

A Importância dos Orbitais Antiligantes nas Reações Orgânicas



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Referência principal: Lewis, D. E., J. Chem. Ed., 76, 1718 (1999)

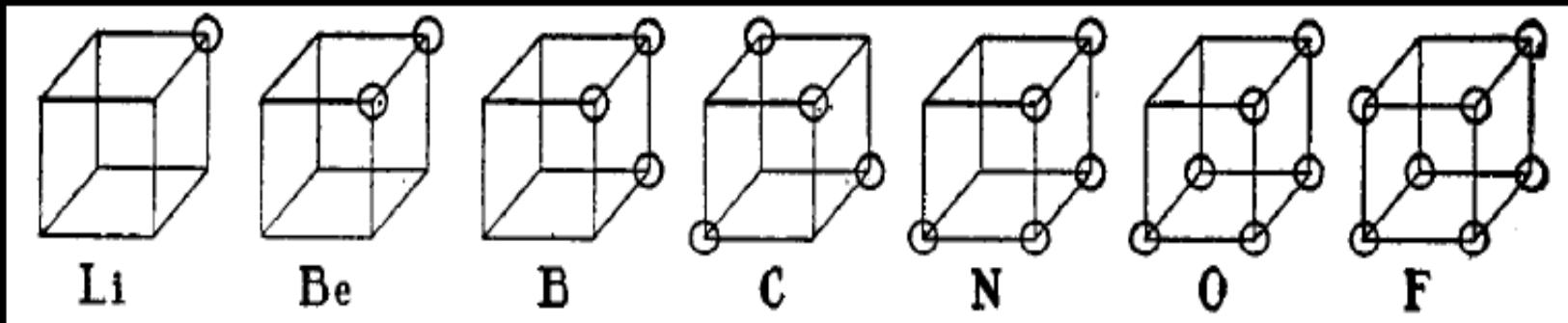
Apresentação disponível em kalilbn.wordpress.com

Introdução



Teoria de Lewis

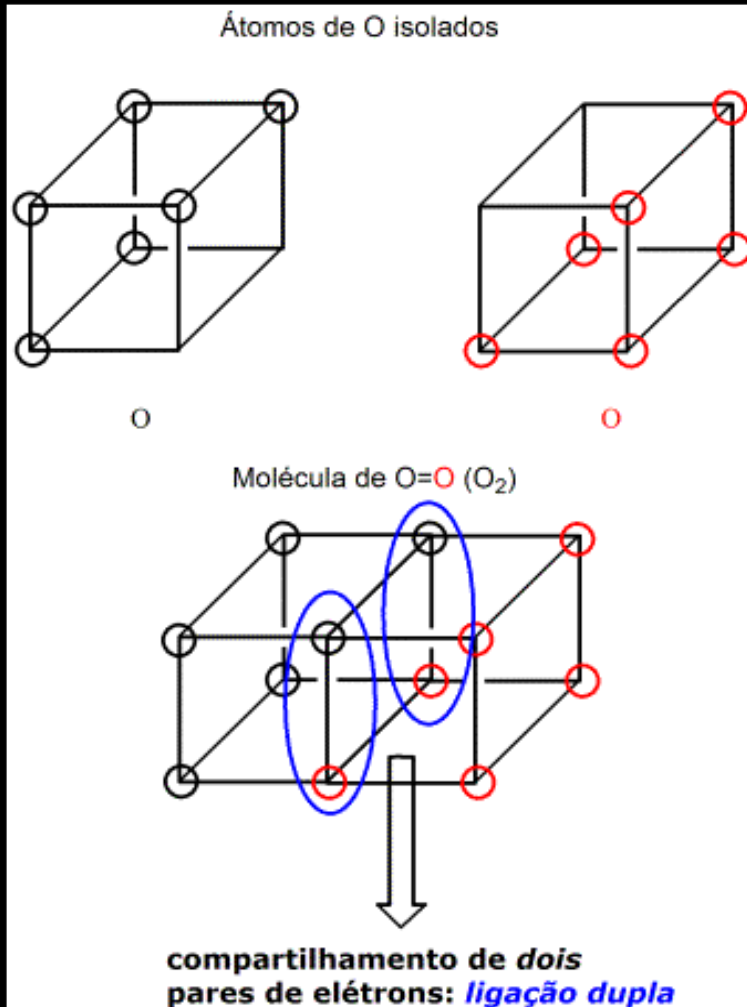
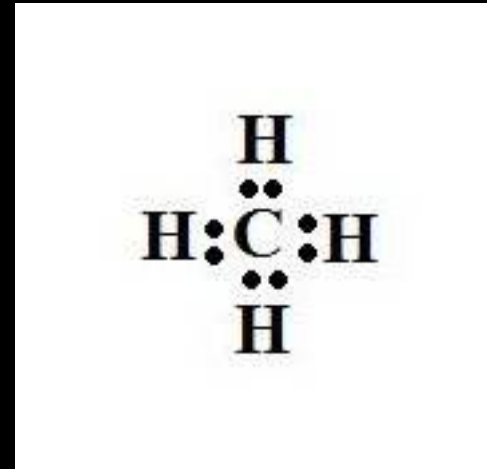
- Proposta em 1916
- Os elétrons de um átomo ocupariam os vértices de um cubo – octeto estável



- Ligação simples: Compartilhamento de dois elétrons (uma aresta)
- Ligação dupla: Compartilhamento de 4 elétrons (uma face)

Mahan, B. M., Myers, R. J., Química um Curso Universitário. Ed. Blücher, 1995
Lewis, G. - The atom and the molecule, J. Am. Chem. Soc., 38, 4 – Abril de 1916

Teoria de Lewis



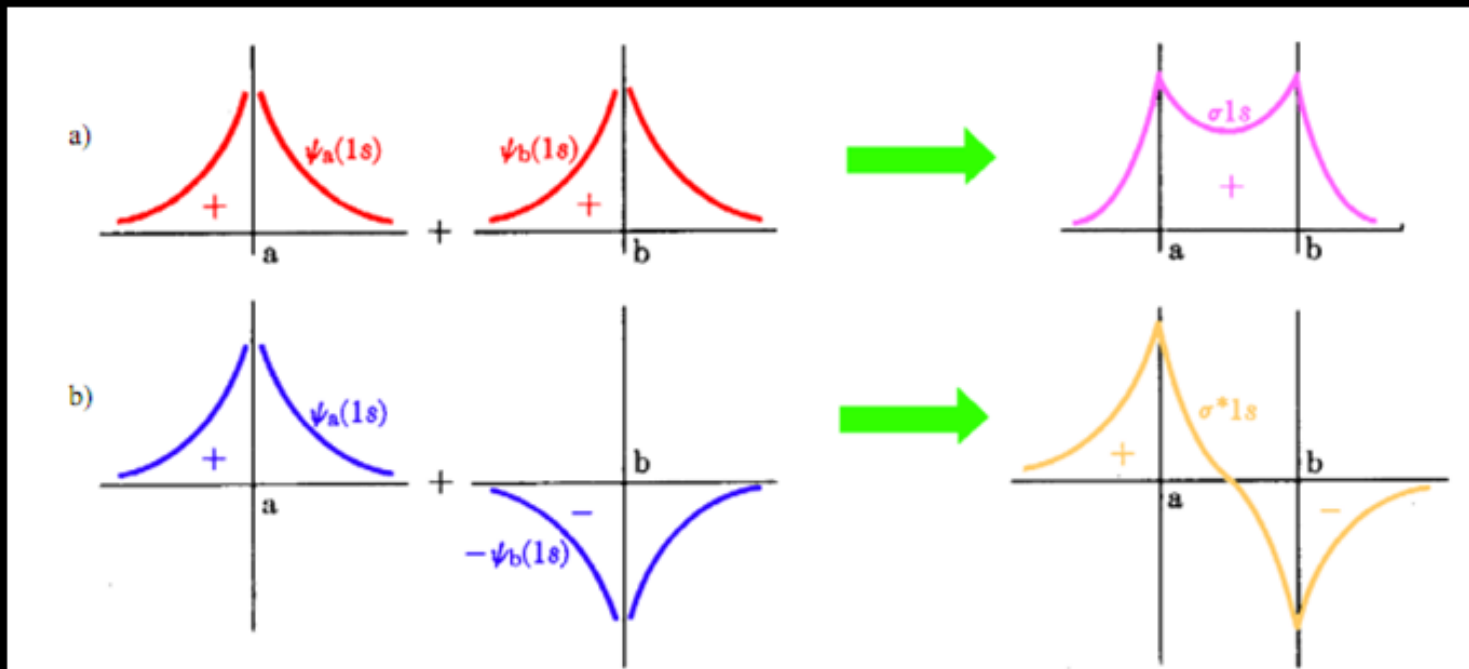
Problemas:

- Octetos incompletos (BF_3)
- Octetos expandidos (SF_4 , SF_6 , XeF_6)
- Baixo poder de predição

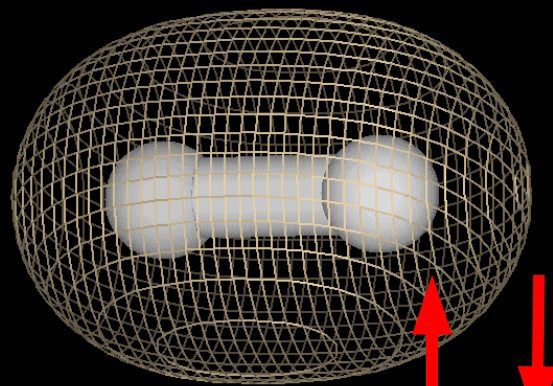
Teoria dos orbitais moleculares

- 1932 ~ 1933
- Milliken – Hund
- Orbitais moleculares seriam formados pela combinação de orbitais atômicos de simetria apropriada
- Os elétrons de valência pertencem à molécula como um todo, e não a um átomo ou ligação em particular
- Preenchimento dos orbitais pelo Princípio de Aufbau
- O preenchimento de orbitais ligantes estabiliza a molécula enquanto o preenchimento de orbitais antiligantes a desestabiliza

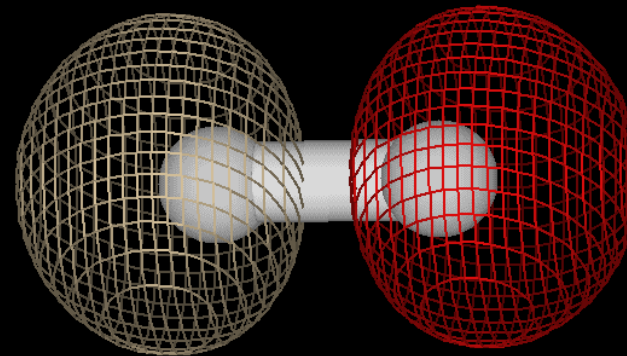
Teoria dos orbitais moleculares



H_2



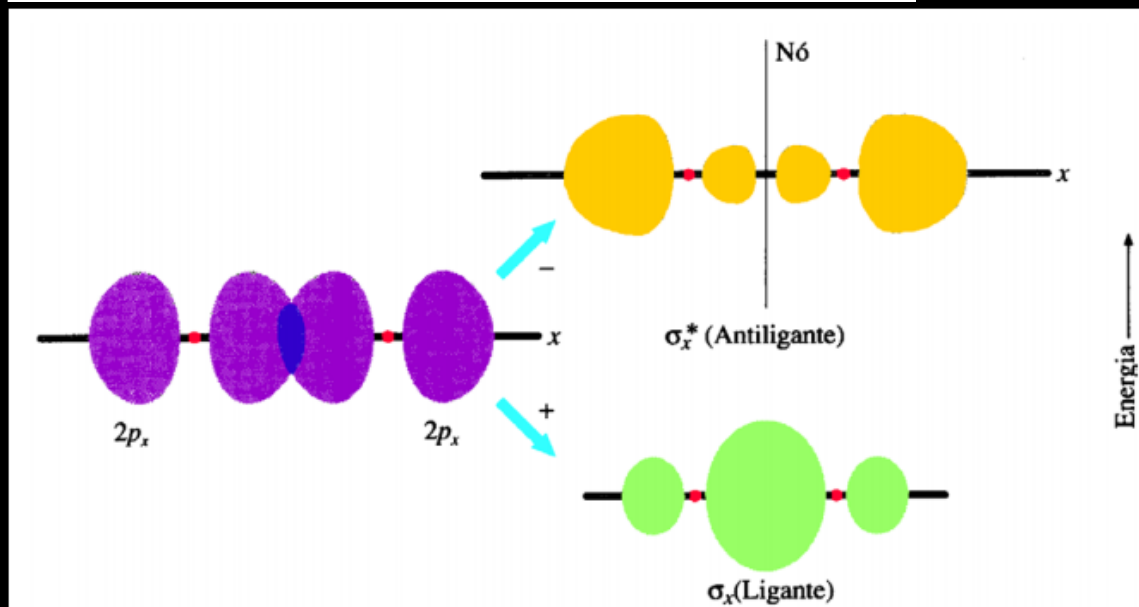
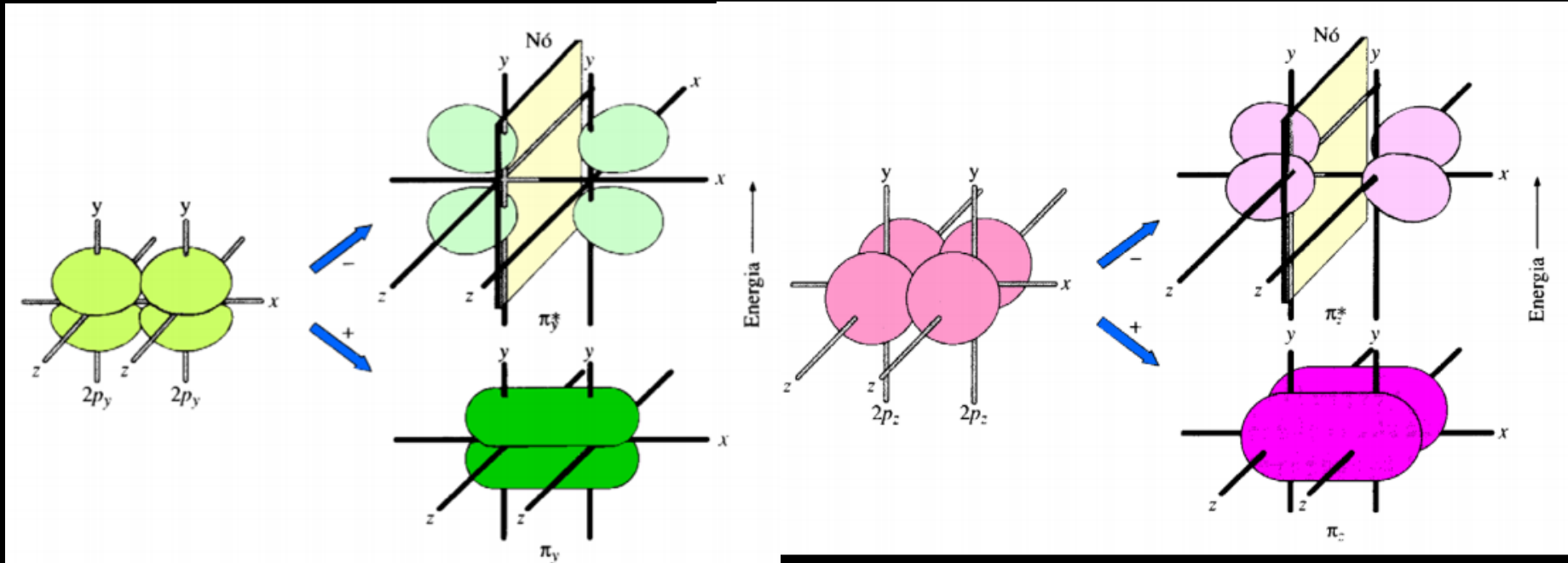
$\sigma(1s)$
 $E = -15,0 \text{ eV}$



$\sigma^*(1s)$
 $E = +7,0 \text{ eV}$

Teoria dos orbitais moleculares

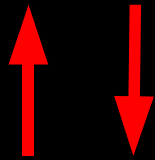
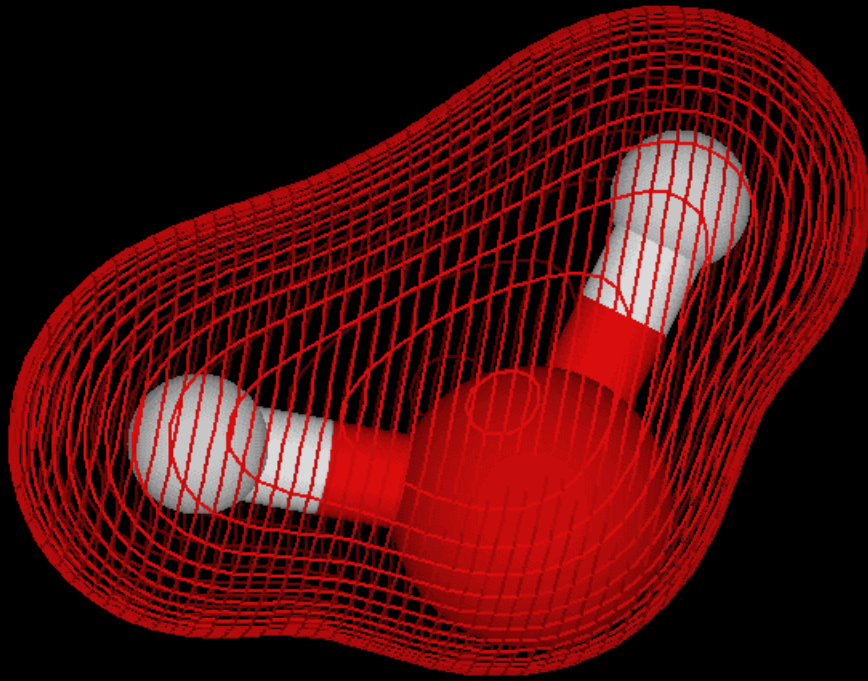
- Combinações de orbitais atômicos tipo p



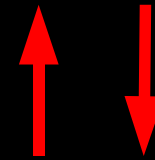
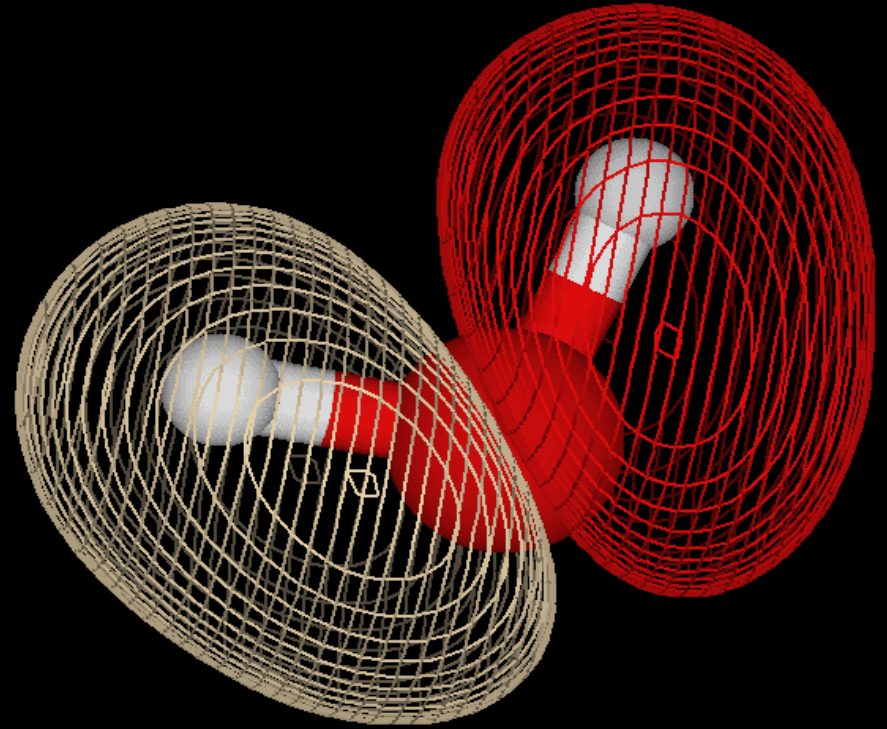
<http://zeus.qui.ufmg.br/~ayala/matdidatico/tom.pdf>
(imagensr)

Orbitais moleculares da água

- Total de elétrons de valência: 1.6 (O) + 2.1 (H) = 8



$$E = -29,9 \text{ eV}$$

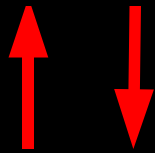
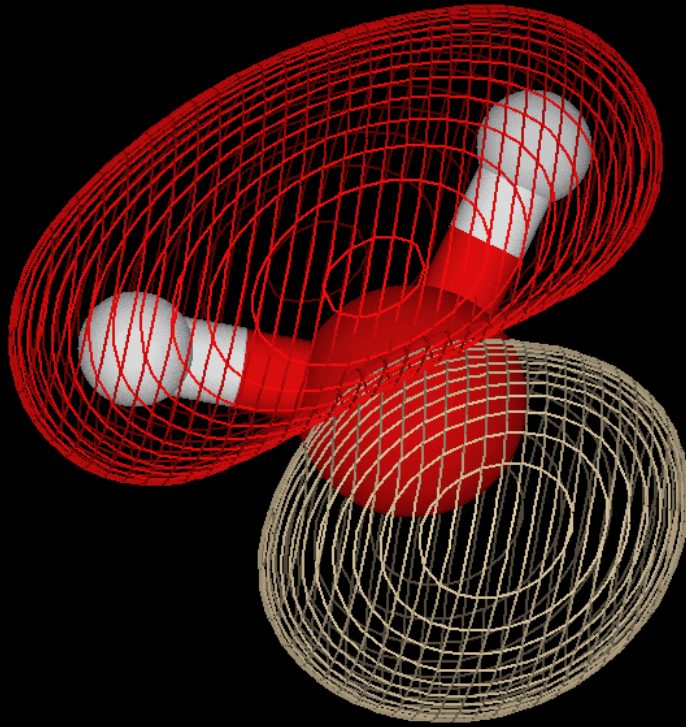


$$E = -18,6 \text{ eV}$$

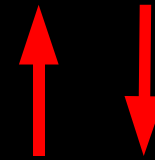
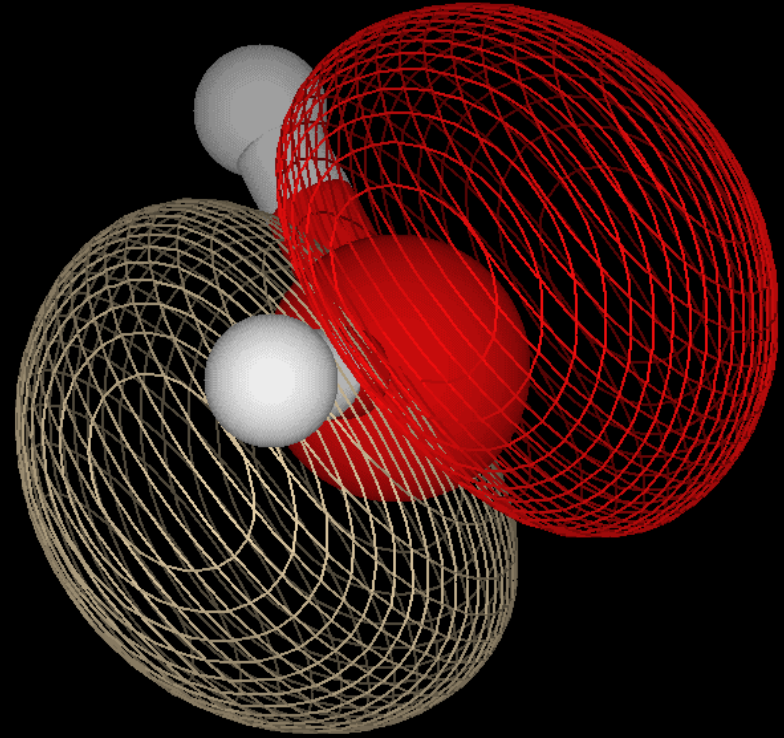


Orbitais moleculares da água

- Total de elétrons de valência: 1.6 (O) + 2.1 (H) = 8



$$E = -14,4 \text{ eV}$$

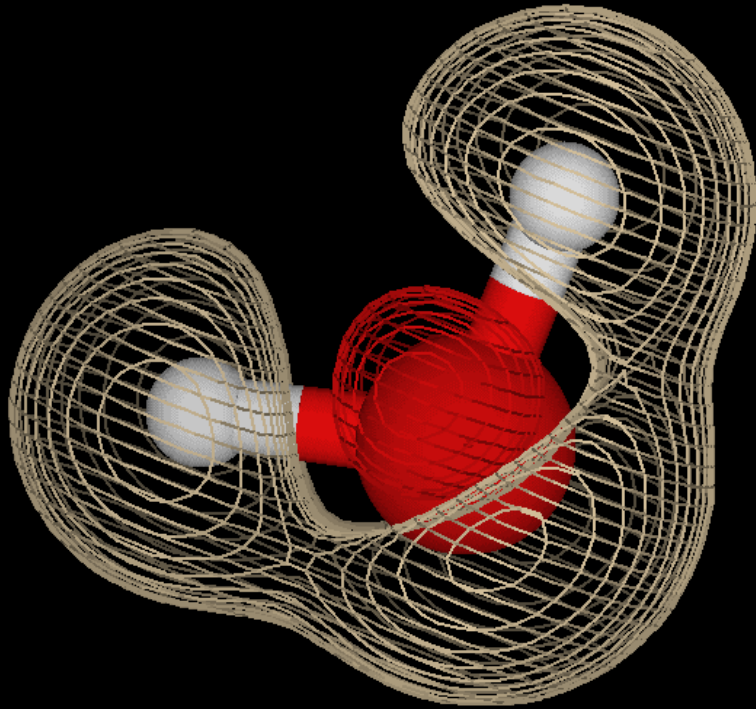


$$E = -12,1 \text{ eV}$$

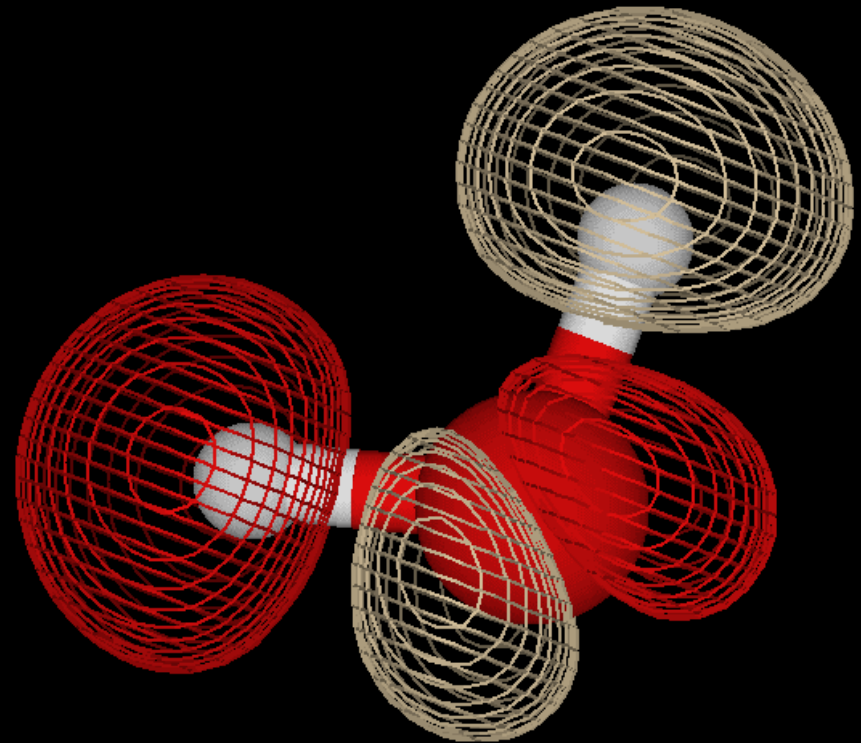
(HOMO)

Orbitais moleculares da água

- Total de elétrons de valência: $1.6 \text{ (O)} + 2.1 \text{ (H)} = 8$

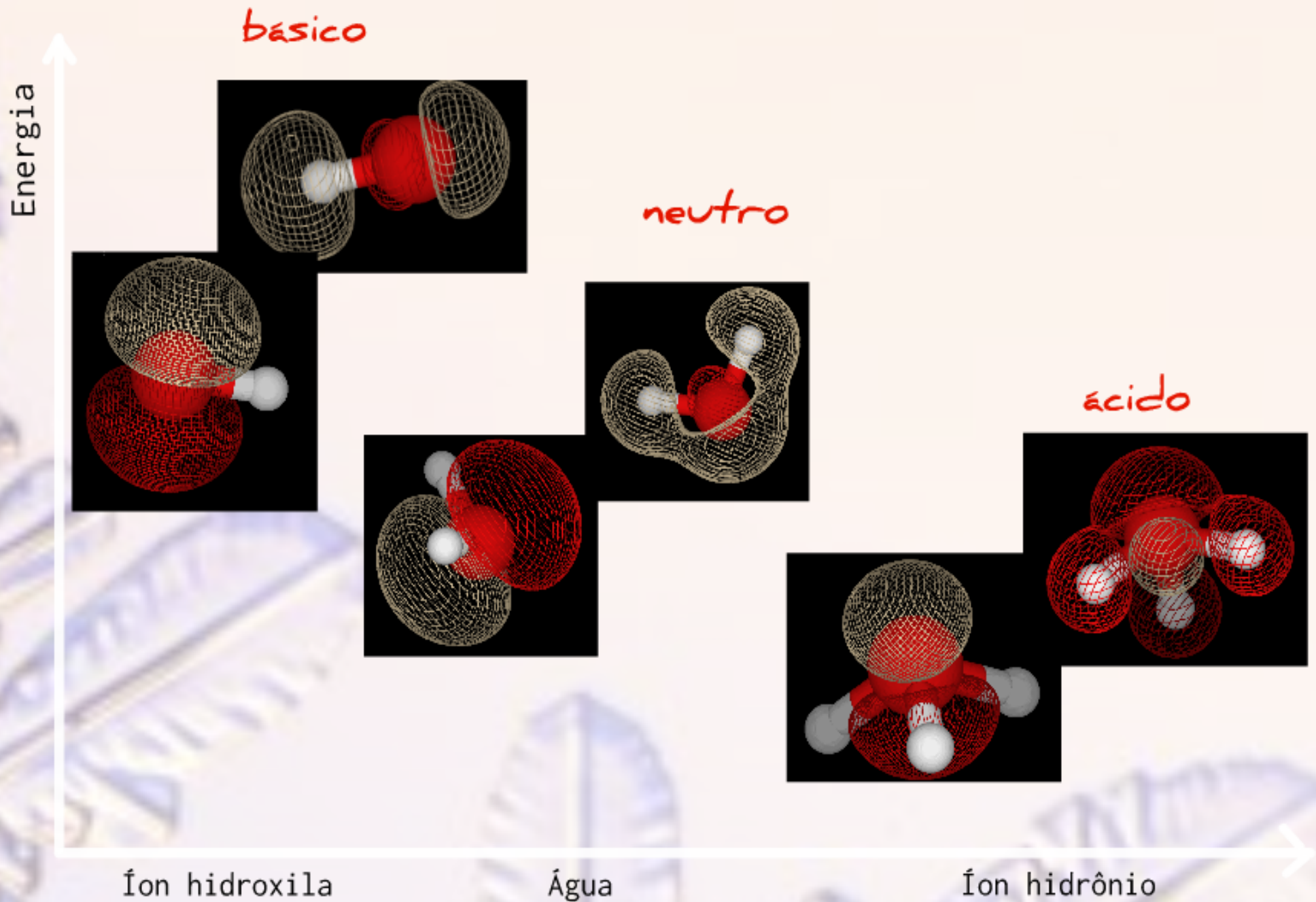


$E = + 4,3 \text{ eV}$
(LUMO)



$E = + 6,1 \text{ eV}$

Acidez e basicidade da água



Metodologia



Metodologia

- Cálculos Semi-empíricos
- Programa: MOPAC 2009
- Hamiltoniano: PM6
- Visualização dos orbitais: MOLDEN

MOPAC 2009, James J. P. Stewart, Stewart Computational Chemistry, Version 9.271L web:
<http://openmopac.net>

Stewart, J. J. P., J. Mol. Mod., 13, 1173 ~ 1213 (2007)

Schaftenaar, G., Noordik, J. H., J. Comput.-Aided Mol. Design, 14, 123~134 (2000)

Aplicação em reações orgânicas



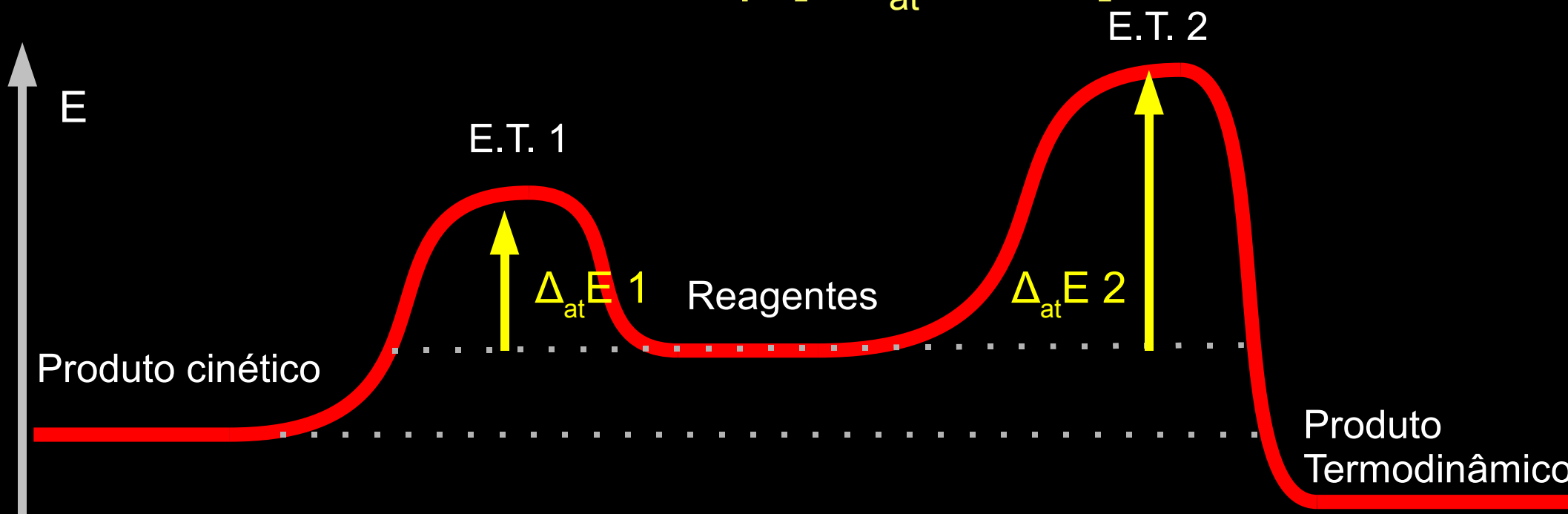
Cinética VS Termodinâmica

- **Termodinâmica:** Constante de equilíbrio

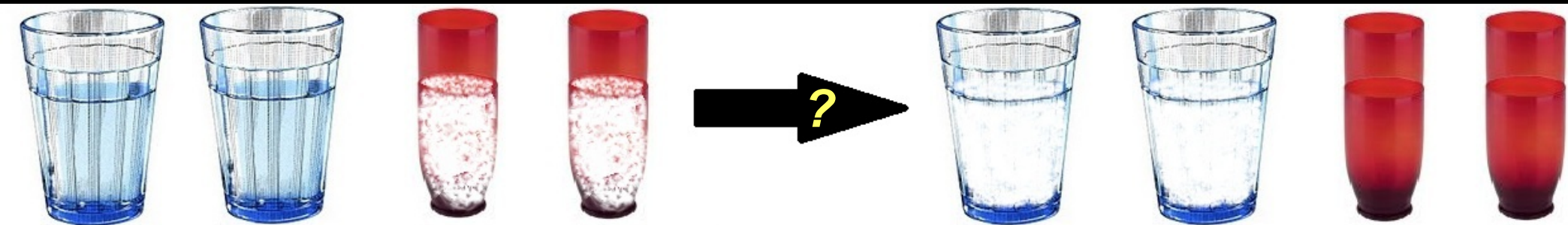
$$K_{eq} = \exp [- \Delta_r G / RT]$$

- **Cinética:** Constante de velocidade (Eq. de Arrhenius)

$$k = A \cdot \exp [- \Delta_{at} E / RT]$$



Reação Química: Reorganização dos elétrons



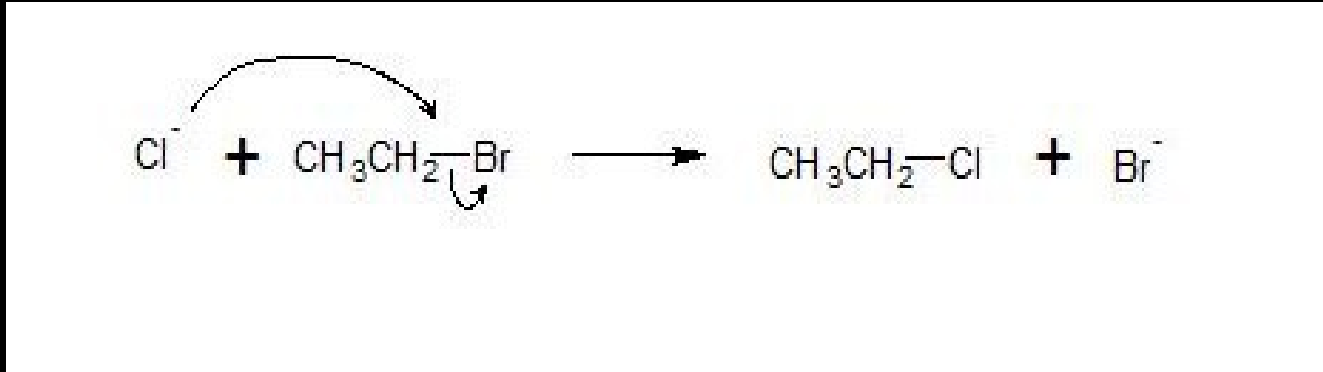
Pode-se interpretar uma reação química através da transferência de densidade eletrônica de um reagente para outro. Como o Princípio da Exclusão de Pauli permite apenas dois elétrons em cada orbital molecular, para que essa transferência seja possível, é necessária a participação de um orbital molecular vazio para acomodar os elétrons transferidos. O orbital desocupado mais acessível é o de menor energia, ou seja, o LUMO da molécula.

LUMO!!!

Lewis, D. E., J. Chem. Ed., 76, 1718 (1999)

S_N2

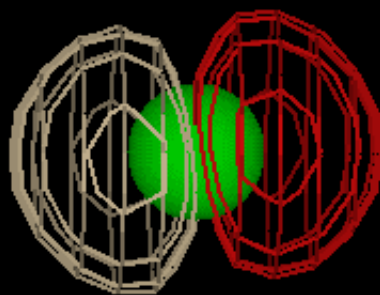
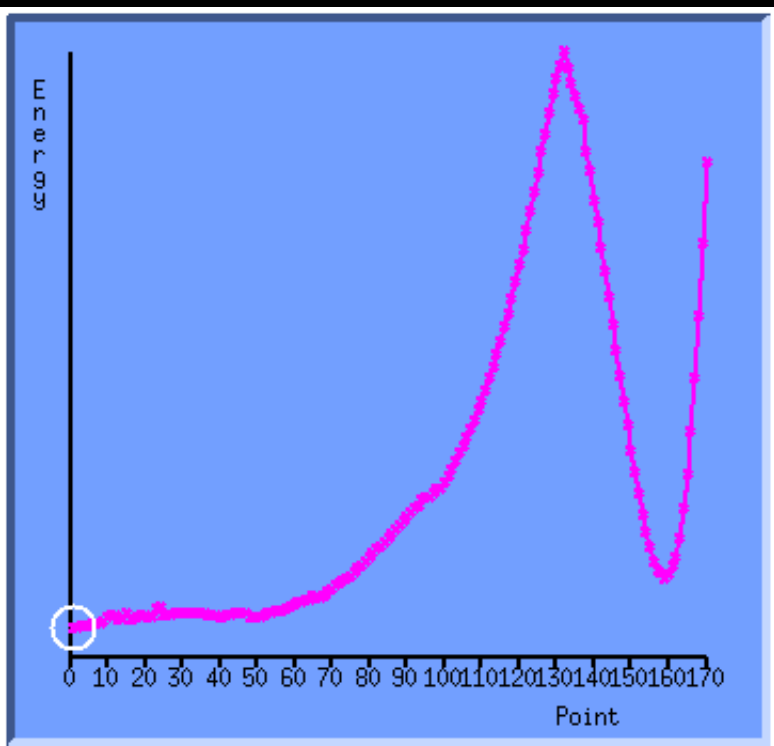
- Reação:



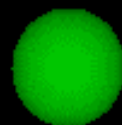
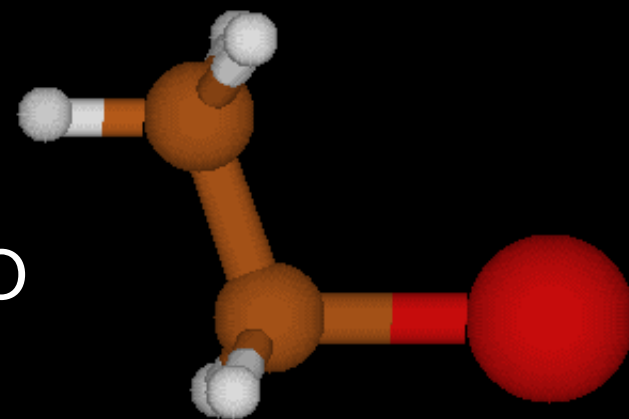
- Solvente: **DMSO, $(\text{CH}_3)_2\text{SO}$, $\text{EPS} = 49$**

Idéia: Ocorre a transferência de elétrons do nucleófilo (cloreto) para o eletrófilo (bromoetano) e essa transferência ocorre por meio dos orbitais de fronteira dos reagentes, ou seja, do HOMO (ocupado) do cloreto para o LUMO (desocupado) do bromoetano. Nos próximos slides é mostrada a evolução desses orbitais ao longo da coordenada de reação, ou seja, a medida em que o cloreto aproxima-se do carbono para realizar o ataque nucleofílico

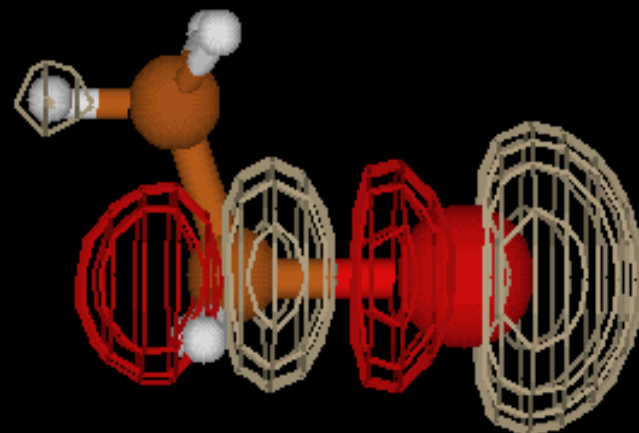
S_N2



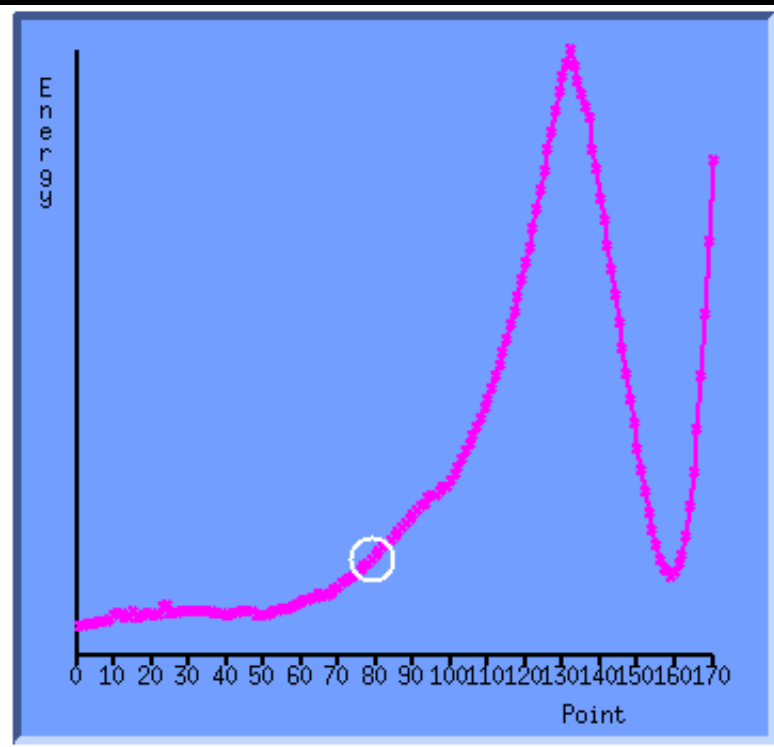
HOMO



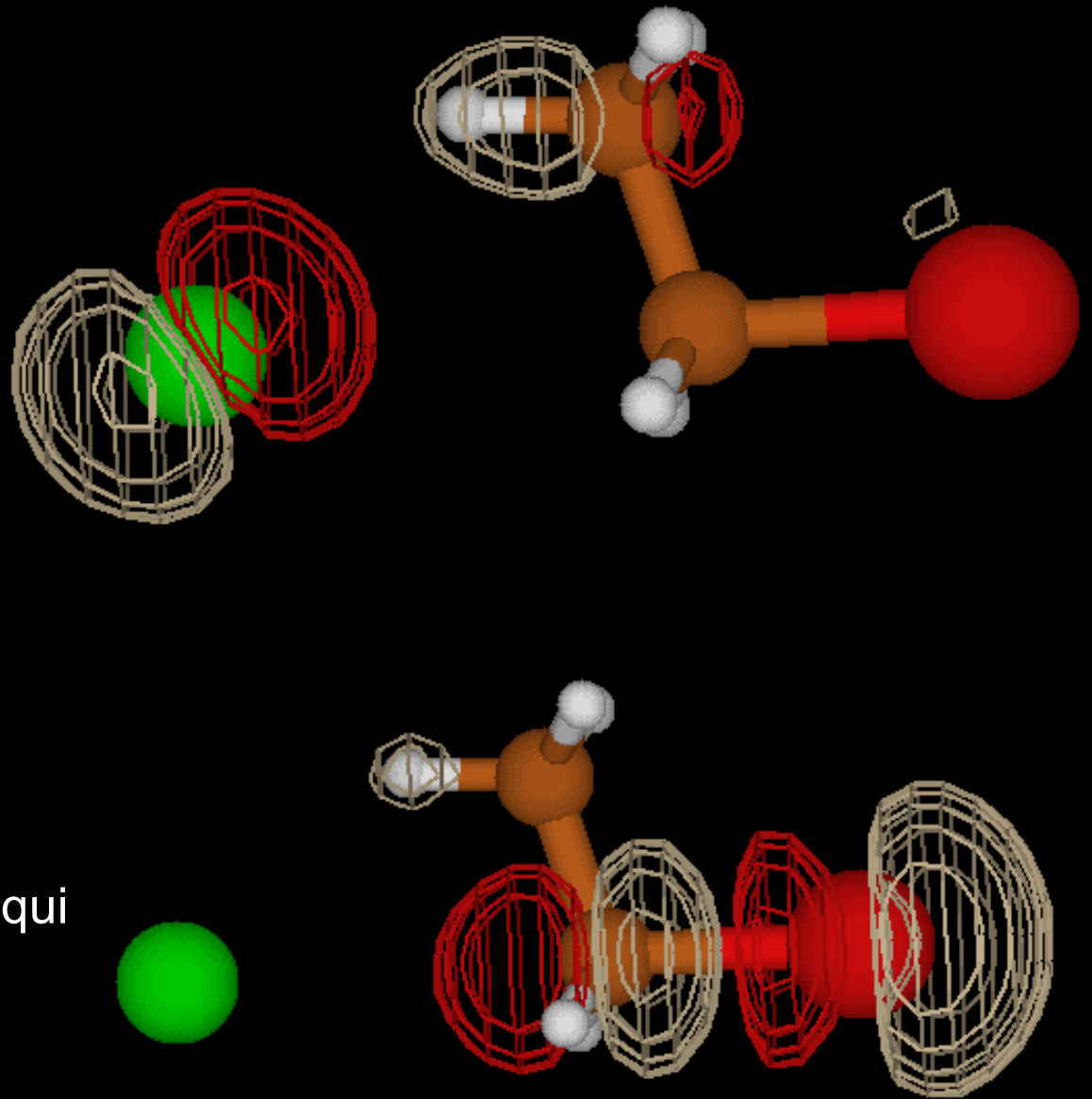
LUMO



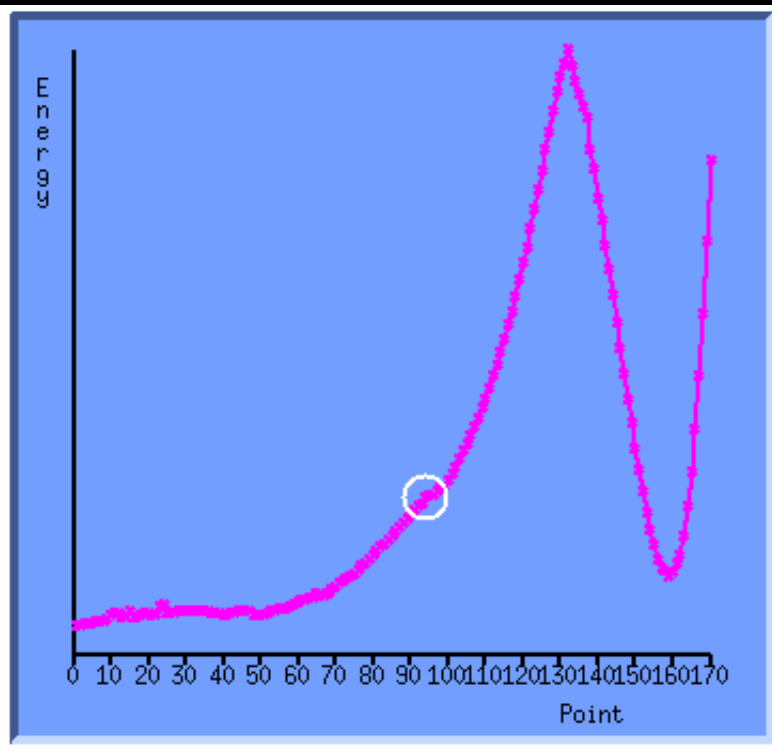
S_N2



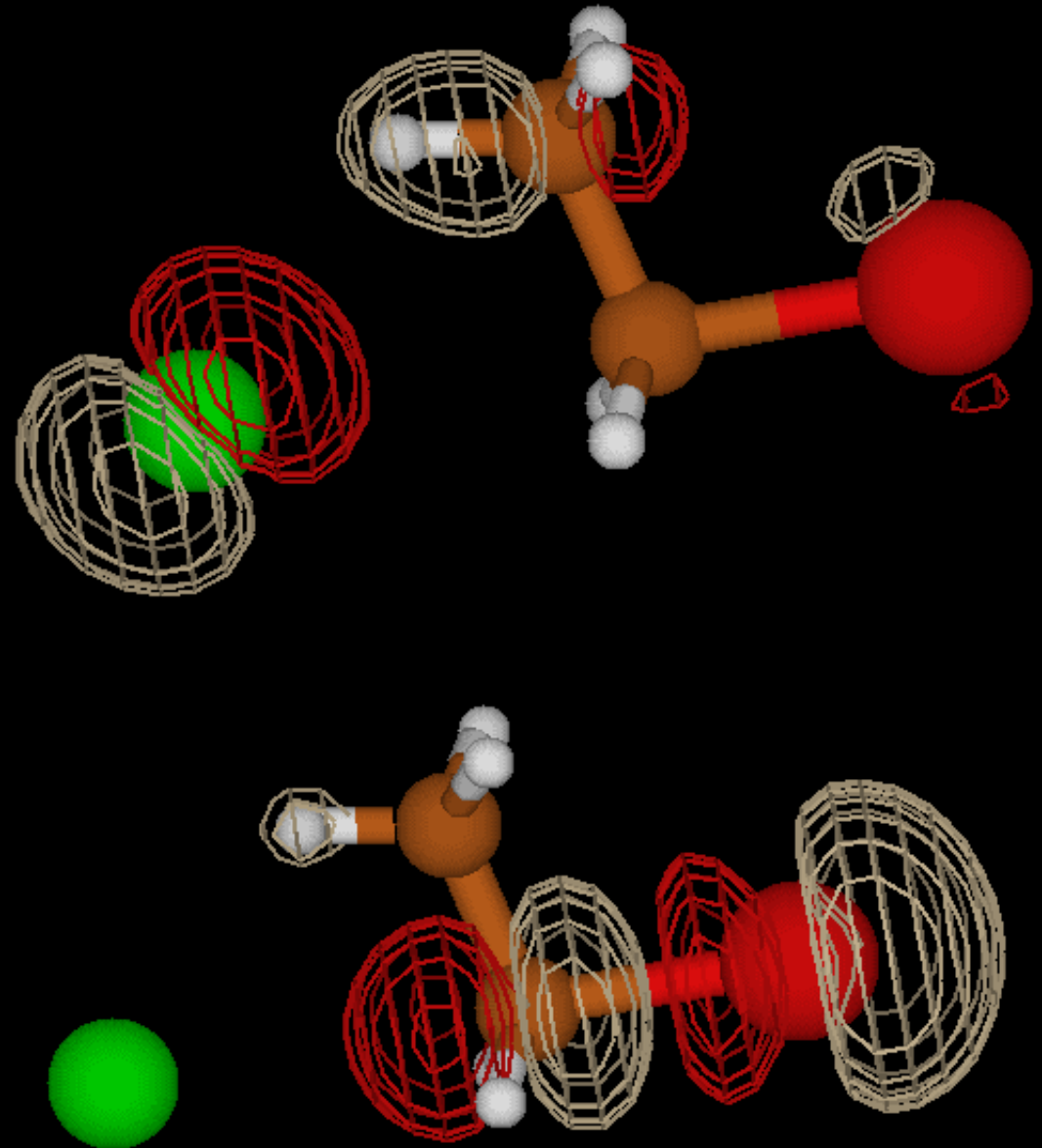
Sabe-se que grupos alquil ligados ao carbono dificultam a ocorrência de reações S_N2 . Isso é evidenciado aqui pela interação antiligante entre o nucleófilo e o grupo CH_3 do eletrófilo, que aumenta a energia do sistema.



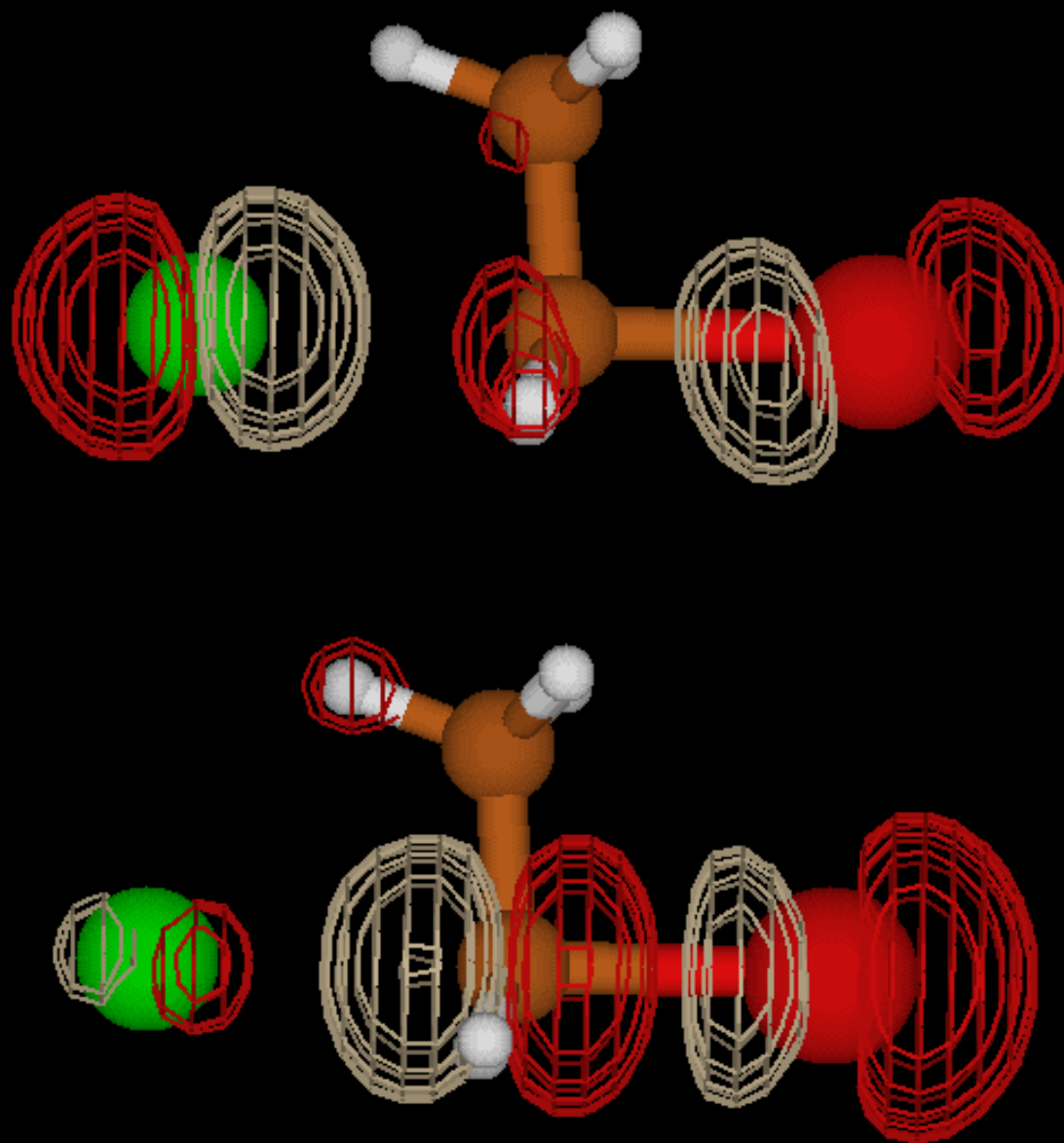
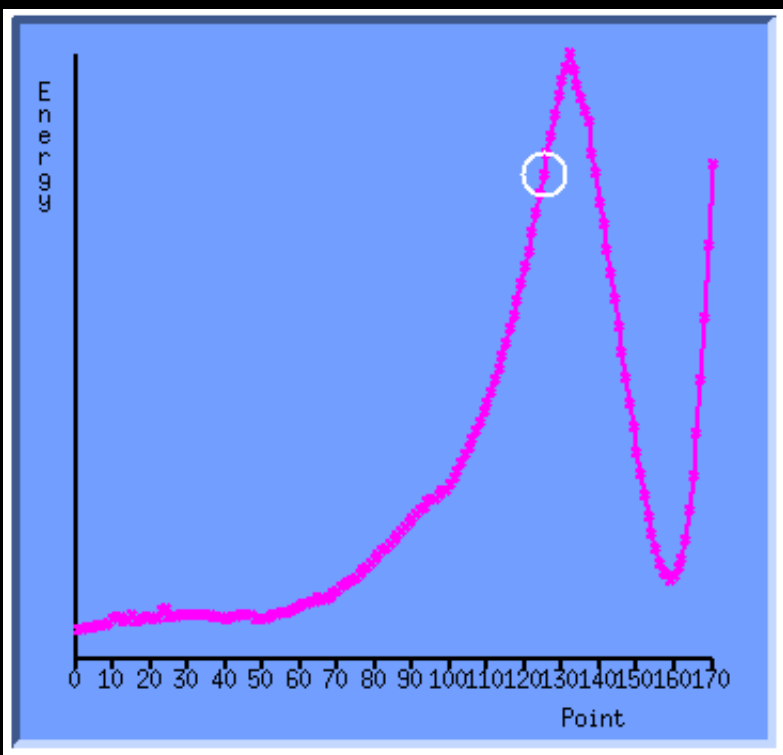
S_N2



Note o surgimento de densidade eletrônica sobre o bromo no HOMO e redução da densidade sobre o cloro, evidenciando a transferência de elétrons do cloreto para o bromoetano

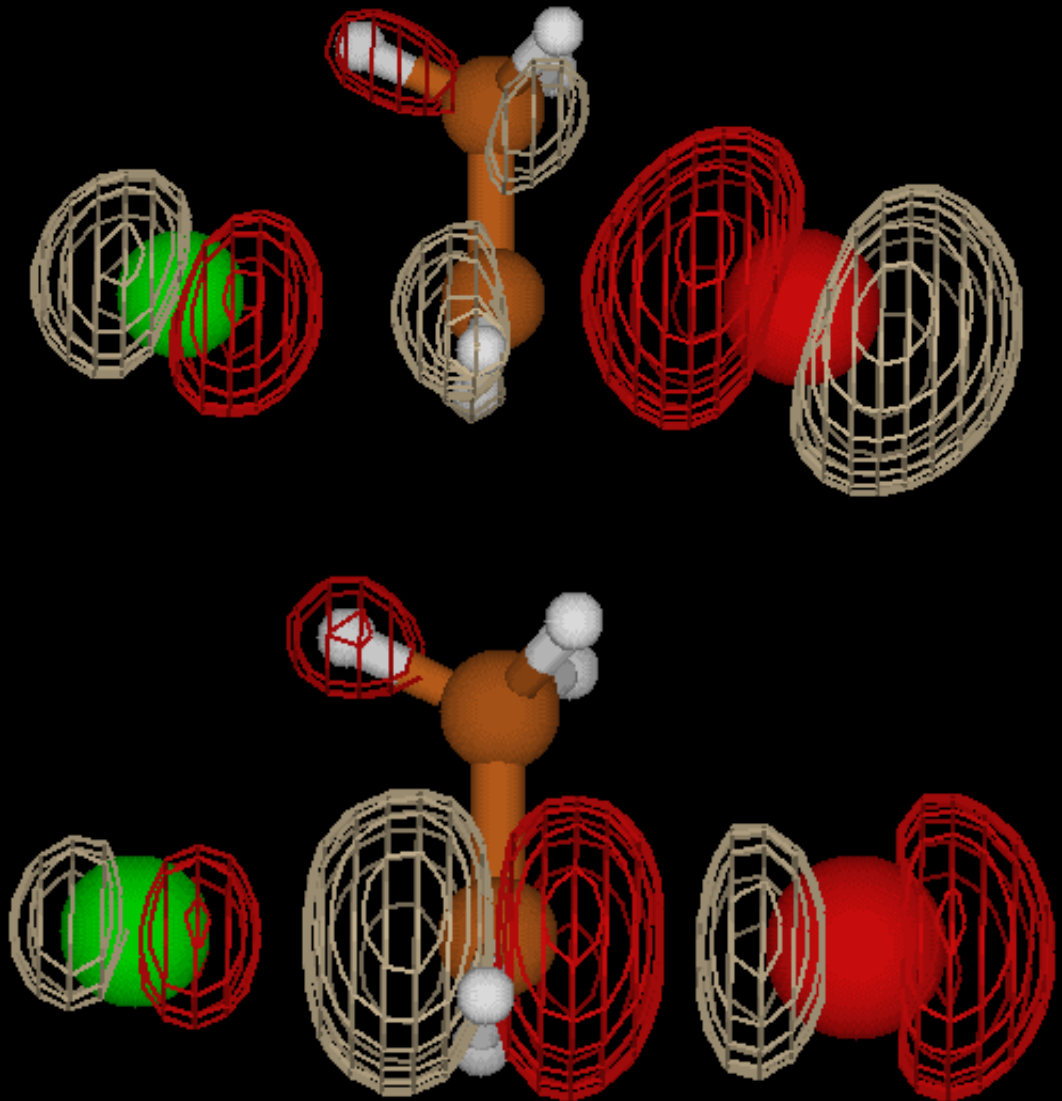
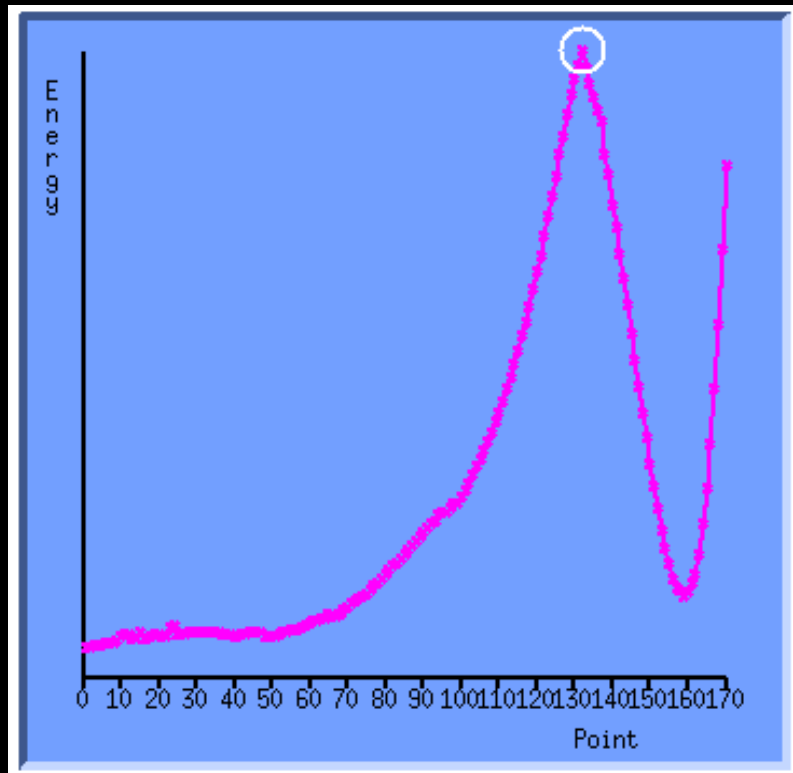


S_N2



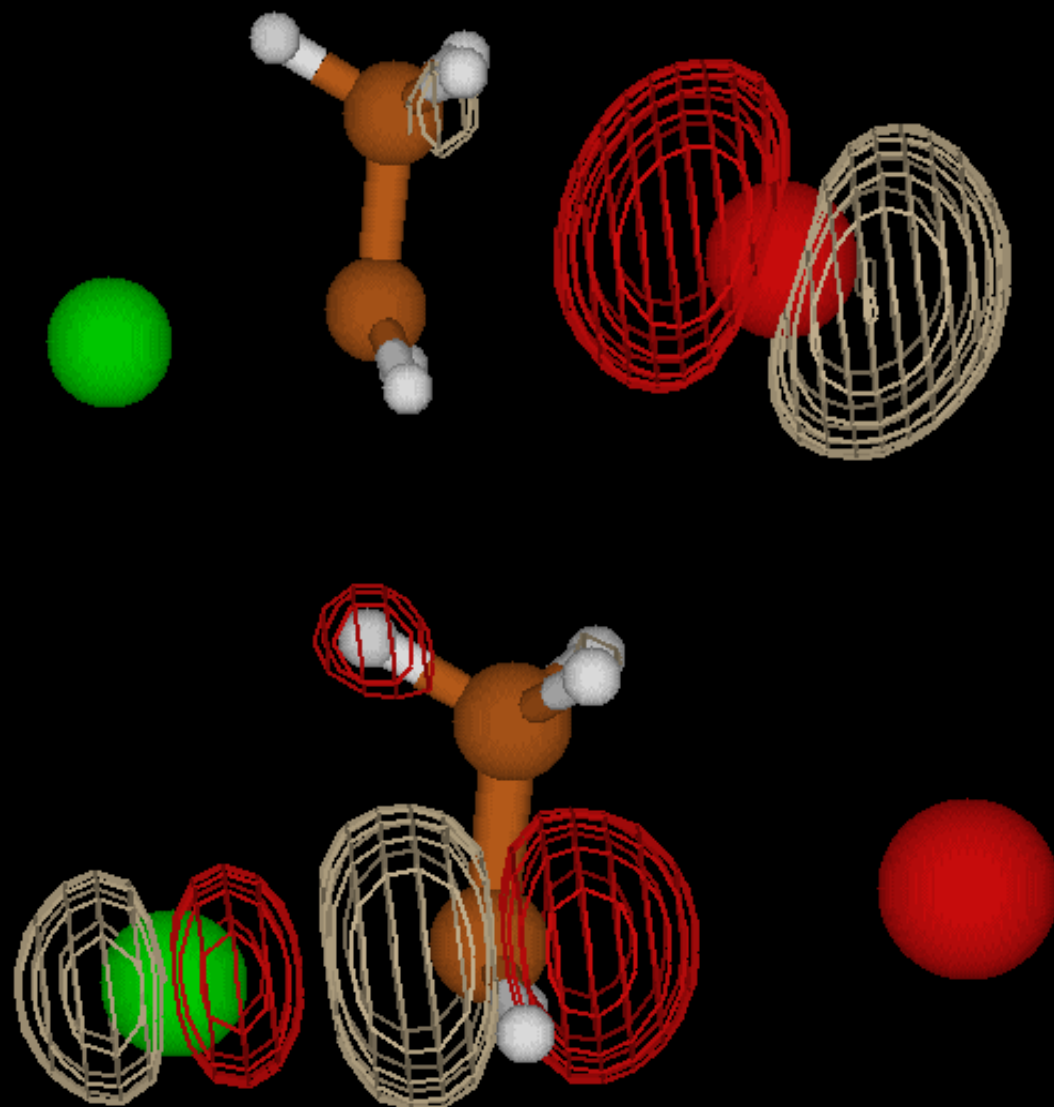
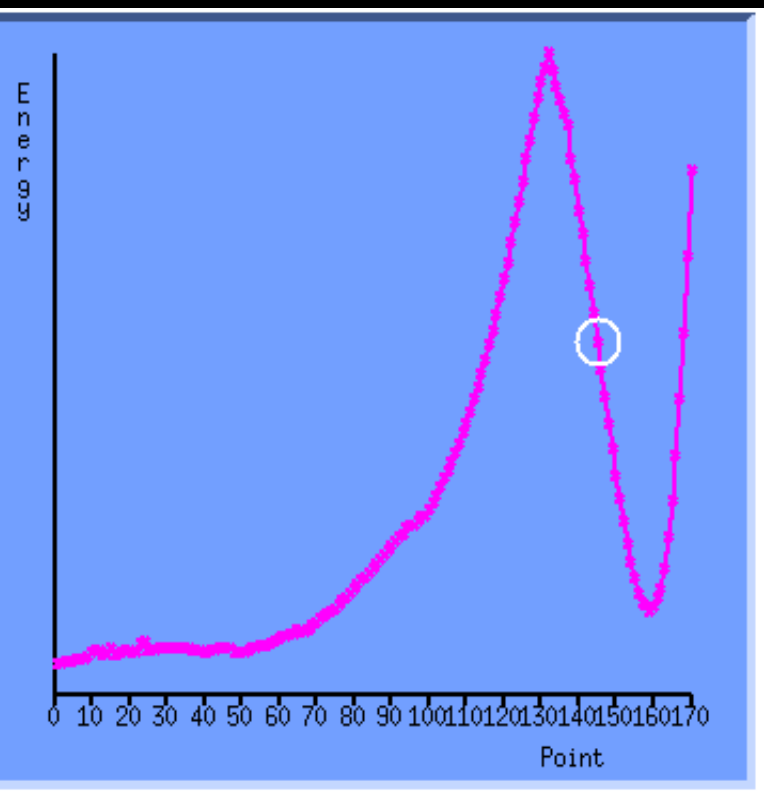
S_N2

Estado de transição!

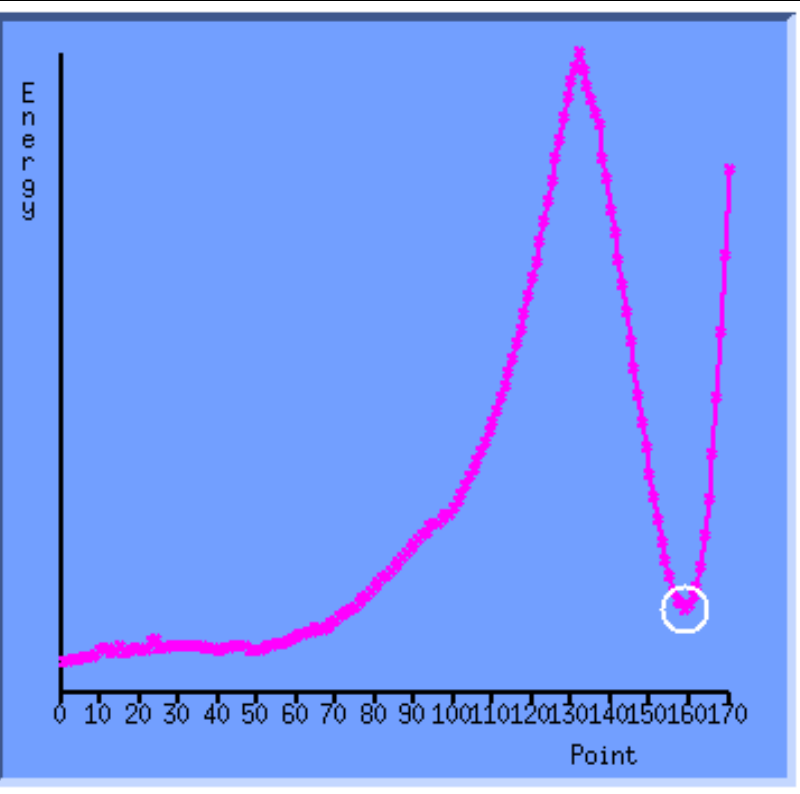


Observe a semelhança entre o HOMO (ocupado) do estado de transição com o LUMO do reagente bromoetano. O HOMO do estado de transição é antiligante tanto entre o carbono e o bromo e entre o carbono e o cloro, assim, em princípio, ambas as ligações podem ser rompidas e o estado de transição é o mesmo para as reações direta e inversa.

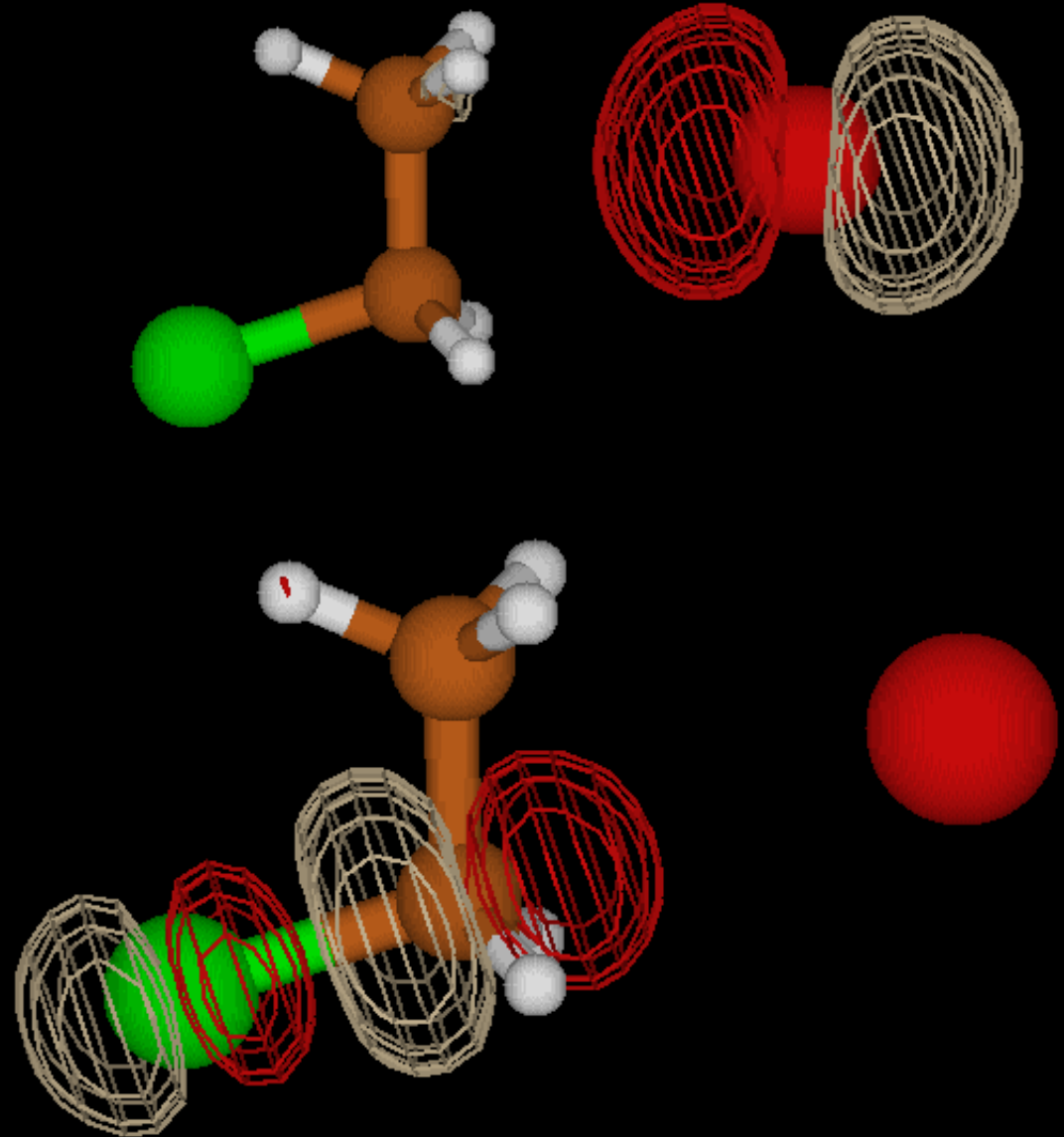
S_N2



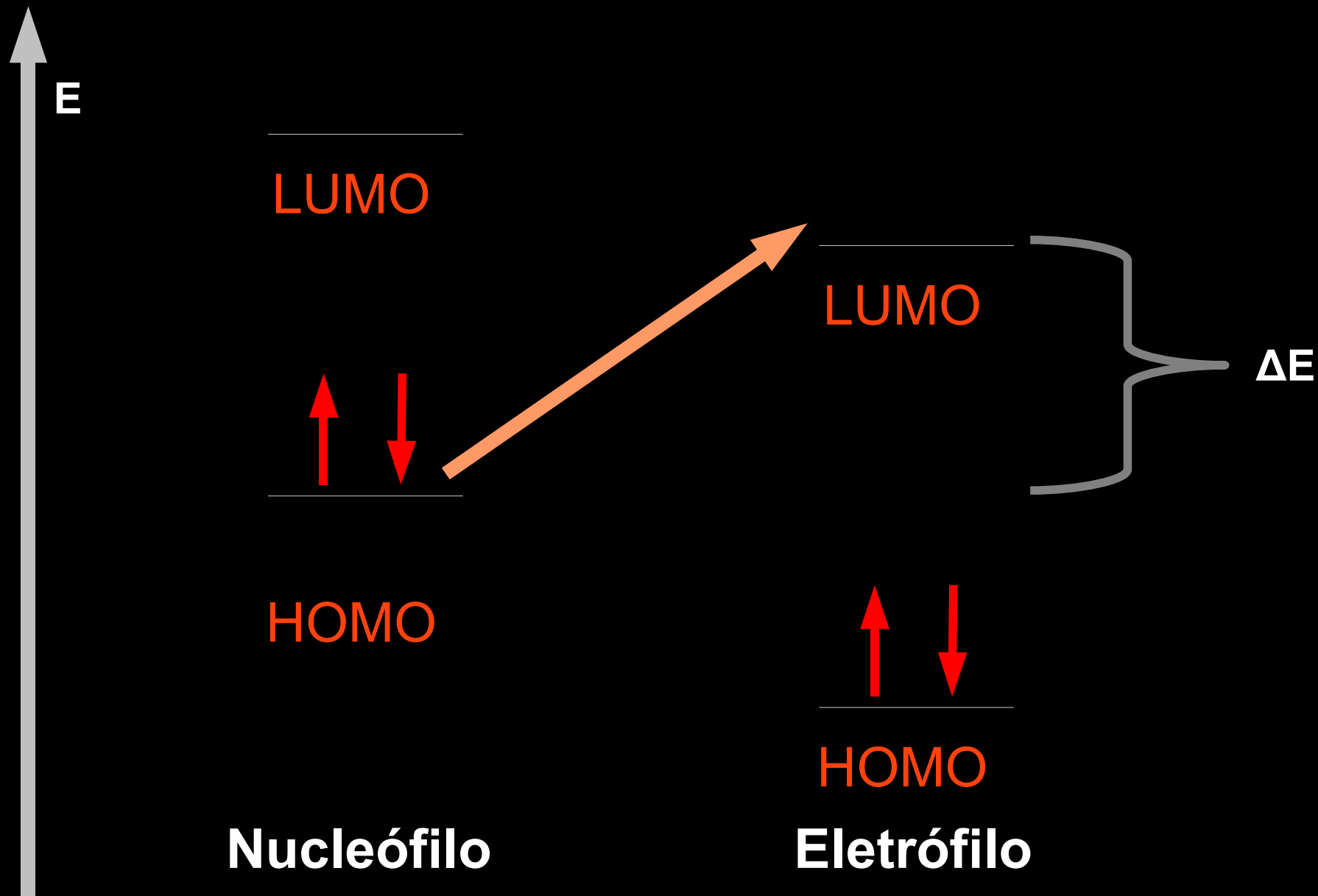
S_N2



Produtos



S_N2 – influência dos orbitais de fronteira



Quanto menor o valor de ΔE , mais fácil será a reação do ponto de vista cinético

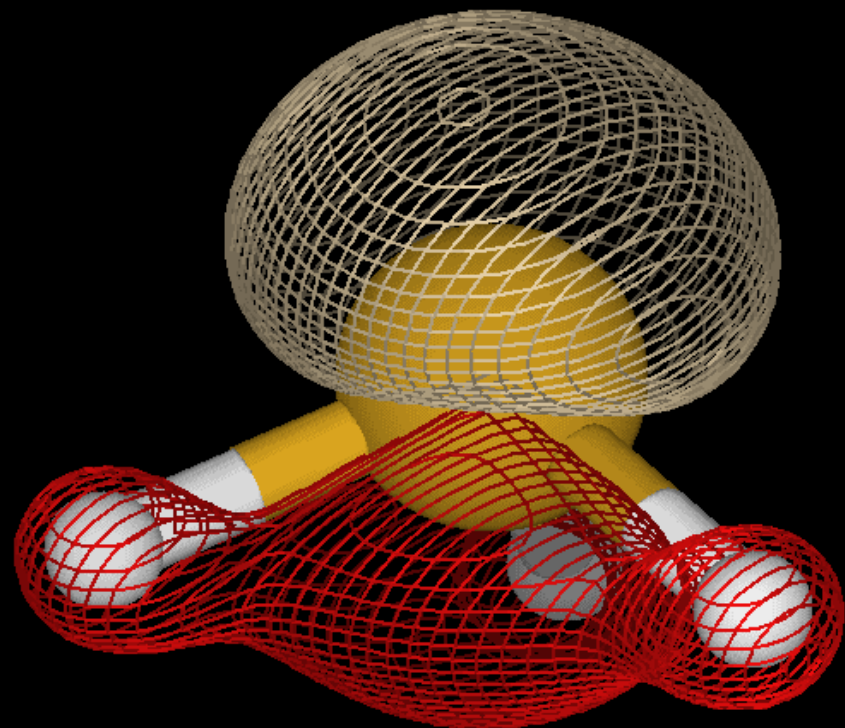
S_N2 – Força do nucleófilo

Nucleófilo	HOMO (eV)	LUMO (eV)
F^-	-11,7	----
Cl^-	-10,7	101,1
Br^-	-10,1	120,7
I^-	-9,1	122,4
NH_3	-10,6	4,7
H_2O	-12,1	4,3
PH_3	-10,0	4,3
H_2S	-9,7	0,5
OH^-	-10,4	7,4
$CH_3CH_2O^-$	-9,0	4,8
HS^-	-9,3	1,7
$CH_3CH_2S^-$	-8,9	1,3
N_3^-	-9,4	1,9
CN^-	-9,3	3,4
HCC^-	-8,9	3,9

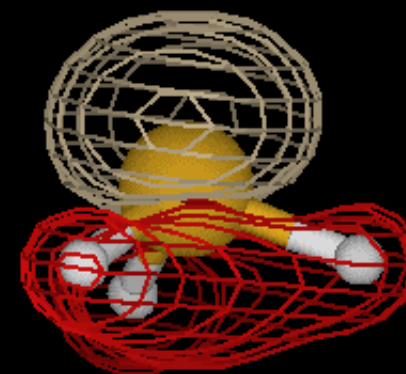
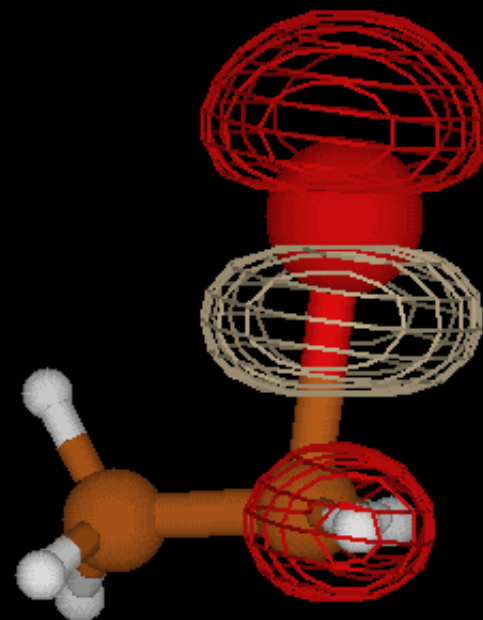
S_N2 – Efeito do Grupo abandonador

Composto	HOMO (eV)	LUMO (eV)
CH ₃ CH ₃	-11,9	4,5
CH ₃ CH ₂ F	-12,1	2,9
CH ₃ CH ₂ Cl	-11,0	0,7
CH ₃ CH ₂ Br	-10,8	-0,2
CH ₃ CH ₂ I	-10,1	-0,8
CH ₃ CH ₂ O ⁻	-9,0	4,8
CH ₃ CH ₂ OH	-10,9	2,6
CH ₃ CH ₂ OH ₂ ⁺	-12,8	-0,1
Solvente	DMSO, (CH ₃) ₂ SO	ESP= 49

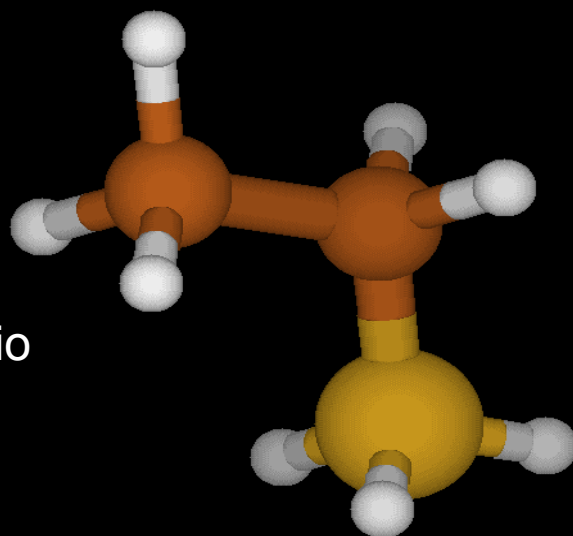
S_N2 – Outros exemplos



HOMO - fosfina



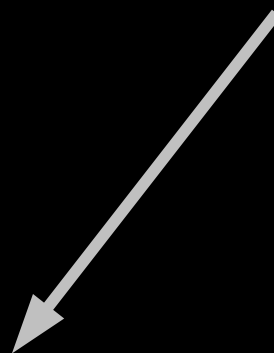
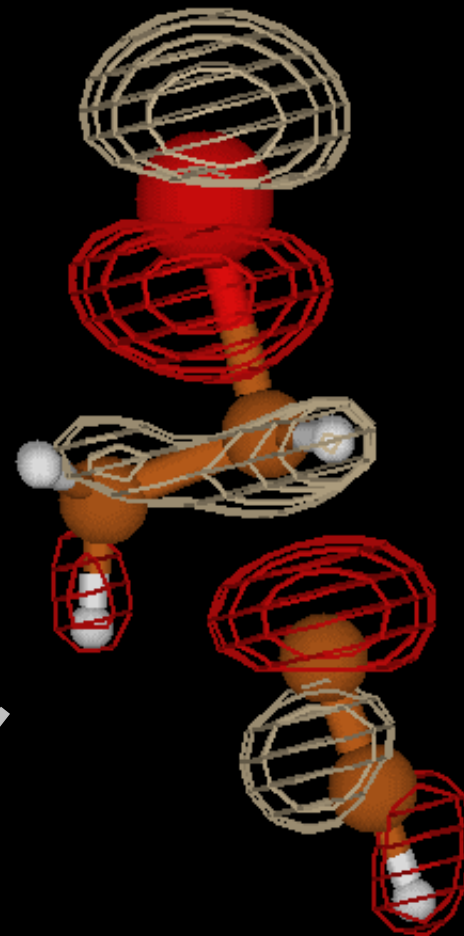
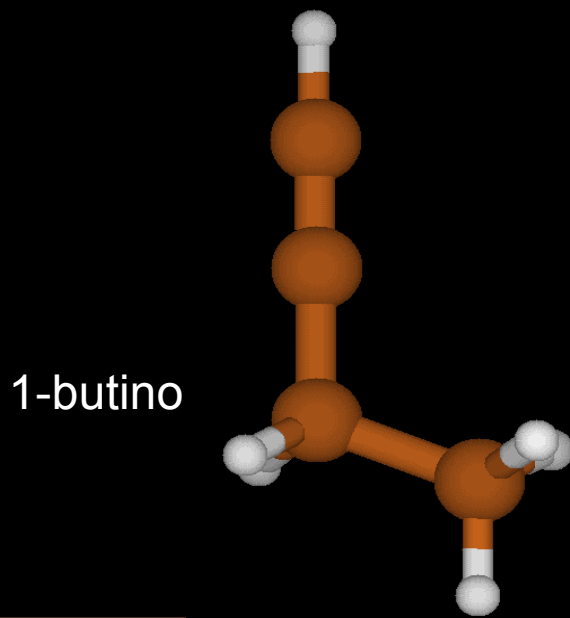
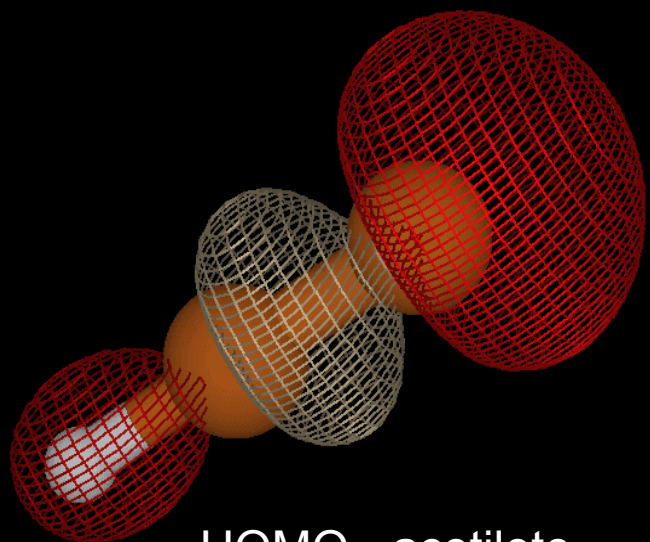
HOMO – estado de transição



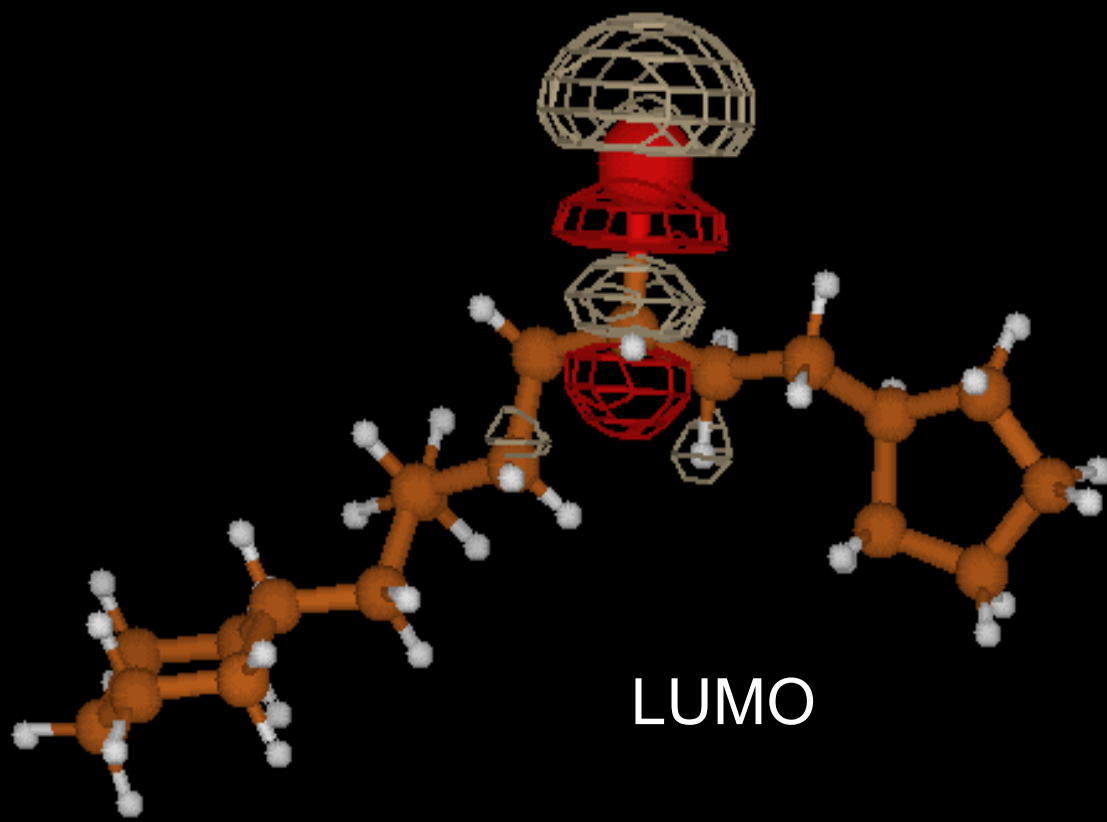
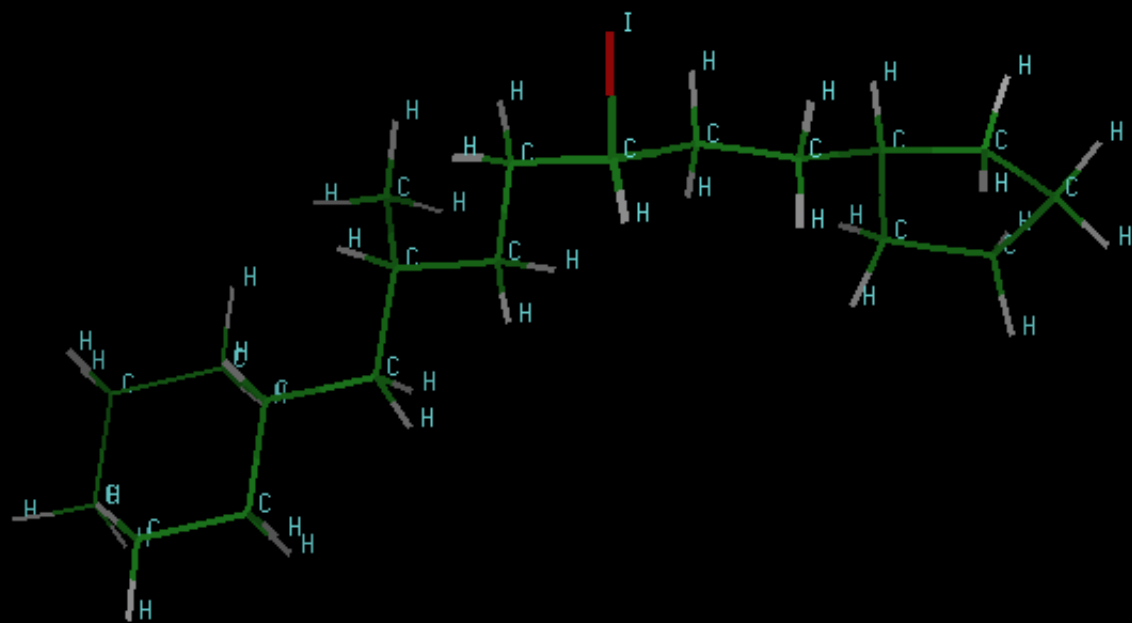
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S_N2 – Outros exemplos

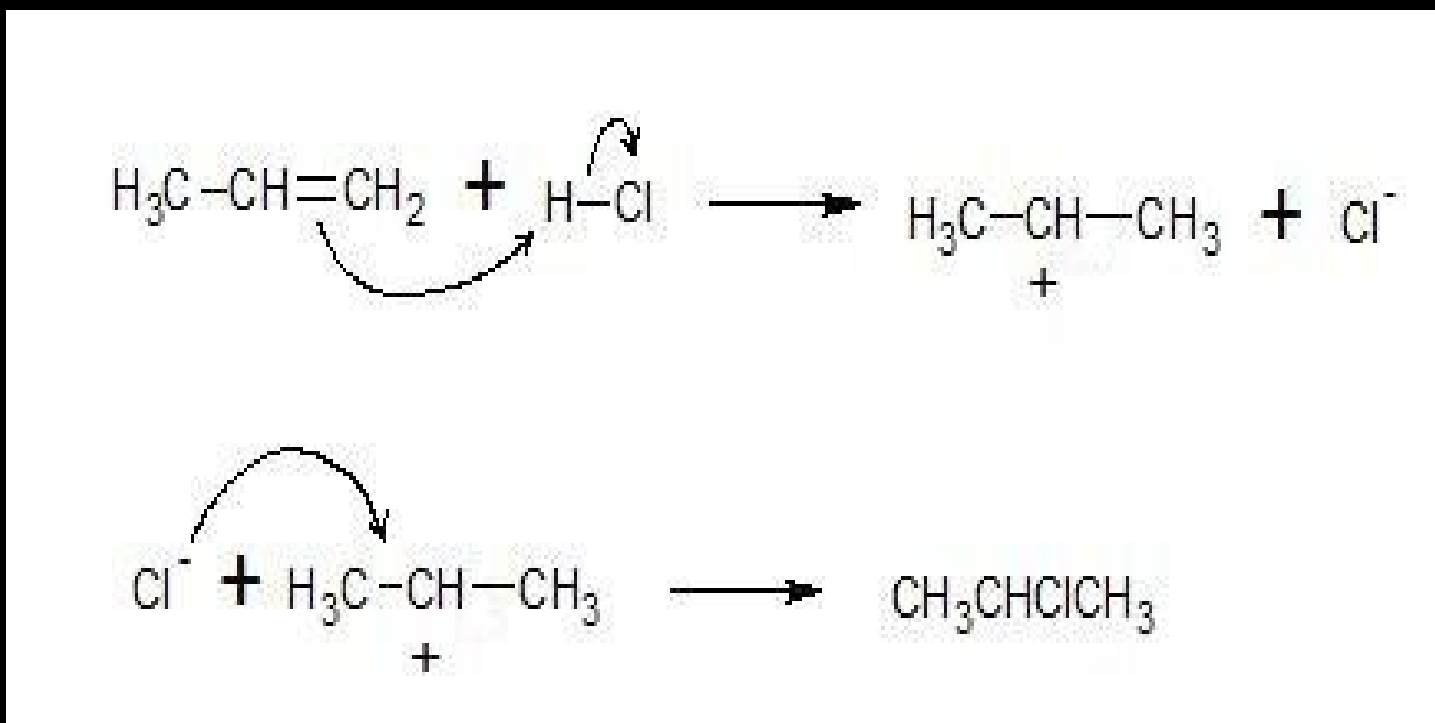


S_N2 – Outros exemplos



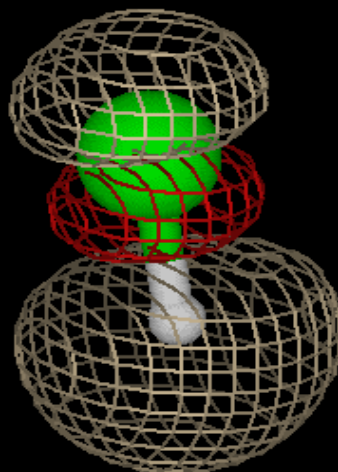
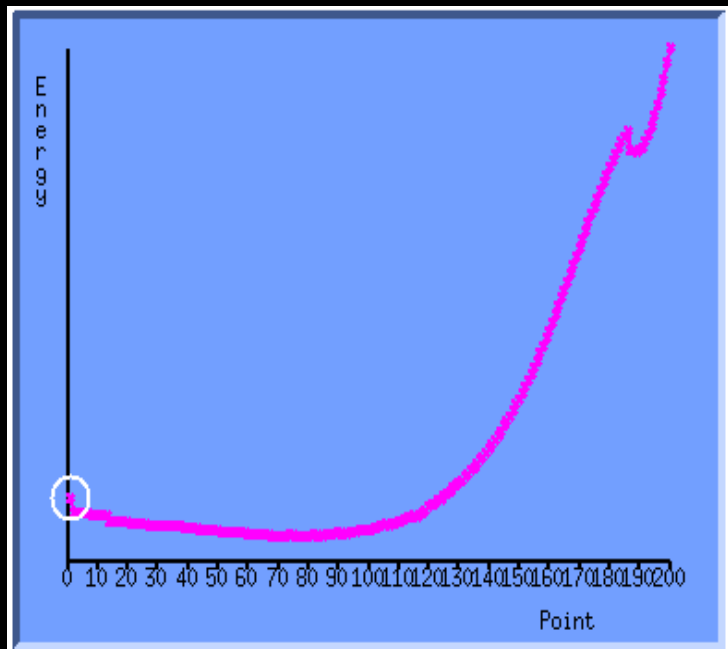
Adição em alcenos

- Reação:

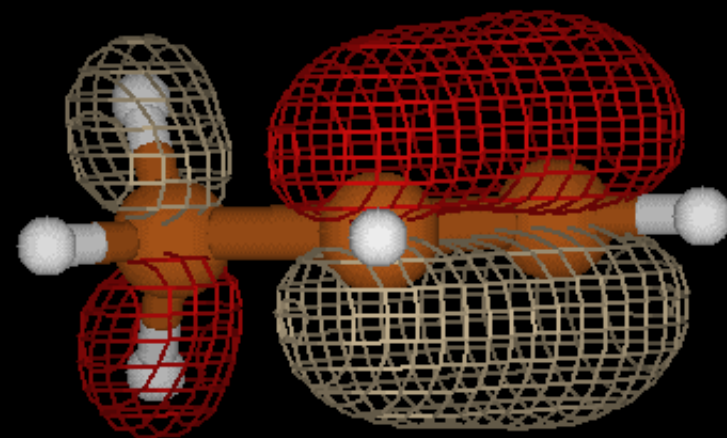


- Solvente: **Água, H₂O, EPS = 80**

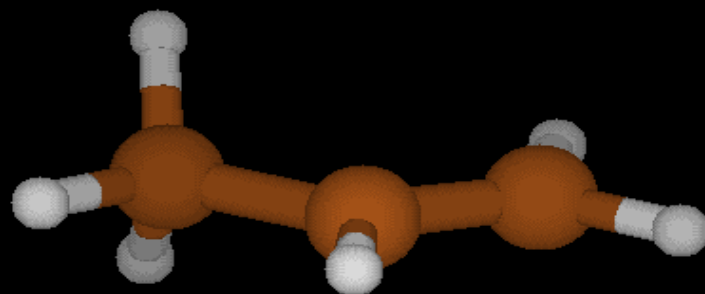
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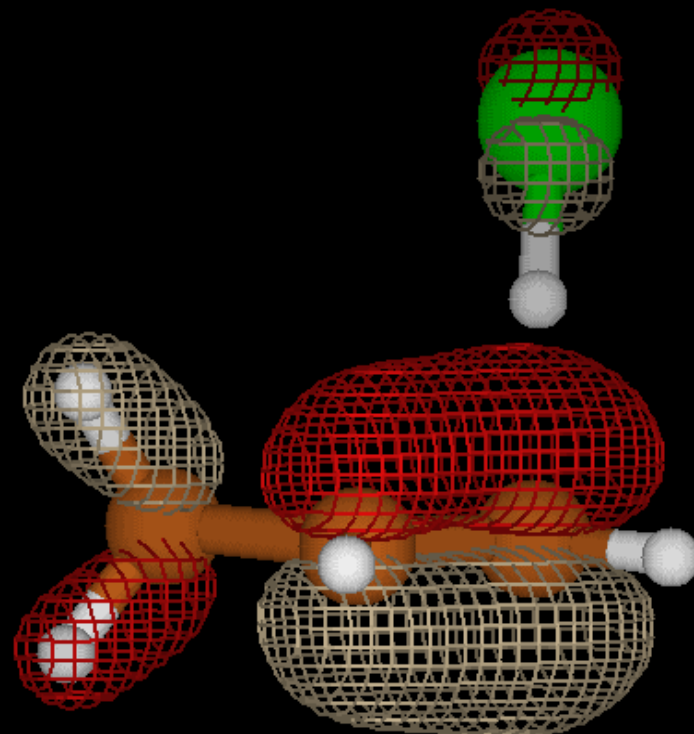
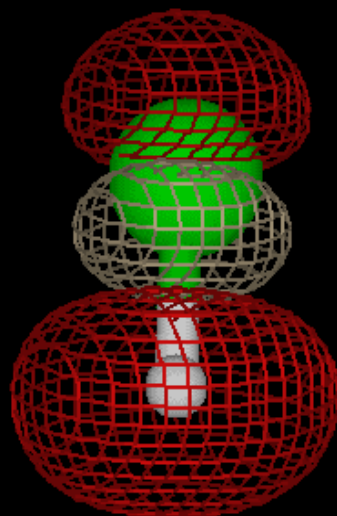
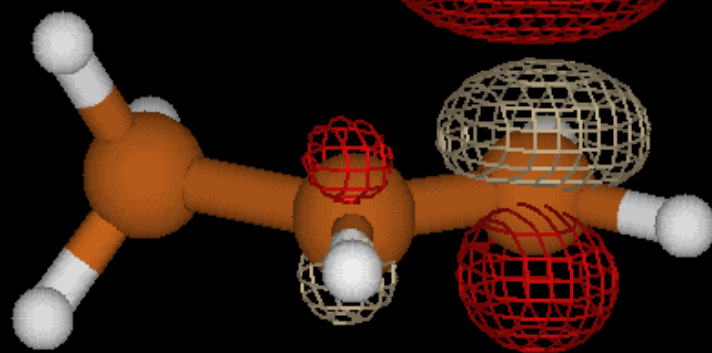
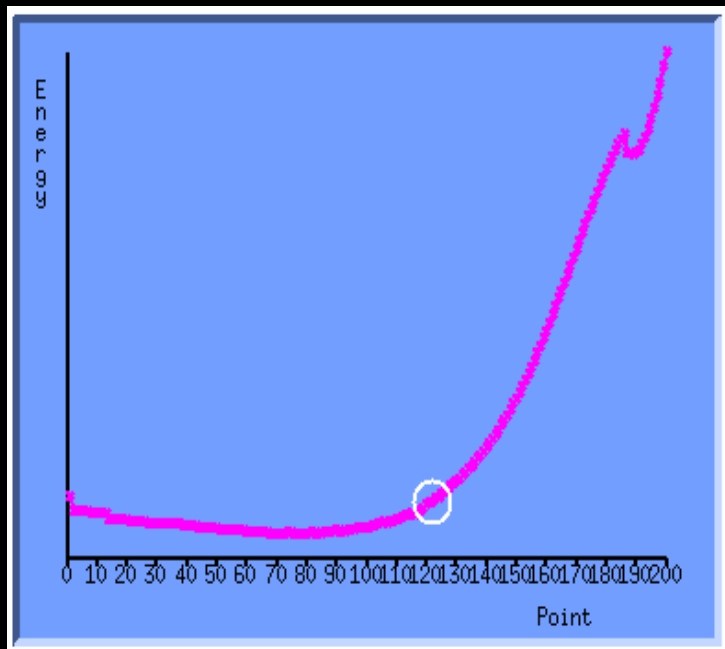
HOMO



LUMO



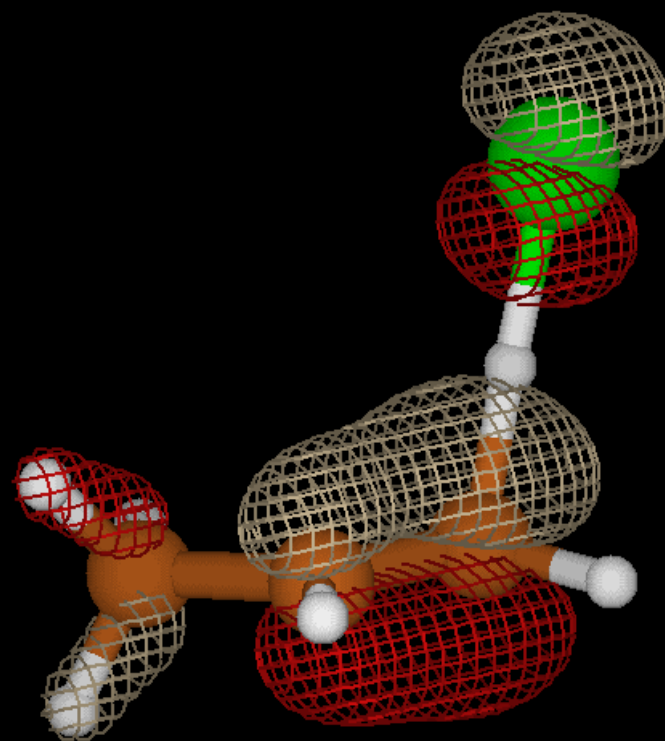
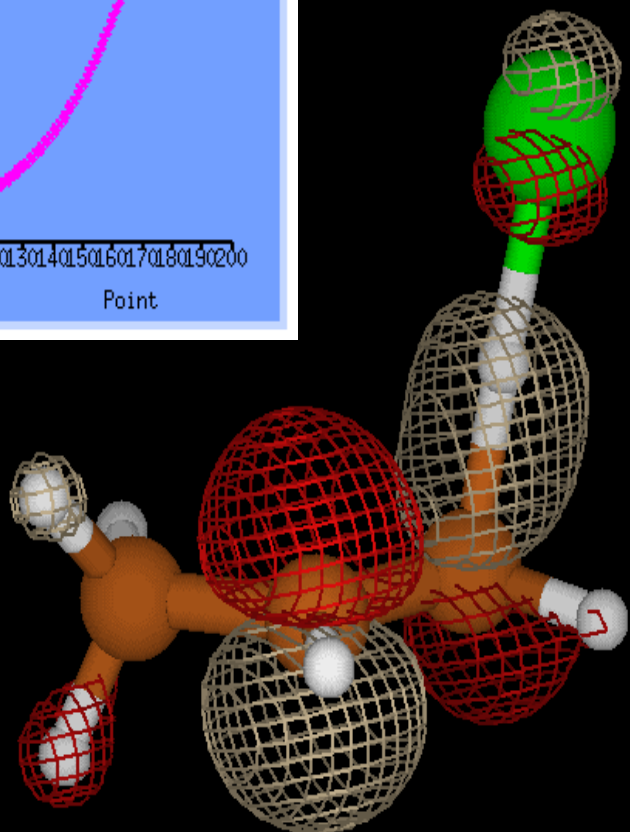
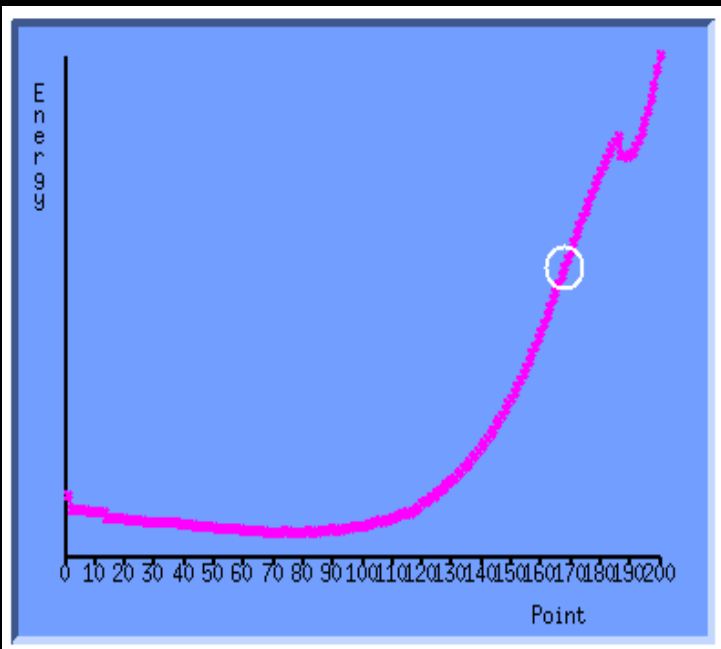
Adição em alcenos



HOMO

LUMO

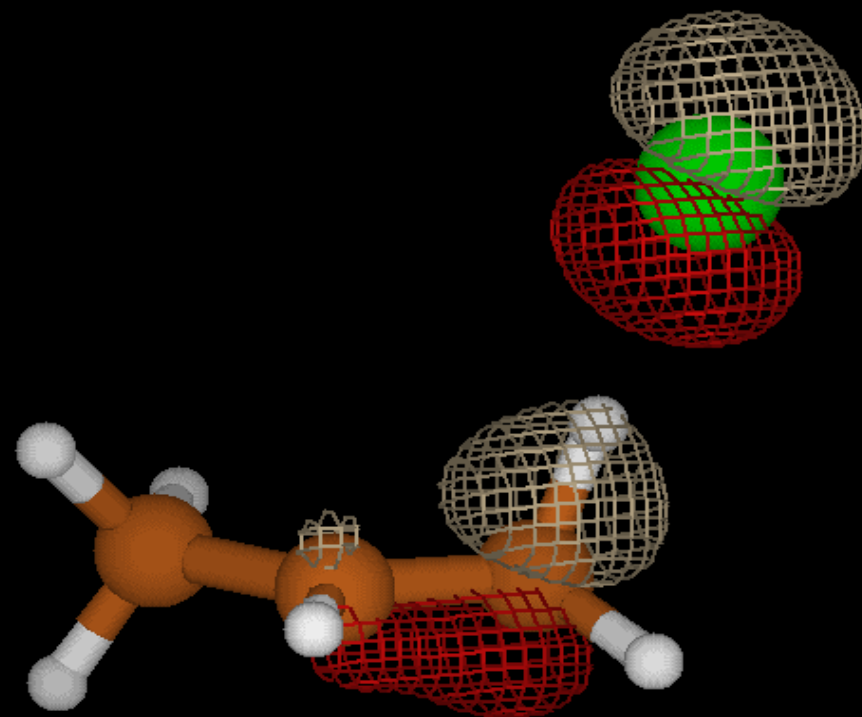
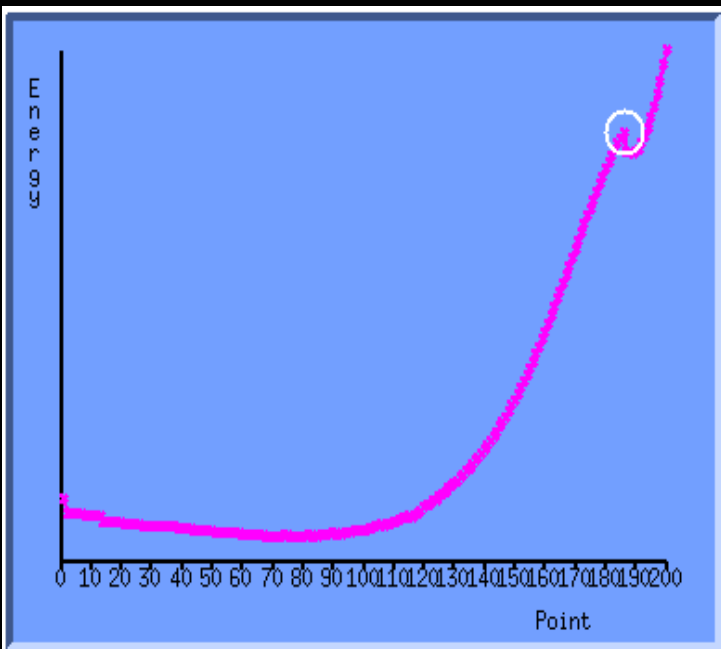
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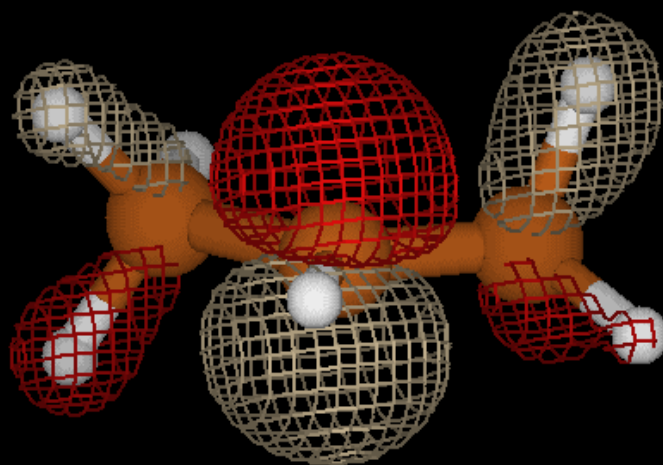
HOMO

LUMO

Adição em alcenos

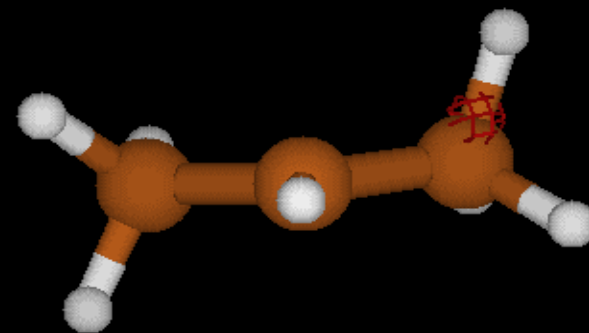
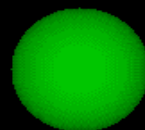
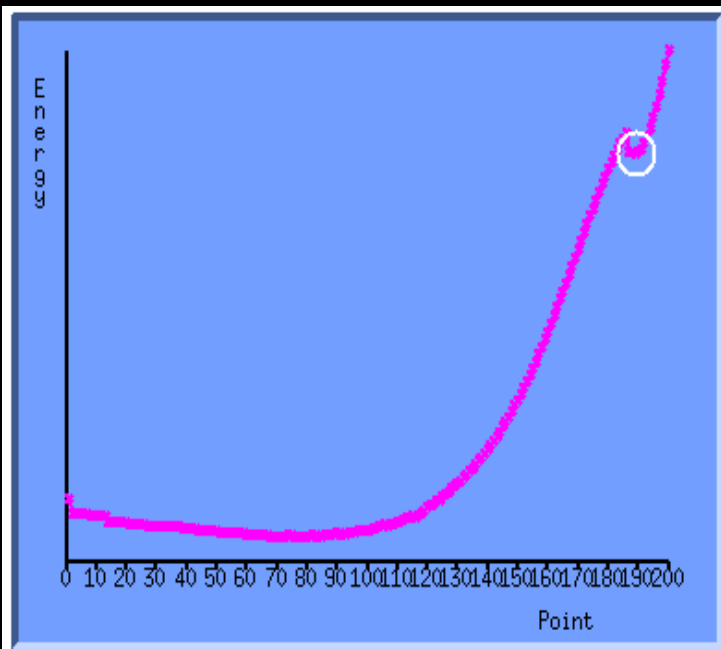


HOMO

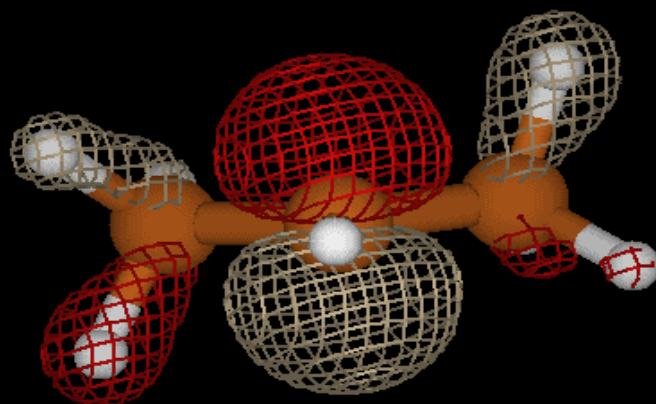


LUMO

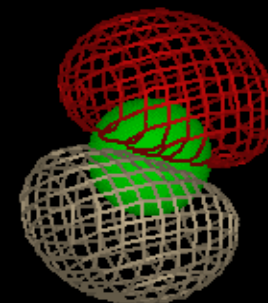
Adição em alcenos



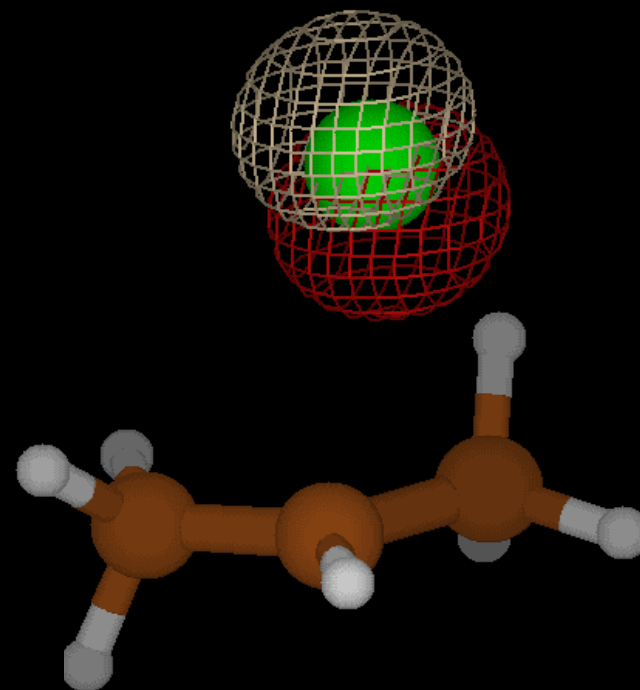
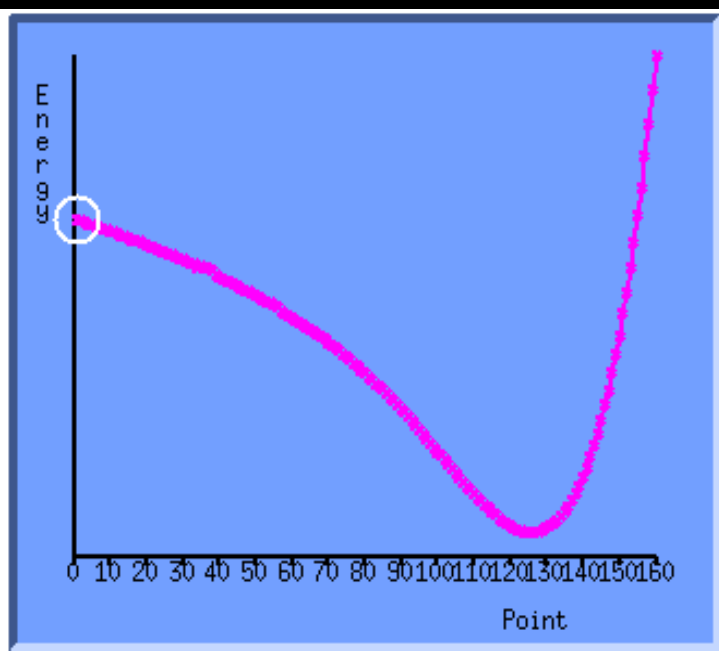
HOMO



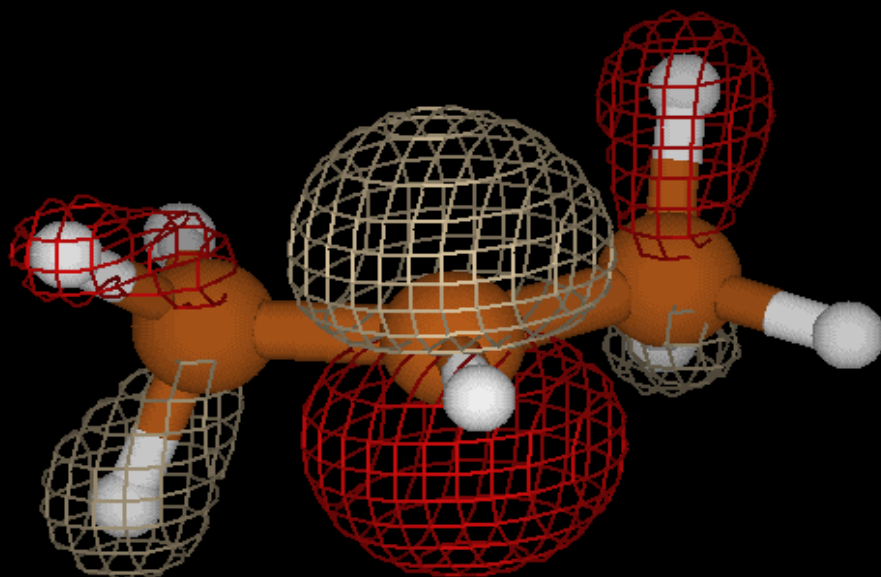
LUMO



Adição em alcenos



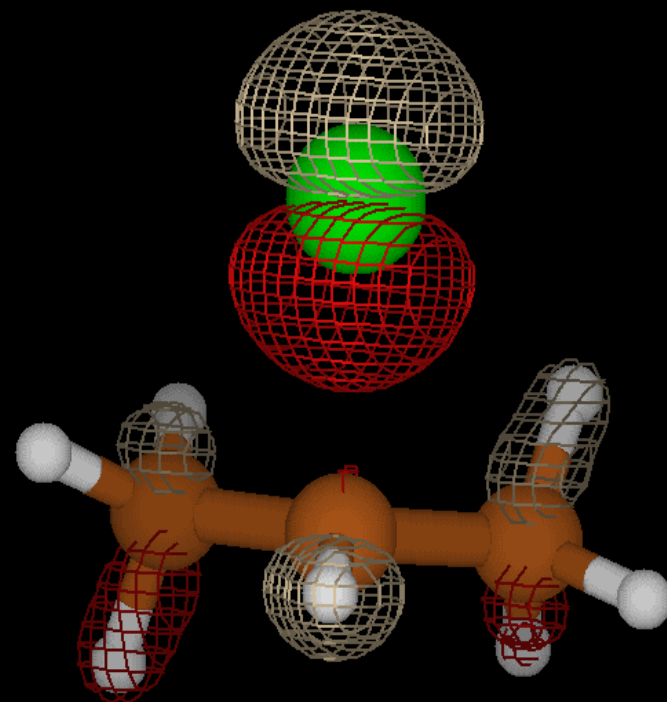
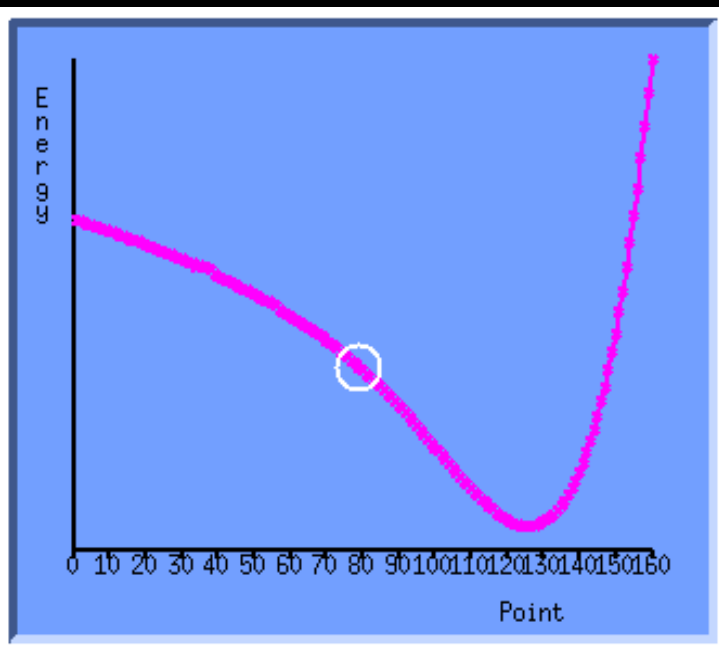
HOMO



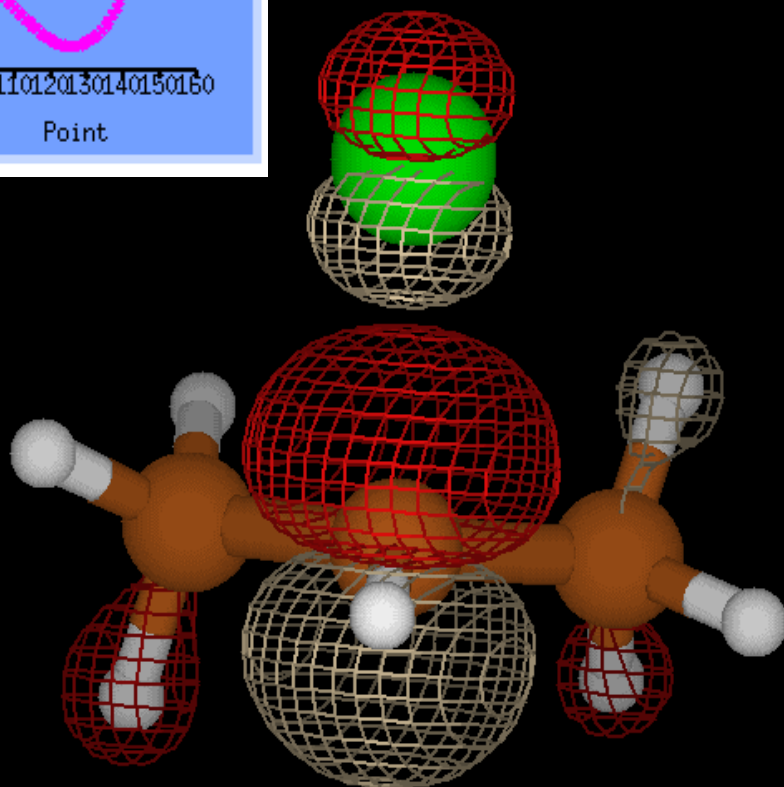
LUMO



Adição em alcenos

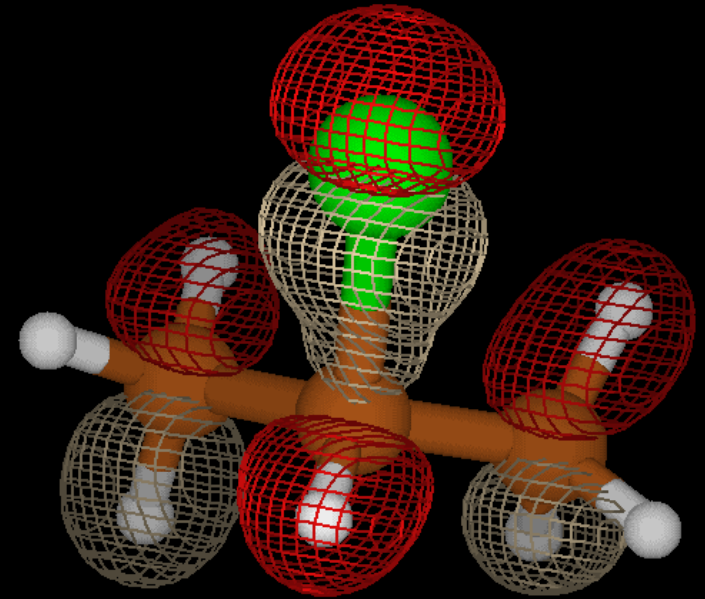
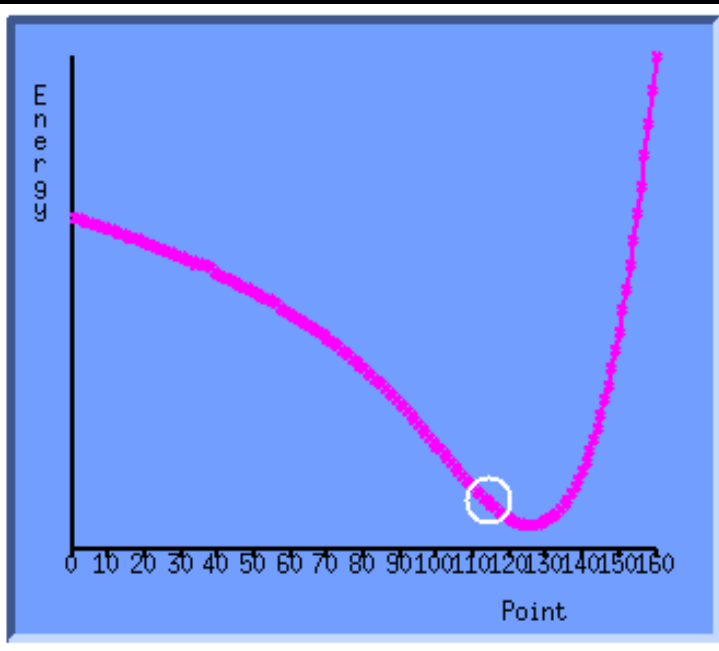


HOMO

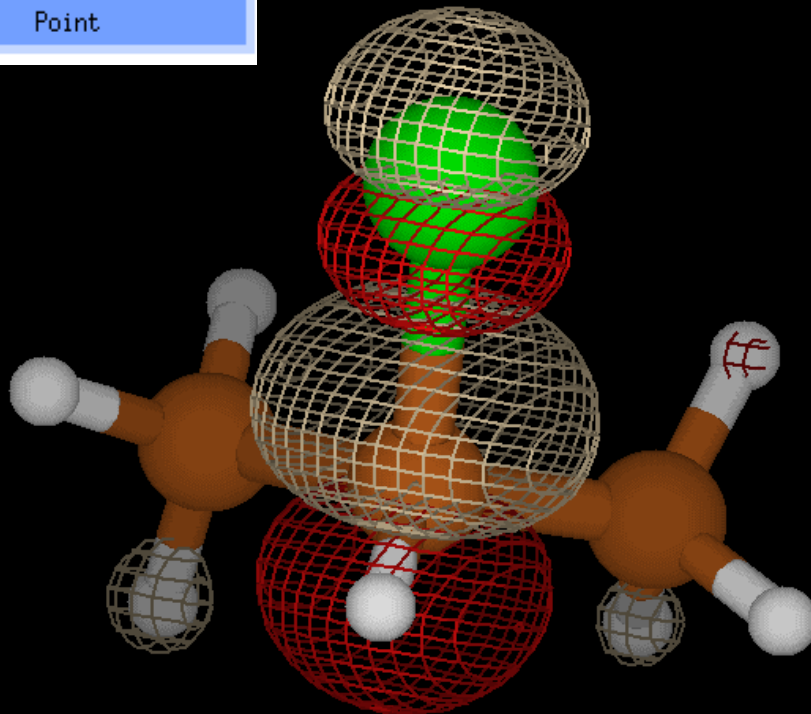


LUMO

Adição em alcenos

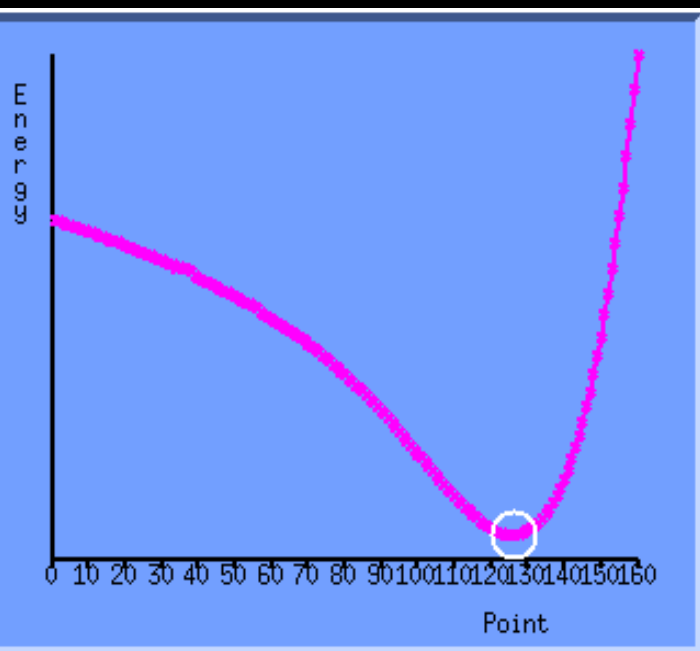


HOMO

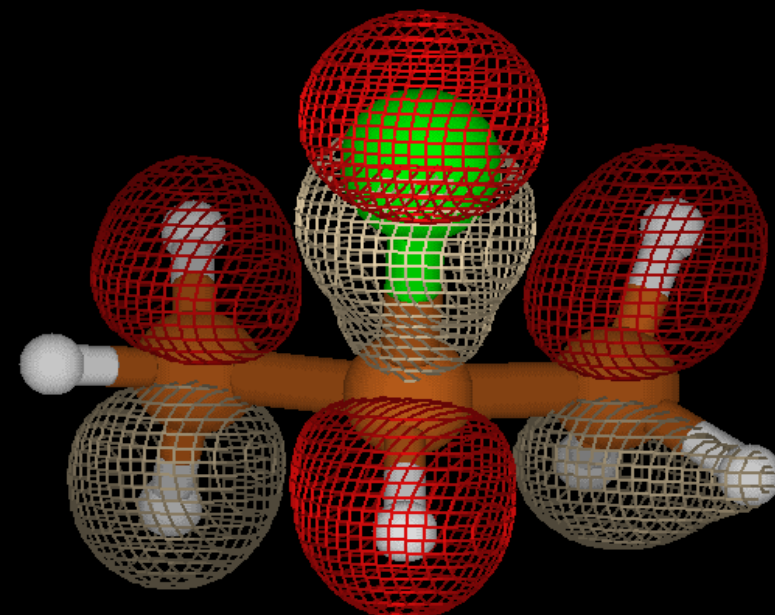
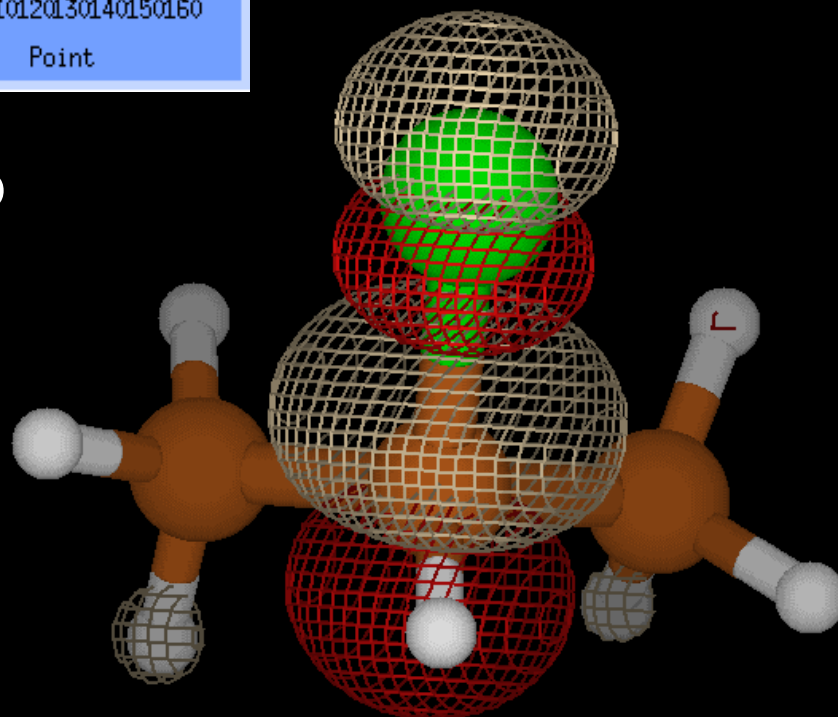


LUMO

Adição em alcenos



Produto

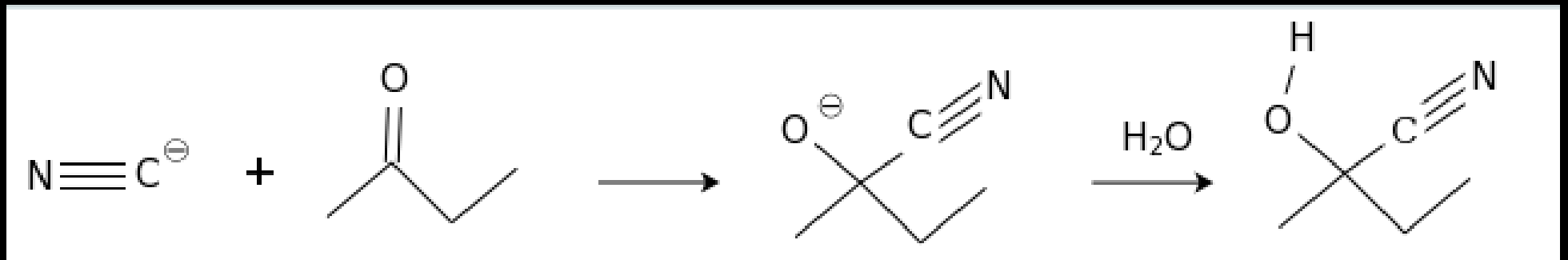


HOMO

LUMO -> Pode sofrer
uma reação S_N2 !

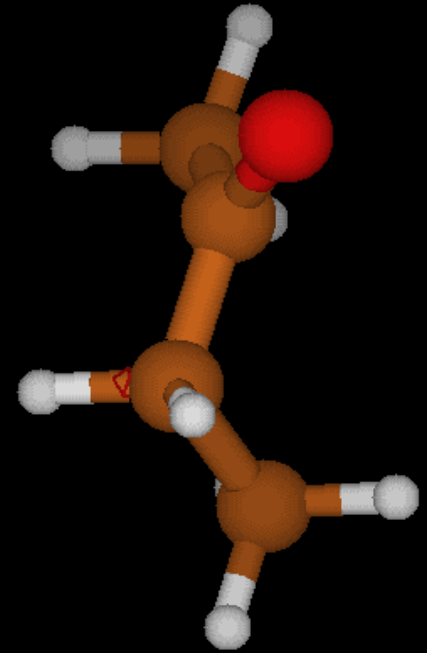
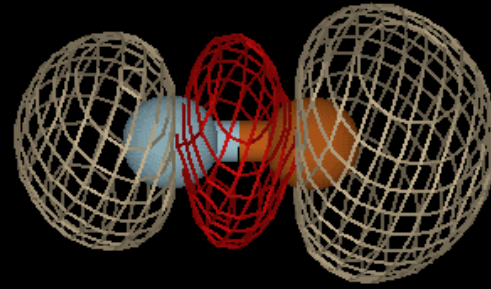
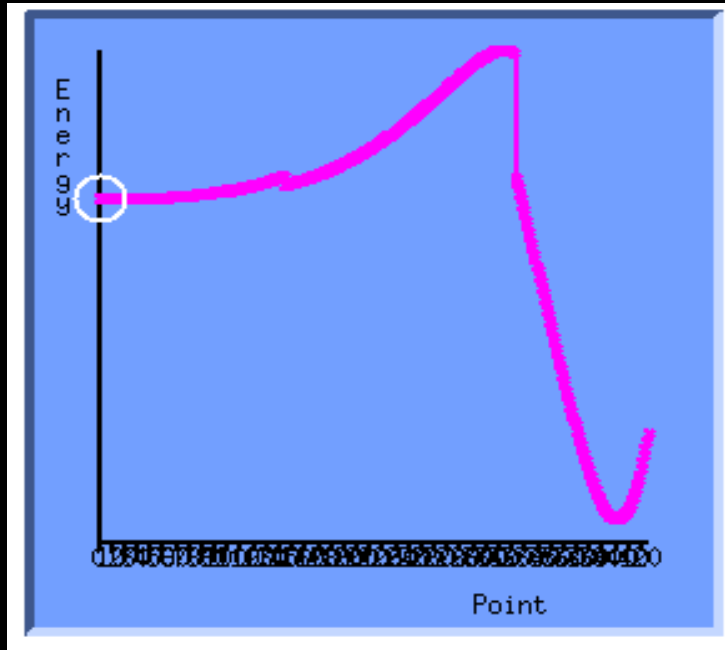
Adição na carbonila

- Reação:

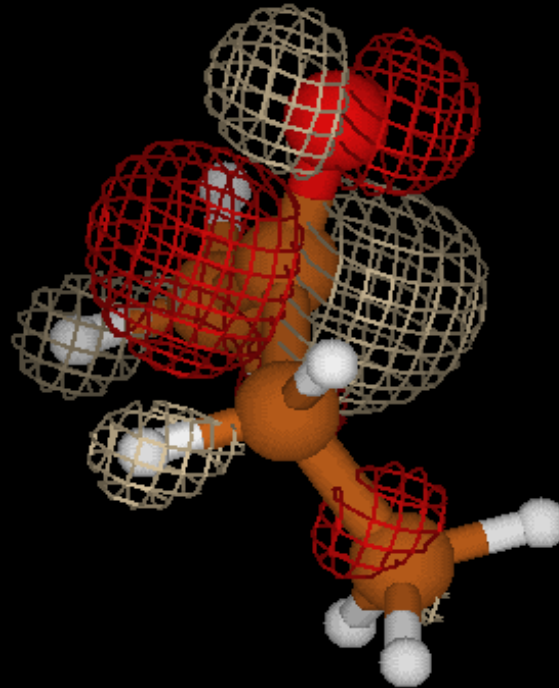
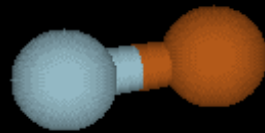


- Solvente: **Água, H_2O , EPS = 80**

Adição na carbonila



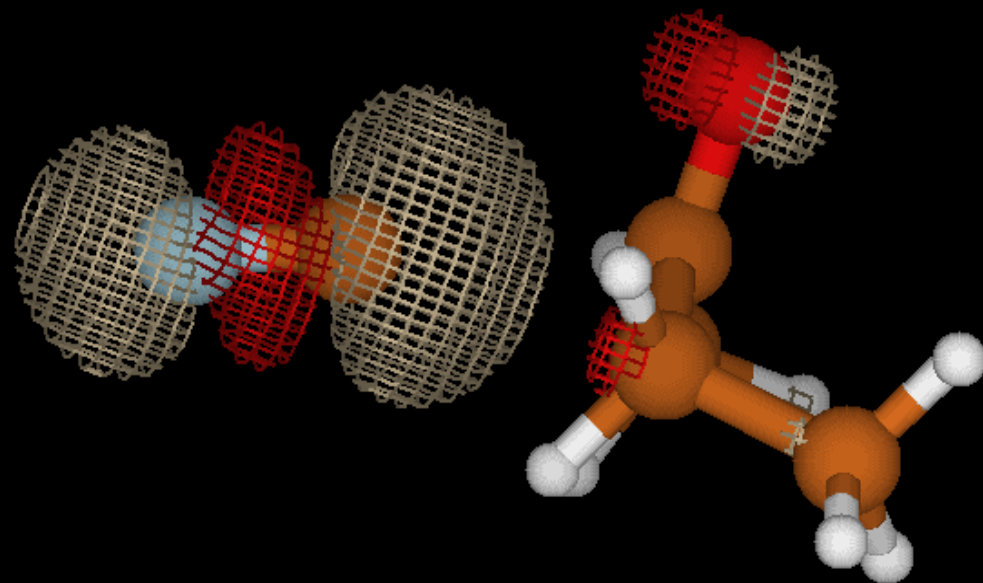
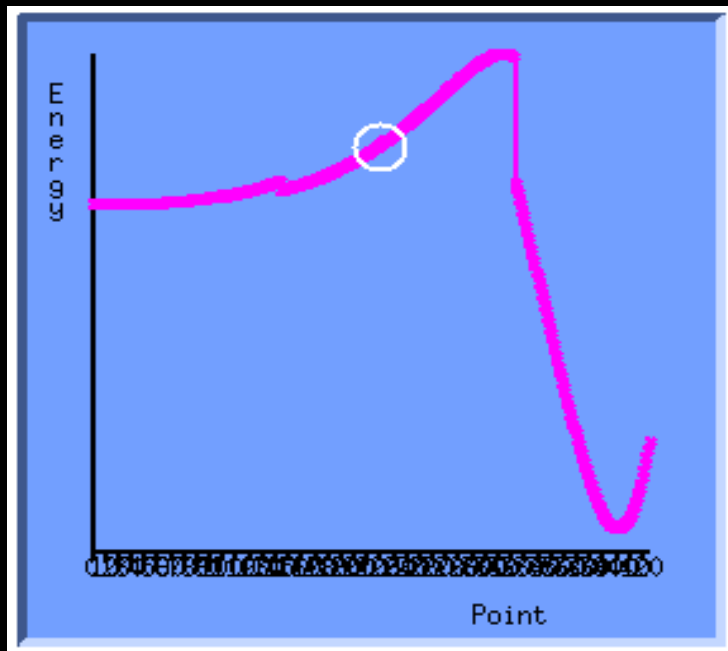
HOMO



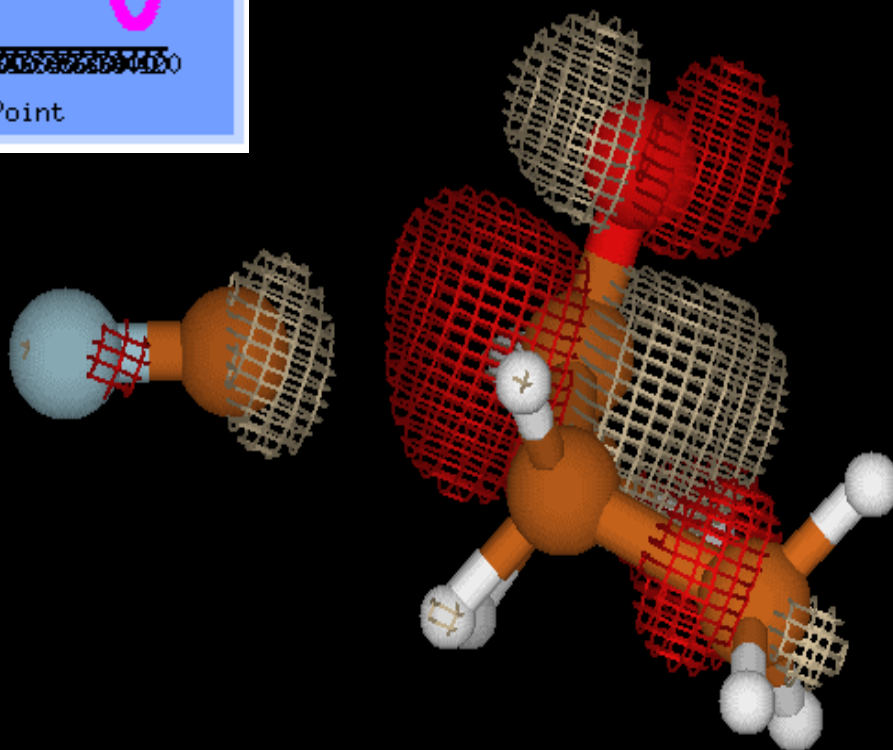
LUMO



Adição na carbonila



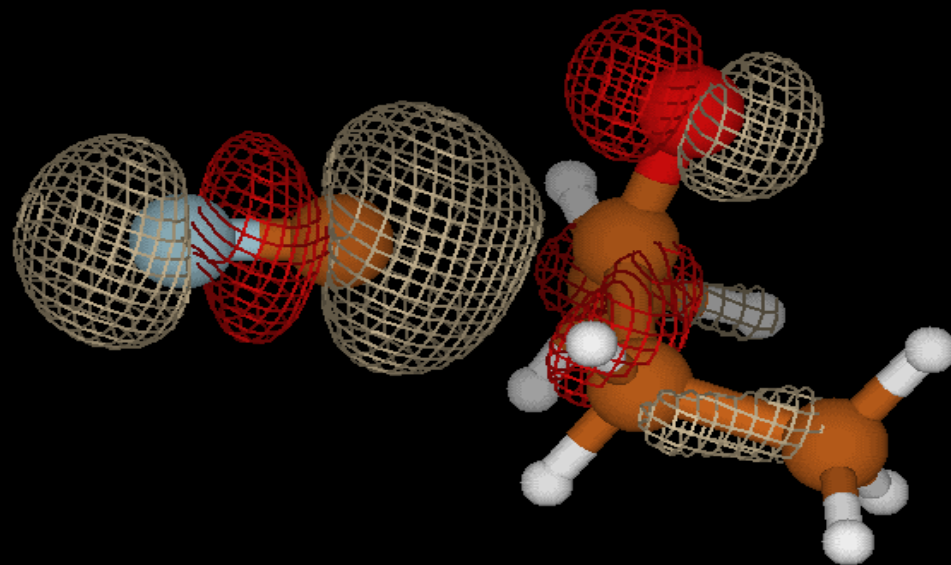
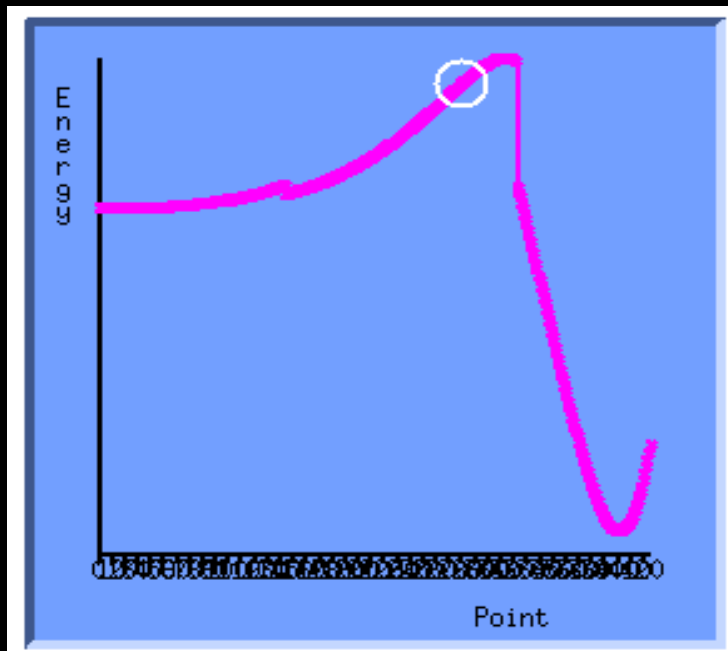
HOMO



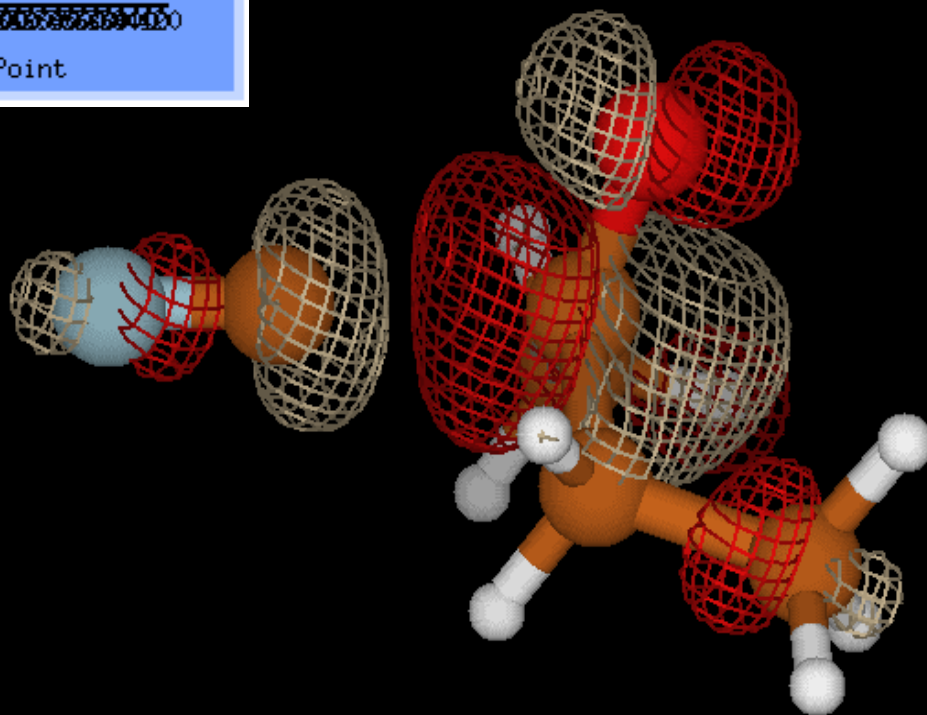
LUMO



Adição na carbonila



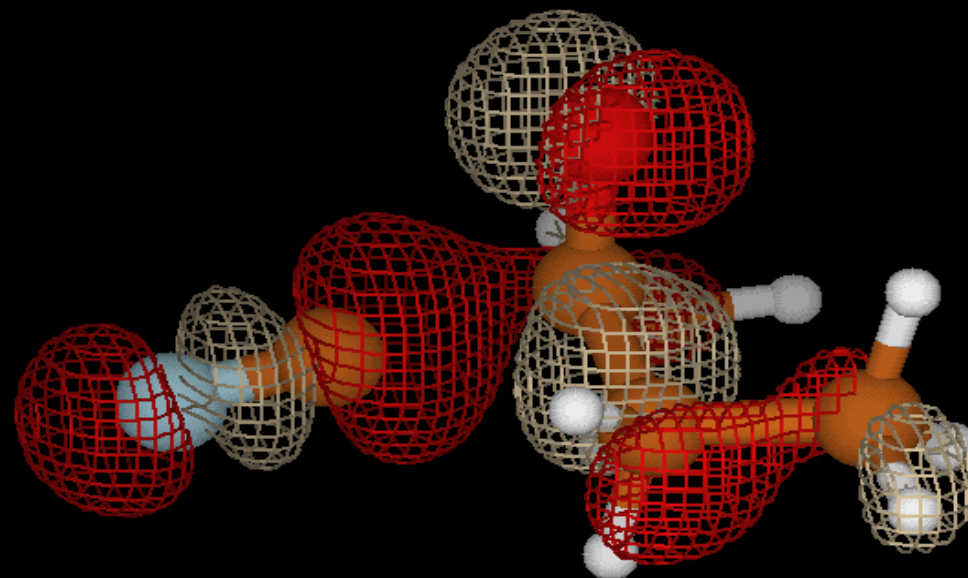
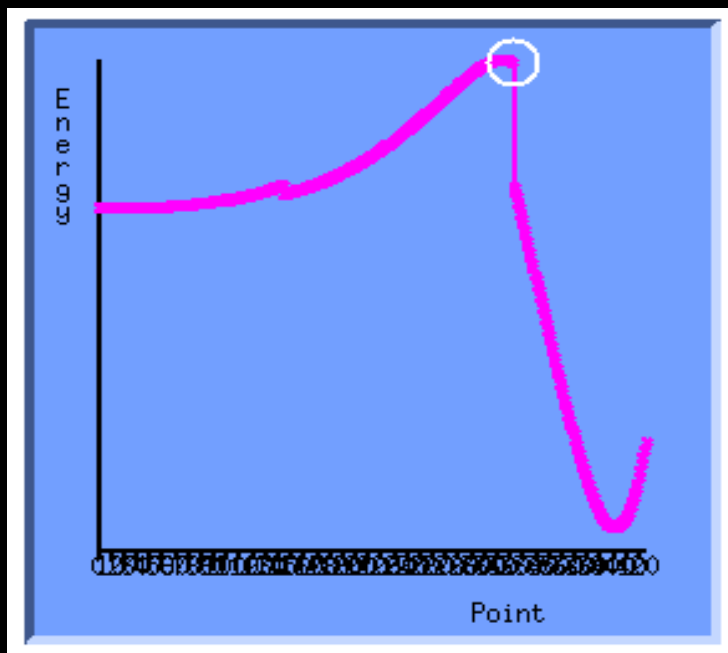
HOMO



LUMO

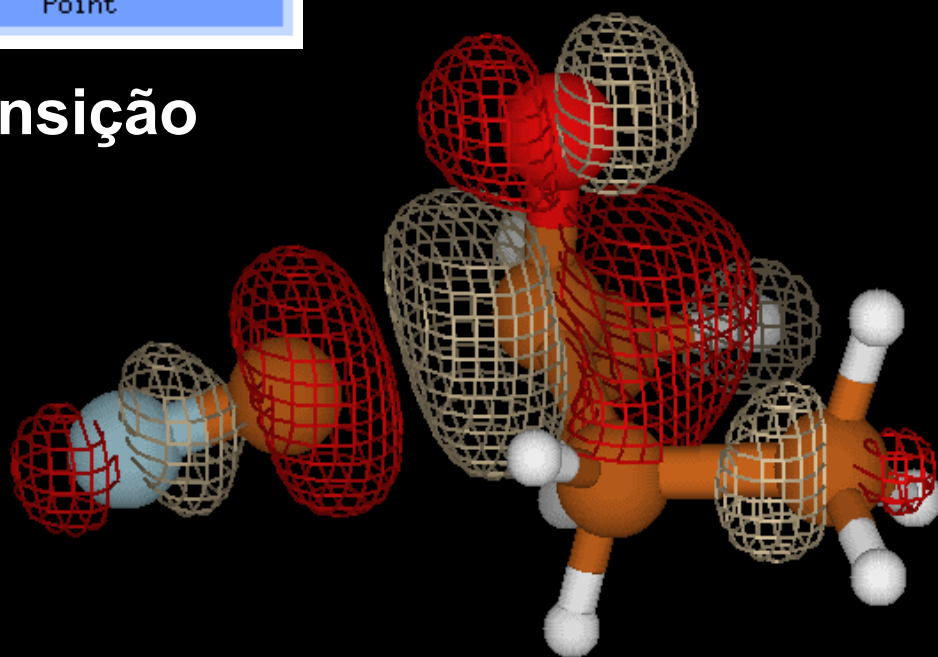


Adição na carbonila



HOMO

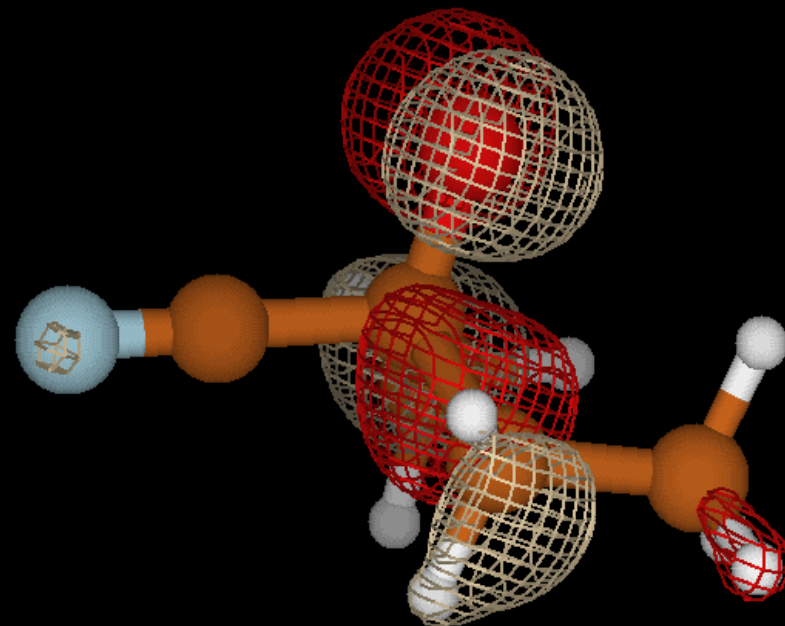
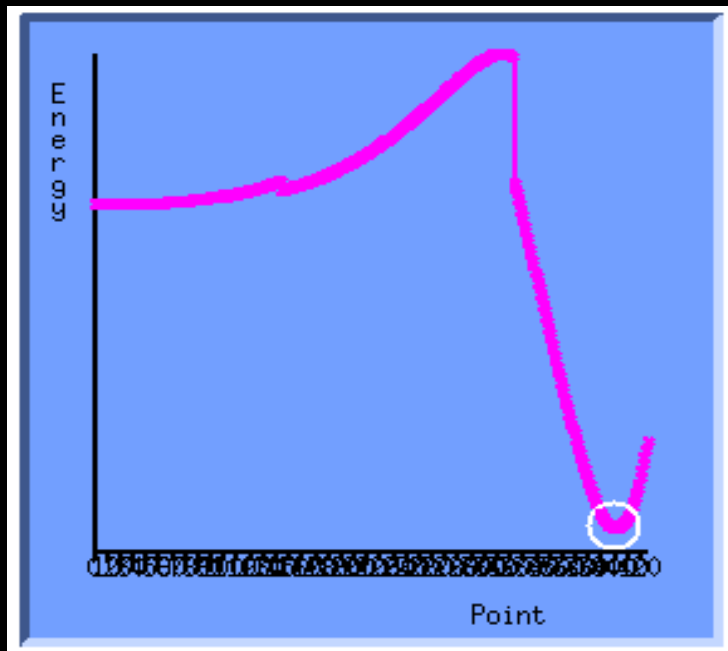
Estado de transição



LUMO

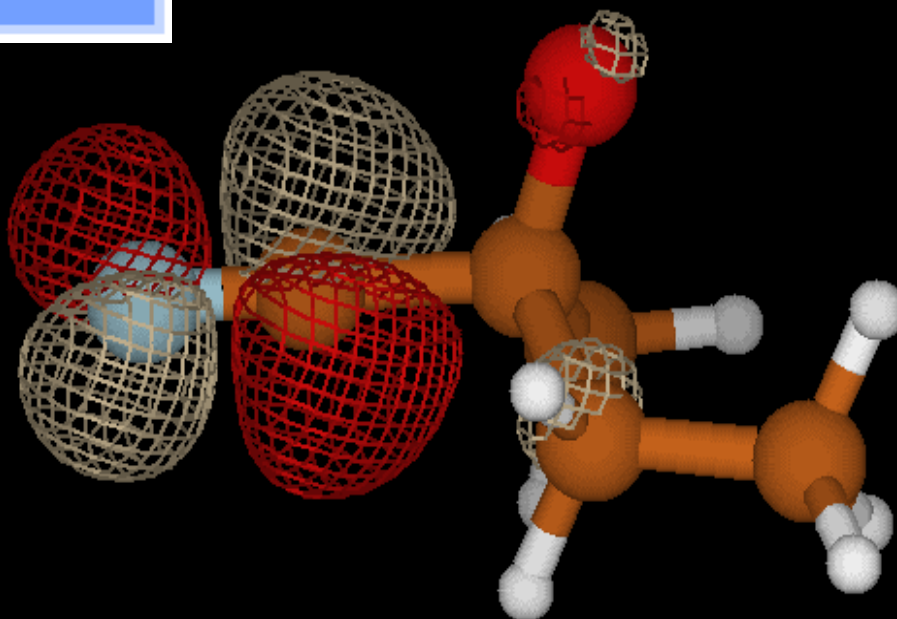


Adição na carbonila



HOMO

É protonado para formar o produto

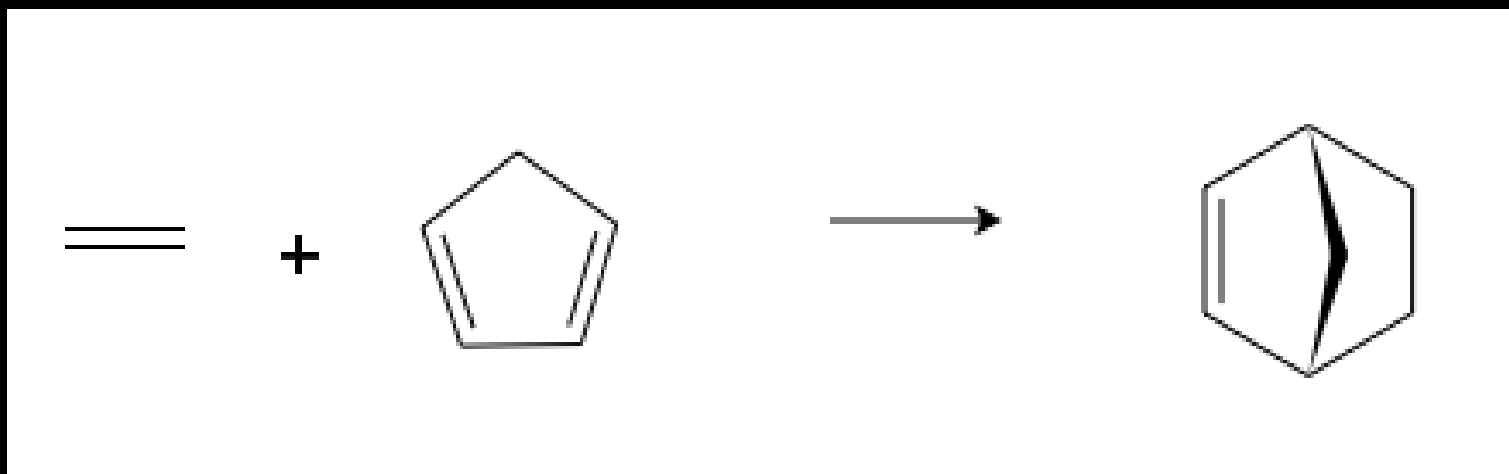


LUMO



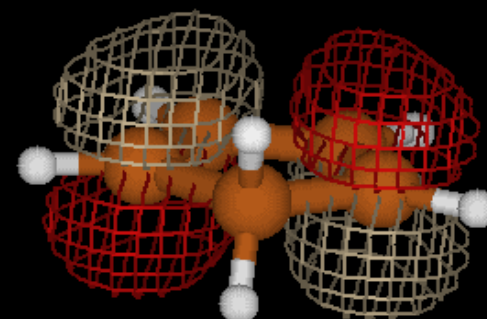
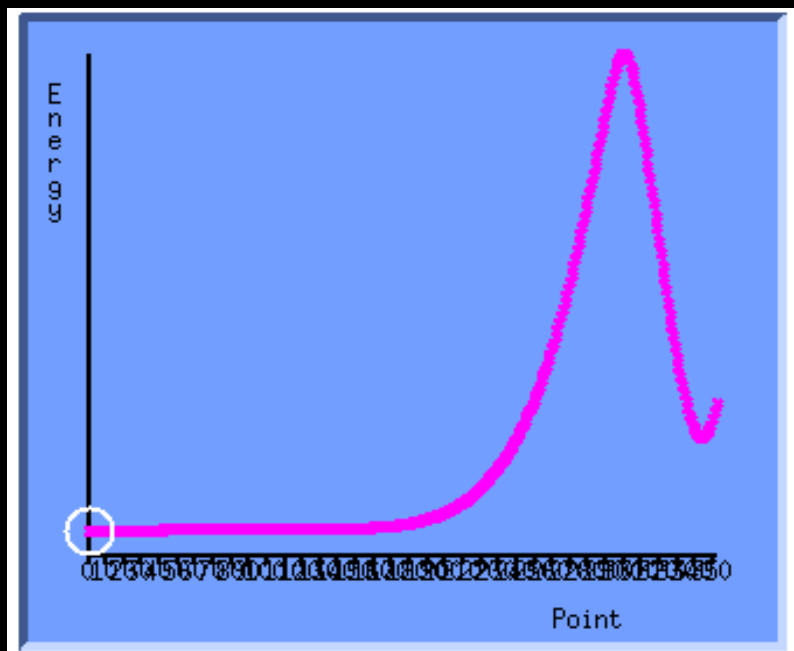
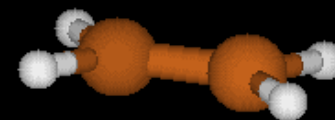
Reação de Diels-Alder

- Reação:

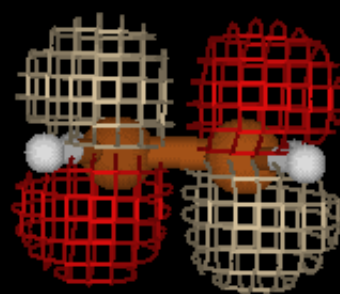


- Solvente: Éter etílico, $(\text{CH}_3\text{CH}_2)_2\text{O}$, EPS = 4
-
-

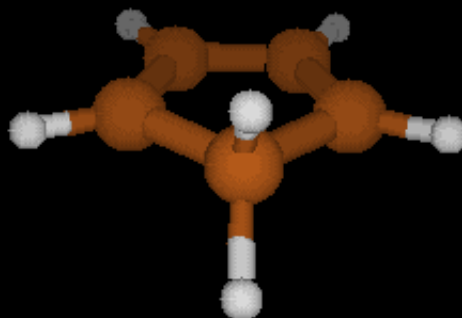
Reação de Diels-Alder



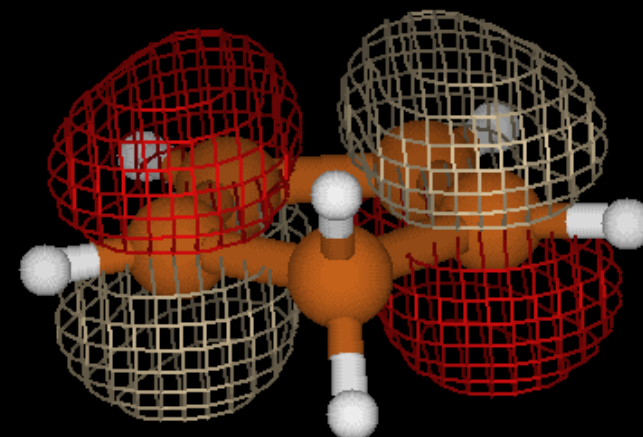
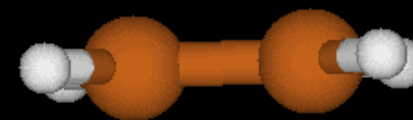
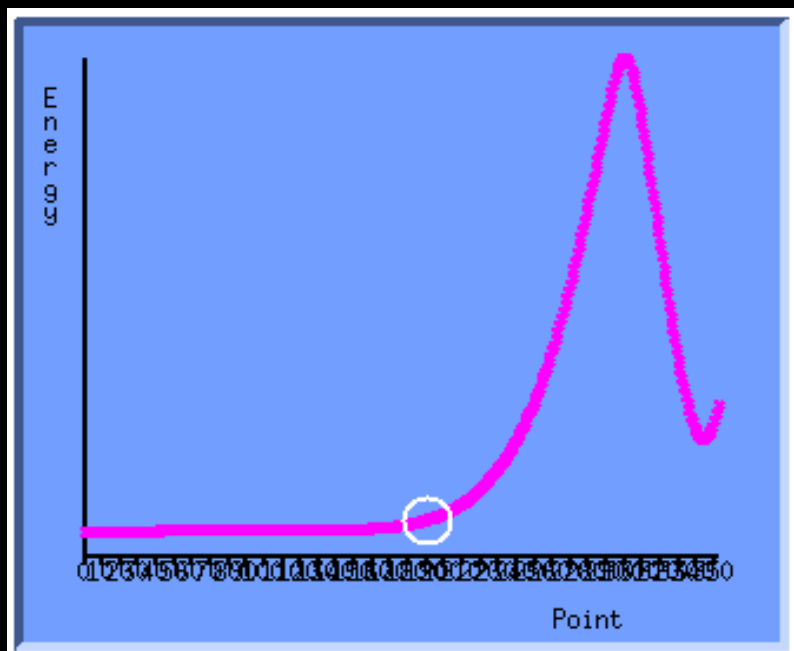
HOMO



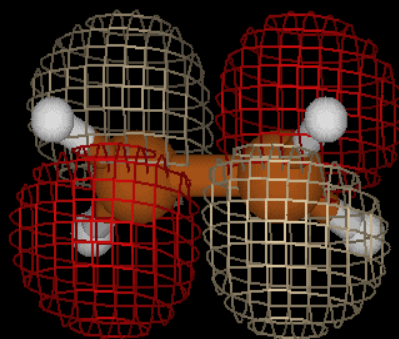
LUMO



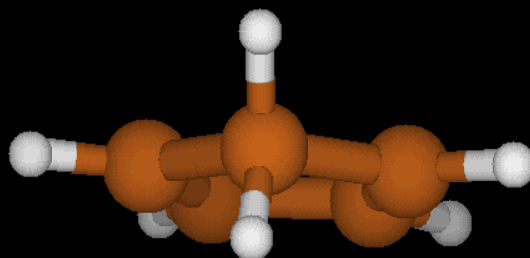
Reação de Diels-Alder



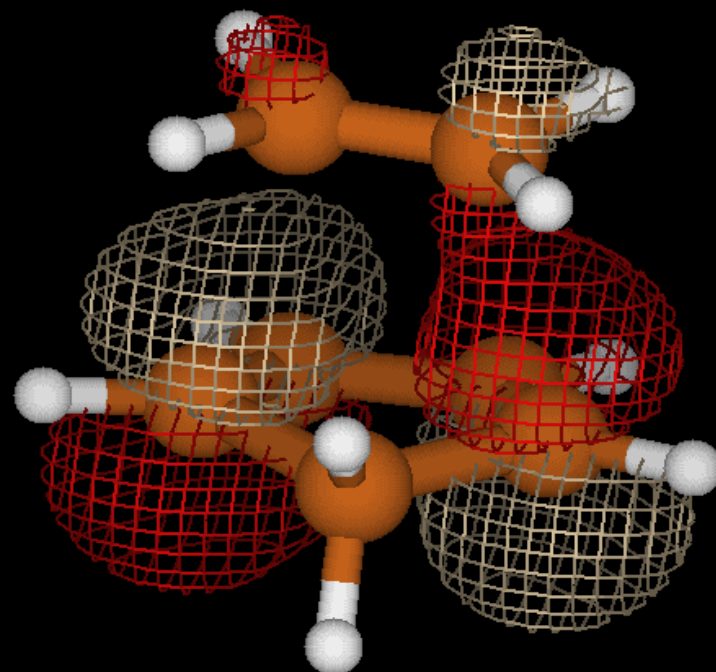
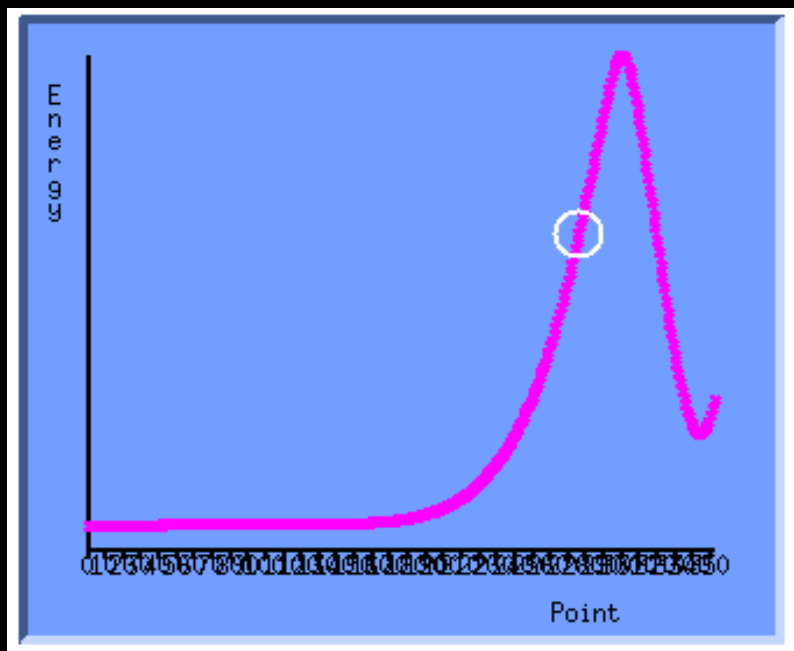
HOMO



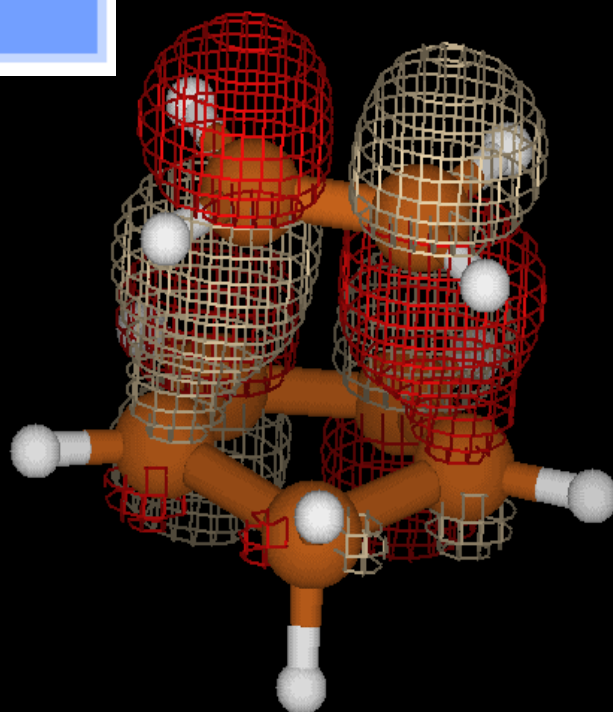
LUMO



Reação de Diels-Alder



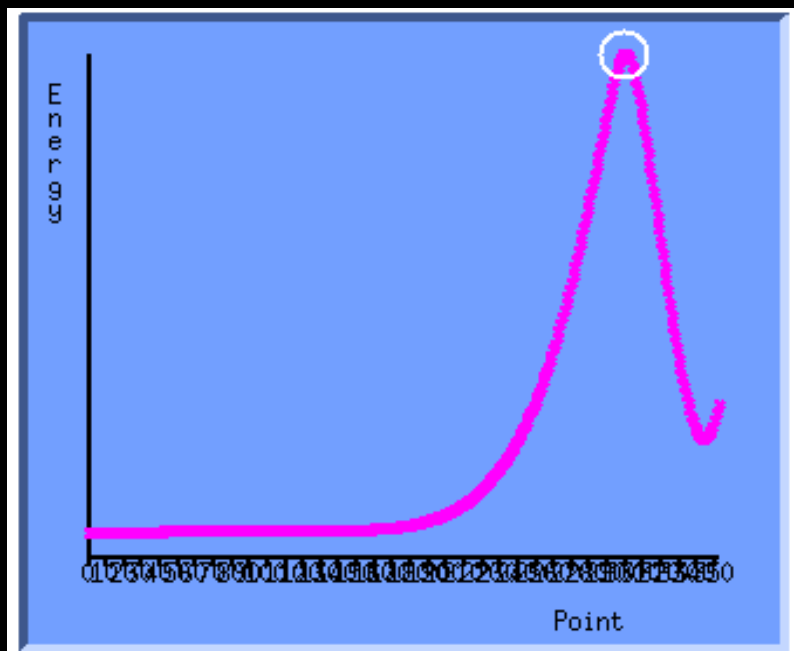
HOMO



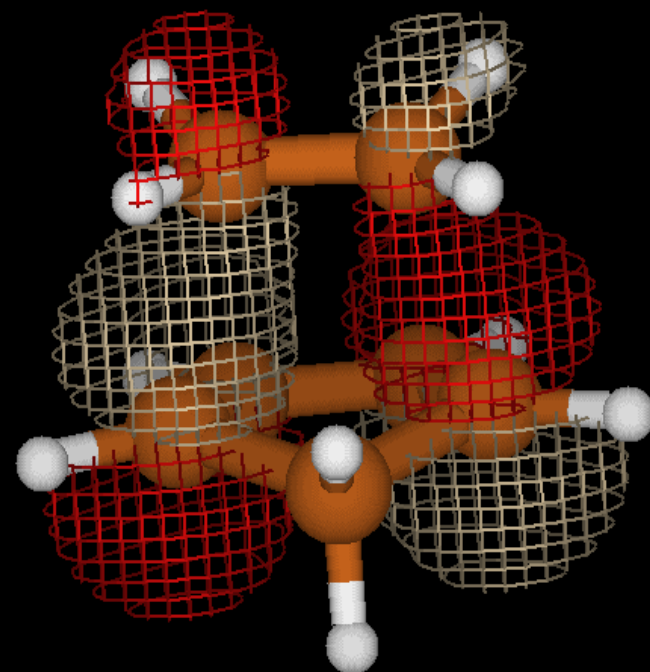
LUMO



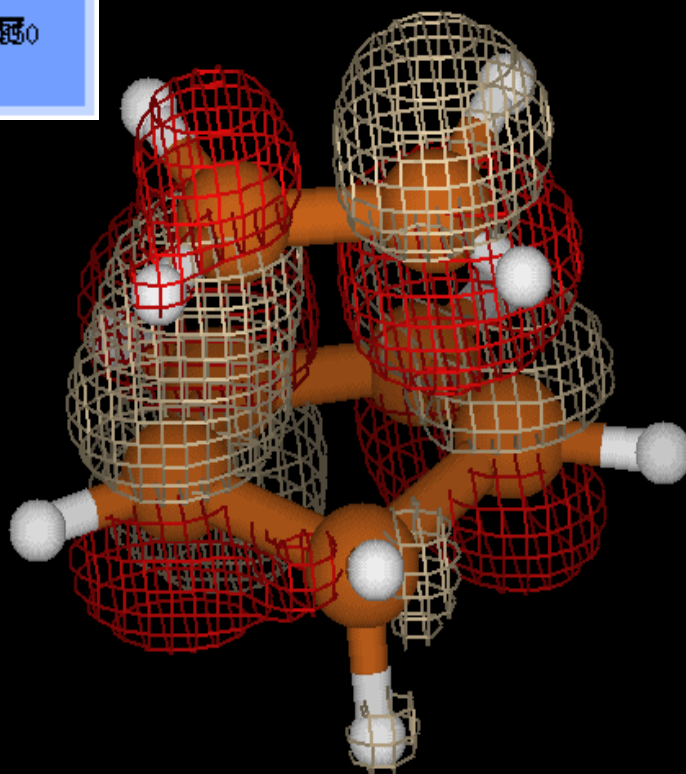
Reação de Diels-Alder



Estado de transição



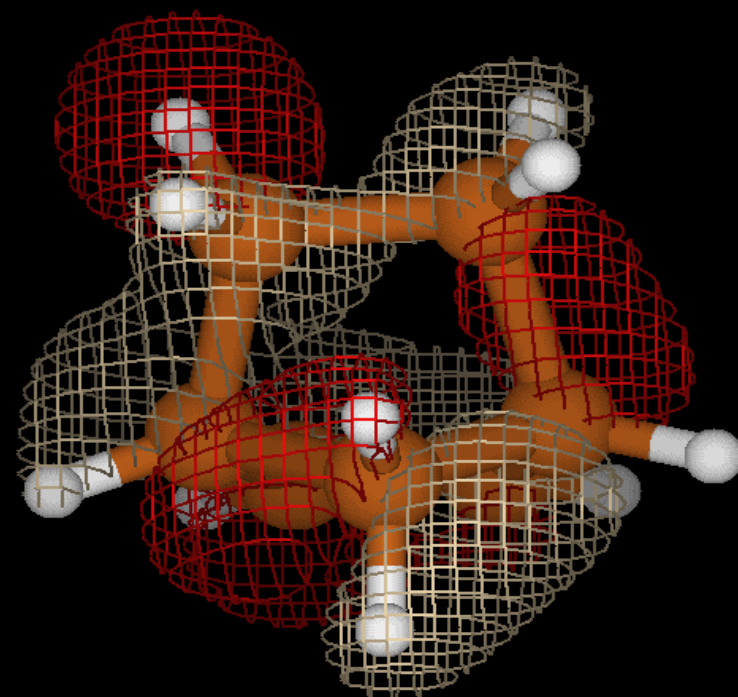
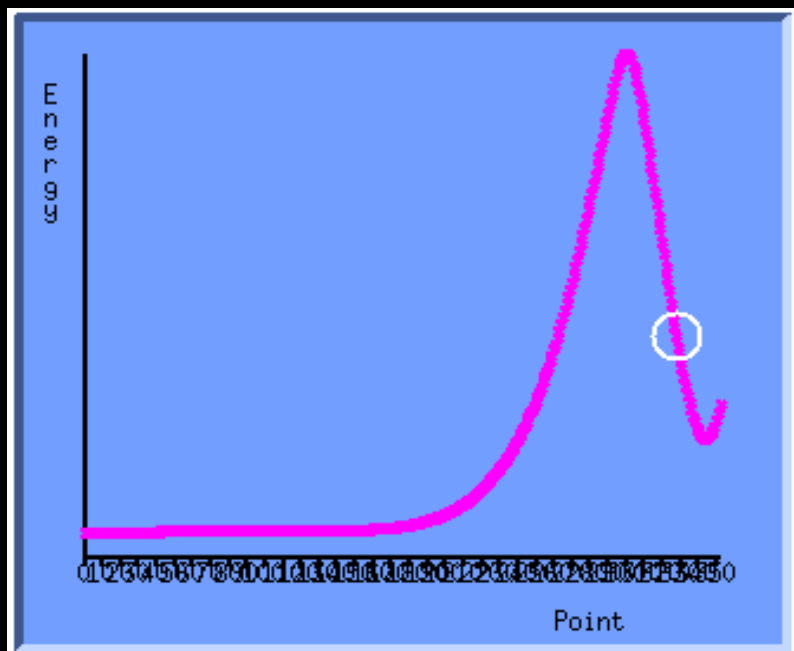
HOMO



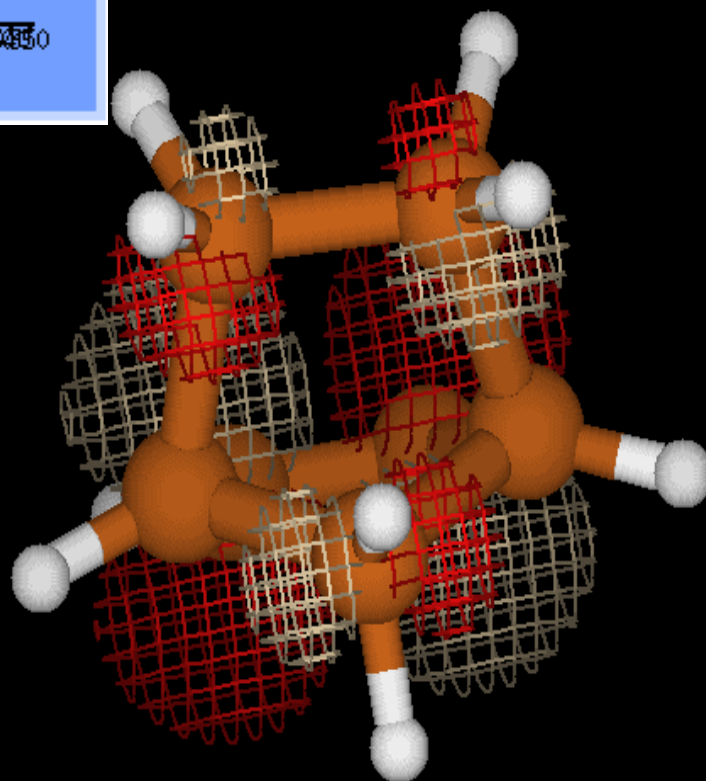
LUMO



Reação de Diels-Alder



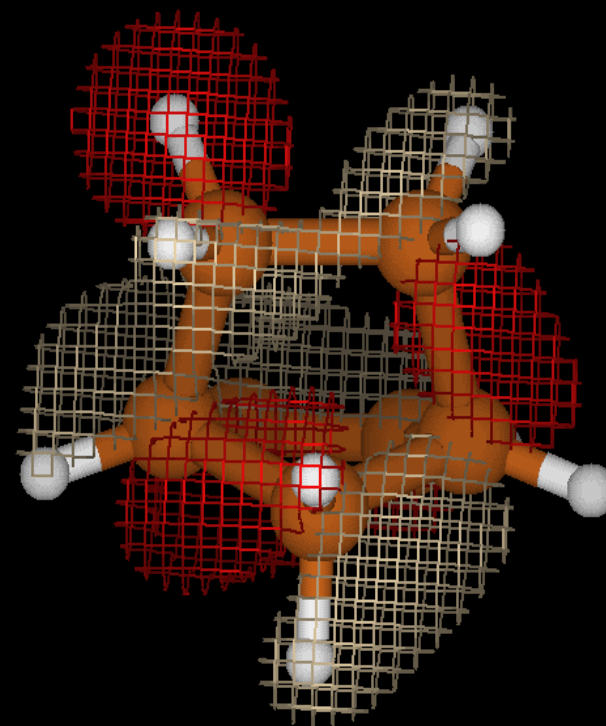
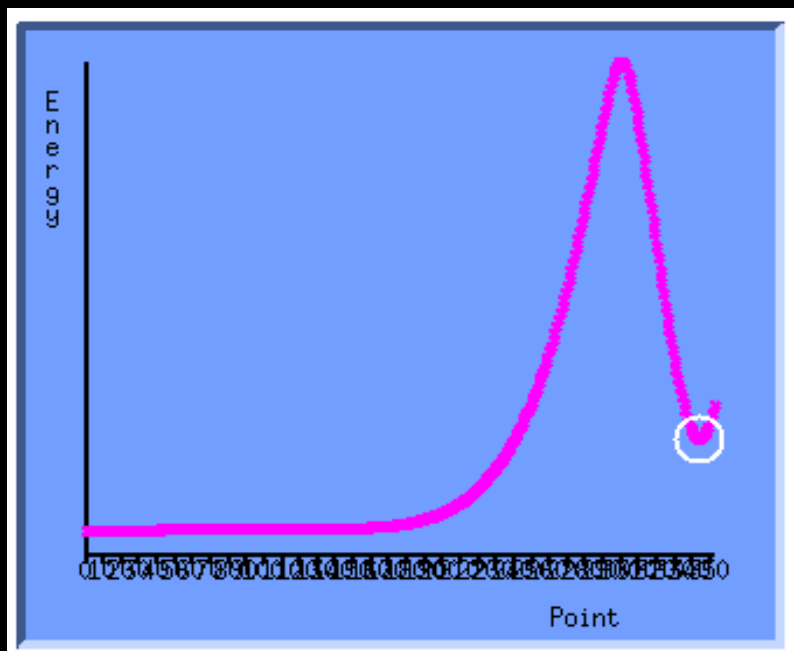
HOMO



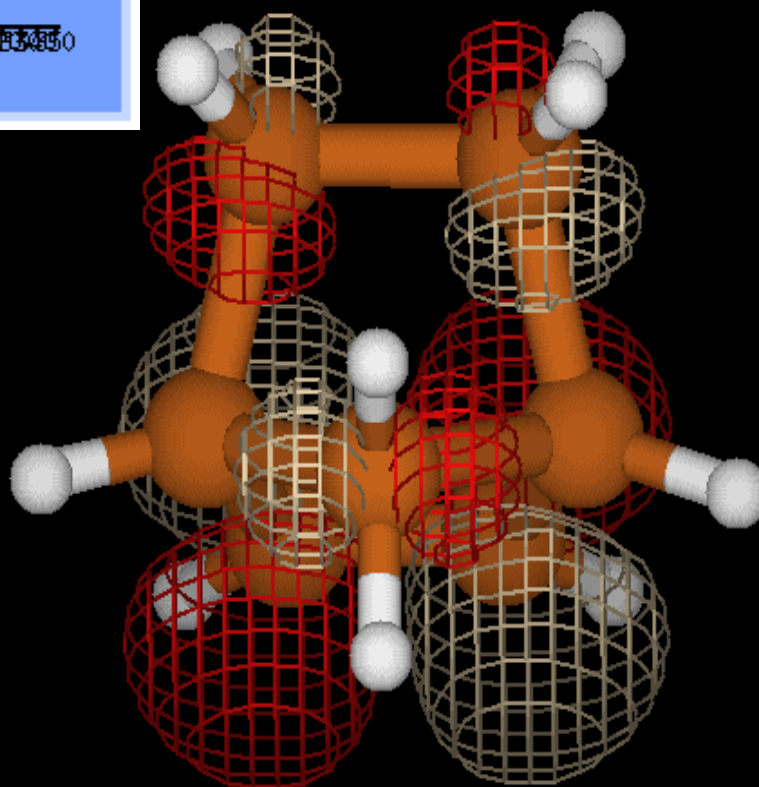
LUMO



Reação de Diels-Alder



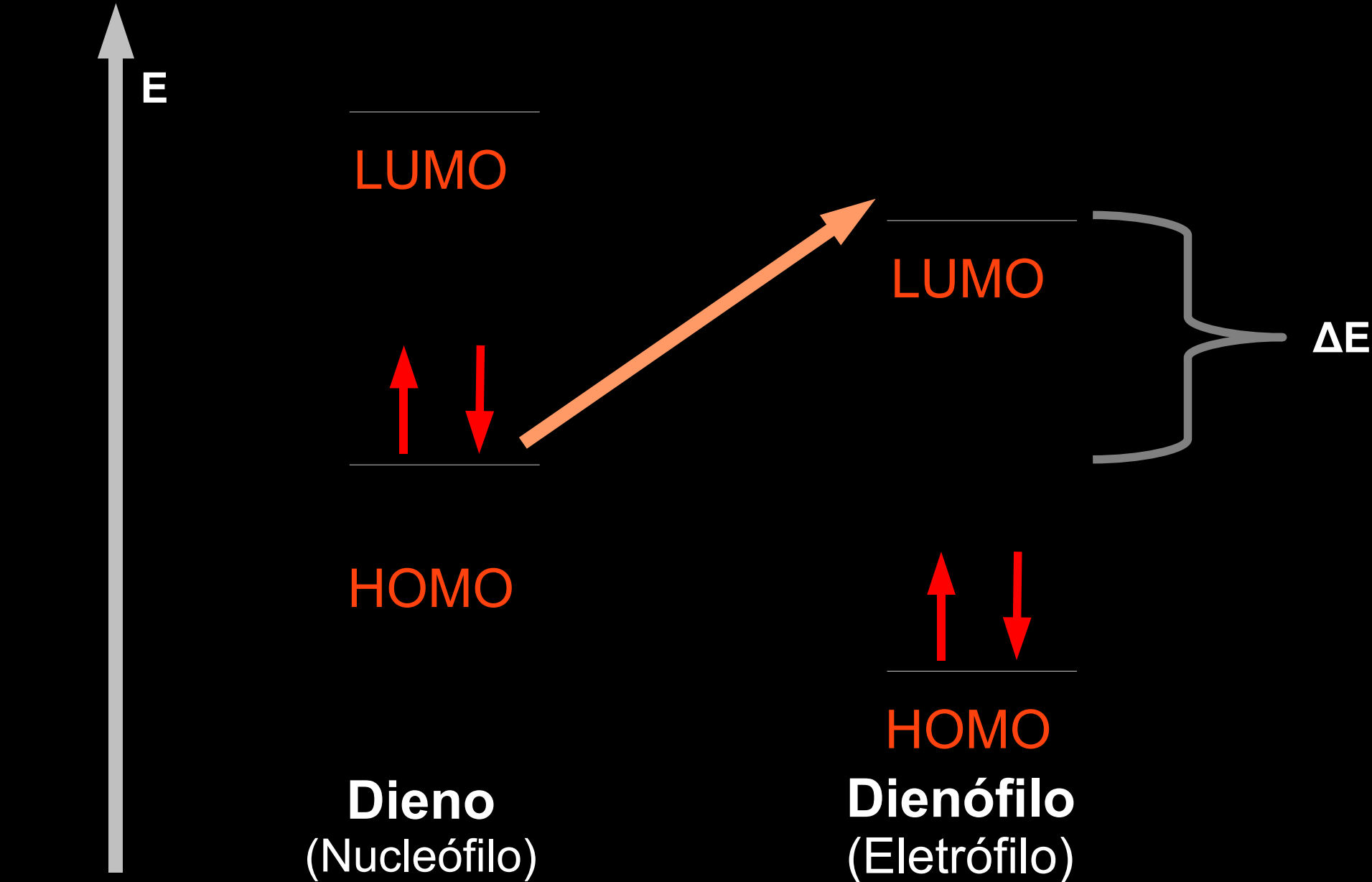
HOMO



LUMO

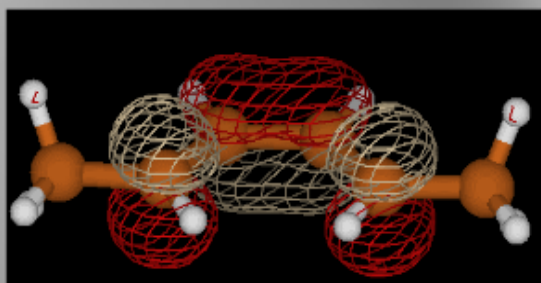


Reação de Diels-Alder – influência dos orbitais de fronteira

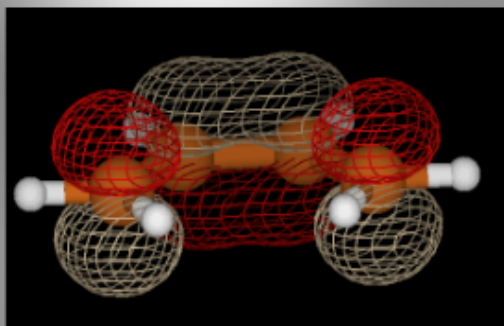


Reação de Diels-Alder – Energias e reatividade

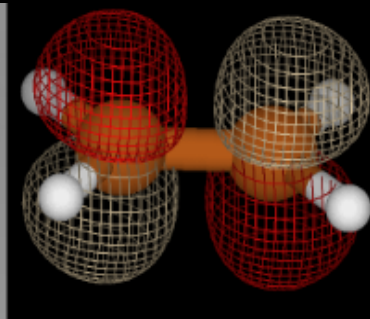
Energia



Hexadieno

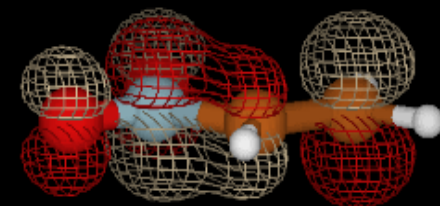


Butadieno

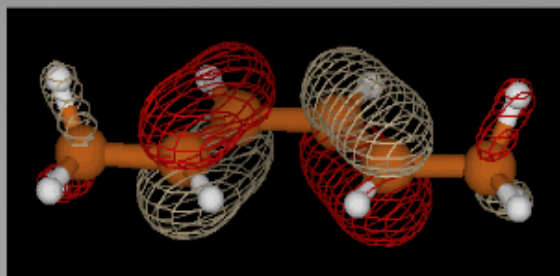


Etileno

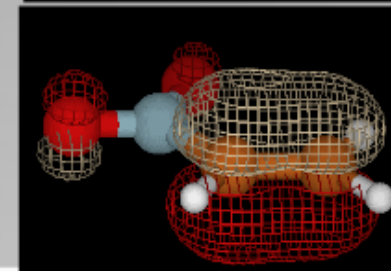
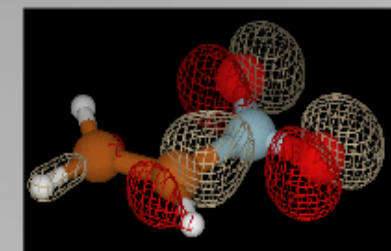
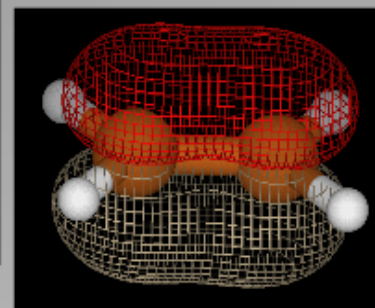
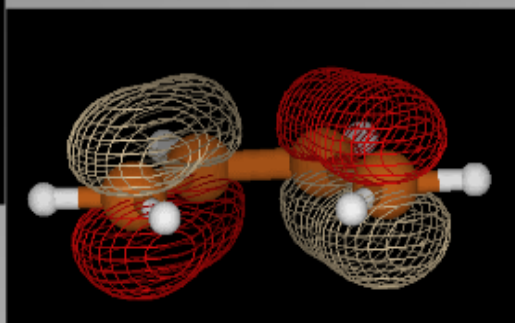
**LUMO mais acessível
Dienonófilo mais reativo**



Nitroetileno



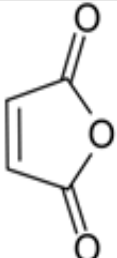
**HOMO mais energético
Dieno mais reativo**



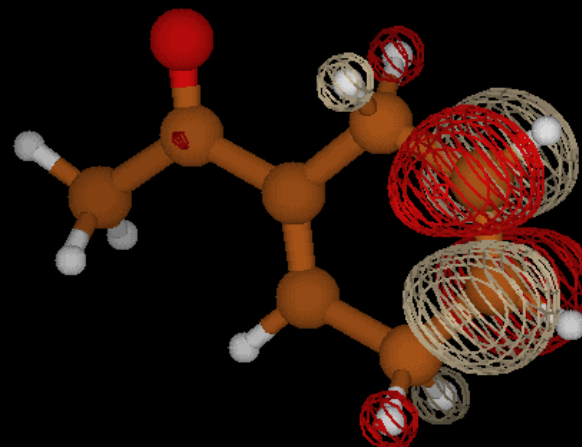
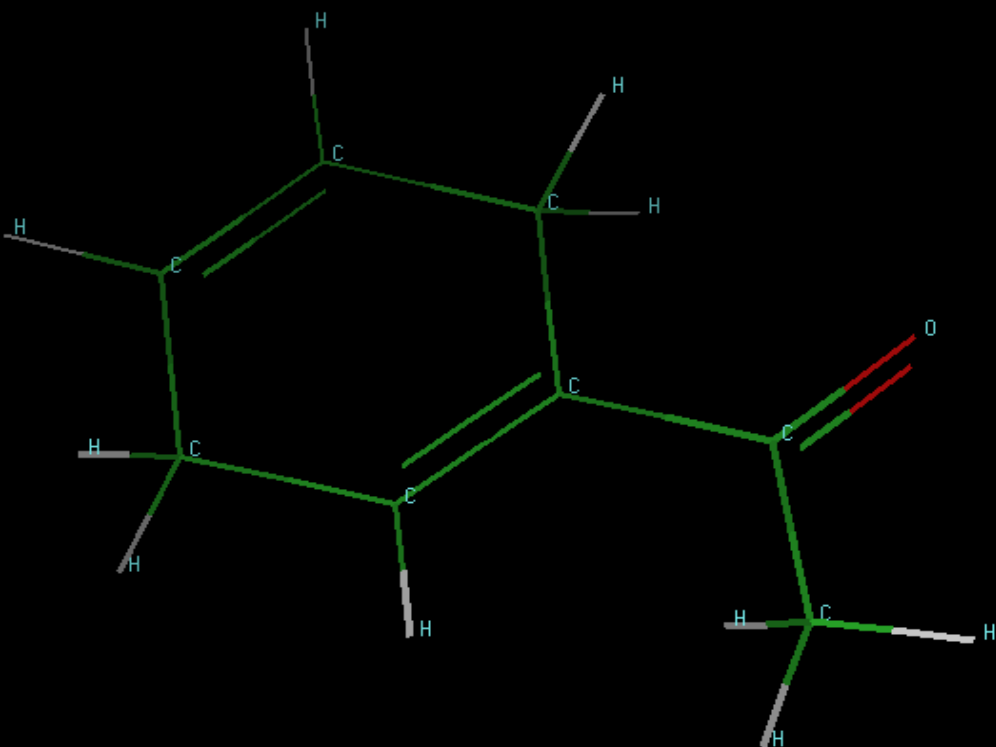
Reação de Diels-Alder – Dienos

Composto	HOMO (eV)	LUMO (eV)
$\text{CH}_2=\text{CH}-\text{CH}=\text{CH}_2$	-9,6	0,2
$\text{CH}_2=\text{CH}-\text{CH}=\text{CH}-\text{CH}_3$	-9,3	0,3
$\text{CH}_2=\text{CH}-\text{CH}=\text{CH}-\text{NH}_2$	-8,6	0,3
$\text{CH}_2=\text{CH}-\text{CH}=\text{CH}-\text{CO}-\text{CH}_3$	-10,1	-0,8
$\text{CH}_2=\text{CH}-\text{CH}=\text{CH}-\text{CN}$	-10,1	-0,8
$\text{CH}_2=\text{CH}-\text{CH}=\text{CH}-\text{NO}_2$	-10,6	-1,6

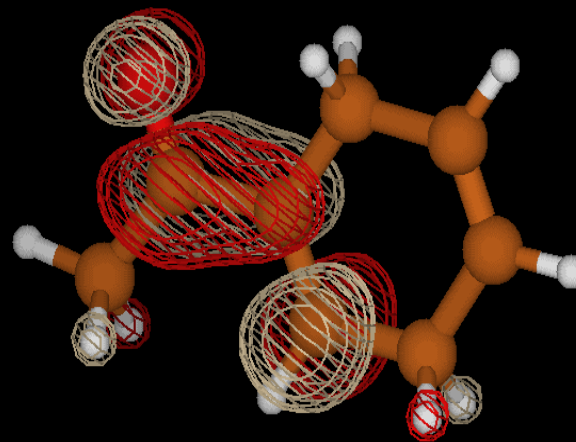
Reação de Diels-Alder – Dienófilos

Composto	HOMO (eV)	LUMO (eV)
HCCH	-11,6	1,6
CH ₂ =CH ₂	-10,8	1,1
CH ₂ =CH-CH ₃	-10,1	1,2
CH ₂ =C(CH ₃) ₂	-9,7	1,3
CH ₂ =CH-CO-CH ₃	-10,6	-0,1
CH ₂ =CH-COOH	-11,5	-0,5
CH ₂ =CH-NH ₂	-9,1	1,1
CH ₂ =CH-NO ₂	-11,6	-1,3
C ₆ H ₁₀ (Ciclohexeno)	-9,5	1,4
	-11,8	-1,9

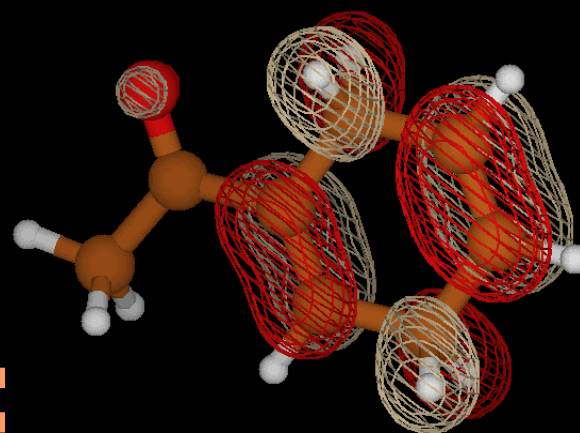
Reação de Diels-Alder – Dienófilos



$E = +1,1 \text{ eV}$

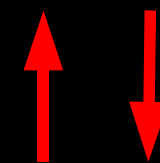


$E = -0,3 \text{ eV}$
(LUMO)

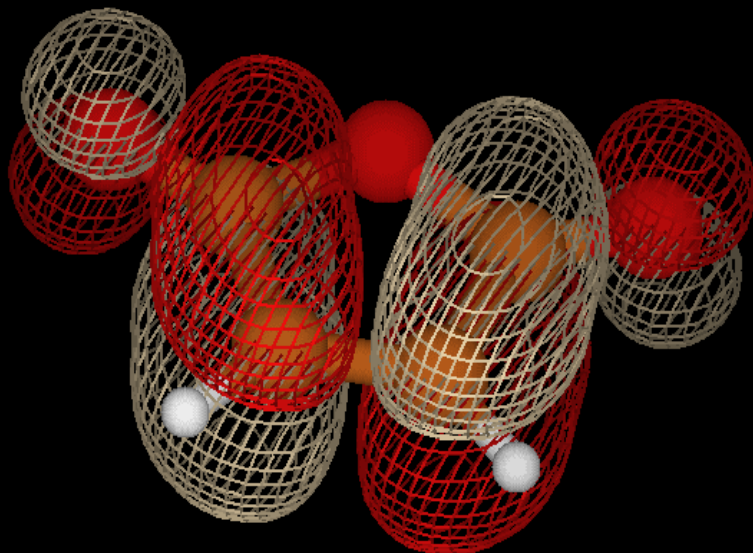


$E = -9,5 \text{ eV}$
(HOMO)

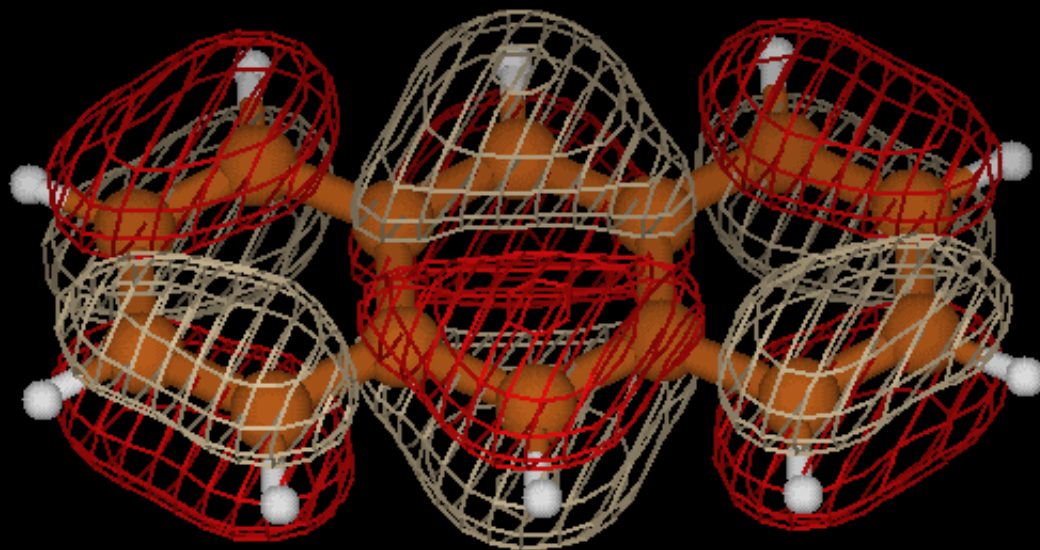
Qual dupla irá reagir?



Reação de Diels-Alder – Um último exemplo



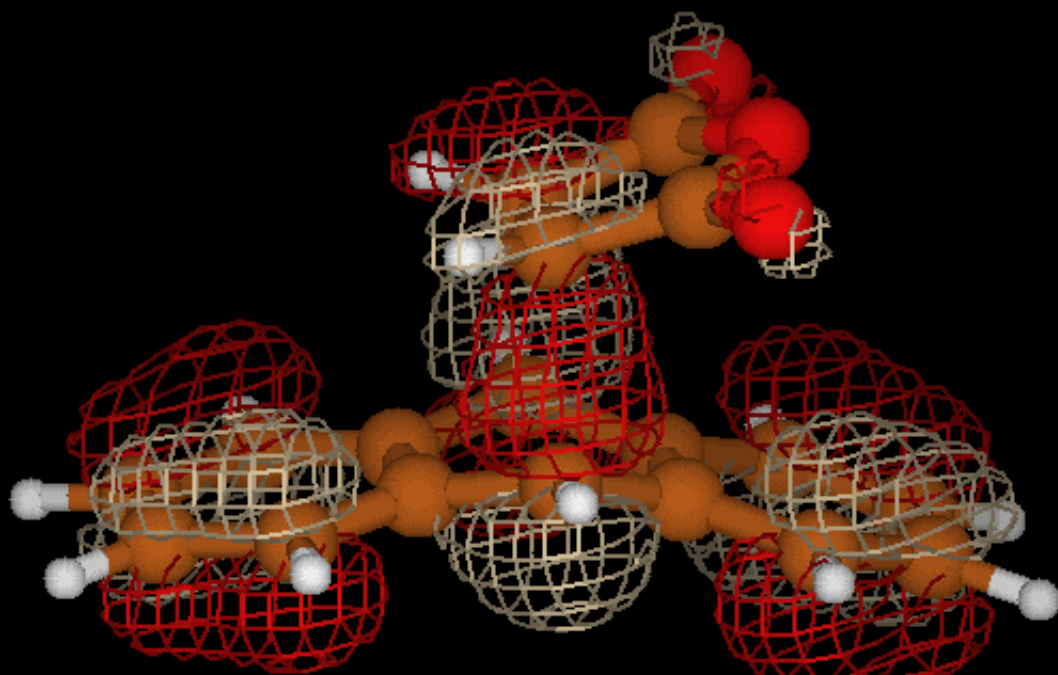
LUMO Anidrido maléico



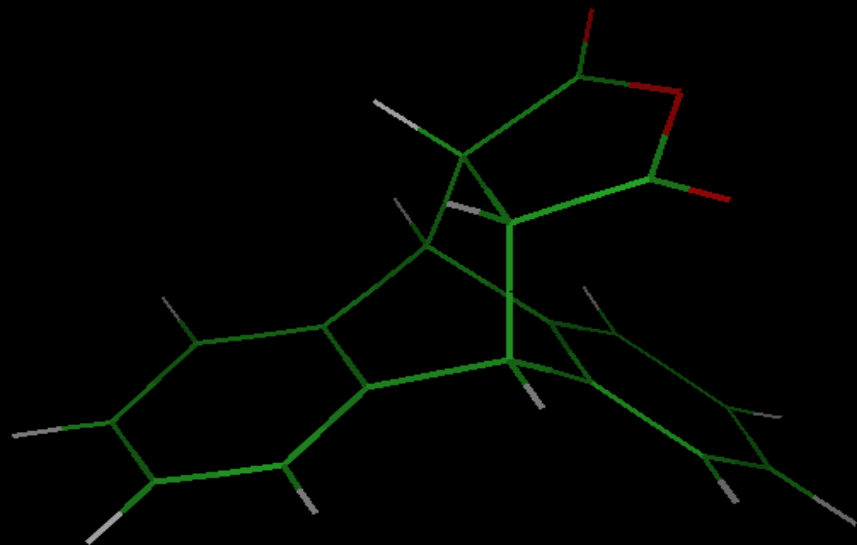
HOMO Antraceno

Apesar de seu caráter aromático, o antraceno atua como dieno na reação de Diels-Alder

Reação de Diels-Alder – Um último exemplo



HOMO Estado de
transição



Estrutura do produto

Conclusões



Conclusões

- ✓ As reações orgânicas podem ser compreendidas considerando a transferência de elétrons do orbital HOMO do nucleófilo para o LUMO do eletrófilo
 - ✓ A análise da simetria e das energias dos orbitais de fronteira dos reagentes permite verificar quais ligações poderão ser rompidas ou formadas em uma reação
 - ✓ Grupos que aumentam a energia do orbital HOMO aumentam a reatividade de nucleófilos
 - ✓ Grupos que diminuem a energia do orbital LUMO aumentam a reatividade de eletrófilos
-
-

Agradecimentos

- ✓ Adriana Yumi Iwata
 - ✓ Rebecca Nogueira e Silva
 - ✓ Camila Daiane
 - ✓ Juliana Marques
 - ✓ Renata Fernandes Siqueira

 - ✓ Ao Prof. Dr. Timothy J. Brocksom, pela sugestão do tema
-
-

Apresentação disponível
para download em

kalilbn.wordpress.com

