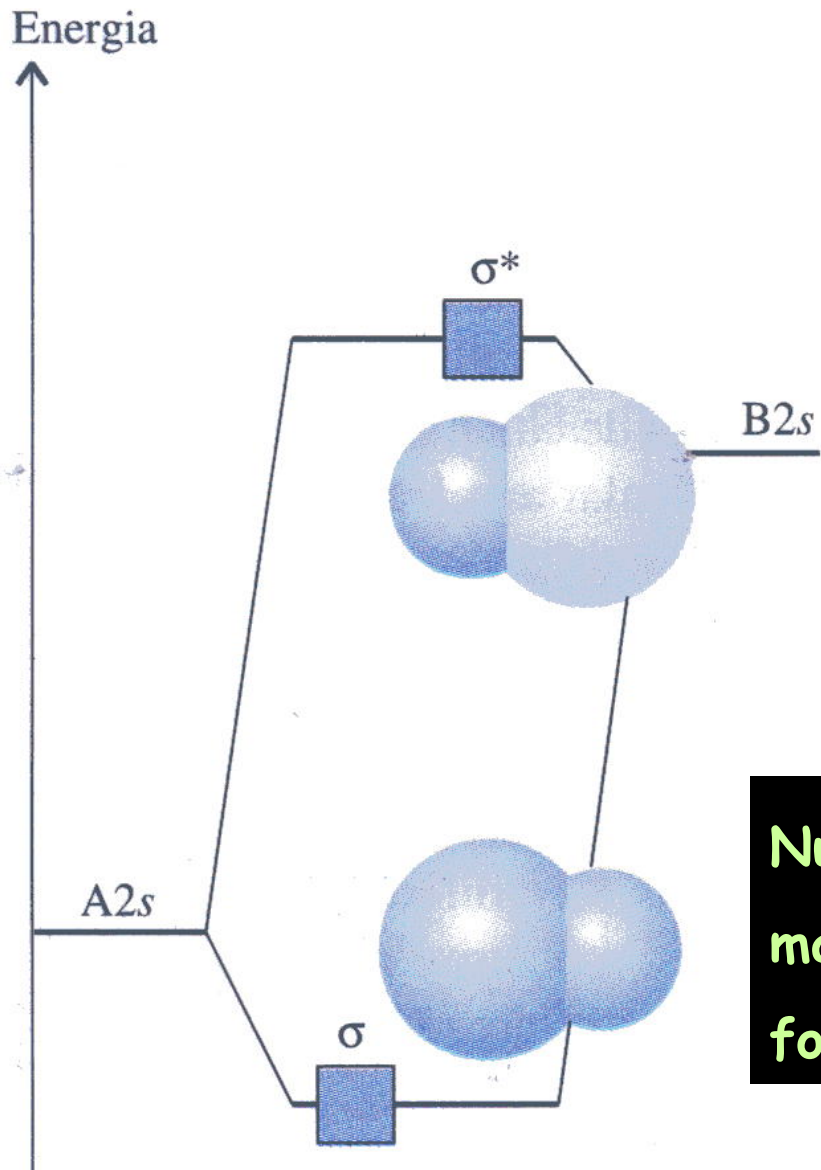


Flúor, F_2



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.

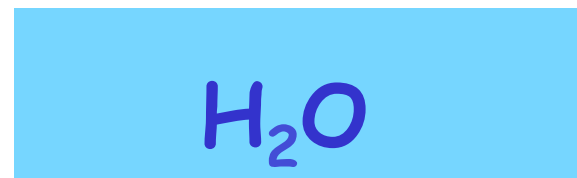
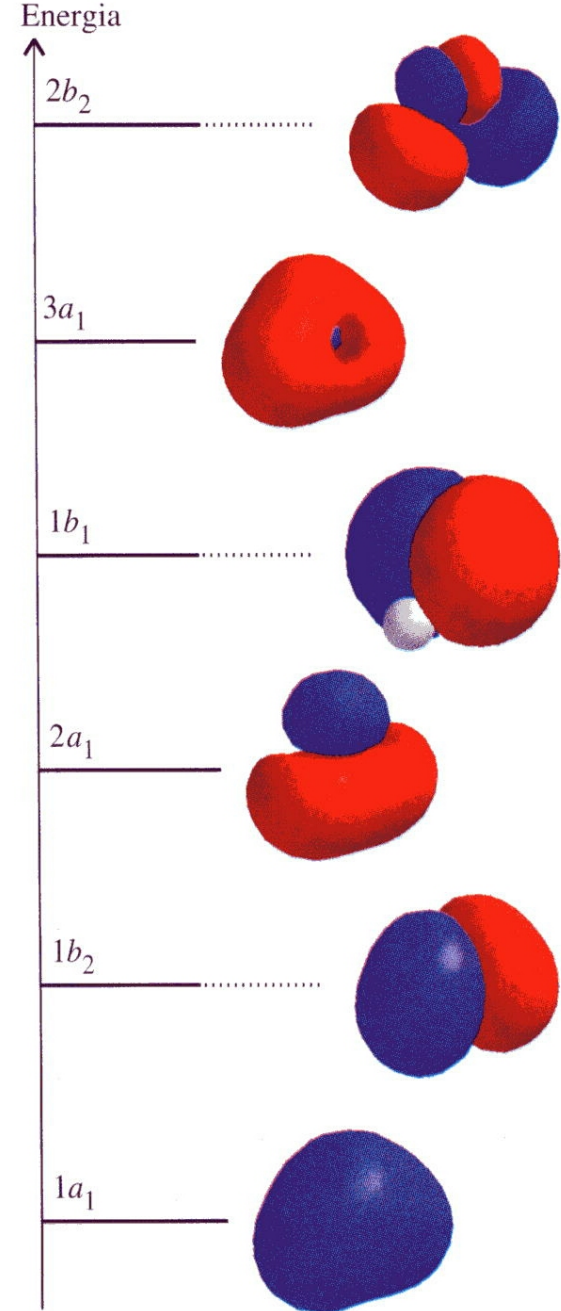
Numa ligação covalente polar o elemento mais eletronegativo contribui mais fortemente com o orbital ligante.

Moléculas poliatômicas

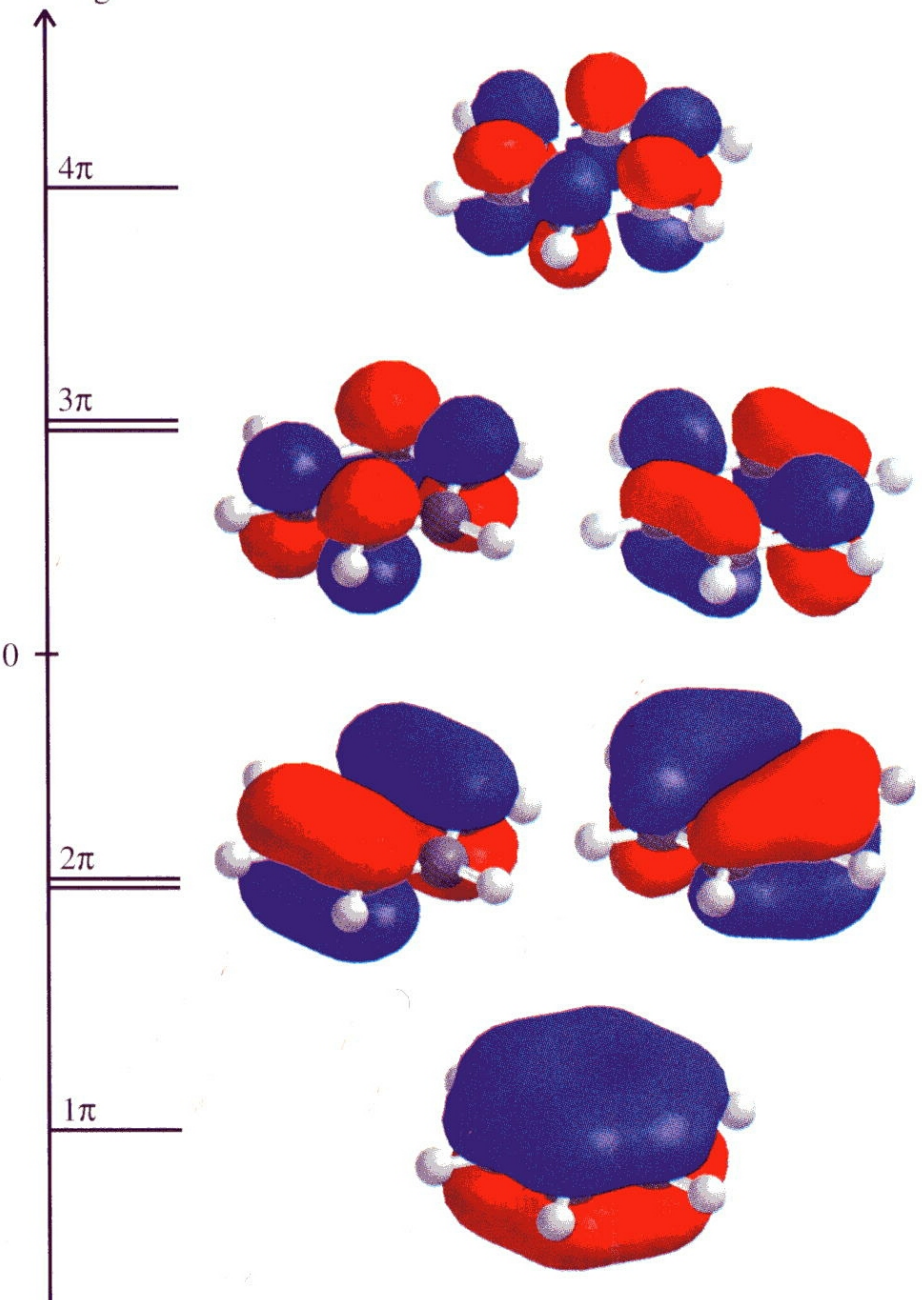
Orbitais ligantes

Orbitais anti ligantes

Orbitais não ligantes



Energia



Benzeno

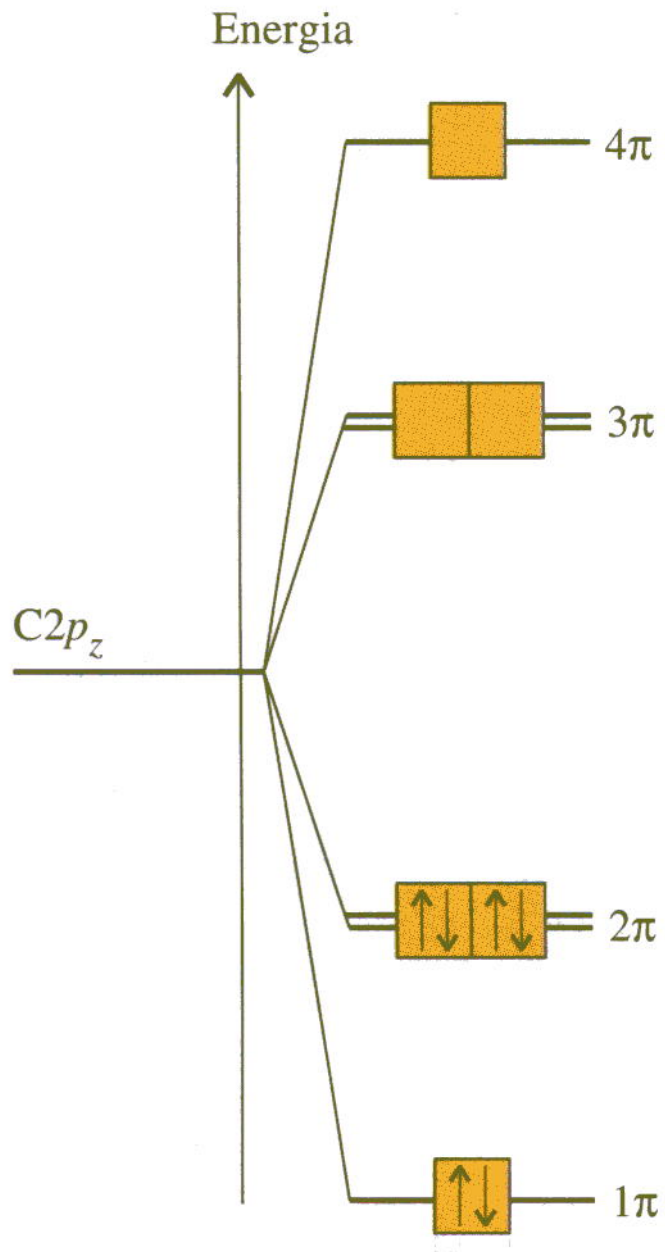
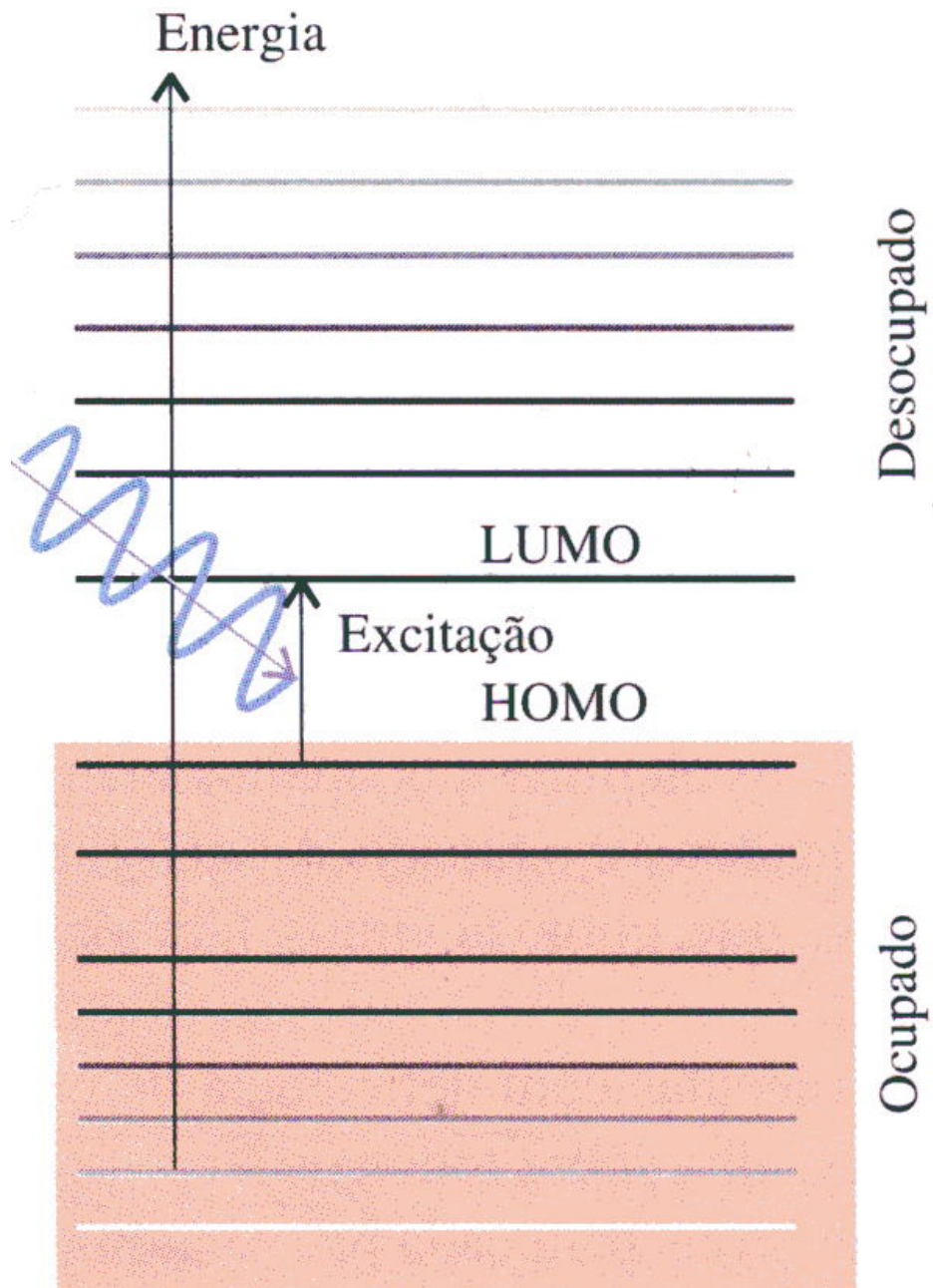
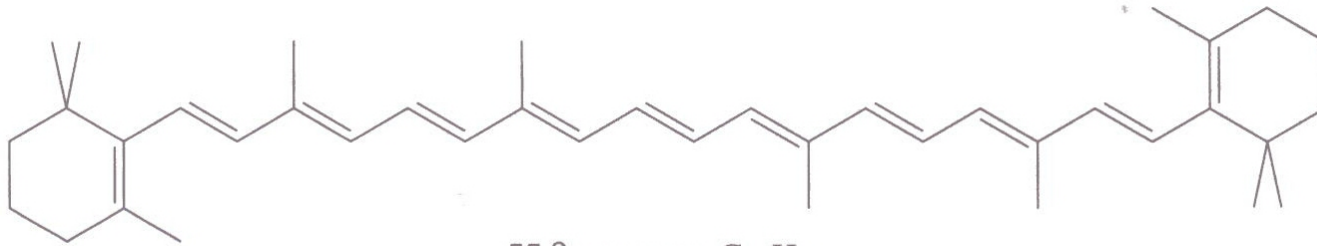


Diagrama de níveis de energia dos orbitais π do benzeno

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 β -caroteno, $C_{40}H_{56}$



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

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

A teoria de bandas no sólidos

Condutores

Semicondutores

Isolantes

Supercondutores

