

Química Geral Estrutural

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2562-7444

Labs 622/629A

<http://interlab.iq.ufrj.br>



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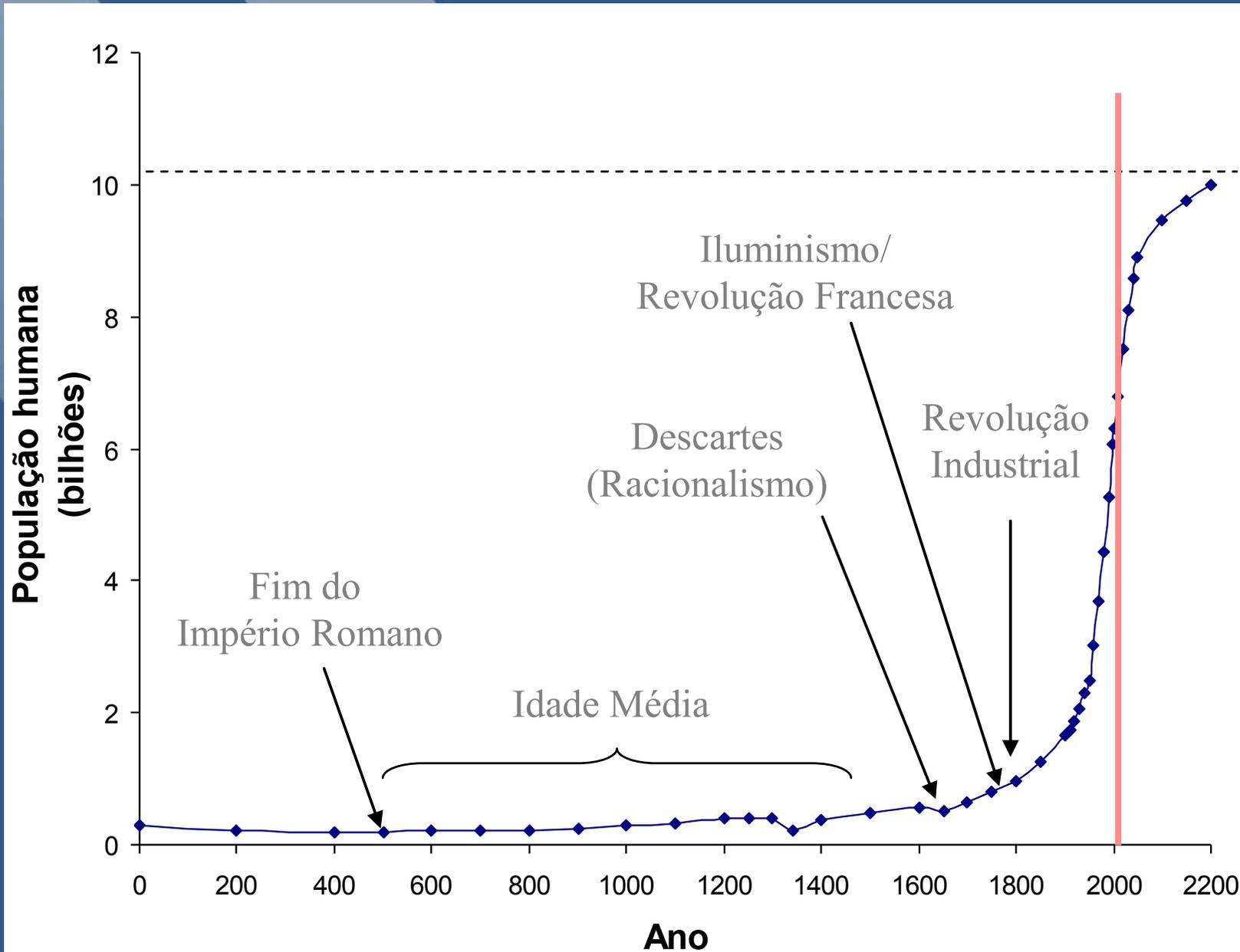
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Quem sou eu?

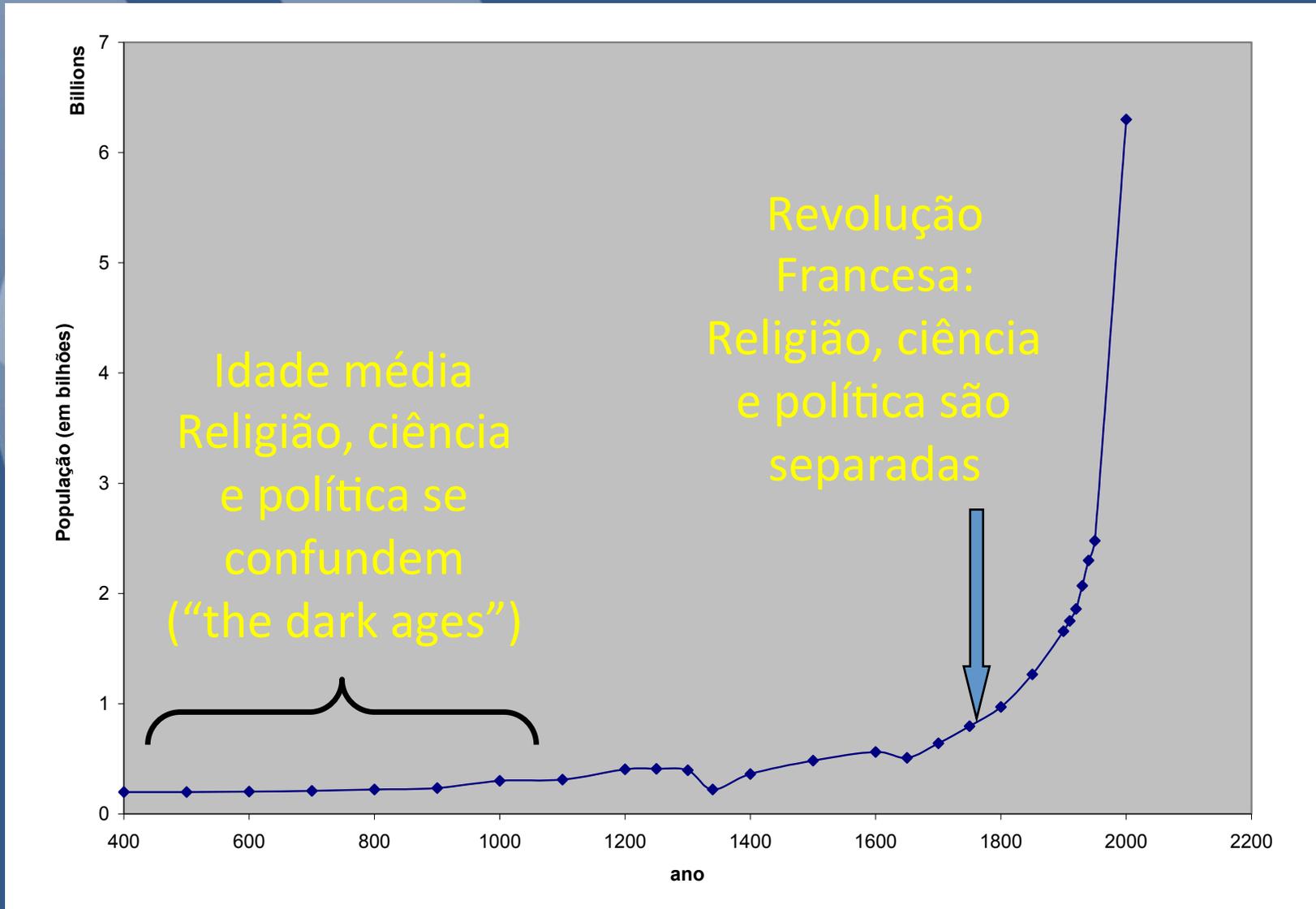


Turma IQ, 1990
sala 601

Crescimento Populacional (Dados da ONU)



Ode à razão e à lógica



No quê trabalhar

- Olhar o passado ajuda a enxergar o futuro
- O que será importante em 2050?
 - População humana estimada: ~ 10 bilhões de pessoas
 - Rio de Janeiro:
 - Hoje: 6 milhões (1 em cada 5 mora em “comunidades”)
 - 2020: 13 milhões (1 em cada 3 mora em “comunidades”)
 - 2050: 23 milhões ? (1 em cada 1 mora em “comunidades”?)
 - Eu terei 78 anos em 2050,
 - E vocês?



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O que vai faltar?

- Água (petróleo do futuro)
- Energia = Conforto
- Saúde
- Planejamento urbano



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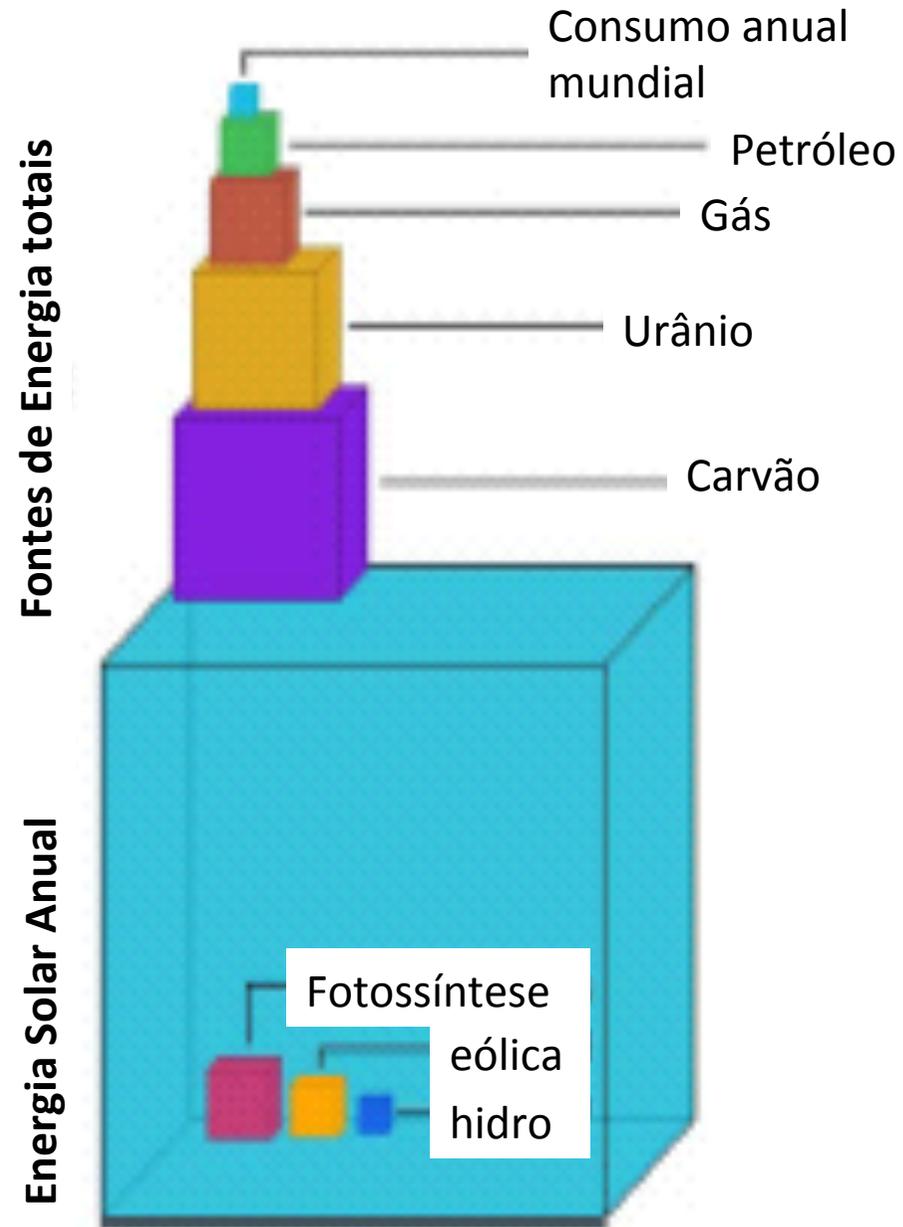
Onde está a Química?

- ✿ Água (petróleo do futuro)
- ✿ Energia = Conforto
- ✿ Saúde
- ✿ Planejamento urbano
- ✿ Etc



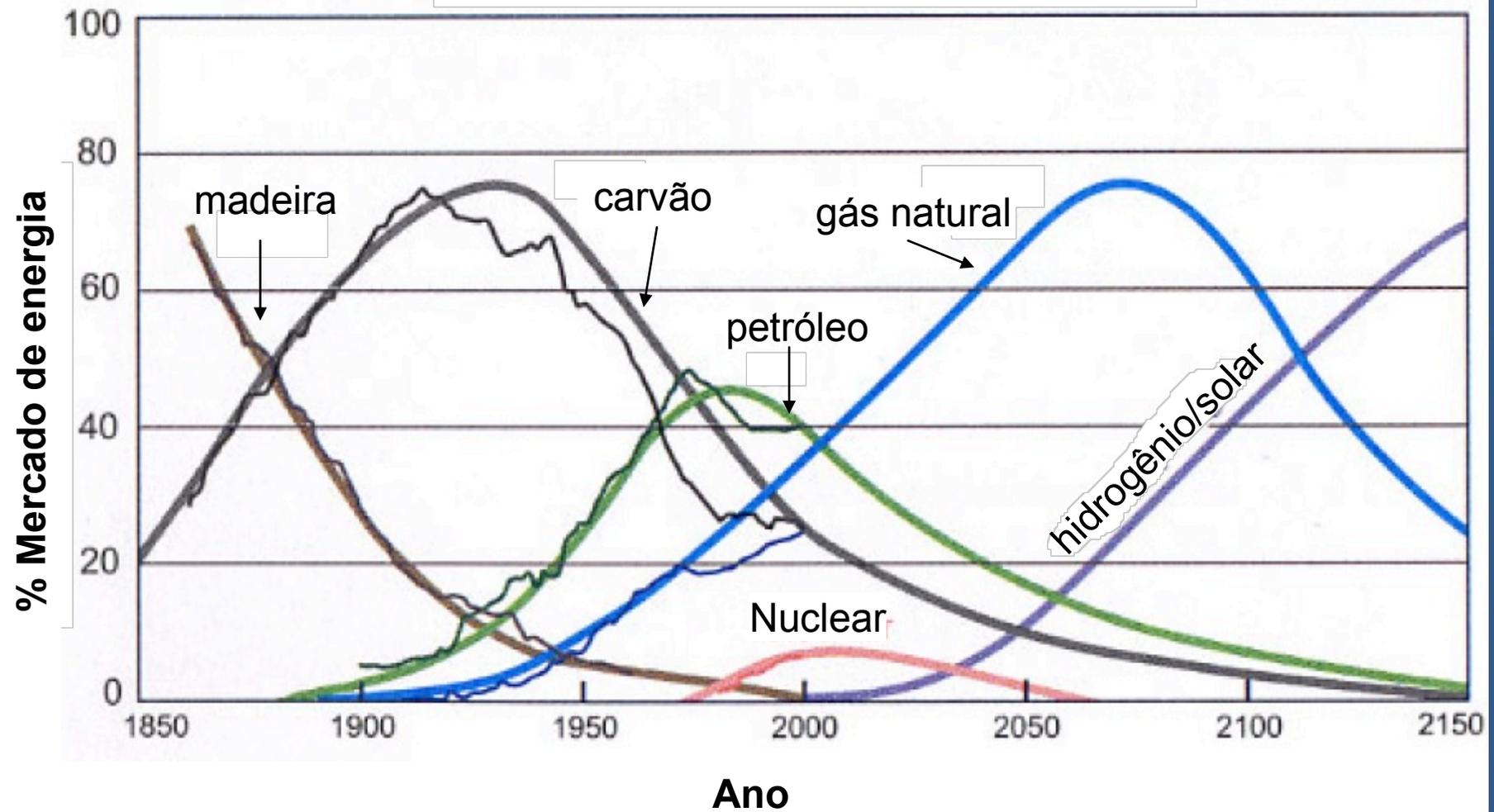
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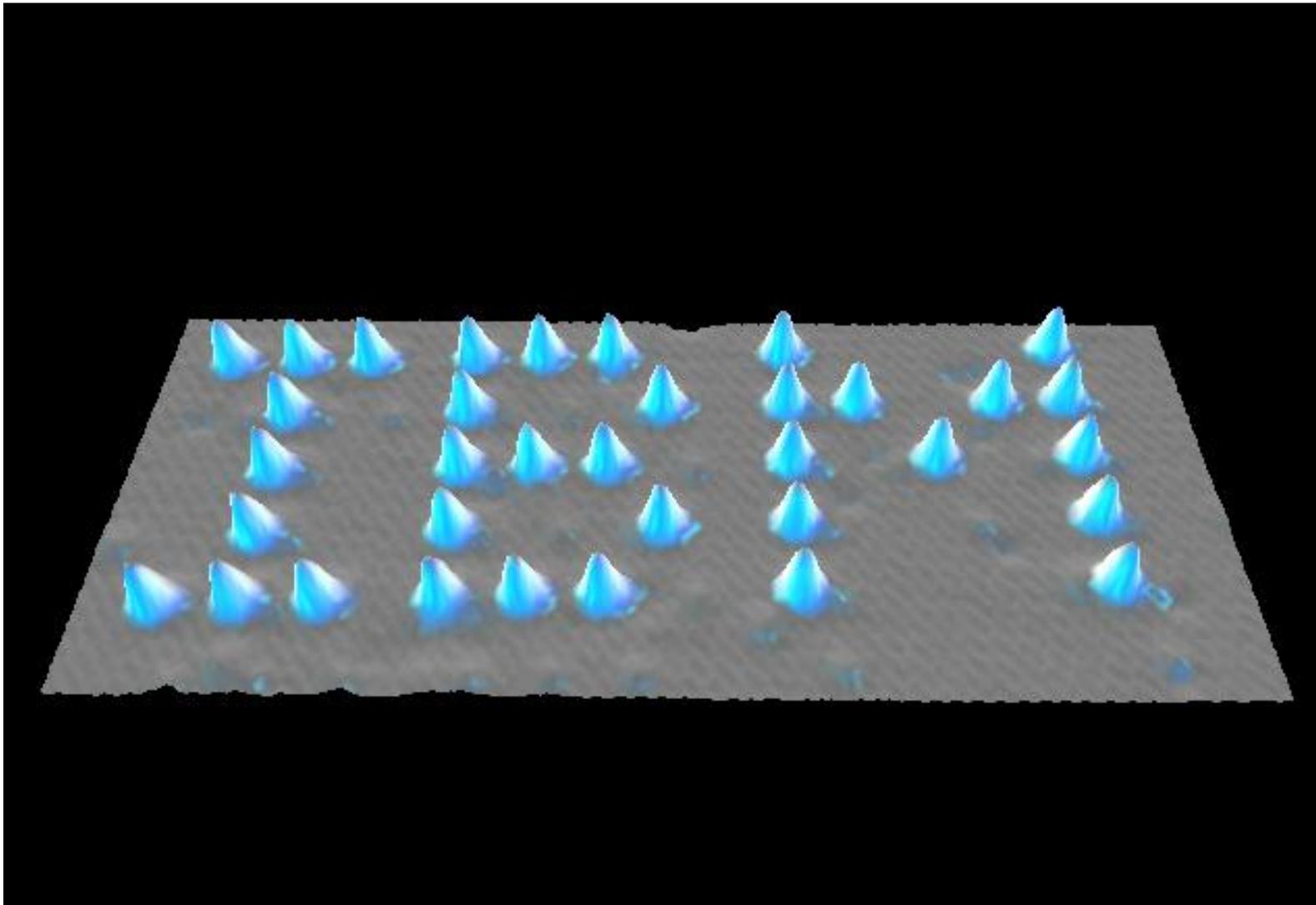


Lomborg, 2001

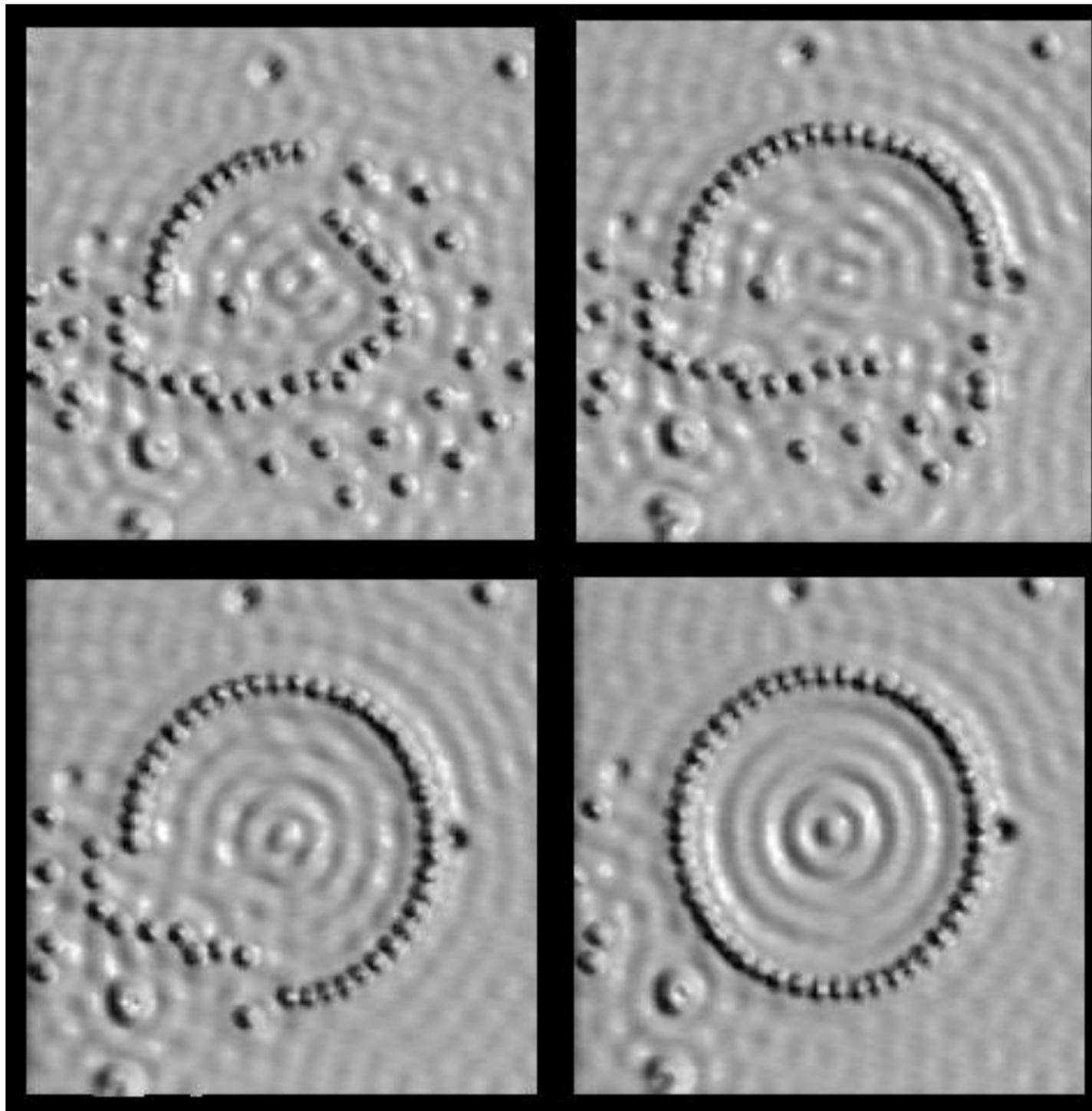
Projeções para o uso de algumas formas de energia no futuro.



Manipulando átomos



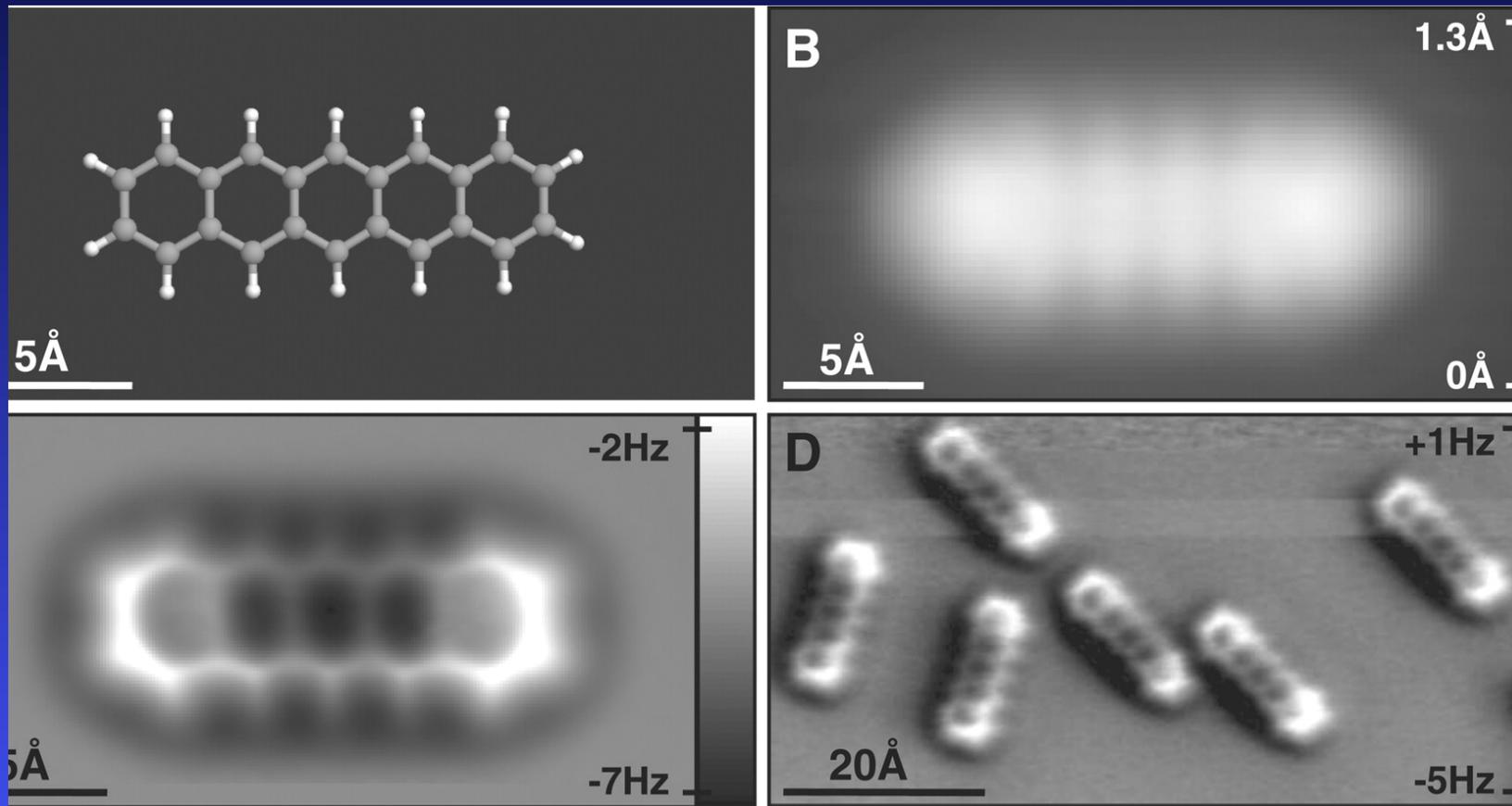
Curral Quântico



Atualidades: Do que somos capazes?

Primeira “foto” de uma molécula (2009)

Imagem STM e AFM do pentaceno em Cu(111)



Gross, Mohn, Moll, Liljeroth, Meyer *Science* 2009, 325(5944),1110
DOI: 10.1126/science.1176210

*The Chemical Structure of a
Molecule Resolved by
Atomic Force Microscopy*

Leo Gross, Fabian Mohn,
Nikolaj Moll, Peter
Liljeroth, Gerhard Meyer
Science

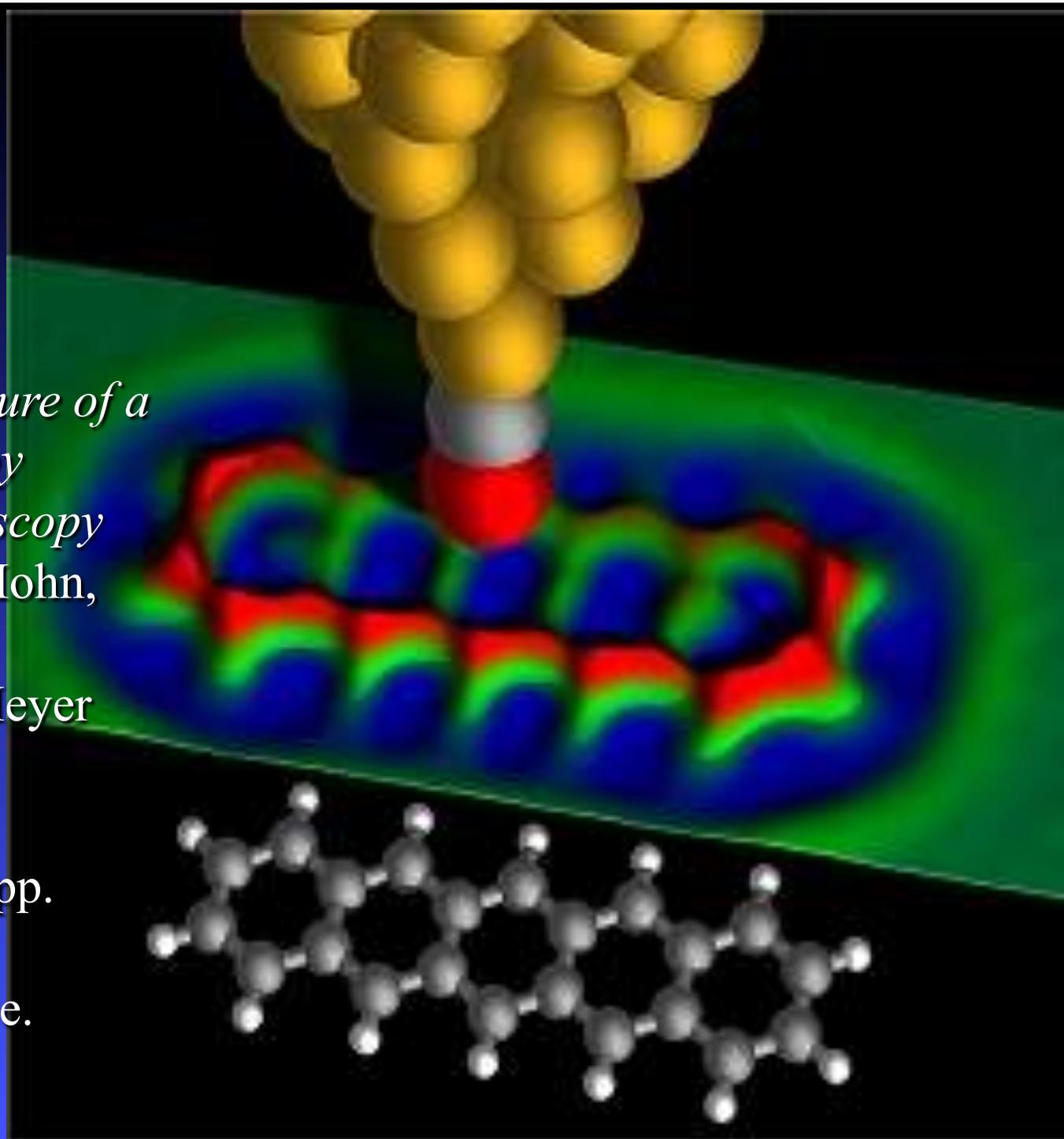
28 August 2009

Vol.: 325. no. 5944, pp.

1110 - 1114

DOI: 10.1126/science.

1176210



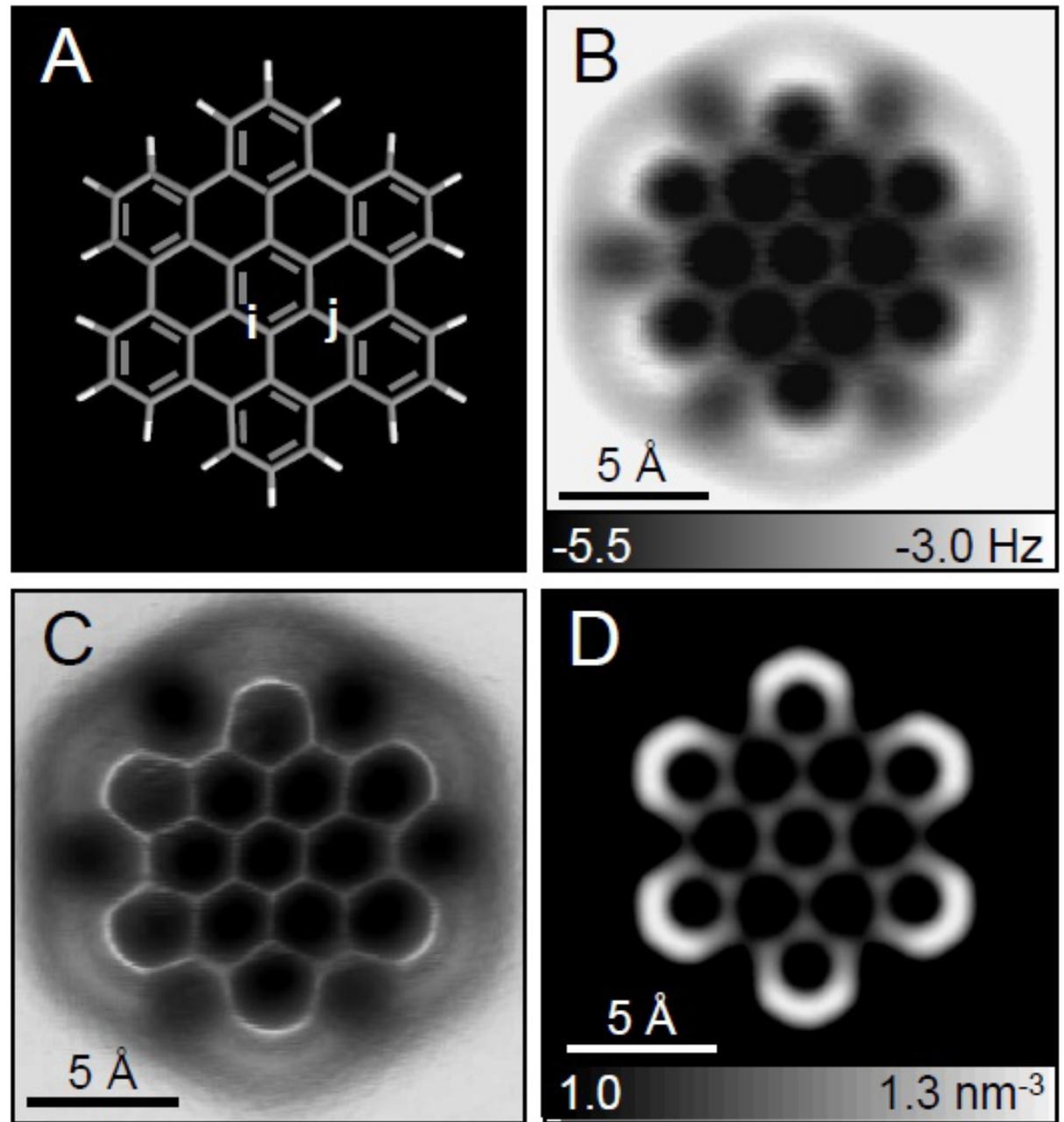


As soon as I mention this, people tell me about miniaturization, and how far it has progressed today. They tell me about electric motors that are the size of the nail on your small finger. And there is a device on the market, they tell me, by which you can write the Lord's Prayer on the head of a pin. But that's nothing; that's the most primitive, halting step in the direction I intend to discuss. It is a staggeringly small world that is below. In the year 2000, when they look back at this age, they will wonder why it was not until the year 1960 that anybody began seriously to move in this direction.

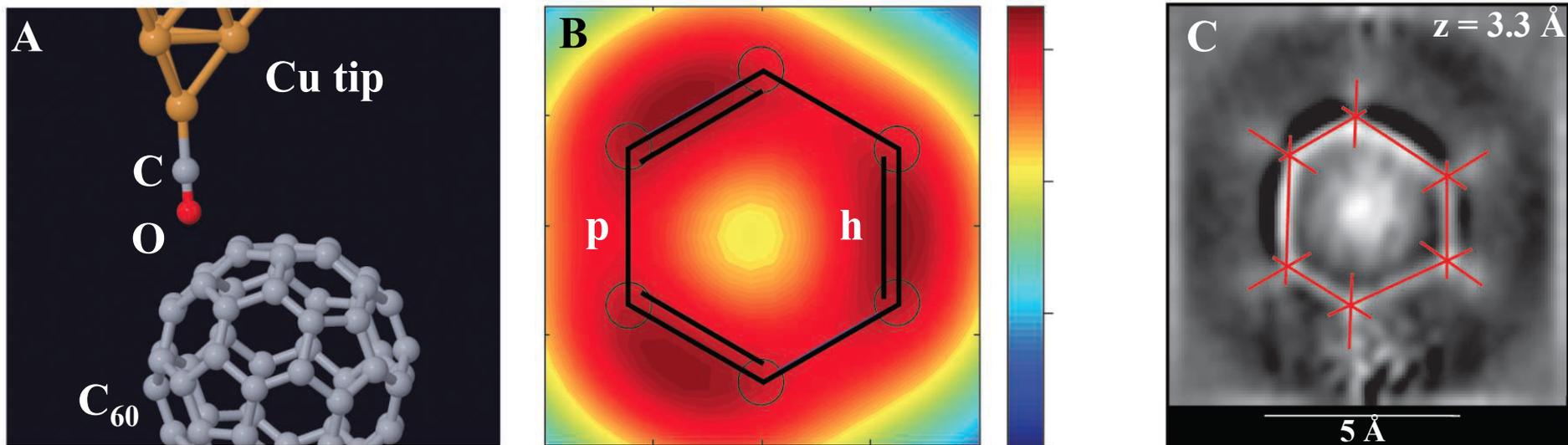


Richard P. Feynman, 1960

Discriminando
ordem de
ligação por AFM



Bond order discrimination By AFM



Forceful discrimination. Gross et al. used AFM with a CO-functionalized tip (A) to map the subtle differences in charge density (B) and bond length (C) associated with nonequivalent C-C bonds in a fullerene (C₆₀) molecule and to correlate them with their bond order.

Gross et al., Science 337, 1326 (2012).



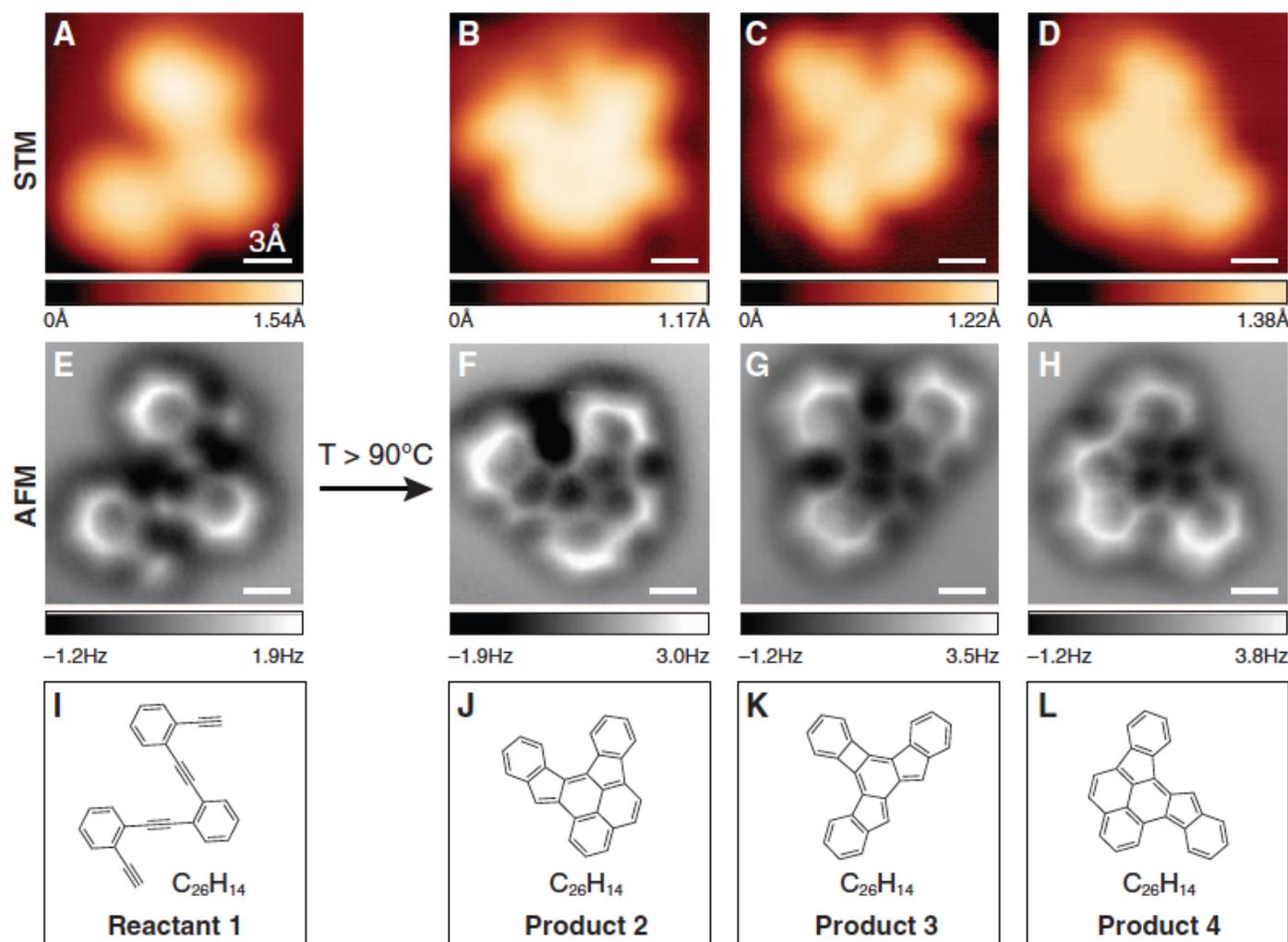
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Seguindo uma reação química por AFM

REPORTS

Fig. 2. Comparison of STM images, nc-AFM images, and structures for molecular reactant and products. (A) STM image of **1** on Ag(100) before annealing. (B to D) STM images of individual products **2**, **3**, and **4** on Ag(100) after annealing at $T > 90^\circ\text{C}$ ($I = 10$ pA, $V = -0.2$ V, $T = 4$ K). (E) nc-AFM image of the same molecule (reactant **1**) depicted in (A). (F to H) nc-AFM images of the same molecules (products **2**, **3**, and **4**) depicted in (B) to (D). nc-AFM images were obtained at sample bias $V = -0.2$ V (qPlus sensor resonance frequency = 29.73 kHz, nominal spring constant = 1800 N/m, Q-value = 90,000, oscillation amplitude = 60 pm). (I to L) Schematic representation of the molecular structure of reactant **1** and products **2**, **3**, and **4**. All images were acquired with a CO-modified tip.



de Oteyza et al. *Science* 340, 1434 (2013);
DOI: 10.1126/science.1238187

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Manipulando átomos: Uso de STM para quebrar uma ligação

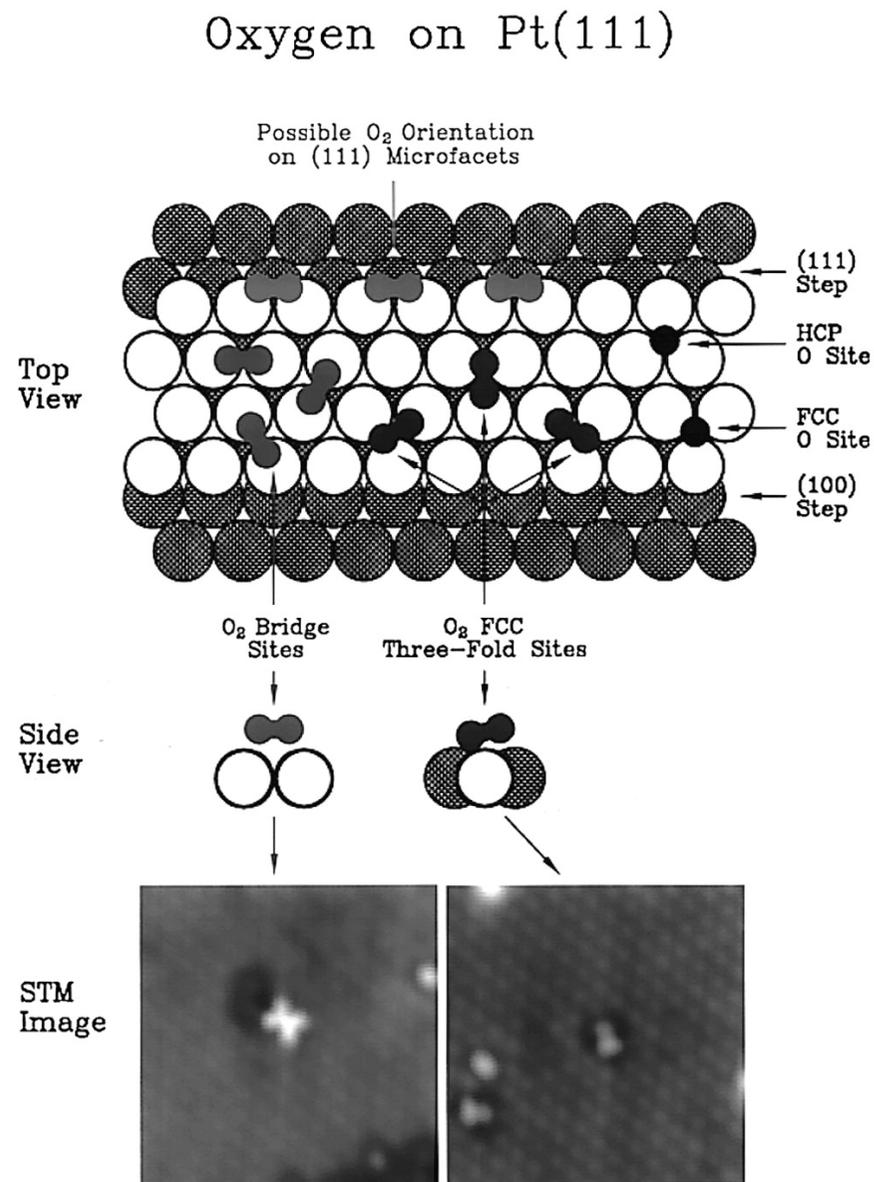
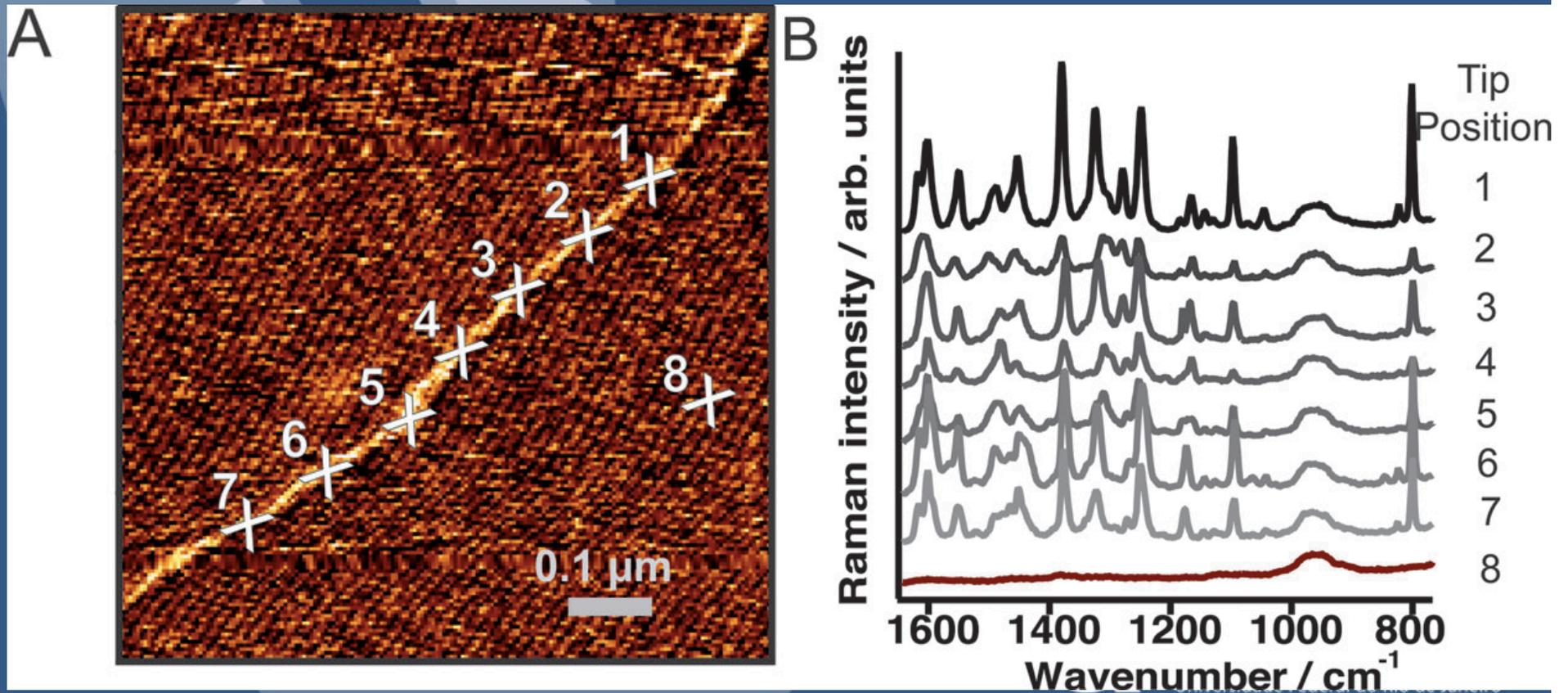


Figure 3 Schematic showing the molecular and atomic oxygen adsorbed on Pt(111) as observed by variable-temperature STM. The oxygen molecules on the 2-fold bridge and 3-fold fcc sites have three equivalent orientations; STM images are shown for one orientation.

Tip Enhanced Raman Spectroscopy (TERS) em uma fita de DNA



E. Bailo and V. Deckert, *Angew. Chem., Int. Ed.*, 2008, 47, 1658.
DOI: 10.1039/b705967c

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Femtoquímica

- Ver trabalhos de Ahmed Zewail
 - <http://www.its.caltech.edu/~femto/>
- Espectroscopia de estados de transição



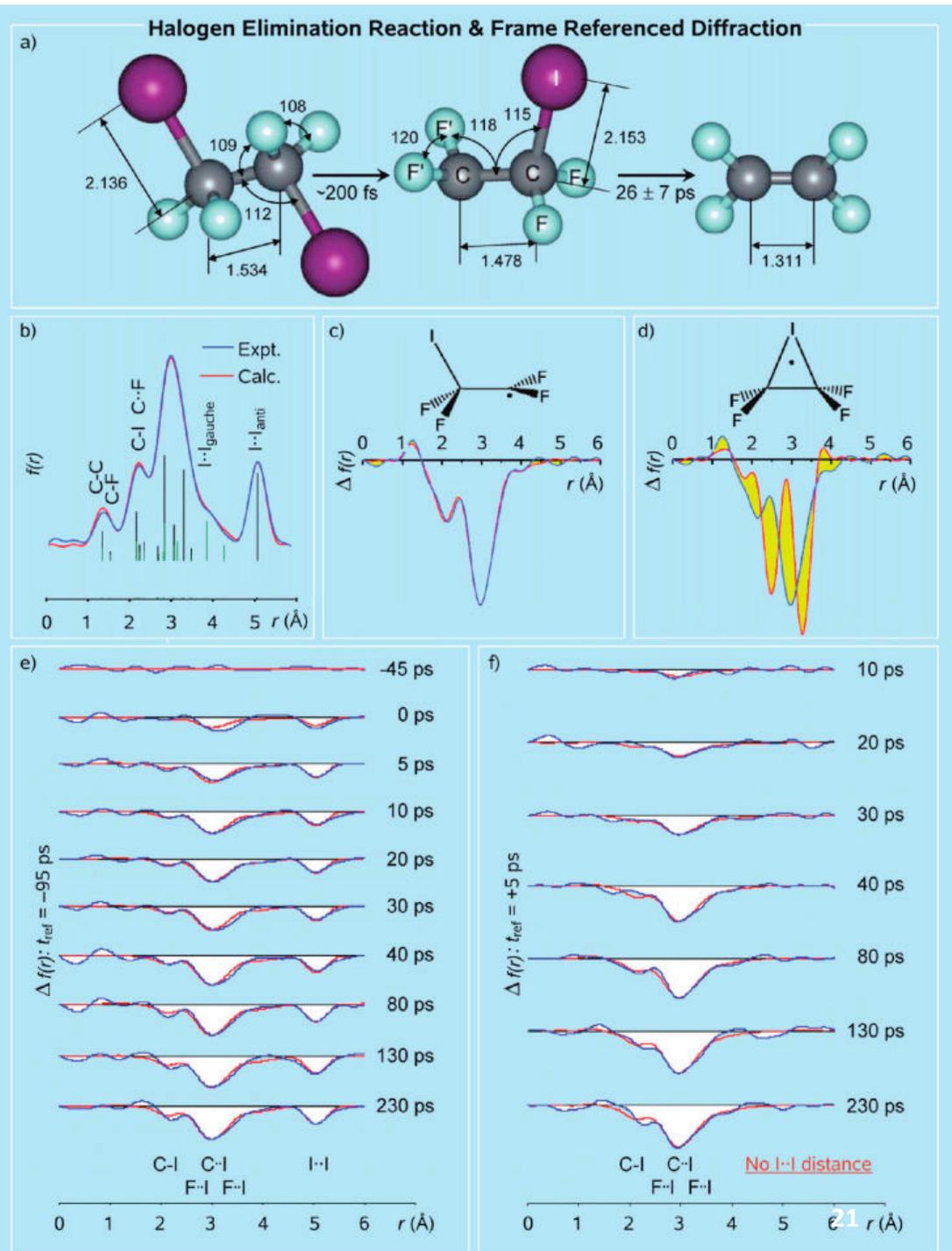
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TEM 4D

- Imagem em escala atômica com resolução temporal
- “Filme” molecular

J. Am. Chem. Soc., 2009, 131 (50), pp 17998–18015
DOI: 10.1021/ja907432p



Novas ferramentas

- Ampliação das antigas ferramentas (RMN, MS, IV, química computacional, etc)
- Novas ferramentas
 - Microscopia
 - com resolução atômica: STM, AFM, SEM, TEM
 - TERS, SERS
 - Raman Confocal
 - com resolução atômica e temporal:
 - ultrafast electron diffraction (UED),
 - ultrafast electron crystallography (UEC),
 - ultrafast electron microscopy (UEM)



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Twenty-first century chemistry represents the forefront of the molecular sciences. New theories, concepts, and ideas facilitated by advances in analytical techniques and instrumentation revolutionized the practice of chemistry in the latter part of the 20th century. Advances in NMR spectroscopy, mass spectrometry, synchrotron and X-ray techniques, single-molecule spectroscopy, microscopy, computations, lasers, and others, along with tremendous strides in synthesis and coupled with tools of biology such as genetic engineering, allow us to examine complex chemical and biological phenomena, unimagined just a few decades ago, at the molecular, atomic, and even subatomic levels.

Peter J. Stang

J. Am. Chem. Soc., 2009, 131 (35), p 12496

DOI: 10.1021/ja903812n



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Algumas coisas não mudam

- Criatividade é a mais valorizadas das habilidades humanas
- Estar em dia com a literatura (estudo contínuado) é a uma das chaves do sucesso
 - Tipos de literatura
 - Notas
 - Comunicações
 - Artigos
 - Revisões
 - Livros
 - Pespectivas



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Algumas coisas não mudam

- Trabalho duro e sério



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Como medir uma propriedade?

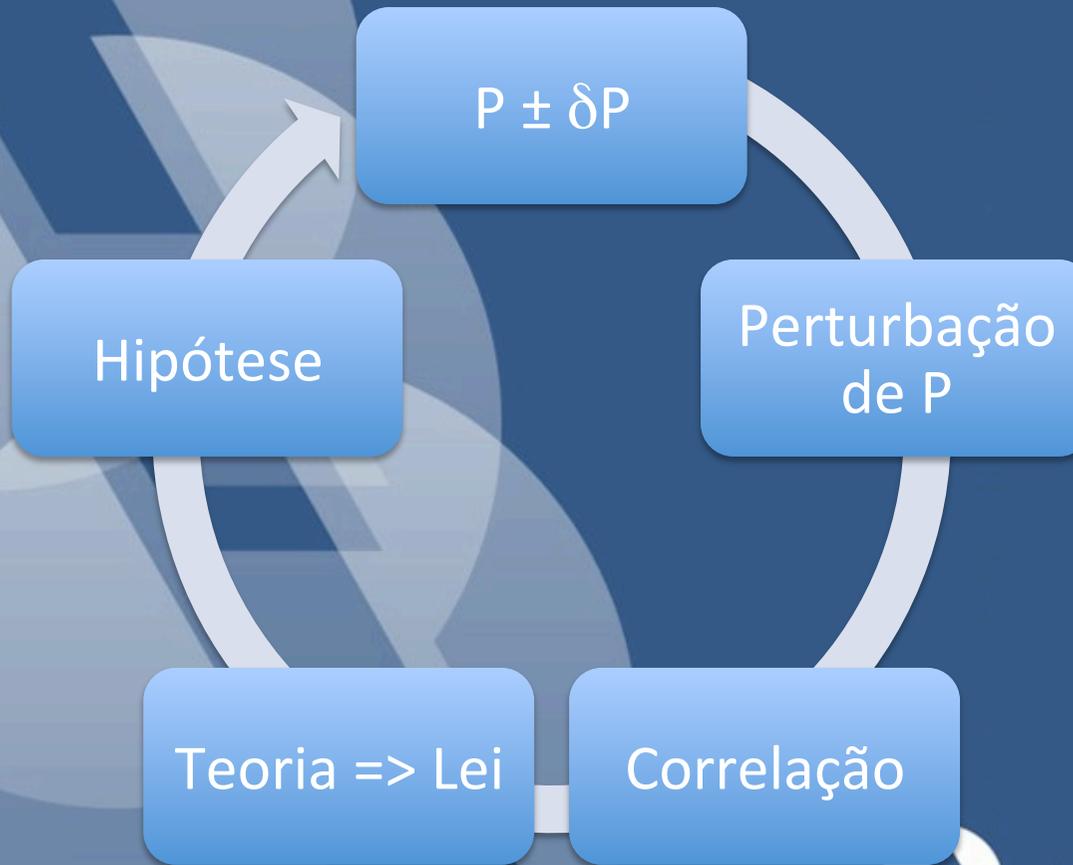
- Qual a propriedade central medida em química?
- Massas
- Volumes
- Concentrações (consequencia dos dois acima)
- Rendimentos (consequencia dos dois acima)



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Como fazer ciência: O ciclo



$$P = \alpha (\text{perturbação}) + \beta$$

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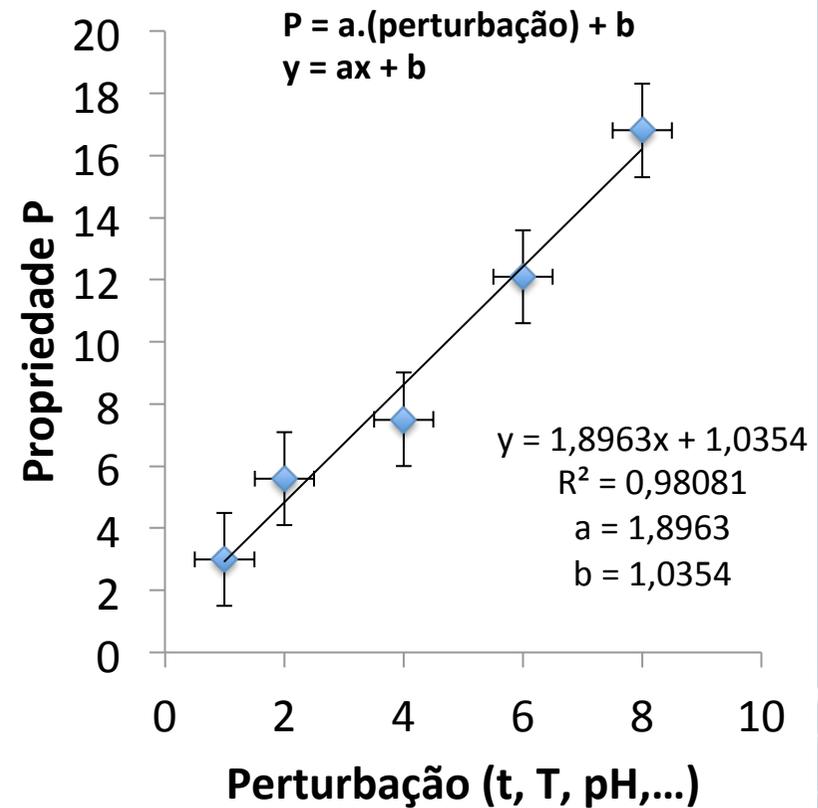
Como fazer ciência: O ciclo

Hipótese

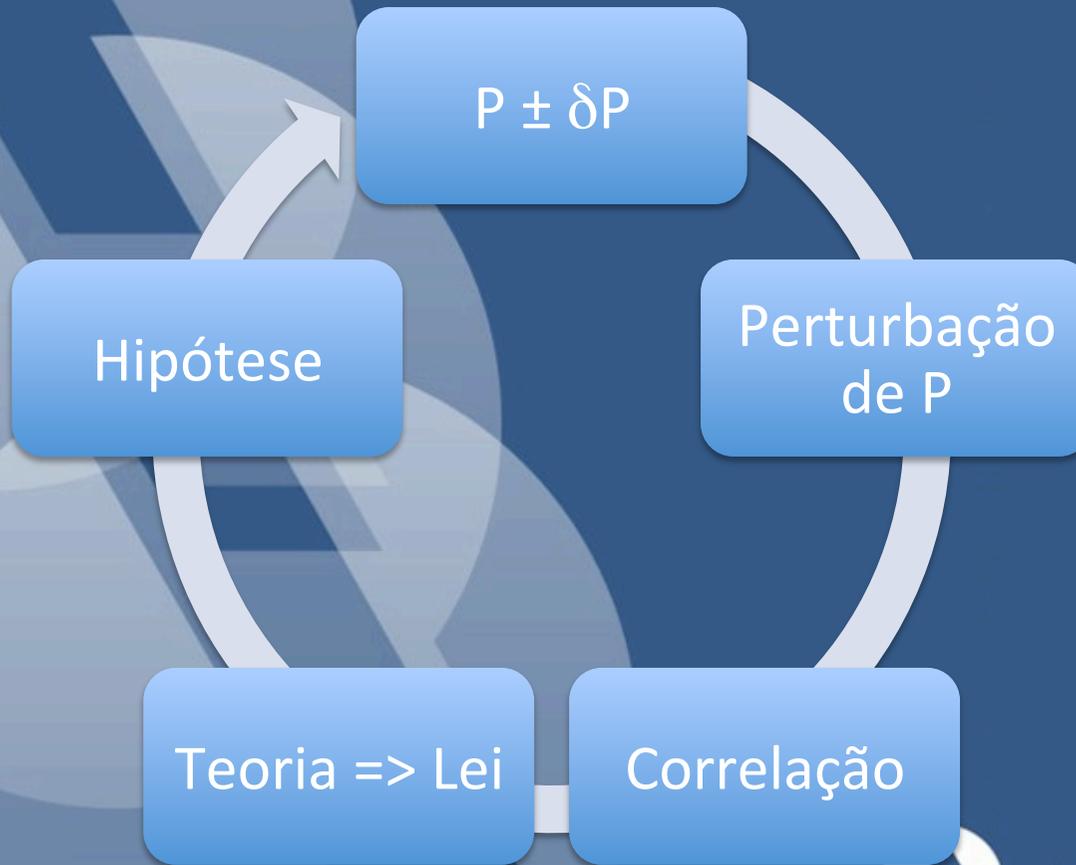
Teoria => Lei

$P \pm \delta P$

$$P = \alpha (\text{perturbação}) + \beta$$



Como fazer ciência: O ciclo



$$P = \alpha (\text{perturbação}) + \beta$$

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Noções Pré-Quânticas

- Teoria Atômica Grécia Antiga
~ 300 a.C.
- **Demócrito** “Nada existe, a não ser átomos e vácuo”
 - Versus
- **Aristóteles**: matéria era composta de água, terra e fogo (idéia original de Empedócles)

Renascença... 2000 anos depois

- Idéias atomísticas resgatadas
 - Giordano Bruno, Francis Bacon, René Descartes, Isaac Newton, Pierre Gassendi
- Iluminismo
 - Robert Boyle → O Químico Cético
 - Chamou atenção para a química
 - 1784 – Antoine Lavoisier
 - Compostos Orgânicos constituídos essencialmente de C, H e O

- 1807 – Dalton:
 - Teoria Atômica: átomo indivisível e indestrutível
- 1807 – Humphry Davy
 - Experimentos em eletroquímica com bateria desenvolvida por Volta
 - Átomos eletropositivos e eletronegativos
- 1811-1831 – Liebig, Berzelius e Dumas
 - Métodos quantitativos para a determinação da composição dos compostos orgânicos

- 1811- Avogadro

Fórmulas: CH_2

- 1860 - Canizarro

Fórmulas:

Empíricas: CH_2

Moleculares: C_2H_4 , C_5H_{10} , $\text{C}_6\text{H}_{12}\text{O}$

- 1858 → 1861

– Couper, Kekulé: Carbono tetravalente

– Butlerov (1861): Ligação Química

Estrutura Química

**Teoria
Estrutural**

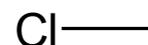
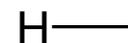
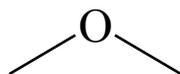
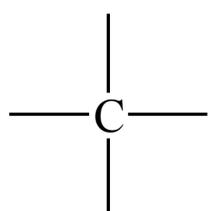
Teoria Estrutural: Premissas Fundamentais

- 1. Átomos dos elementos nos compostos orgânicos podem estabelecer um número fixo de ligações  **Valência**

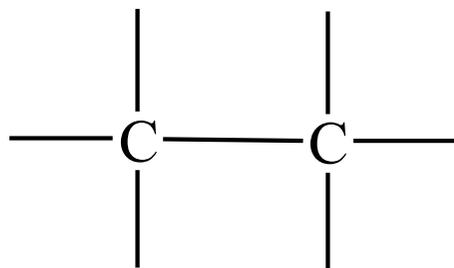
- C → Tetravalente
- O → Divalente
- H, Cl → Monovalente

– Brown (1861) e Erlenmeyer

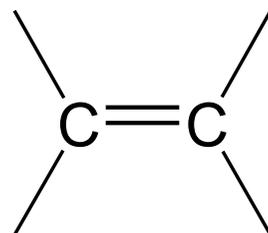
- Representação Gráfica da Valência → Conectividade



- 2. Um átomo de carbono pode usar uma ou mais valências para formar ligações coim outro átomo de carbono



Lig. Simples



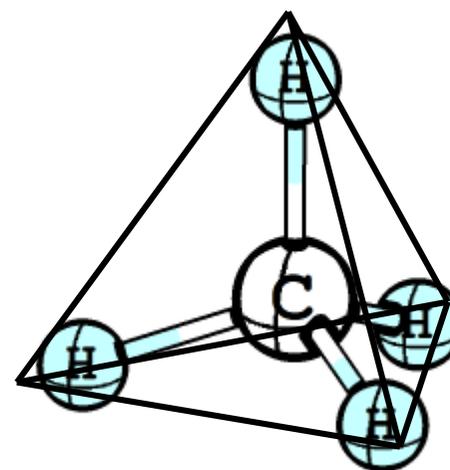
Lig. Dupla

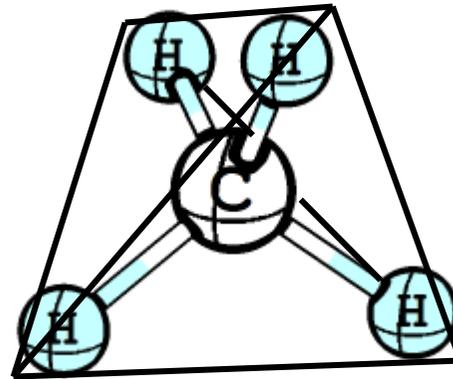
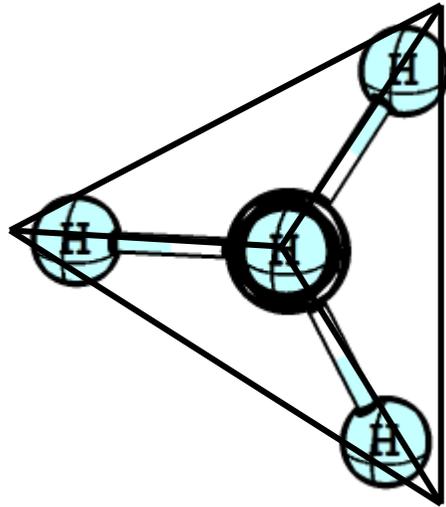
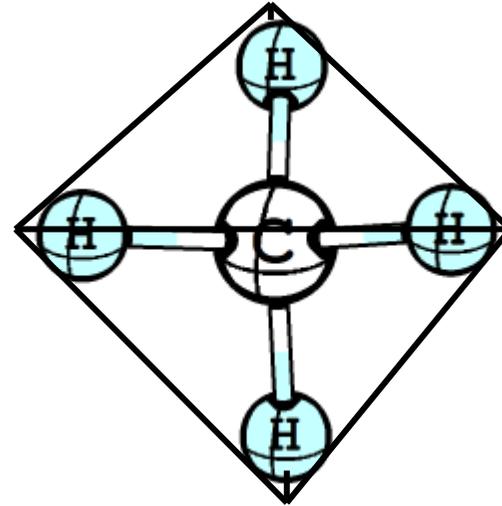
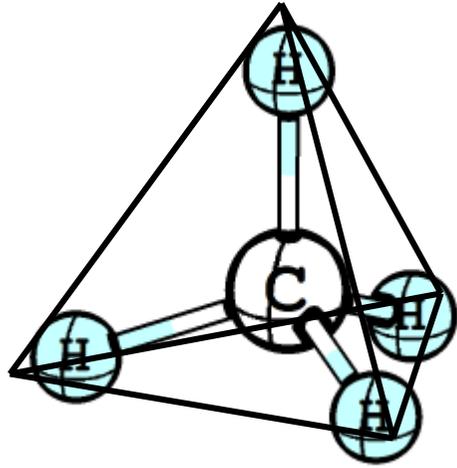


Lig. Tripla

1860-1870

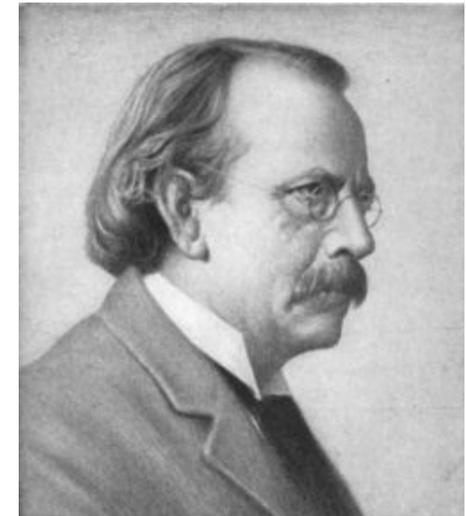
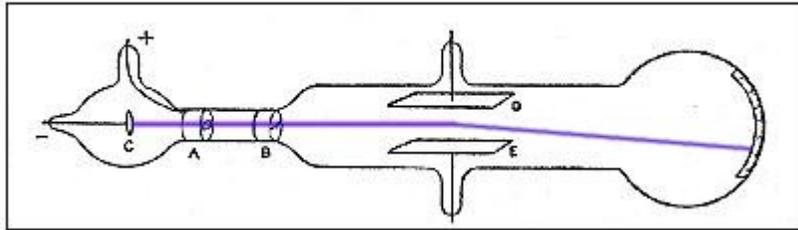
- Medeleiev, Lothar Meier
 - Correlação entre valência e posição na tabela periódica
- Pasteur, Kekulé, Butlerov
 - Assimetria
- 1874 – van't Hoff e Le Bel
 - Arranjo tridimensional →
 - Isomeria ótica e espacial





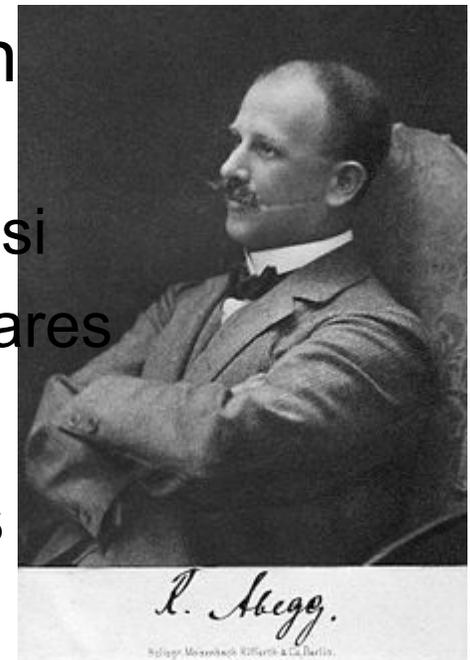
A descoberta do elétron

- 1897- Thomson
 - Descobre o elétron graças à invenção das bombas de vácuo



J. J. Thomson

- 1904 – Thomson → Modelo de Thomson
 - Ligação química seria formada quando dois átomos trocam ou transferem elétrons entre si
 - Dificuldades para explicar ligações homopolares
- 1904 – Abegg → Regra do Octeto para explicar a estabilidade dos gases nobres



Elétrons: consequências

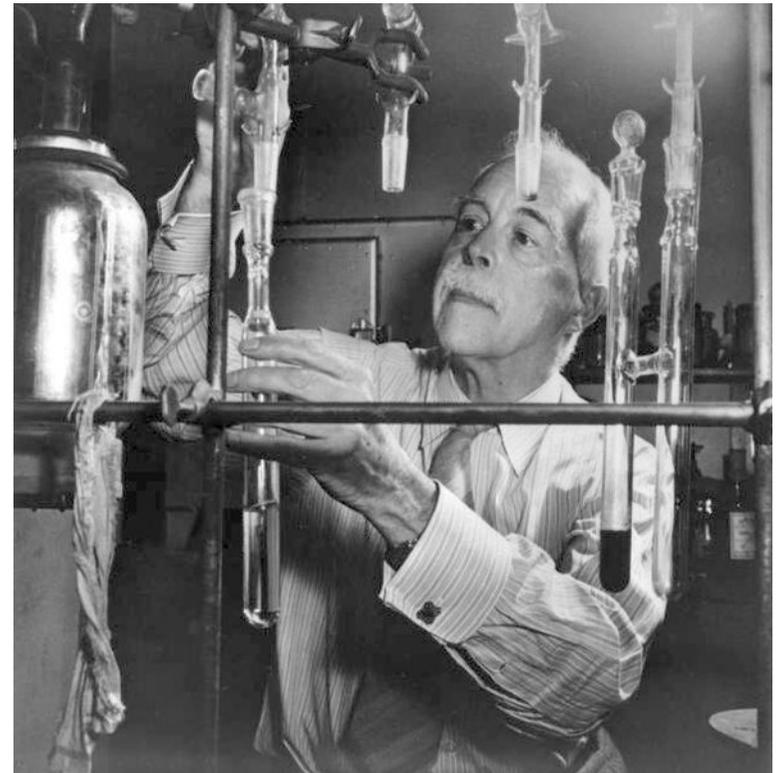
- 1915 – W. Kössel (Munich) → Ligação iônica
 - Átomos reagem para assumir a configuração de um gás nobre
- 1916 – G. N. Lewis (Califórnia)
 - Emparelhamento de elétrons para a formação da ligação química
 - Reconhecimento de que elétrons, por estarem localizados na parte externa do átomo são responsáveis pela ligação química

Livro clássico (divisor de águas)

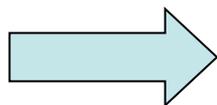
- 1923 – “Valence and Structure of Atoms and Molecules” G. N. Lewis
 - Reconhecimento do conceito de par de elétrons na ligação química

Trunfo da lógica cartesiana

**Qualquer sistema de N elétrons
pode ser subdividido em
subsistemas de 2 elétrons!!!
(usamos até hoje!!!)**



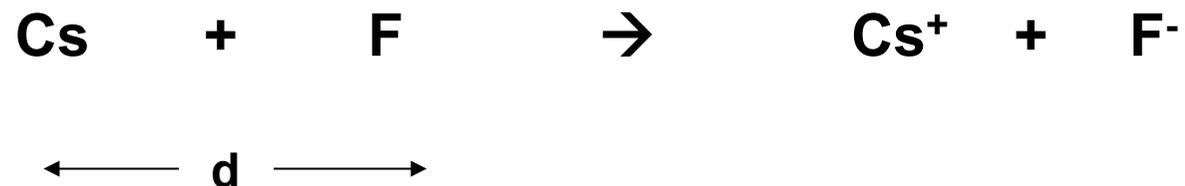
Reatividade
Química



Depende dos elétrons

Transferências de 1 elétron:

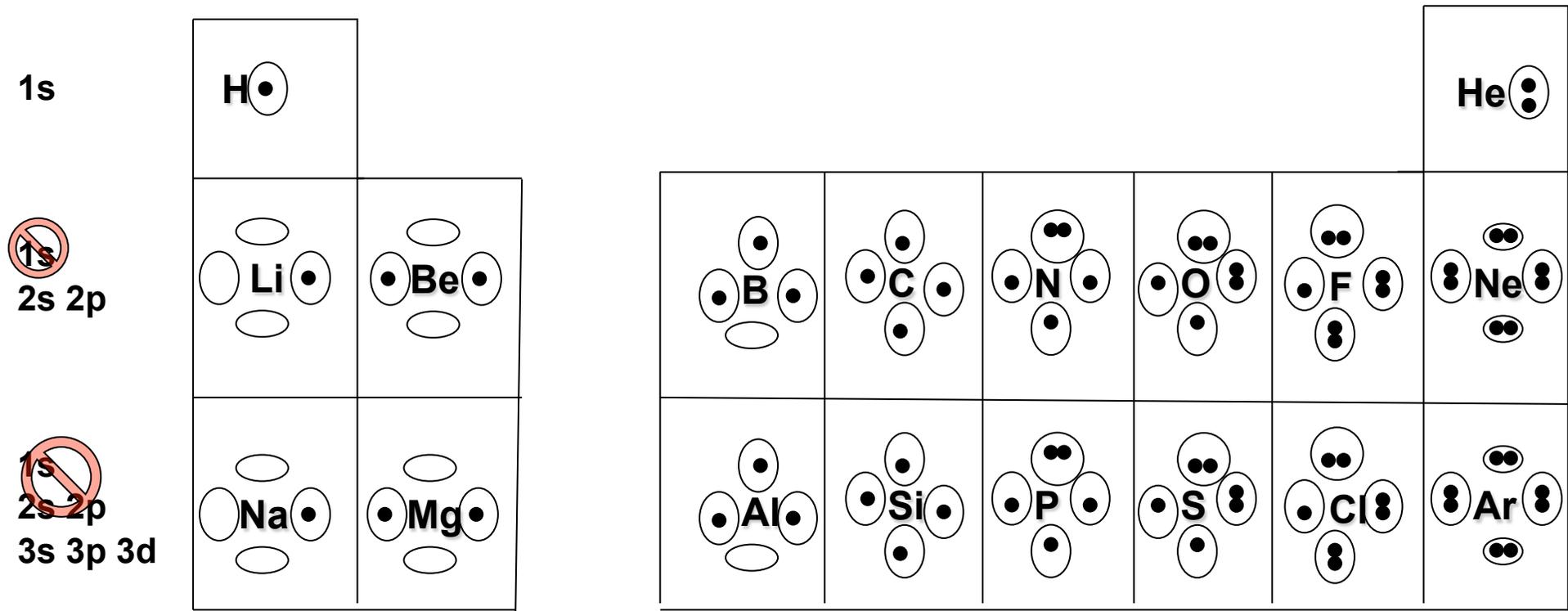
Desde curtas distâncias
até 150 Å



d ~ 58 Å !!!!

Tabela Periódica e Estruturas de Lewis

- Contagem de Elétrons de **Valência** é **Fundamental** para Entender **Reatividade Química**



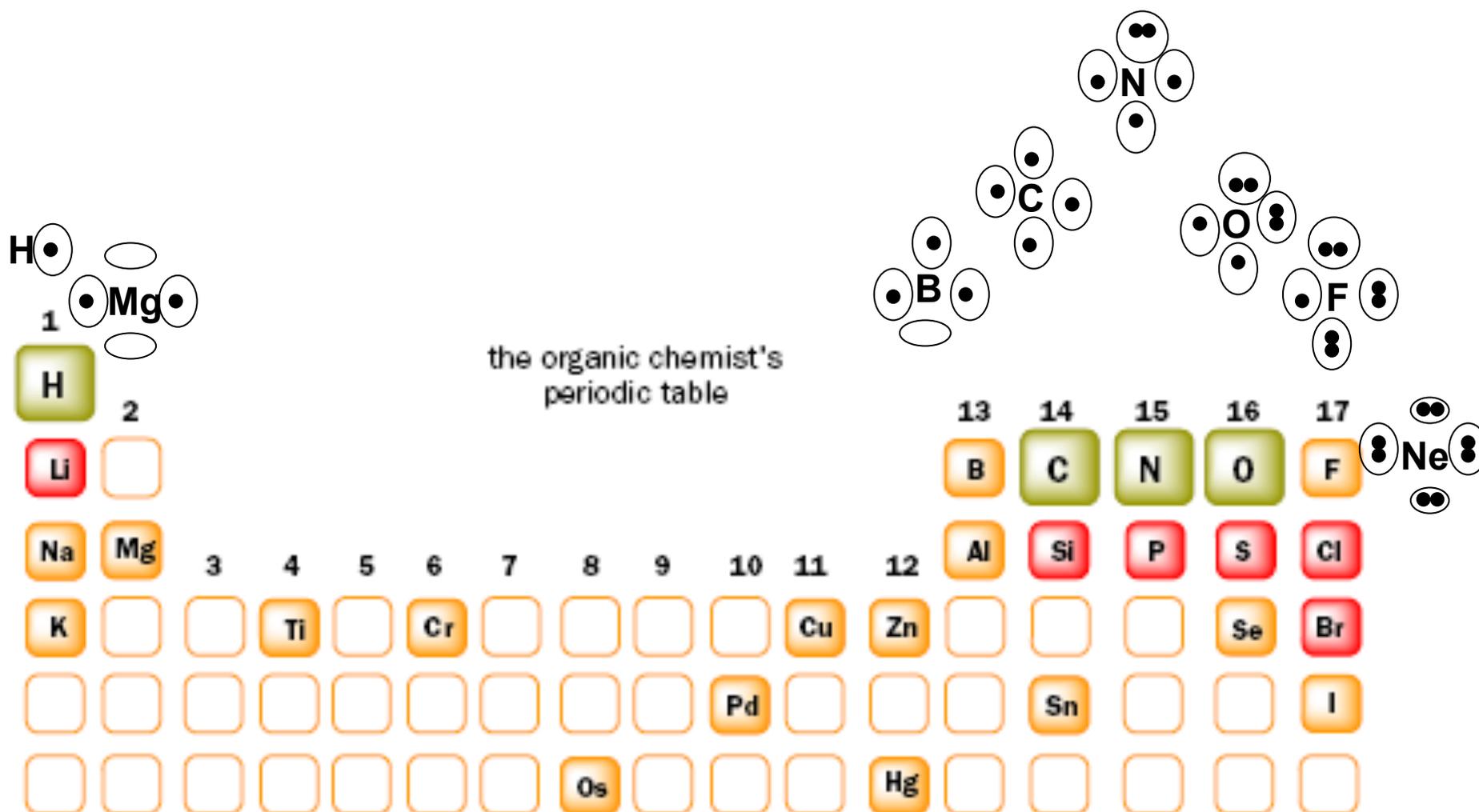
Basicamente 3 tipos de reação em toda a Química Orgânica

- Oxidação-Redução de 1 elétron (SET)
- Ácido-Base: Transferência de 2 elétrons
- Pericíclicas: N elétrons

Estimo que cerca de **80 %** das reações sejam classificadas como ácido-base

Tabela Periódica e Estruturas de Lewis:

Contagem de Elétrons é Fundamental para Entender Reatividade Química



Quer relaxar um pouco? Baralho Químico

- [Jogos.iq.ufrj.br](http://jogos.iq.ufrj.br)
- <http://www.ekmfsites.com.br/q/jogos.php?idJogo=1>

QUÍMICA JOGOS

Principal

Paciência Periódica

Ranking

Cadastre-se Já!

Login

Pilha de Descarte

Distribuir Cartas

Ver Regras

00:37:59

35 bromo Br 79.90

14 silício Si 28.09

16 enxofre S 32.07

20 cálcio Ca 40.08

113 urânio Uut 284.18

34 selênio Se 78.96

50 estanho Sn 118.71

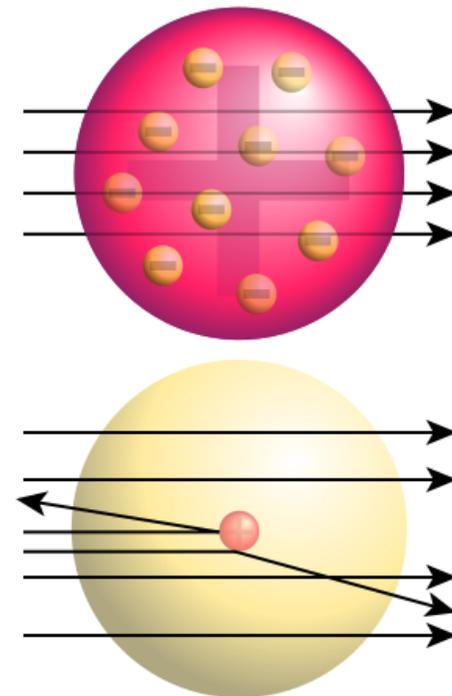
84 polônio Po 209.98

Paralelamente na Física...

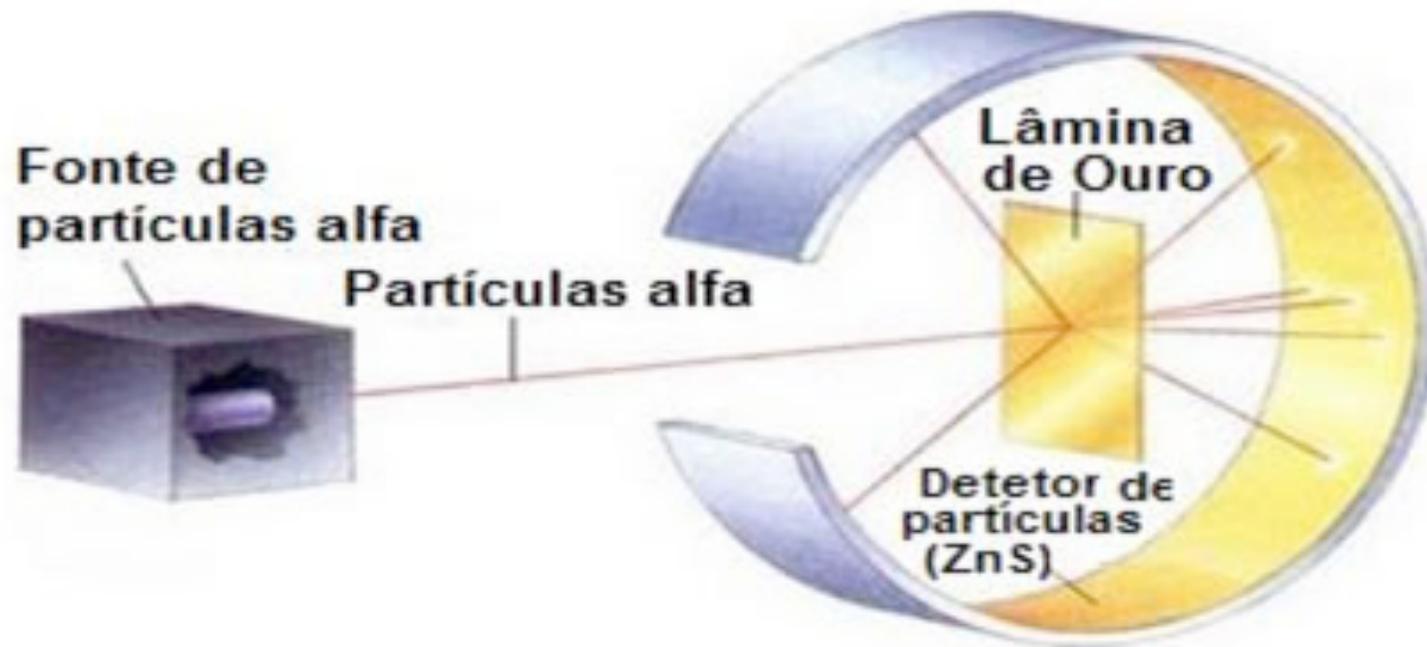
- 1904 – Thomsom
 - Descoberta do elétron
- Rutherford, Geiger e Marsdsen
 - Descoberta do núcleo



Modelo atômico (planetário) de Rutherford



Folhas de Ouro... O Experimento de Geiger-Marsden

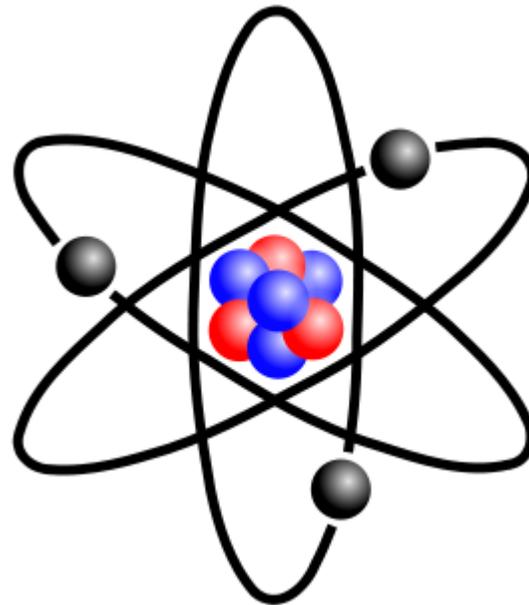


Geiger-Marsden (1909)

O modelo de Rutherford



Ernest Rutherford



**Átomo não teria estabilidade → do eletromagnetismo sabe-se que uma carga acelerada emite radiação (energia)
Se sistema perde energia, elétrons deveriam cair no núcleo, o que não acontece.**

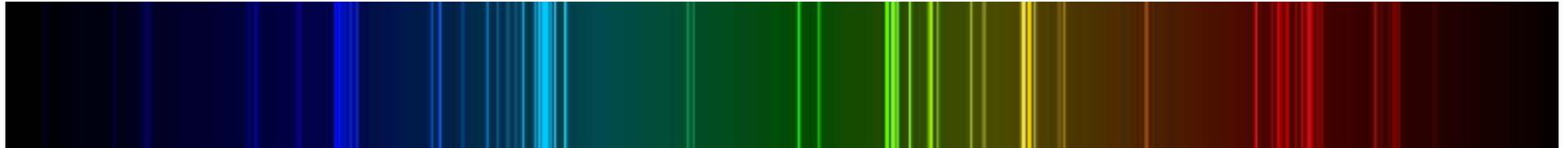
Efeito Fotoelétrico

- 1900 – Max Planck
 - Estudo dos corpos negros
- 1905 – Einstein
 - Efeito fotoelétrico: Luz, partícula ou onda?
- Espectroscopia atômica → Linhas de absorção
- Quantização de energia: Física de Newton começa a ruir...

Linhas de absorção hidrogênio

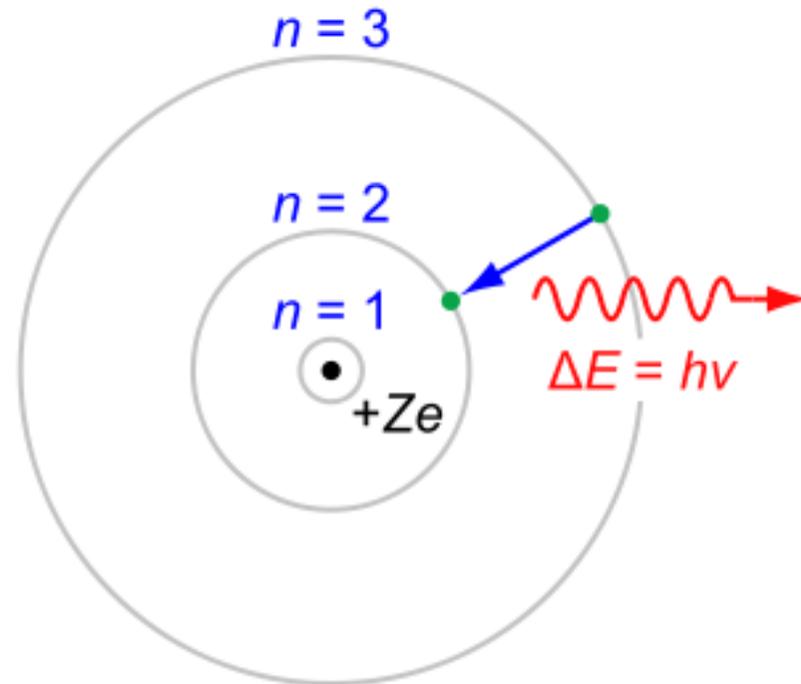


Linhas de absorção do nitrogênio



Estrutura do Átomo

1913 – Niels Bohr



- Quantização do momento angular dos elétrons (órbitas constantes)
- Explicava linhas em espectroscopia

Física de Newton começa a ruir...

- 1924 - De Broglie

$$E = mc^2 \therefore E = \frac{hc}{\lambda}$$

$$mc^2 = \frac{hc}{\lambda}$$

$$mc = \frac{h}{\lambda}$$



De Broglie

Átomo de Hélio

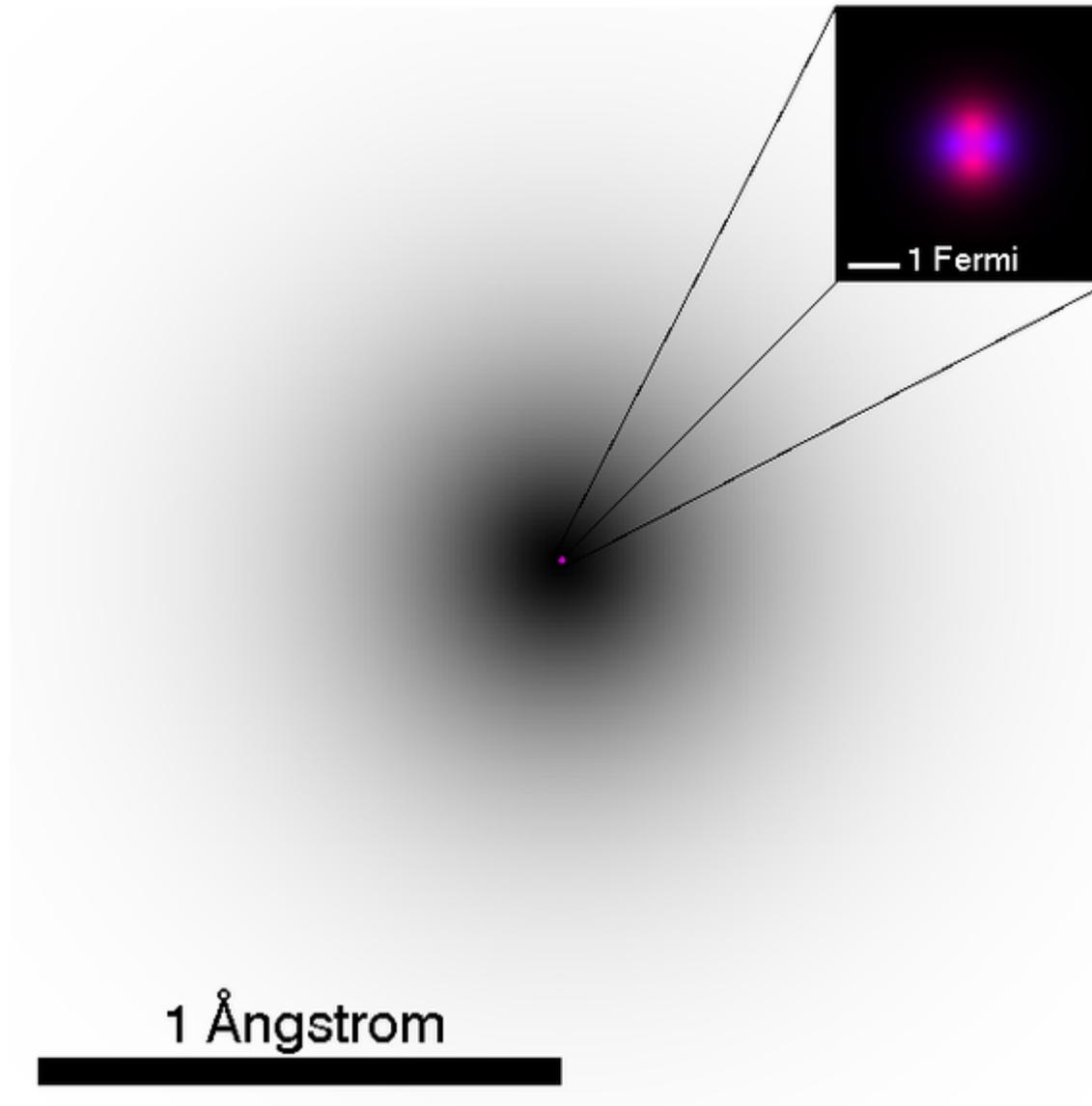


Figura 1.28 Previsão clássica para a passagem de elétrons através de fendas.

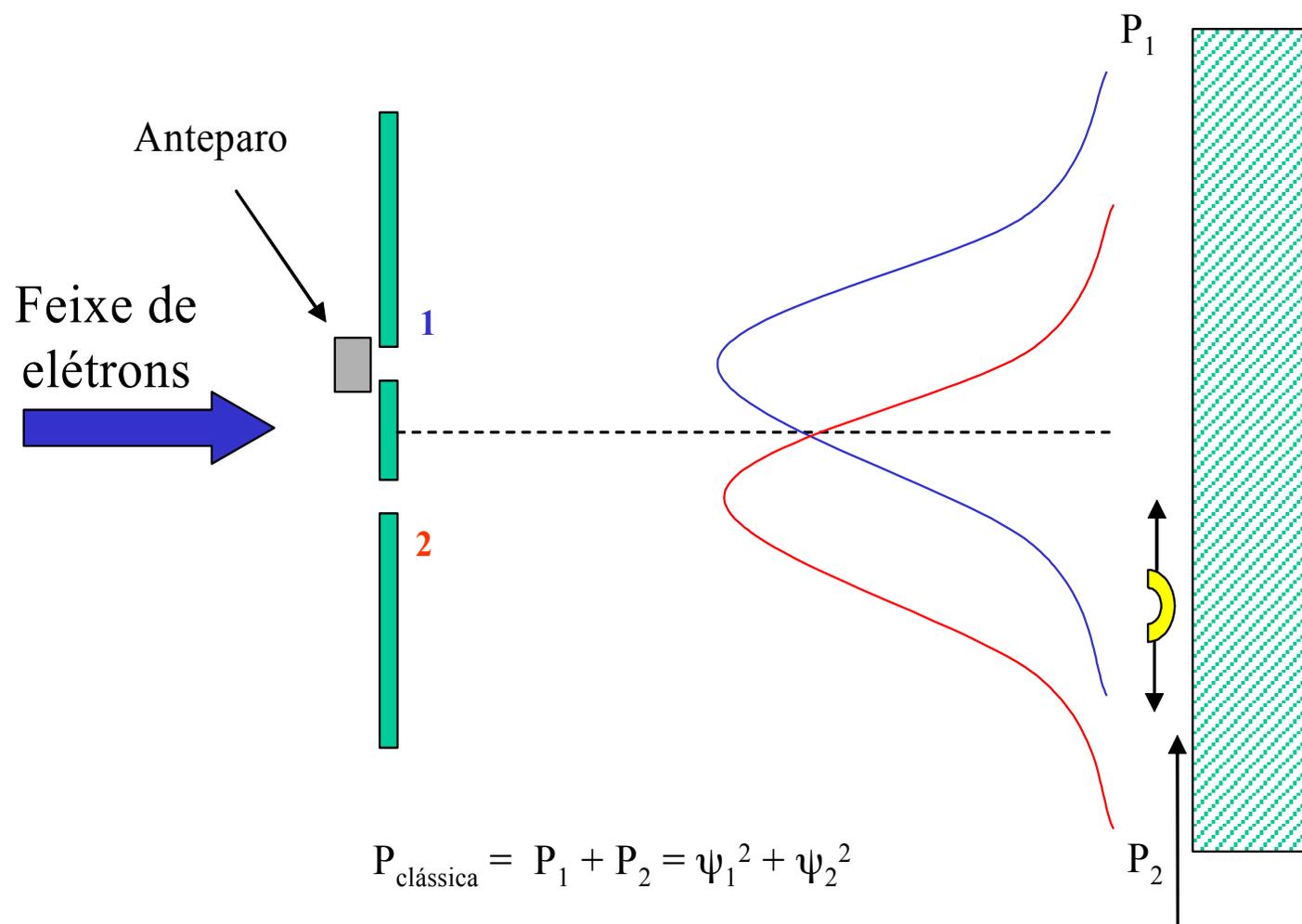
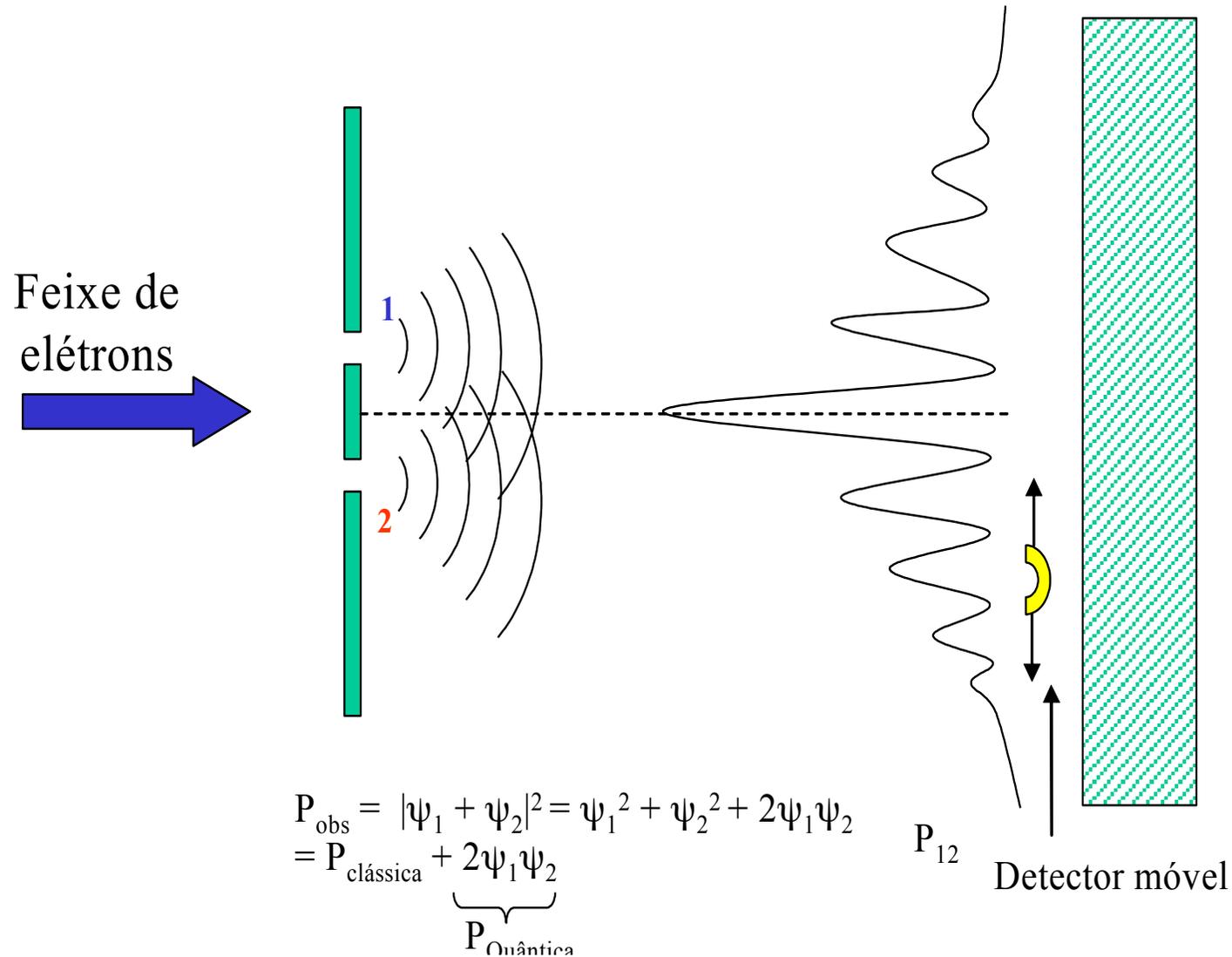
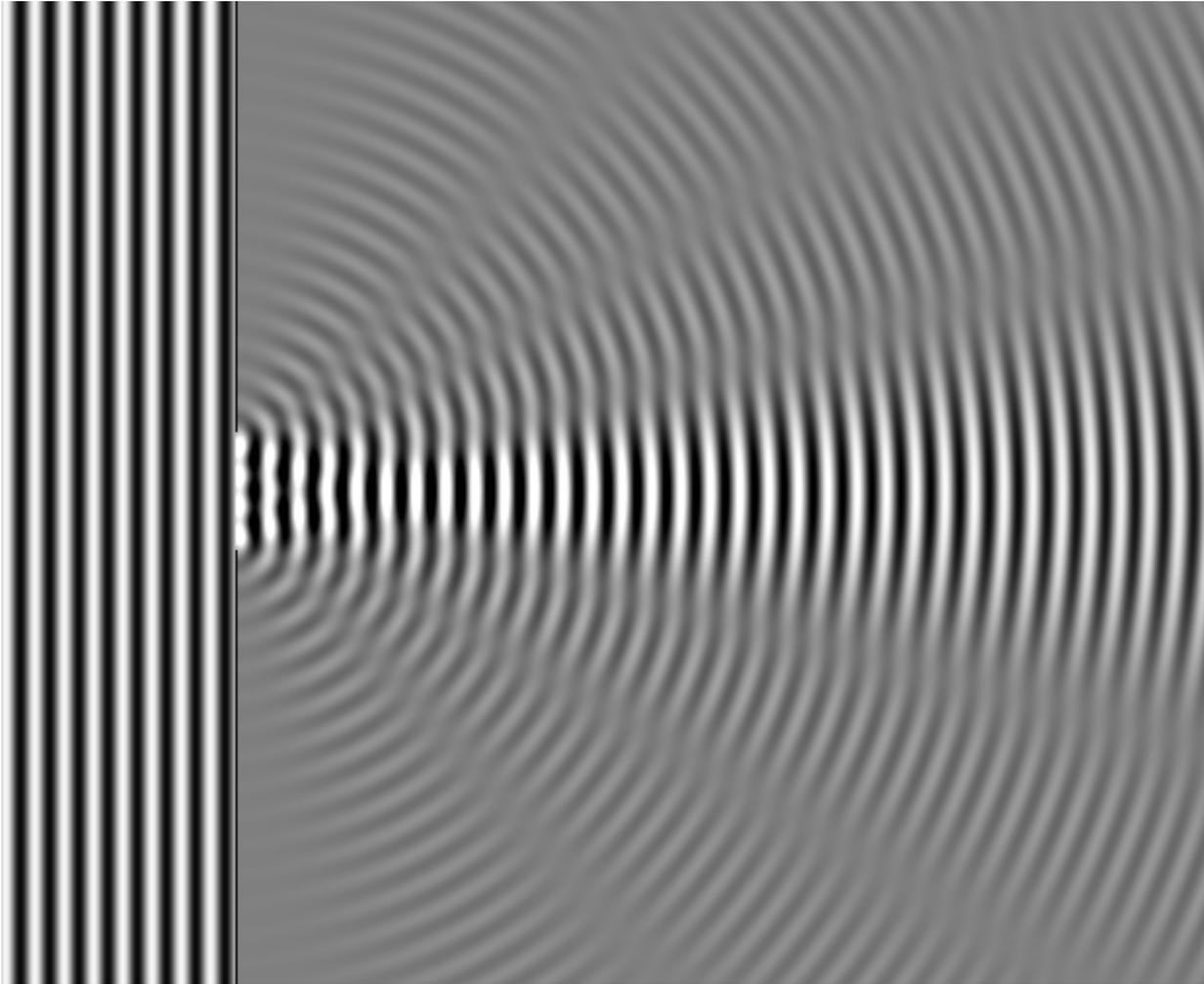


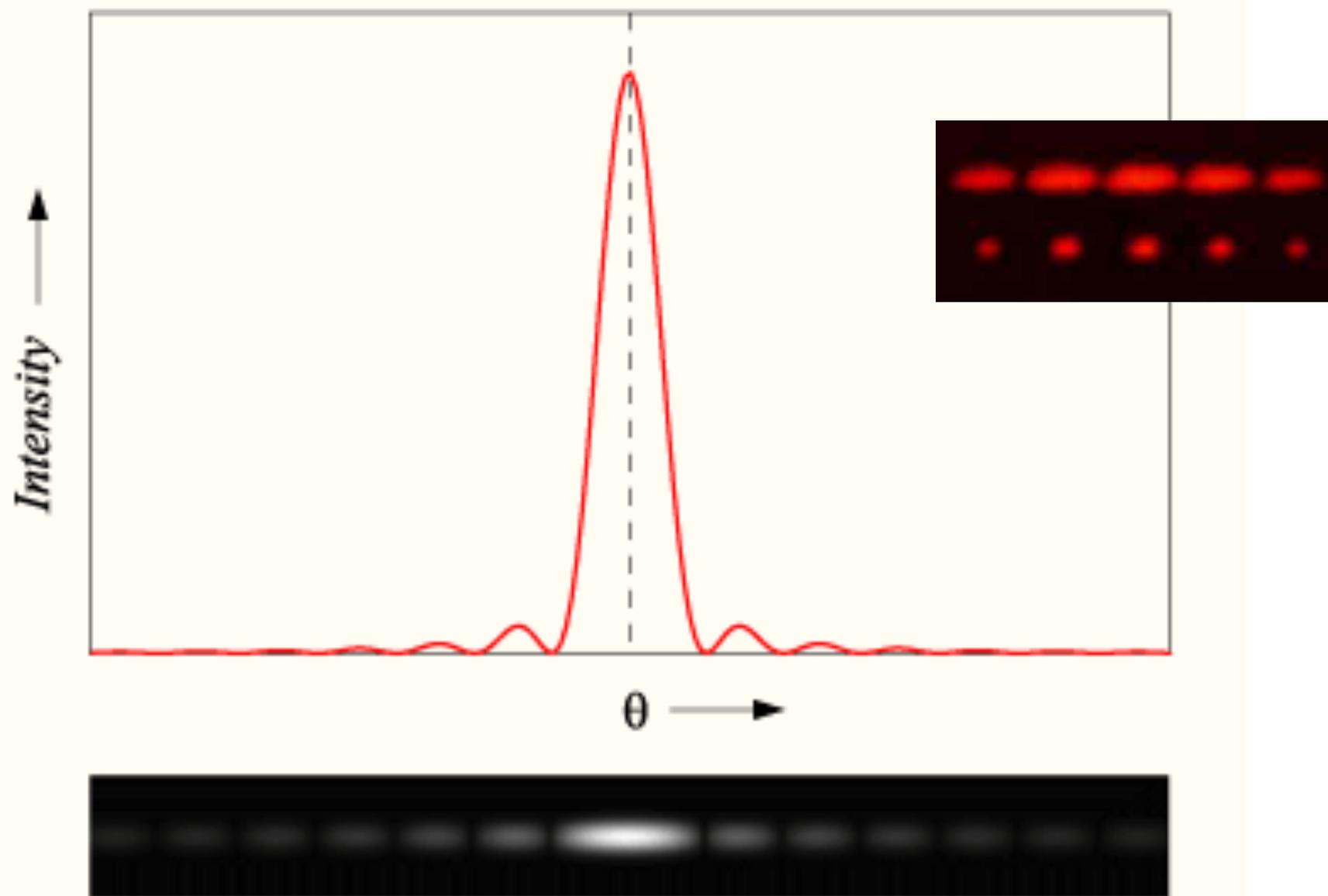
Figura 1.29 Experimento de Davidson e Germer de difração de elétrons em cristais de níquel



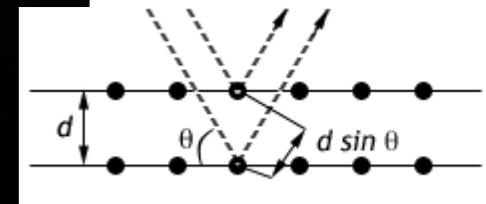
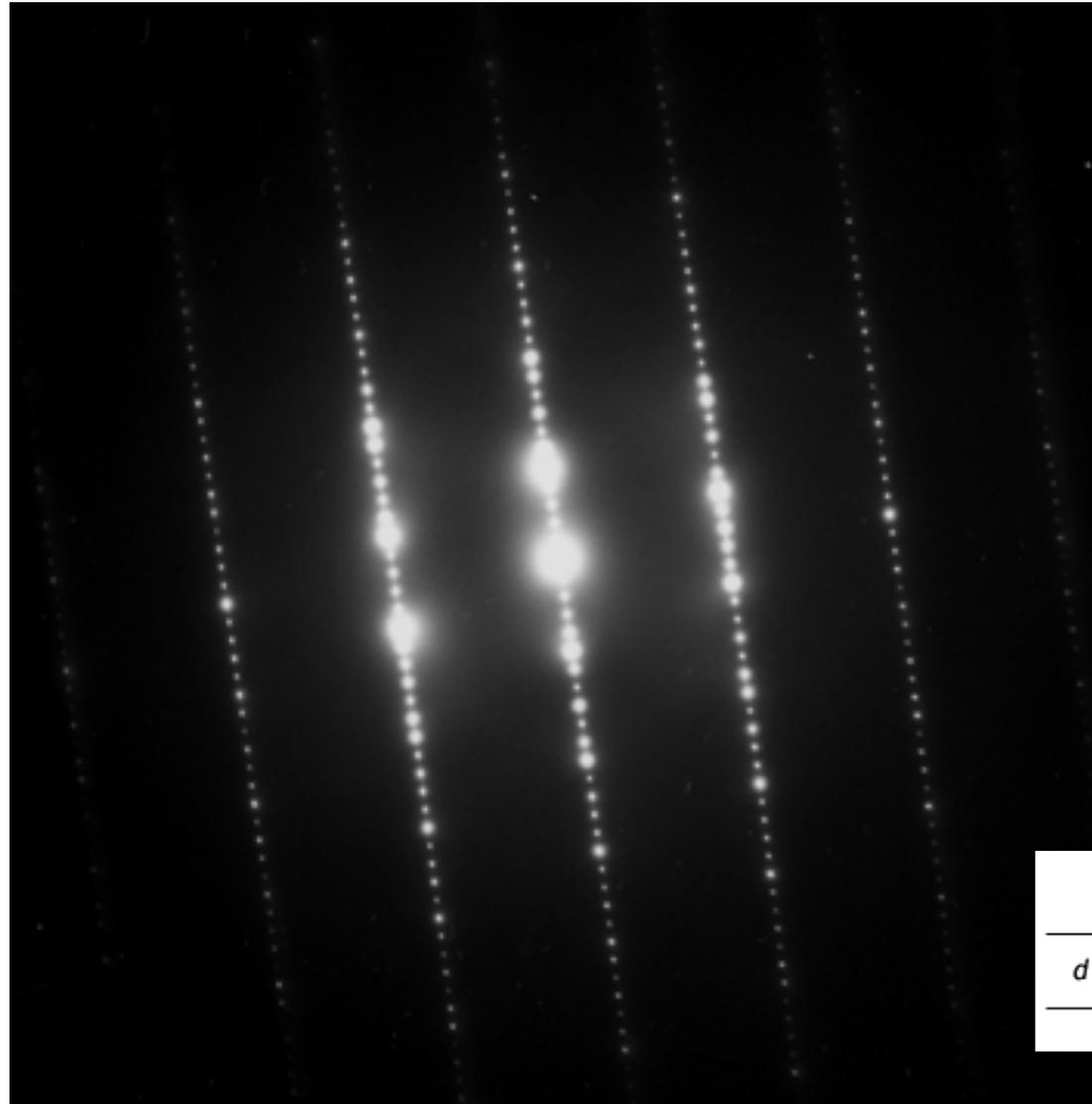
Interferência...



Single-slit diffraction pattern

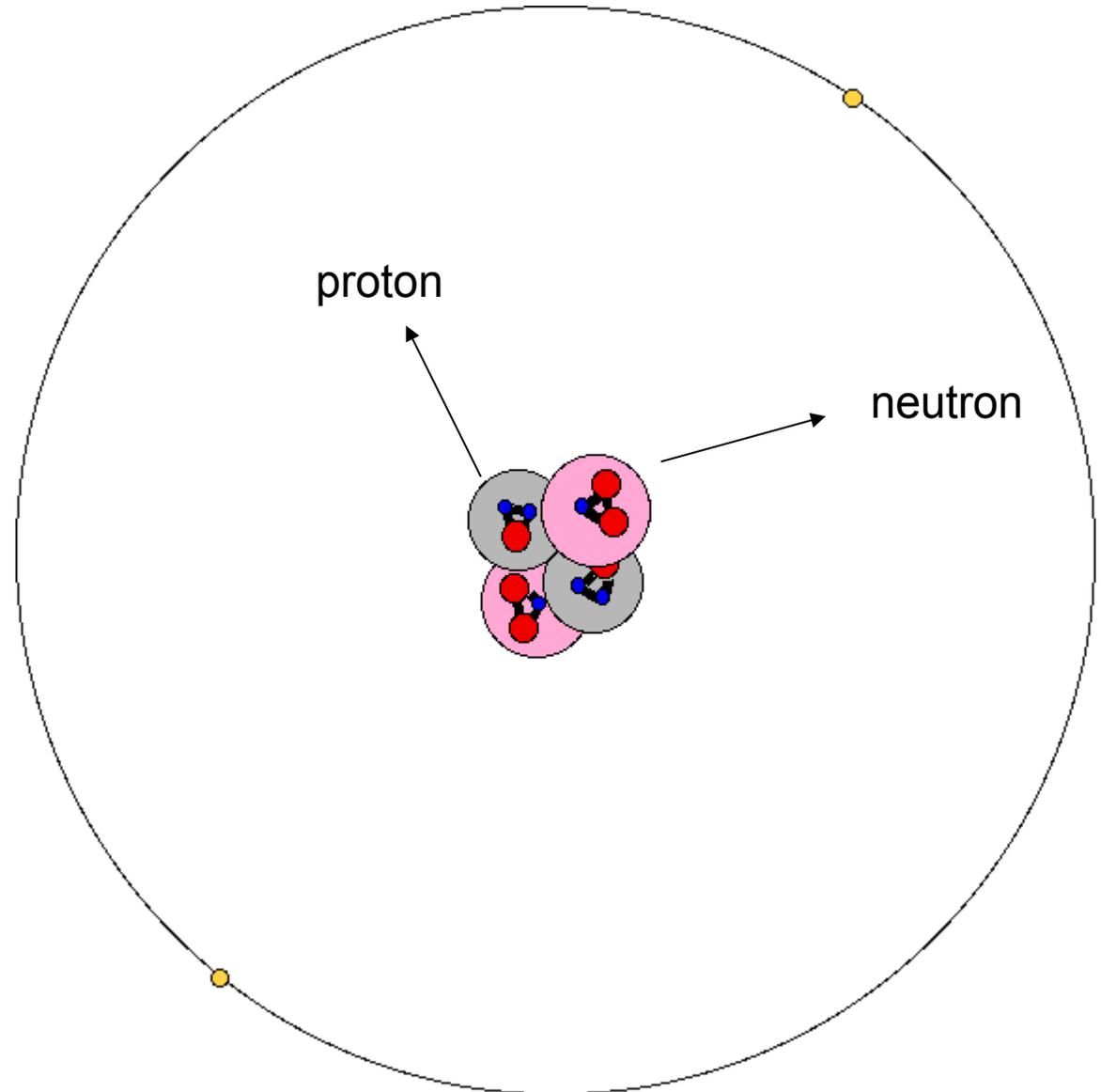


Difração de elétrons: microscópio TEM (Transmission Electron Microscope)



Estrutura do Átomo

- Núcleo feito de quarks e gluons
- Neutron: 2 quarks up (vermelho) e 1 quark down (azul)
- Próton: 1 quark up e 2 quarks down
- Gluons mantém núcleo junto



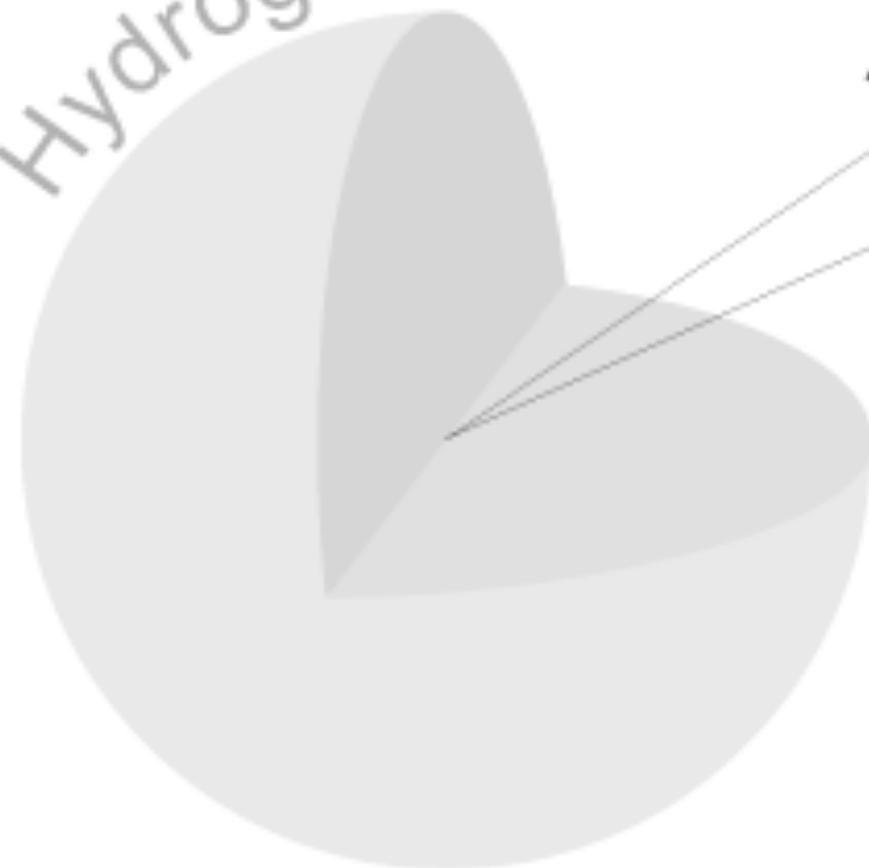
Hydrogen

Proton



1.6 to 1.7×10^{-5}
Ångstrom

1.20 Ångstrom



1925-1926

- Erwin Schrödinger// Nascimento da mecânica quântica ondulatória

$$\frac{\partial^2 \Psi(x, t)}{\partial x^2} = \frac{1}{v^2} \frac{\partial^2 \Psi(x, t)}{\partial t^2}$$

$$H\Psi(x, t) = E\Psi(x, t)$$

Erwin Schrödinger (1887-1961)

- Em 1910 recebeu seu doutorado pela Universidade de Viena. Foi bastante interessado em Filosofia.
- Em 1921 foi para Zurich, onde trabalhou com a mecânica estatística dos gases, teoria da cor e teoria atômica. Sempre esteve a par dos avanços na área, principalmente de Bohr e De Broglie.

Erwin Schrödinger estava interessado em achar uma equação única e definitiva, cujas soluções descrevessem a onda de De Broglie independentemente das circunstâncias...



No Natal de 1925, inventou sua equação de onda esquiando nos Alpes suíços.

Uma sugestão lógica...



- P. Debye havia sugerido a Schrödinger que partisse das equações fundamentais da Mecânica Ondulatória...

$$\frac{\partial^2 \Psi}{\partial x^2} = \frac{1}{v^2} \cdot \frac{\partial^2 \Psi}{\partial t^2} \Rightarrow \Psi(x, t) = C \cdot \exp \left[2\pi i \cdot \left(\frac{x}{\lambda} - vt \right) \right]$$

Segundo as relações de Planck-Einstein $E = h\nu$

... e De Broglie $p = h/\lambda$... e daí sai direto

$$\Psi(x, t) = C \cdot \exp \left[2\pi i \cdot \left(\frac{px}{h} - \frac{Et}{h} \right) \right]$$

Onde Ψ é uma função que daria a “intensidade” da onda de De Broglie em várias posições no espaço.

As derivadas da função Ψ com relação ao tempo (t) e o deslocamento (x) são fáceis de obter:

$$\frac{\partial \Psi}{\partial t} = \left(-\frac{i}{\hbar} \right) E \cdot \Psi \quad \text{e} \quad \frac{\partial \Psi}{\partial x} = \left(\frac{i}{\hbar} \right) p_x \Psi$$

Um rearranjo trivial destas equações fornece

$$\left(-\frac{\hbar}{i} \right) \frac{\partial \Psi}{\partial t} = E \cdot \Psi \quad \text{e} \quad \left(\frac{\hbar}{i} \right) \frac{\partial \Psi}{\partial x} = p_x \cdot \Psi$$

A partir destas expressões podemos definir os operadores associados à energia total

$$\tilde{E} = -\frac{\hbar}{i} \frac{\partial}{\partial t}$$

e momento linear

$$\tilde{p}_x = \frac{\hbar}{i} \frac{\partial}{\partial x}$$

Como na descrição clássica as partículas têm energia

$$E = E_c + V = \frac{mv^2}{2} + V = \frac{p^2}{2m} + V$$

podemos tentar estabelecer uma correspondência direta (ver Primeiro Postulado) e escrever

$$\tilde{E}_c = \frac{\tilde{p}^2}{2m} = \frac{1}{2m} \tilde{p}\tilde{p} = \frac{1}{2m} \frac{\hbar}{i} \frac{\partial}{\partial x} \frac{\hbar}{i} \frac{\partial}{\partial x} = -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2}$$

para o operador de energia cinética.

$$\tilde{H} = \tilde{E}_c + \tilde{V} = -\frac{\hbar^2}{2m} \tilde{\nabla}^2 + \tilde{V}$$

para o operador Hamiltoniano associado à energia total do sistema. Consideramos aqui o operador $\tilde{V}(\mathbf{r})$ como uma energia potencial genérica, e a equação fica na forma

$$\tilde{H}\Psi = -\frac{\hbar^2}{2m} \nabla^2 \Psi + \tilde{V} \Psi = E \cdot \Psi$$

Observe que se o operador Hamiltoniano não contém explicitamente o tempo, é sempre possível separar as variáveis supondo que

$$\Psi(q, t) = \Psi(q) \cdot \Phi(t)$$

E obtemos sem dificuldades

$$\Phi(t) \cdot \tilde{H}\Psi(q) = i\hbar \cdot \Psi(q) \frac{\partial \Phi(t)}{\partial t}$$



$$\frac{\tilde{H}\Psi(q)}{\Psi(q)} = i\hbar \cdot \frac{1}{\Phi(t)} \frac{d\Phi}{dt}$$

Como o membro da esquerda só depende das coordenadas e o membro da direita só depende do tempo, cada membro tem de ser igual a uma constante à qual chamamos de E (que tem de ser uma energia por causa das unidades).

Assim, as duas equações resultantes formam um simpático sistema...

$$\begin{cases} \tilde{H}\Psi(q) = E \cdot \Psi(q) \\ \frac{d\Phi}{dt} = \frac{E}{i\hbar} \cdot \Phi(t) \end{cases}$$



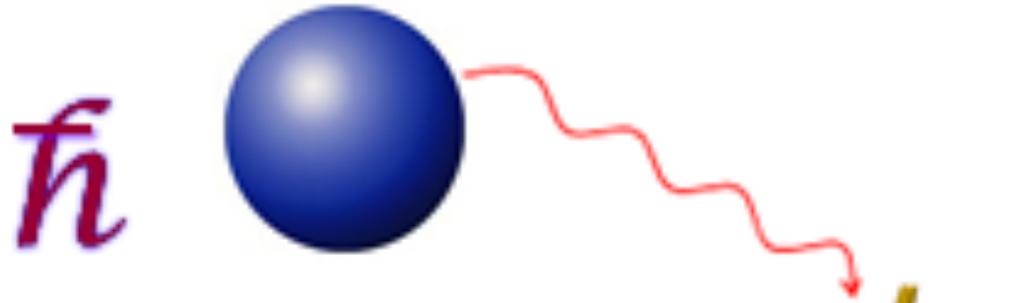
Schrödinger assumiu que as energias permissíveis (E) não são funções do tempo, logo a segunda equação pode ser resolvida imediatamente dando

$$\Phi(t) = \exp\left[-\frac{i}{\hbar}Et\right]$$

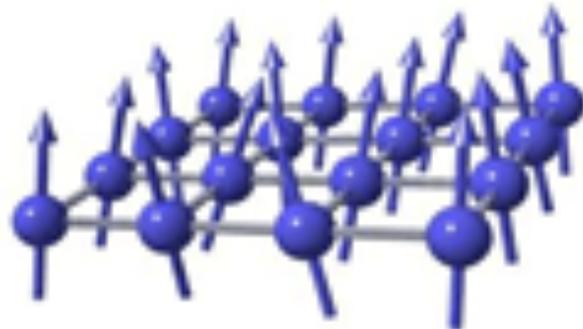
A evolução temporal do sistema!

A primeira equação do sistema é chamada de “equação de Schrödinger independente do tempo” ou “equação de Schrödinger para níveis estacionários”. É uma equação de autovalor, que pode ser resolvida (usando as técnicas usuais, aprendidas anteriormente em Cálculo) para achar o conjunto de autofunções (Ψ) e energias (E) permitidas dos níveis estacionários de qualquer sistema.

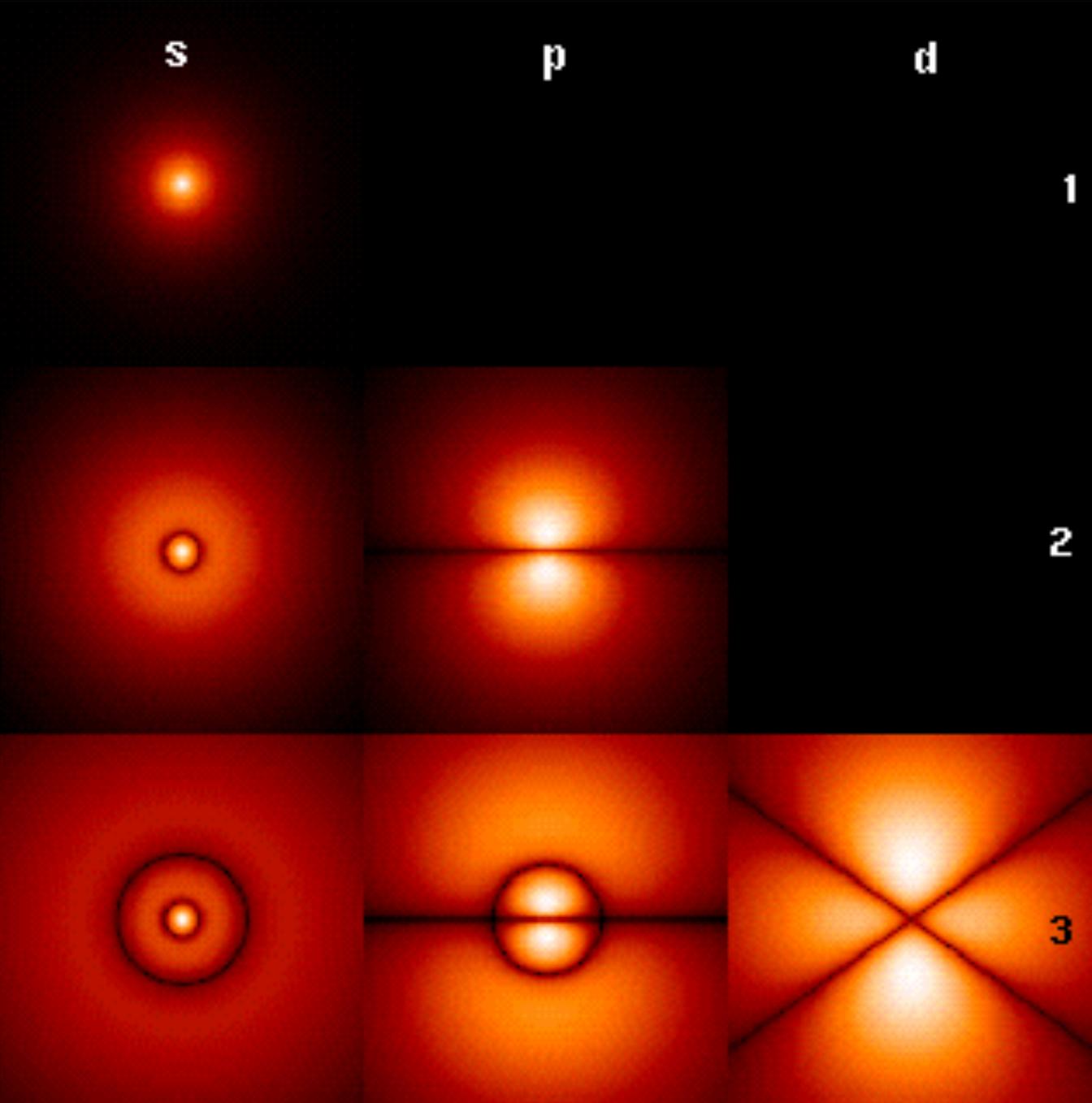
$$\tilde{H}\Psi = E \cdot \Psi$$



Heisenberg

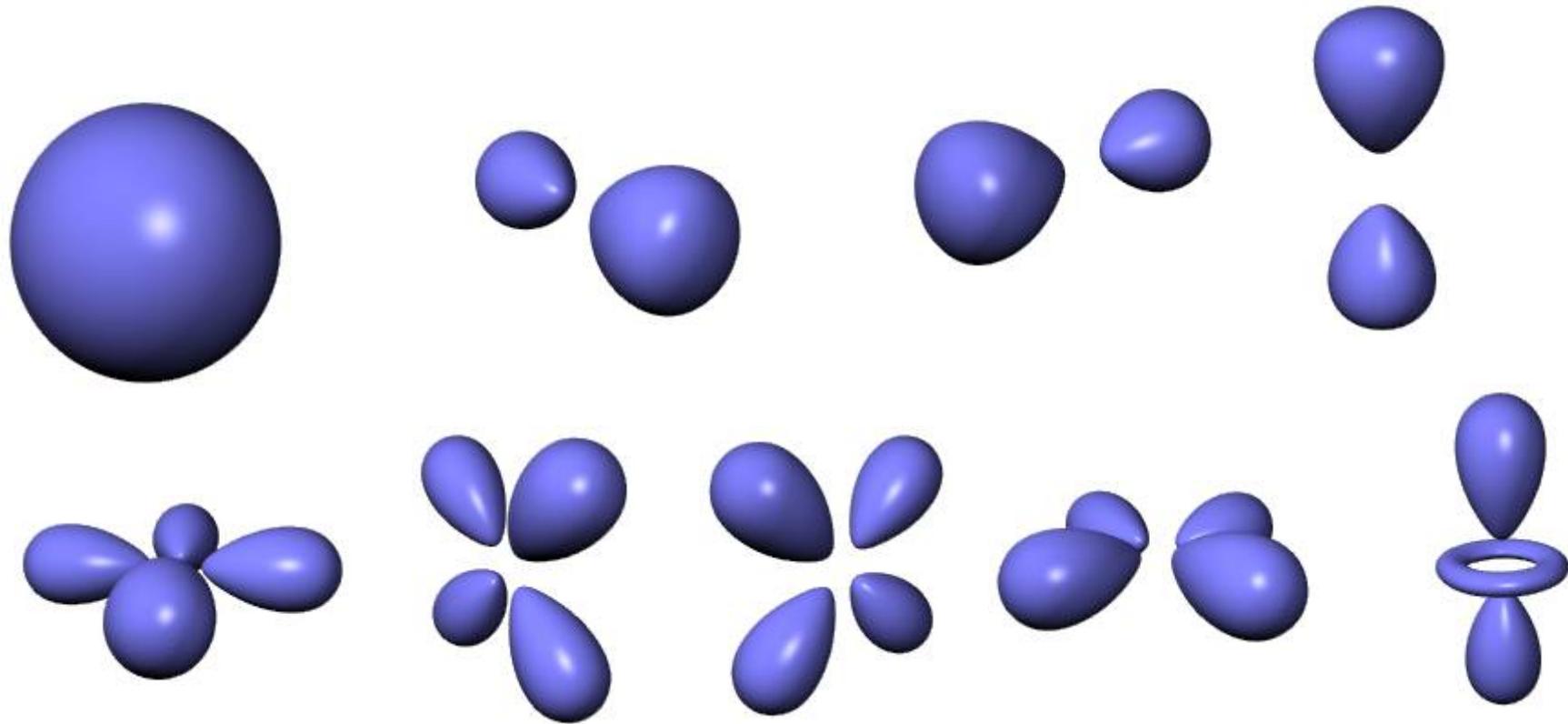


Schrödinger

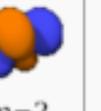
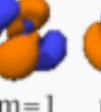
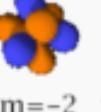
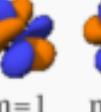
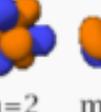
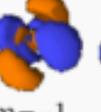
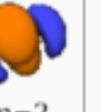


Orbitais: Raízes da Equação de Schrödinger

- Orbitais hidrogenóides



Soluções para o átomo de hidrogênio

	$s (l=0)$	$p (l=1)$	$d (l=2)$	$f (l=3)$
$n=1$	 m=0			
$n=2$	 m=0	   m=-1 m=0 m=1		
$n=3$	 m=0	   m=-1 m=0 m=1	     m=-2 m=-1 m=0 m=1 m=2	
$n=4$	 m=0	   m=-1 m=0 m=1	     m=-2 m=-1 m=0 m=1 m=2	       m=-3 m=-2 m=-1 m=0 m=1 m=2 m=3
$n=5$	 m=0	   m=-1 m=0 m=1	     m=-2 m=-1 m=0 m=1 m=2	
$n=6$	 m=0	   m=-1 m=0 m=1		
$n=7$	 m=0			

Átomos e moléculas multieletrônicos

- Eq. de onda de Schrödinger

$$H\Psi(x, t) = E\Psi(x, t)$$

- Ψ depende das coordenadas de todas as partículas (N elétrons e M núcleos) e do tempo.

$$\Psi = \Psi(x_1, y_1, z_1; x_2, y_2, z_2; \dots; x_N, y_N, z_N; X_1, Y_1, Z_1; X_2, Y_2, Z_2; \dots; X_M, Y_M, Z_M; t)$$

Hamiltoniano: operador da energia total ($E_c + V$) do sistema

$$H = E_c + V$$

$$H = (E_c)_{\text{elétrons}} + (E_c)_{\text{núcleos}} + V_{\text{elétron-núcleo}} + V_{\text{núcleo-núcleo}} + V_{\text{elétron-elétron}}$$

$$E_c = -\frac{\hbar\nabla^2}{2m}$$

$$V = \frac{1}{4\pi\epsilon_0} \frac{q_1 \cdot q_2}{r_{12}}$$

Átomos e moléculas com mais que 1 elétron

- Não há solução analítica (nos falta matemática)
- Soluções somente numéricas
- Aproximações para simplificar o problema
 - Processos independentes do tempo
 - Modelo de Born-Oppenheimer
 - Modelo da partícula independente

Processos independentes do tempo

- Ex.: Moléculas serão sempre as mesmas independente do tempo
- Tira tempo fora da jogada

$$H\Psi(x) = E\Psi(x)$$

Equação Schrödinger
independente do tempo

Aproximação de Born-Oppenheimer (1927)



Max Born



J. Robert Oppenheimer

- Elétrons são mais rápidos do que o núcleo mais leve
- Tira núcleos fora da jogada

$$\Psi = \Psi_{\text{eletron}}(x_1, y_1, z_1; \dots; x_N, y_N, z_N; \{R_M\}) \cdot \Psi_{\text{nuclear}}(R_M)$$

Aproximação do modelo da partícula independente

- Eq. onda eletrônica:
 - 1 equação de N partículas
- Modelo de partícula independente
 - N equações de 1 partícula (orbitais)

Sistema de N equações $\left\{ \begin{array}{l} h\psi_1(r_1) = \varepsilon_1\psi_1(r_1) \\ h\psi_2(r_2) = \varepsilon_2\psi_2(r_2) \\ \vdots \\ h\psi_N(r_N) = \varepsilon_N\psi_N(r_N) \end{array} \right. \quad \psi_i$

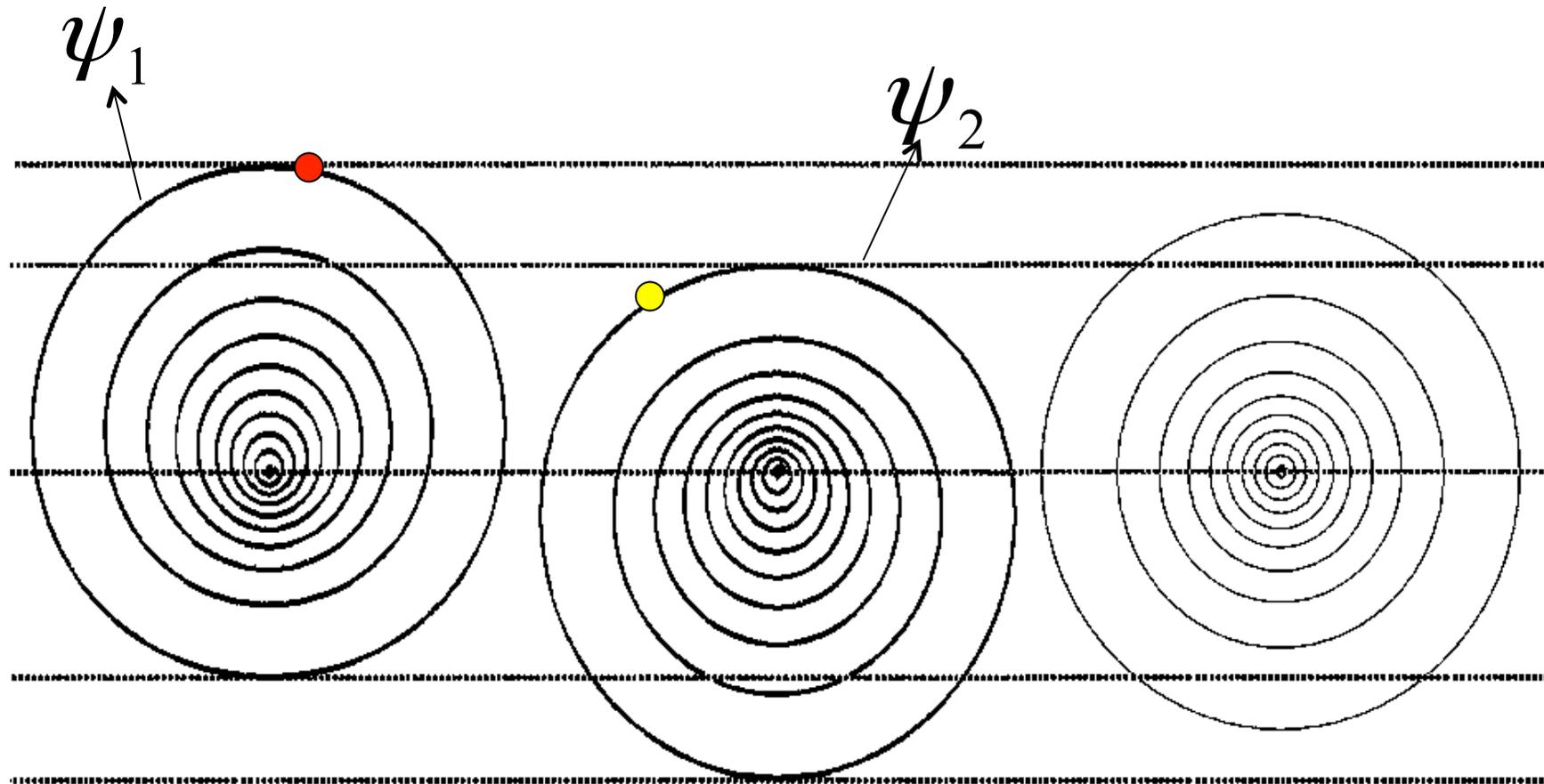
- Funções monoelétrônicas (orbitais)
- Descrevem apenas um dos elétrons (na presença dos outros)

Heisenberg → átomo de hélio (1926)

- Teoria da ressonância
- Troca de elétrons (ressonância) para tornar os elétrons indistinguíveis estabiliza o sistema

$$\Psi_{HL}(He) = [\psi_1(1)\psi_2(2) \pm \psi_1(2)\psi_2(1)]$$

Átomo de hélio: 1 núcleo, 2 elétrons



lobo
(+x)

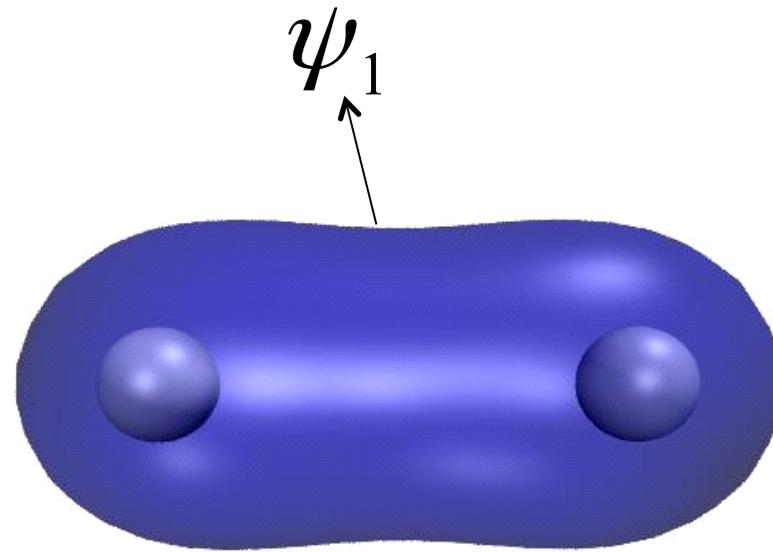
lobo
(-x)

“1s²”

$$\Psi = \psi_1 (\text{red dot}) \cdot \psi_2 (\text{yellow dot})$$

Proj. Final de curso (2008)
Gabriel do Nascimento Freitas e
Marco Antonio Chaer Nascimento

Dois núcleos, 1 elétron: H_2^+



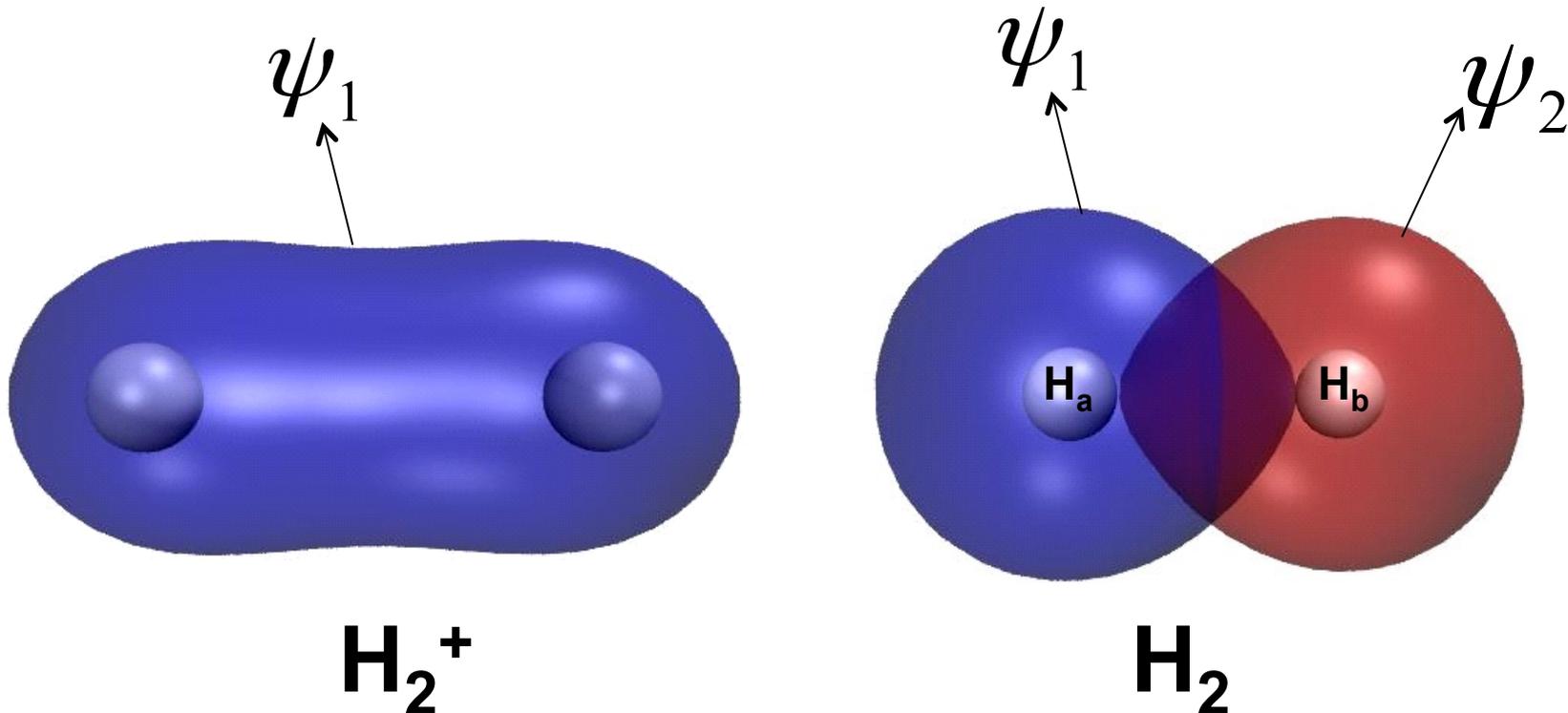
H_2^+

Heitler e London → molécula de H₂ (1927)

- Nascimento do modelo de ligação de valência moderno

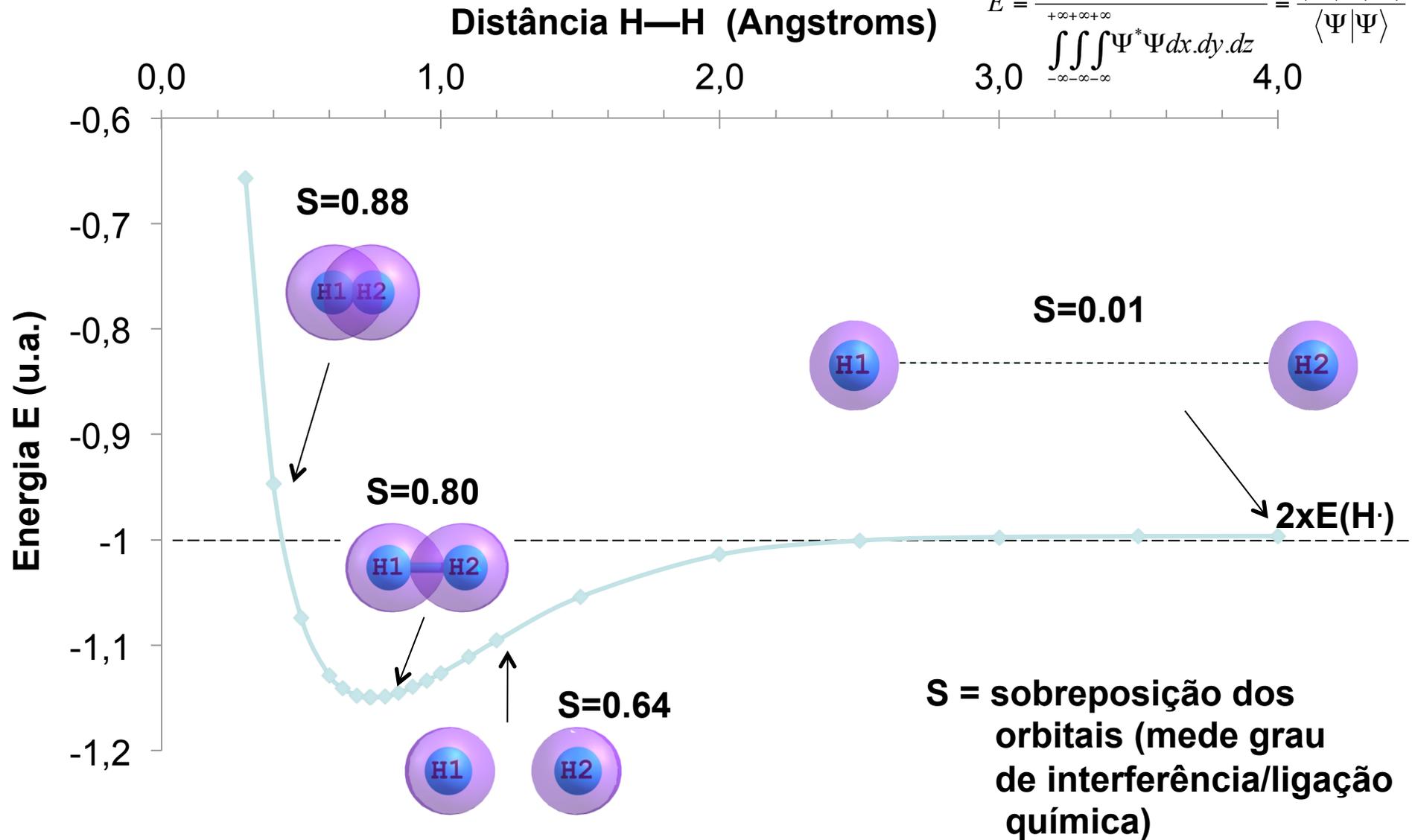
$$\Psi_{HL}(H_2) = [\psi_1(1)\psi_2(2) \pm \psi_1(2)\psi_2(1)]$$

$$\Psi_{HL}(H_2) \approx [1s_a(1)1s_b(2) \pm 1s_a(2)1s_b(1)]$$

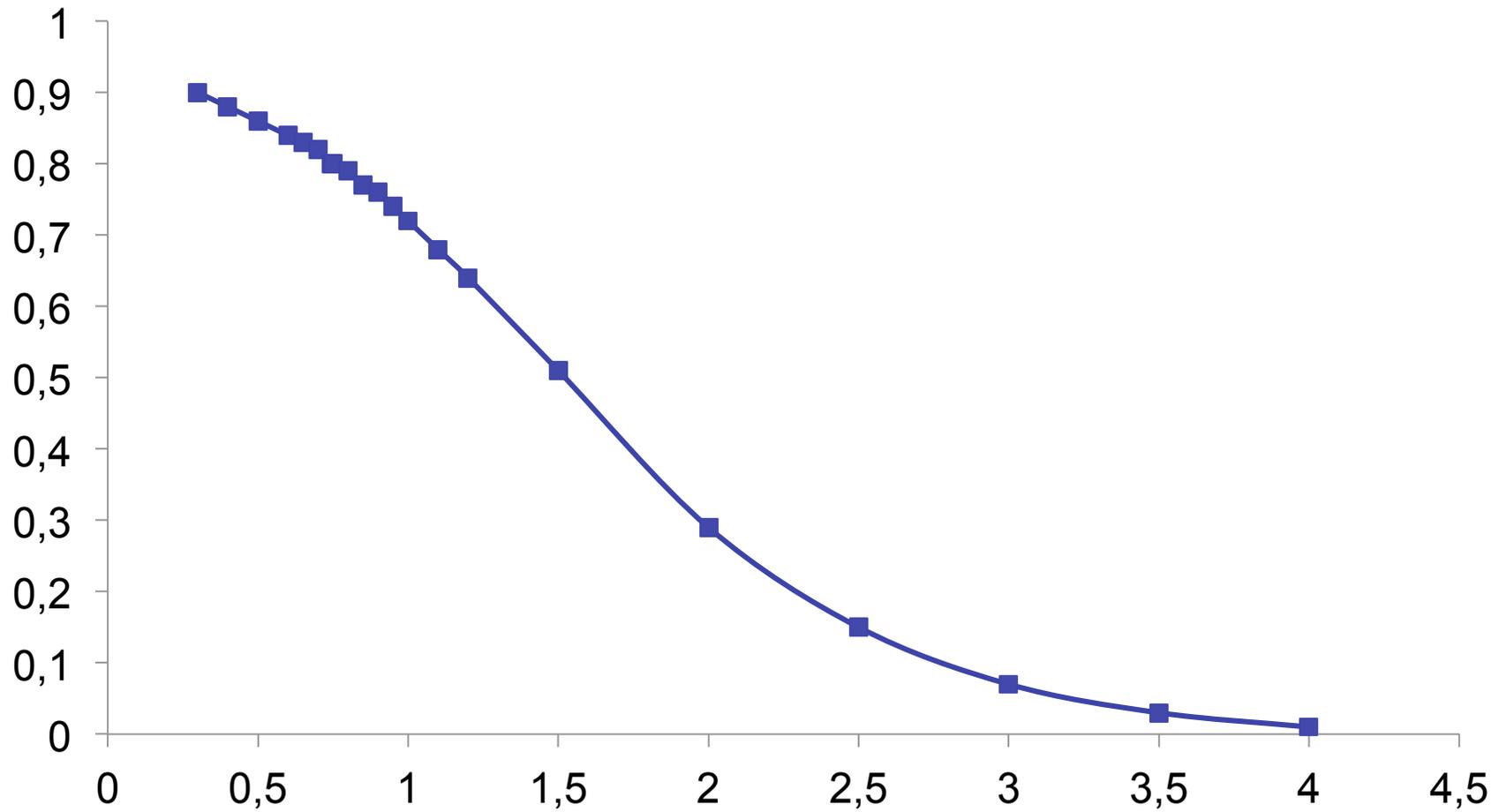


Energia total x distância H—H

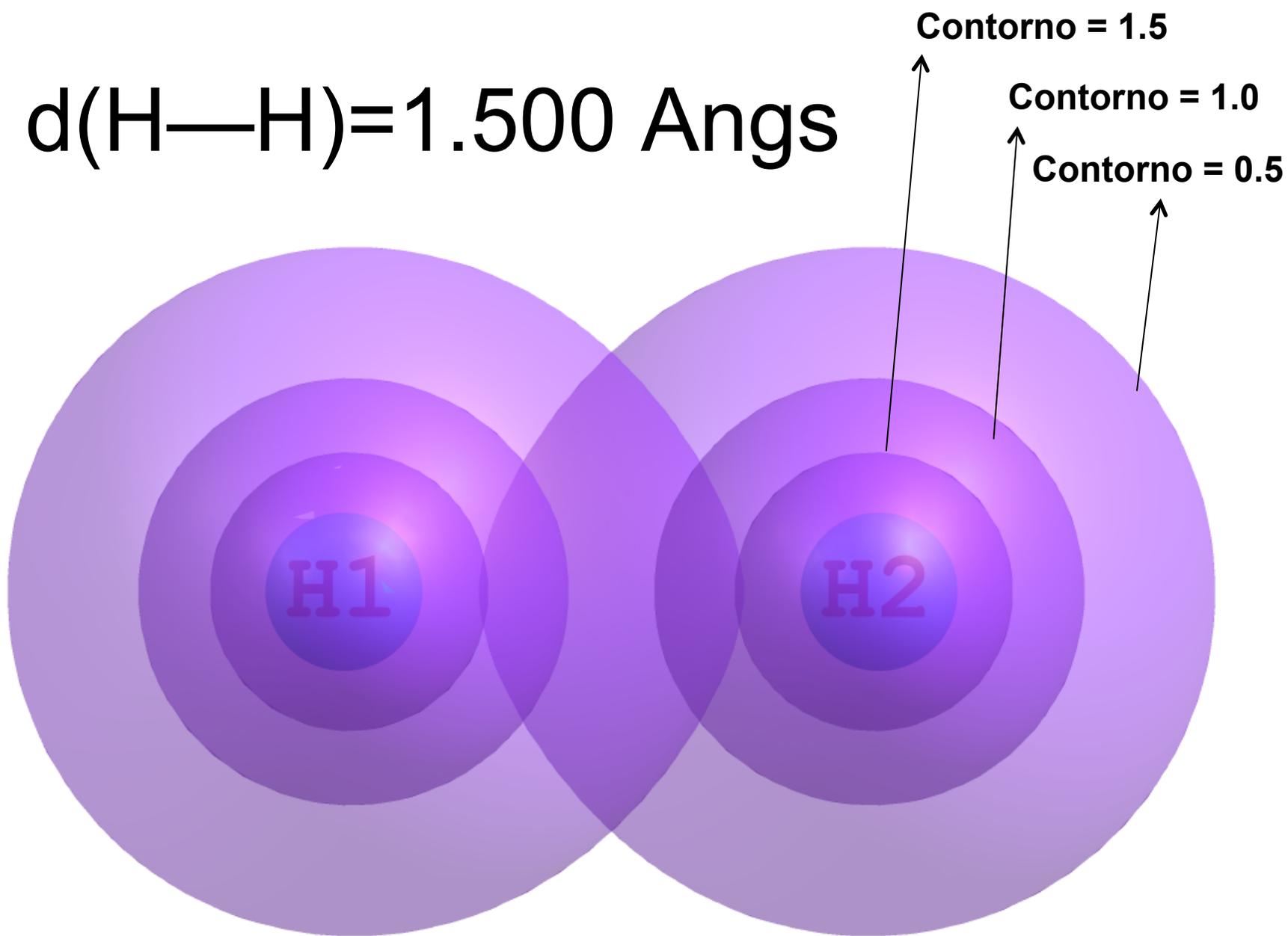
$$E = \frac{\int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} \Psi^* H \Psi dx dy dz}{\int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} \Psi^* \Psi dx dy dz} = \frac{\langle \Psi | H | \Psi \rangle}{\langle \Psi | \Psi \rangle}$$



Sobreposição (S) x Distância

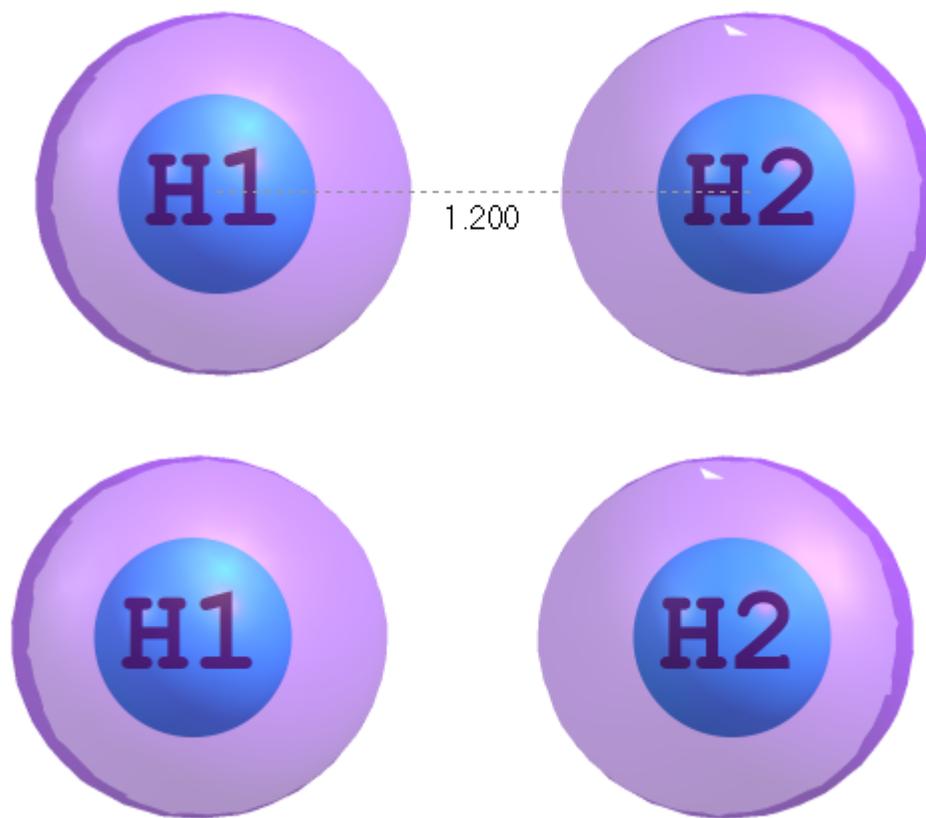


$d(\text{H—H}) = 1.500 \text{ Angs}$

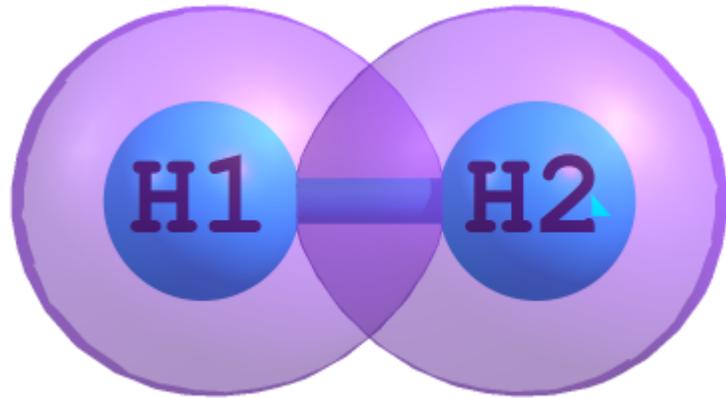




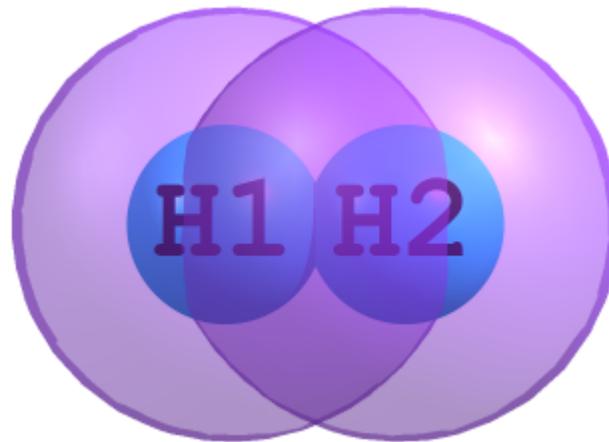
$d(\text{H—H})=1.200$ Angs

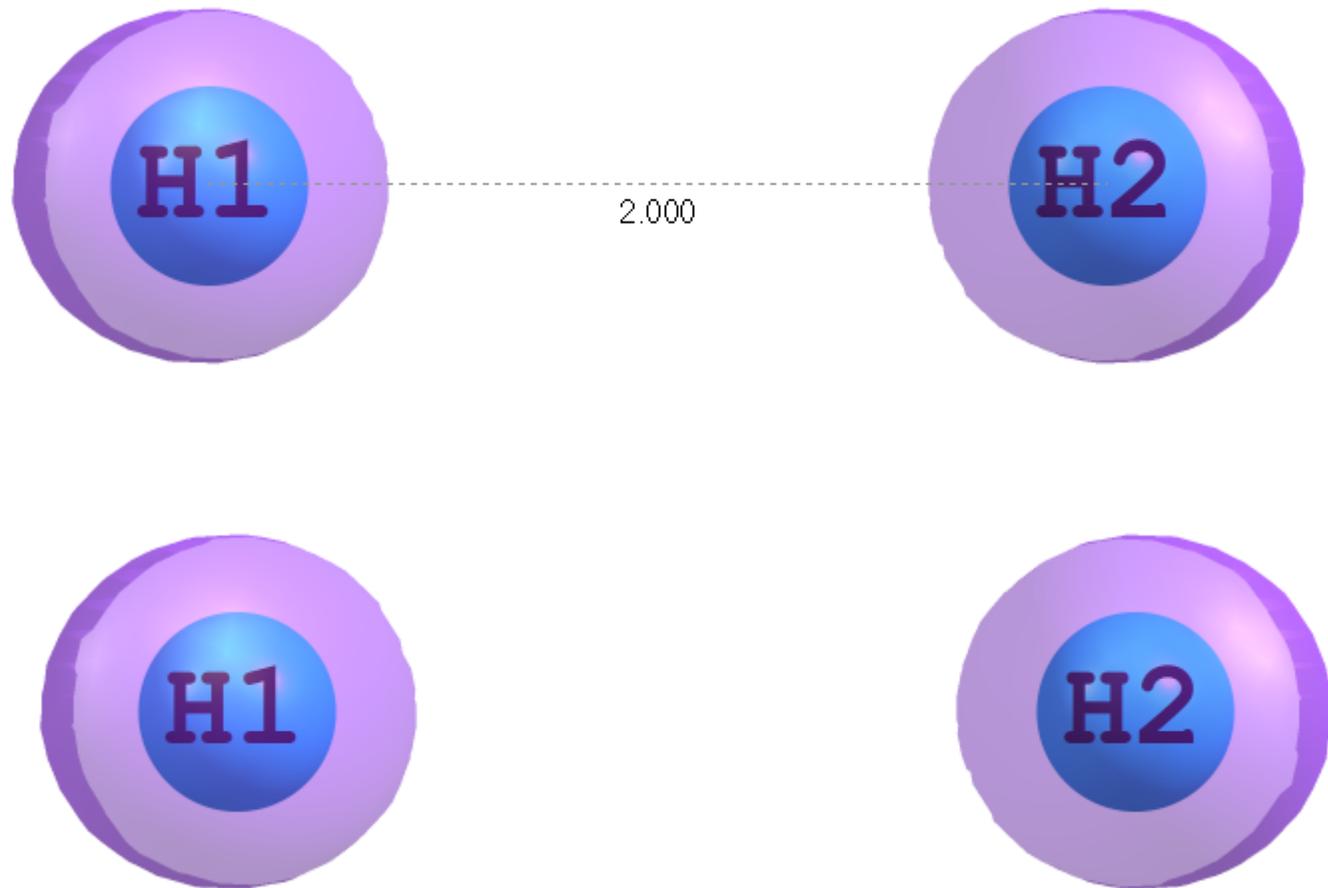


$d(\text{H—H})=0.74 \text{ Angs}$

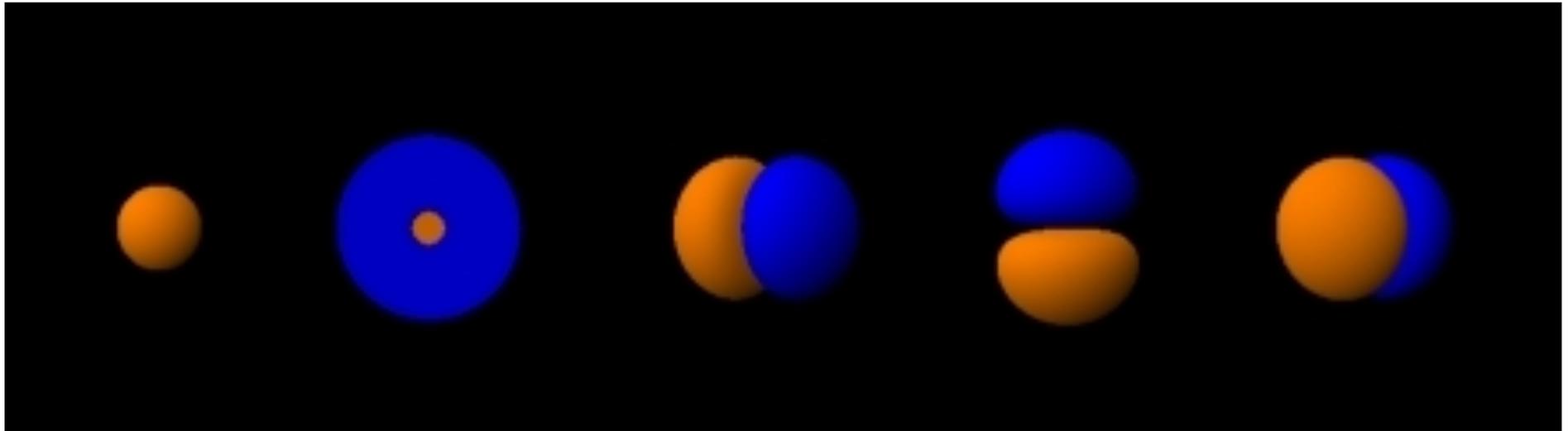


$d(\text{H—H})=0.400 \text{ Angs}$



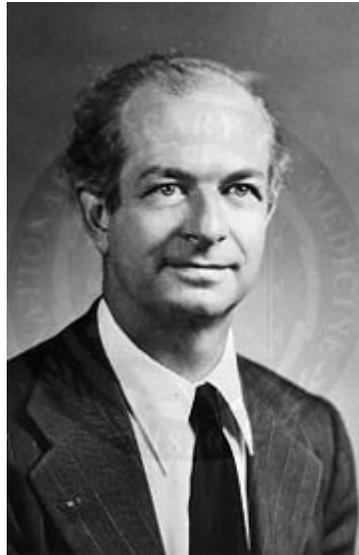


Orbitais do Ne



Linus Pauling

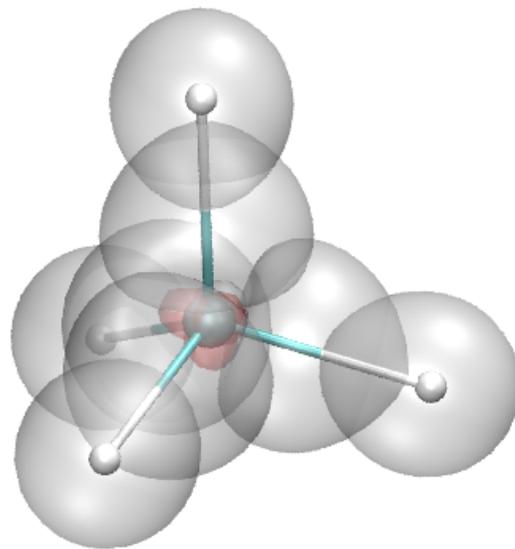
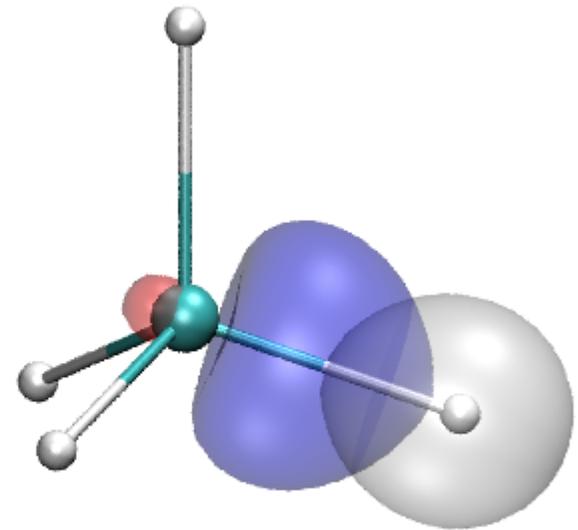
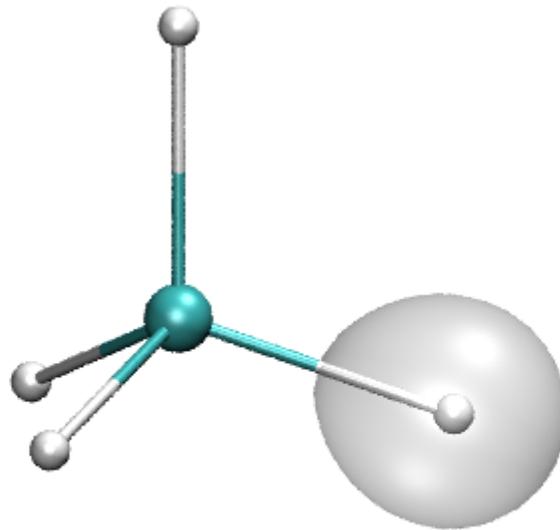
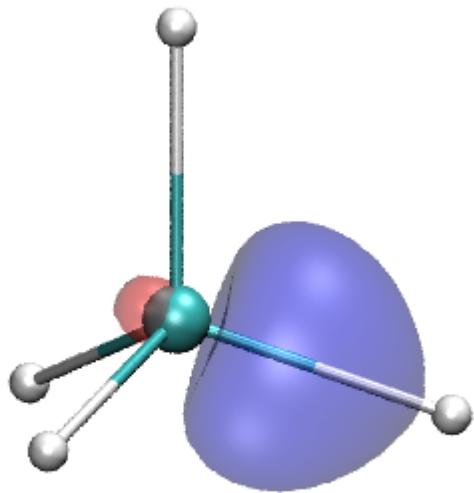
- Estudou com
 - Sommerfeld (Munique)
 - Bohr (Copenhagem)
 - Schrödinger (Zurique)
- Estudos de difração de raios-X em moléculas

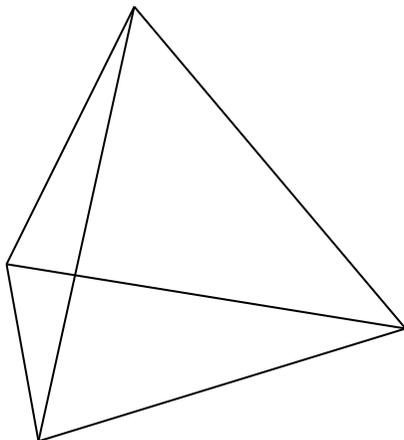


Linus Pauling 1931-1933

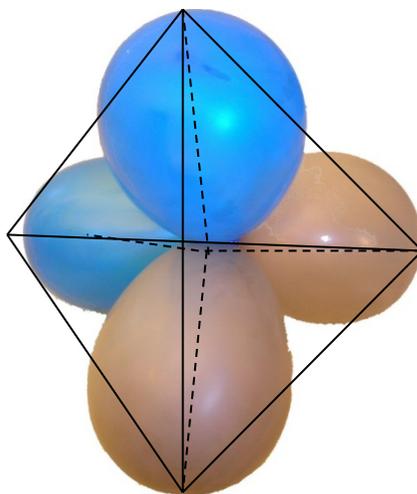
- Reconheceu o modelo de Heitler-London poderia se estendido para moléculas maiores
- Reconheceu também que este modelo (VB) poderia servir como ponte entre o modelo de valência clássico de Lewis e a recém surgida mecânica quântica

Orbitais VB para o CH_4

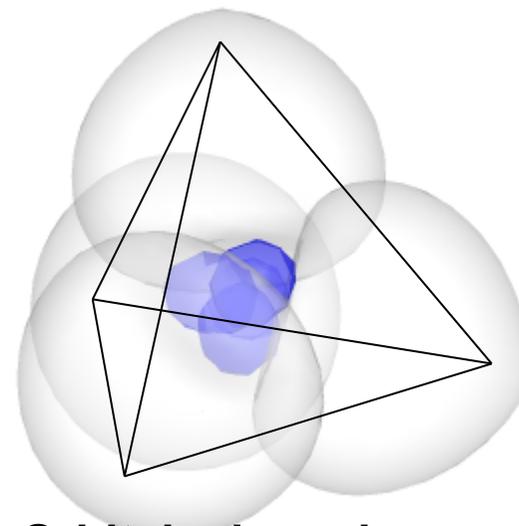




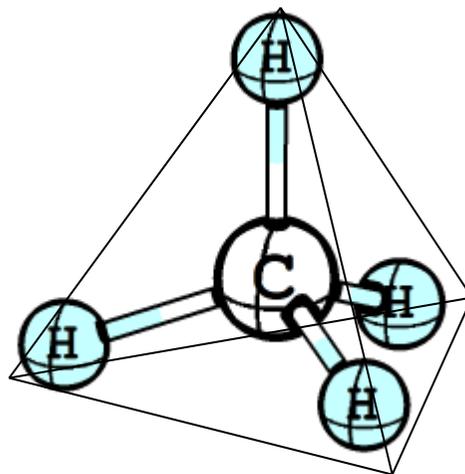
tetraedro



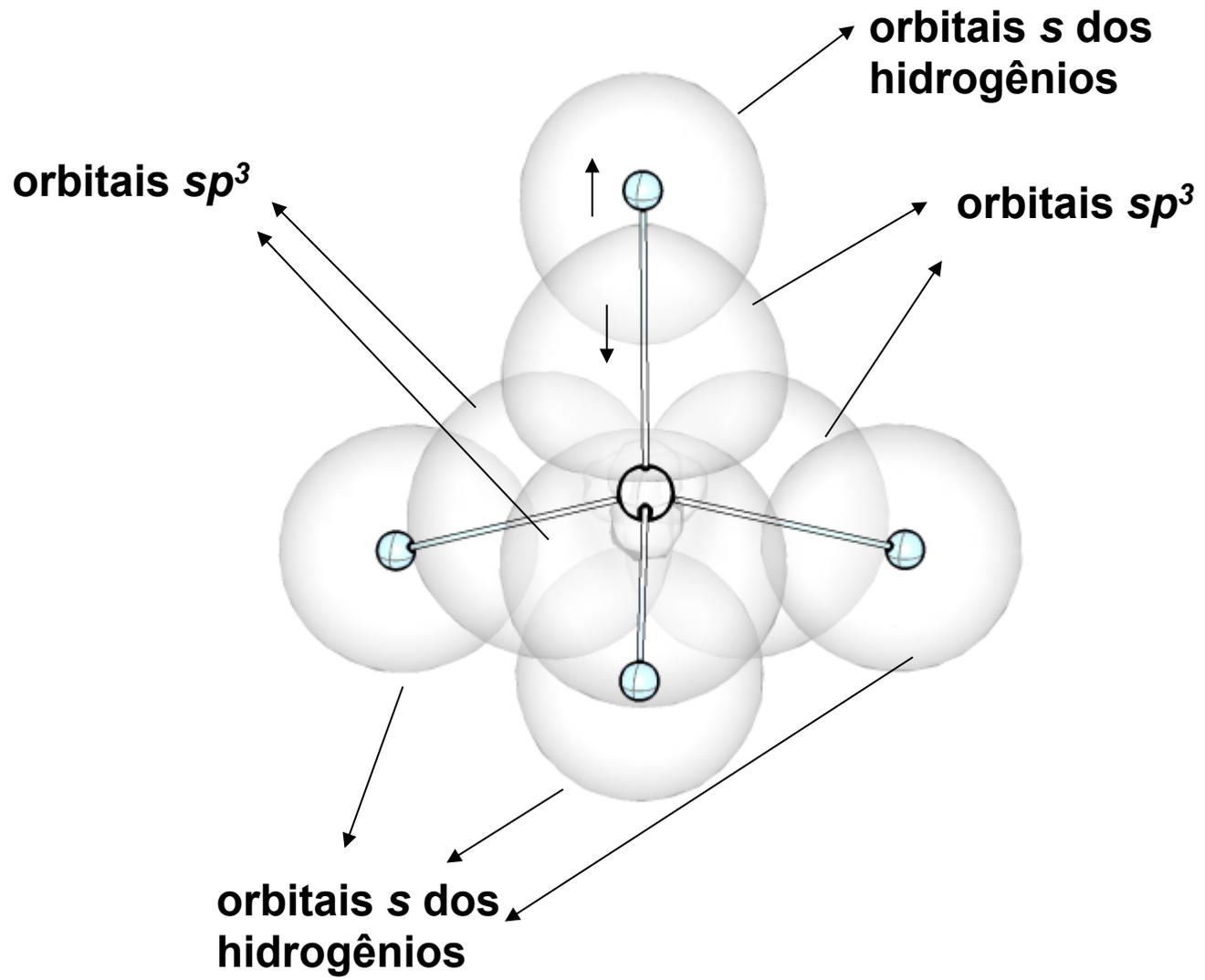
**Bolas de aniversário
(arranjo tetraédrico)**

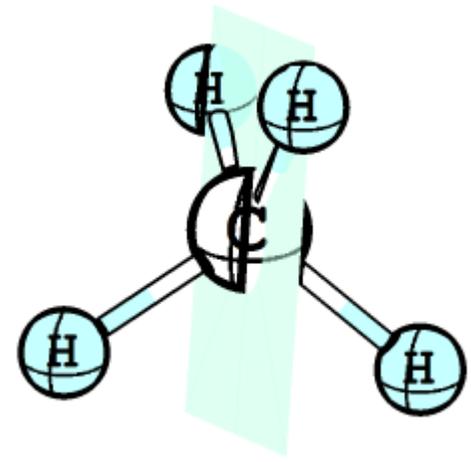
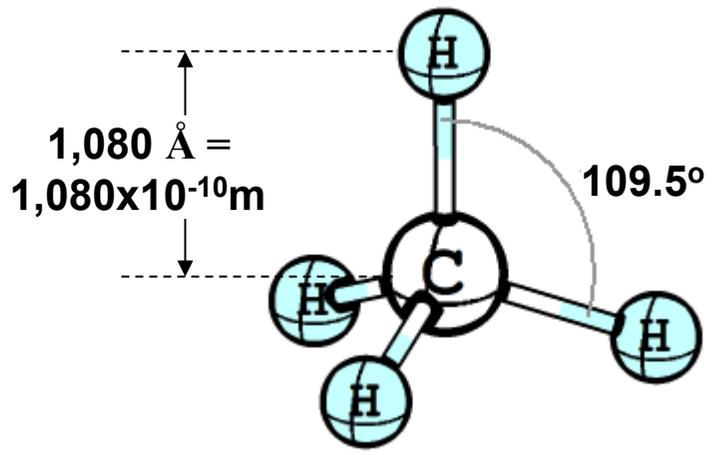


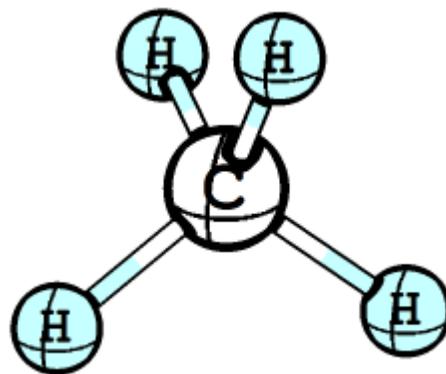
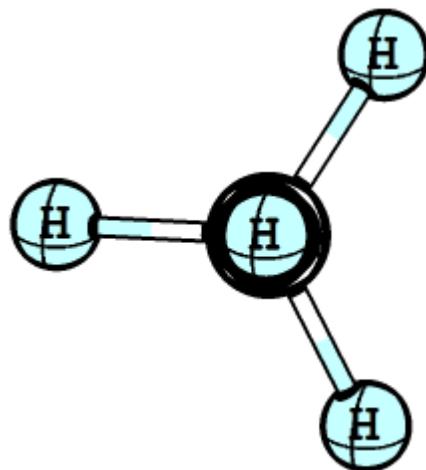
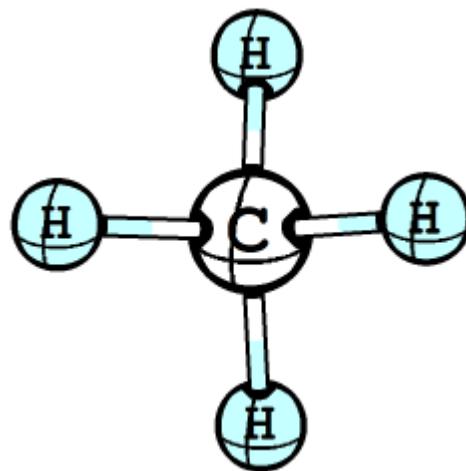
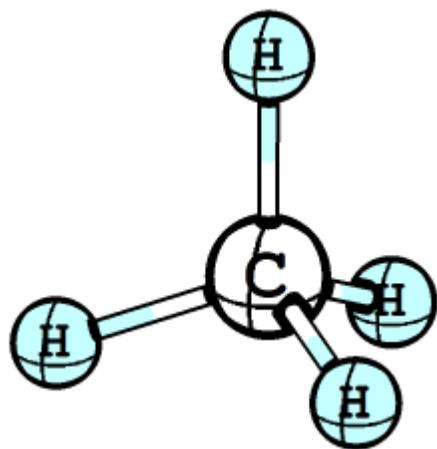
**Orbitais do carbono
(arranjo tetraédrico)**

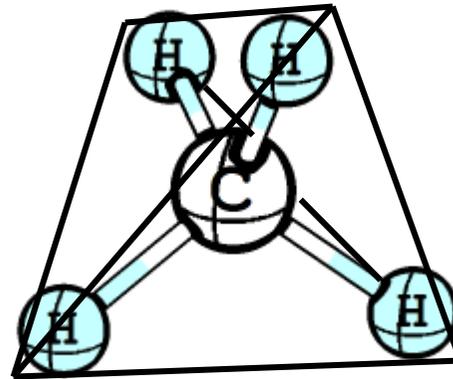
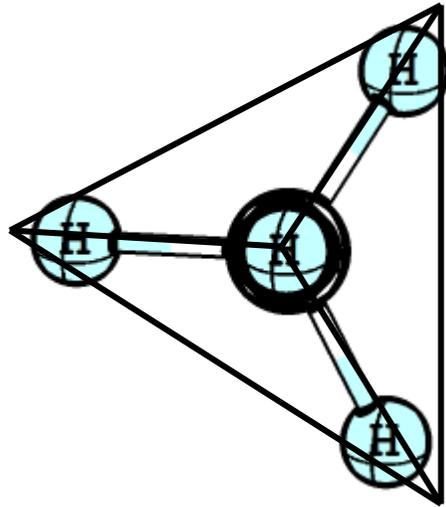
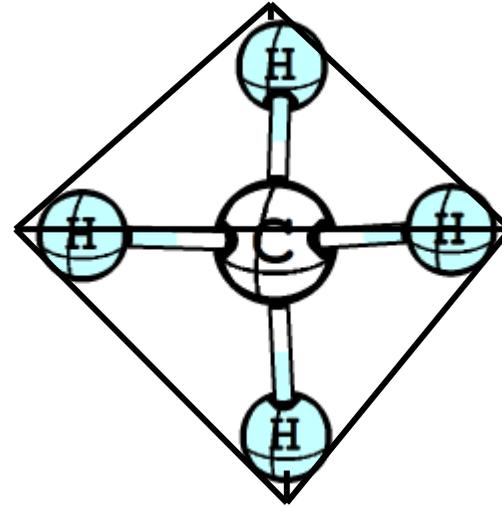
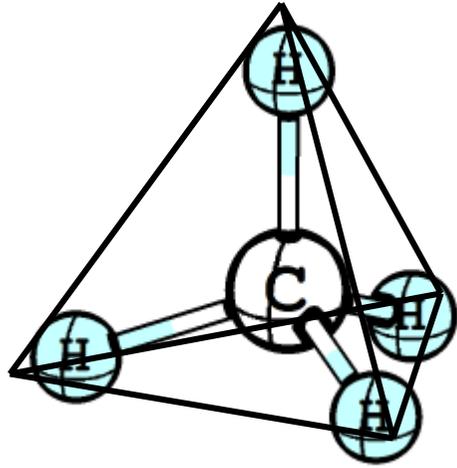


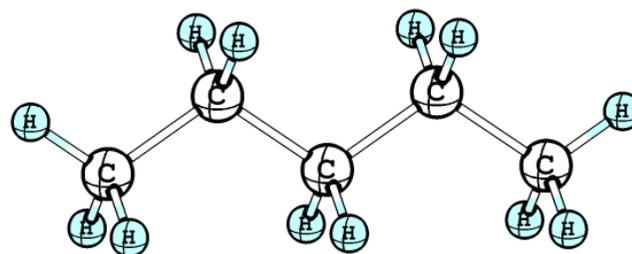
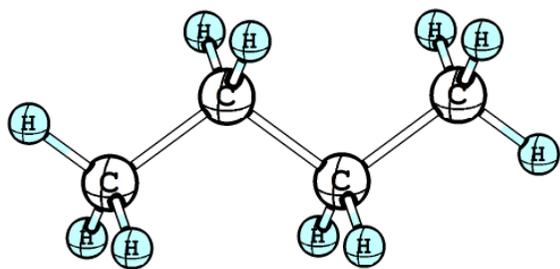
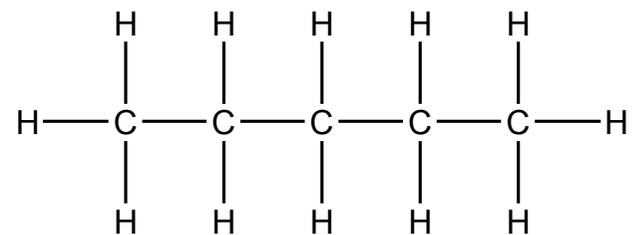
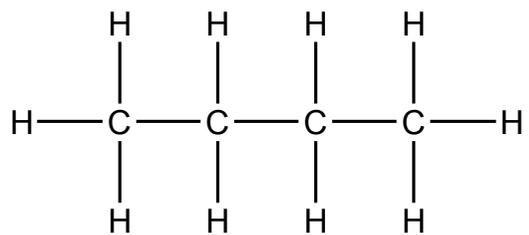
**Metano dentro
em um tetraedro**

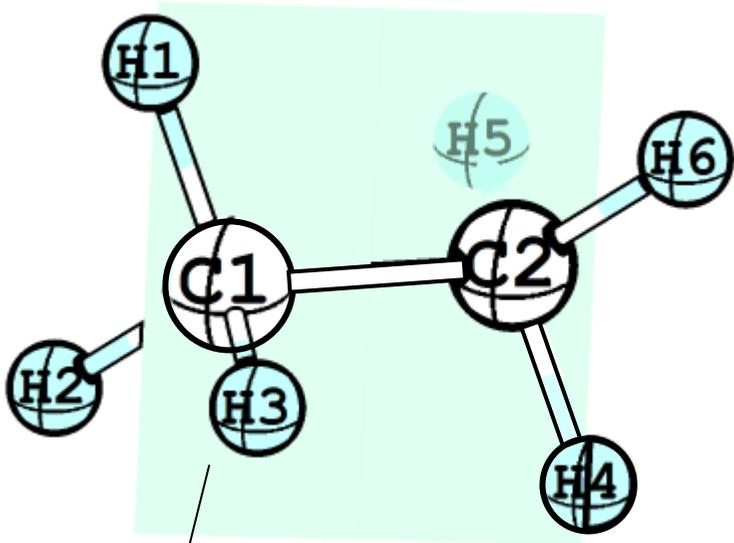








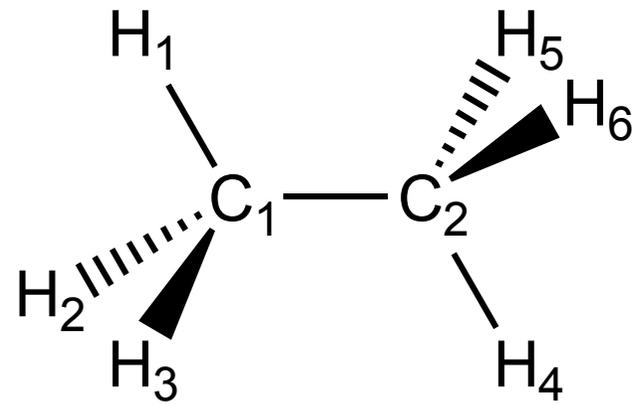


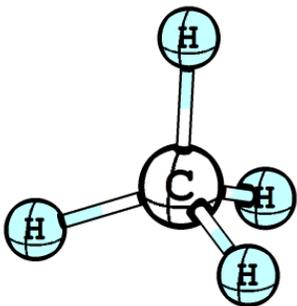


**Plano definido
pelos átomos**

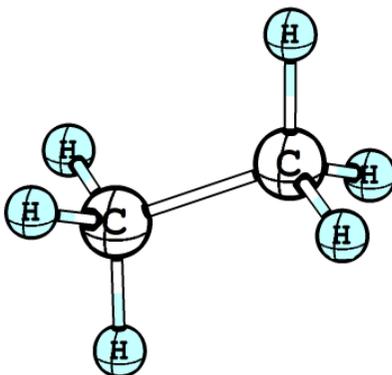
H1-C1-C2-H4

(Plano A)

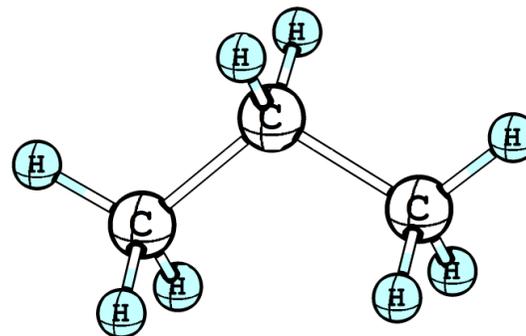




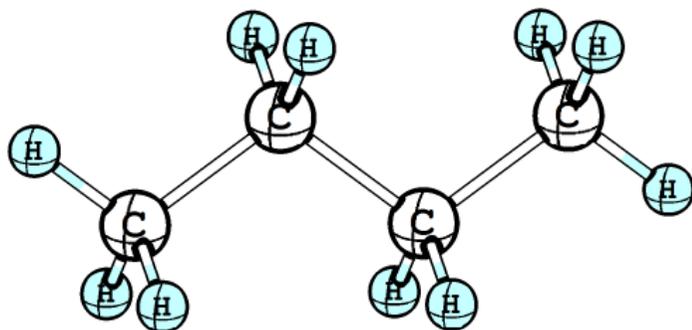
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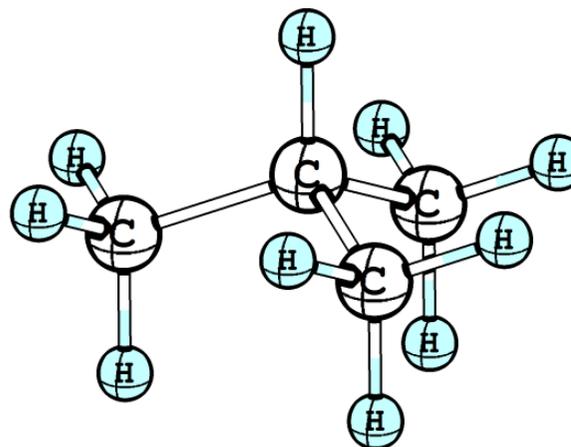
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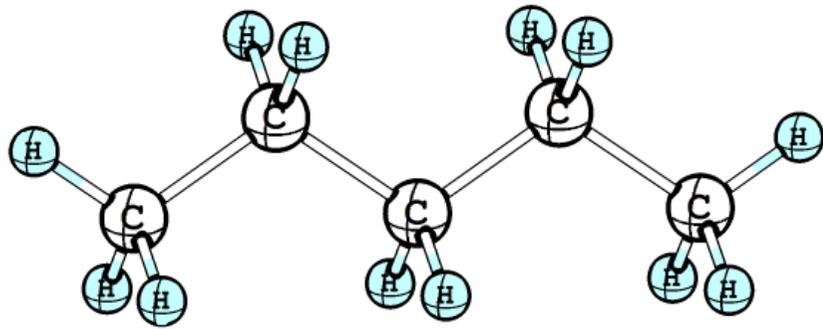
propano



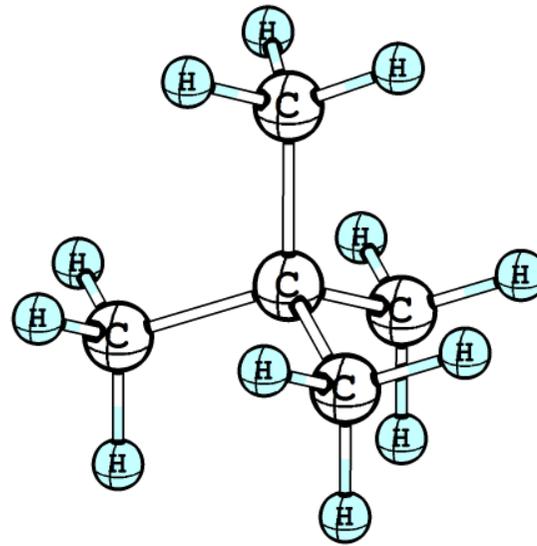
butano



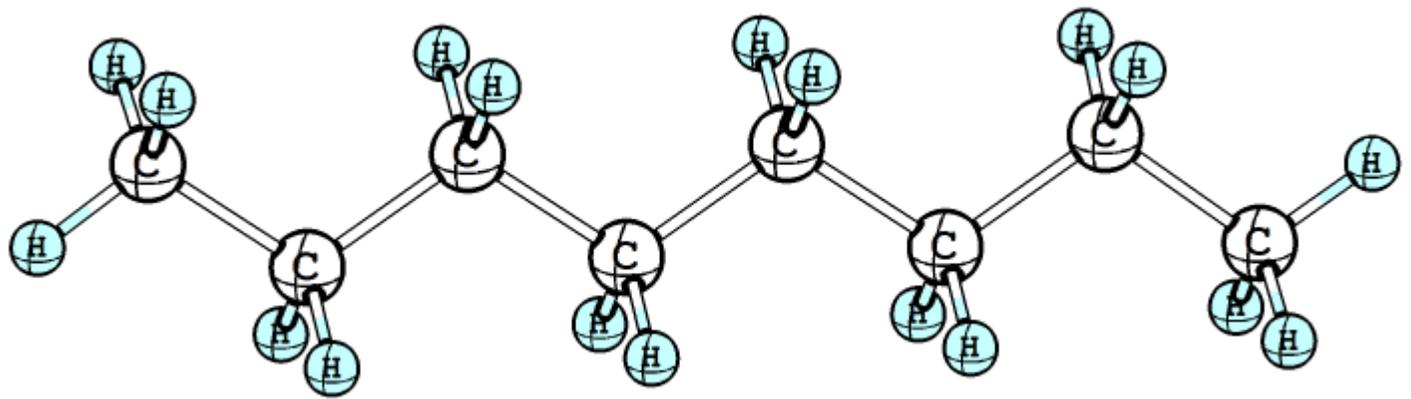
isobutano

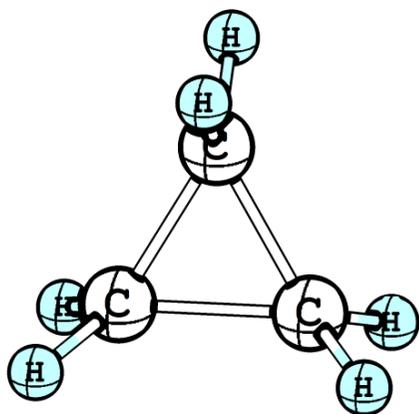


pentano

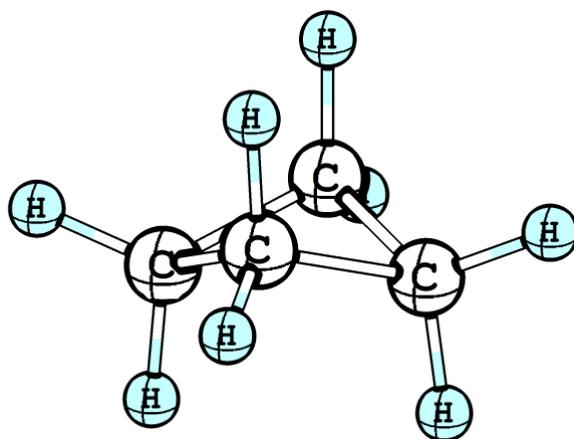


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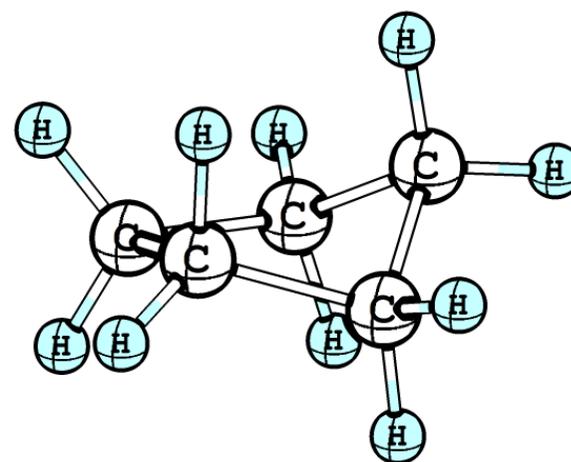




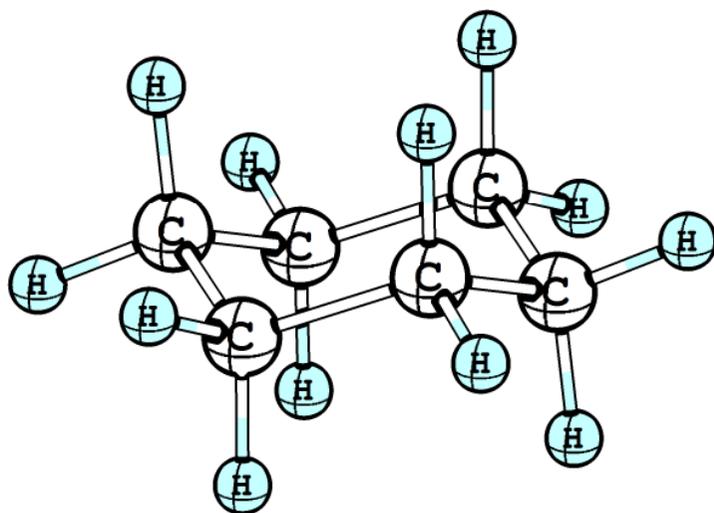
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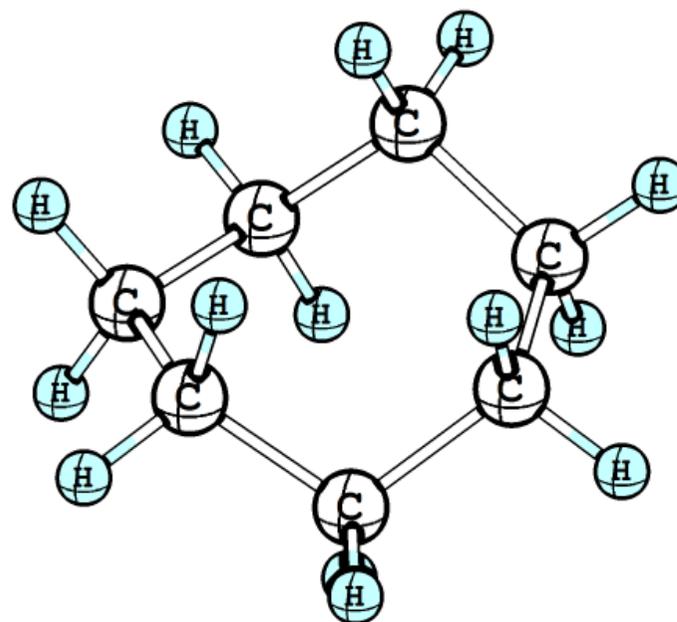
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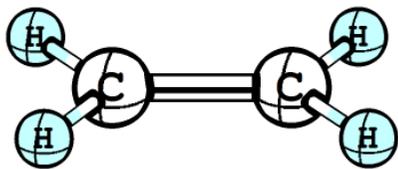
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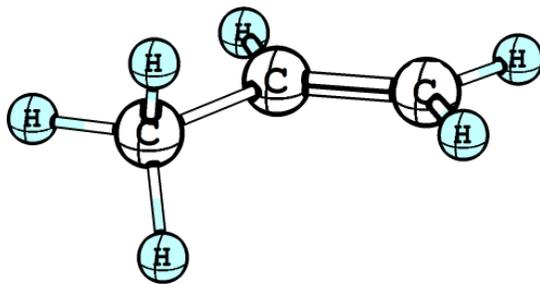
ciclo-hexano



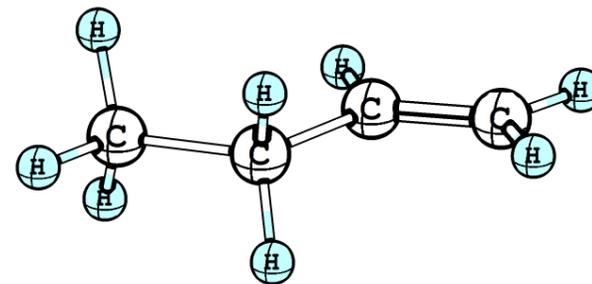
Ciclo-heptano



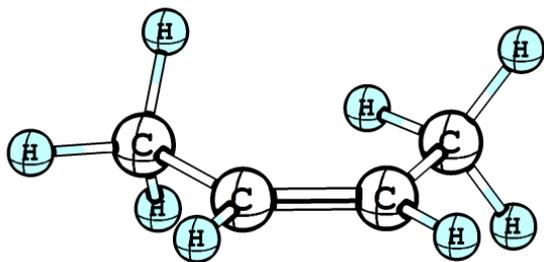
Eteno/etileno



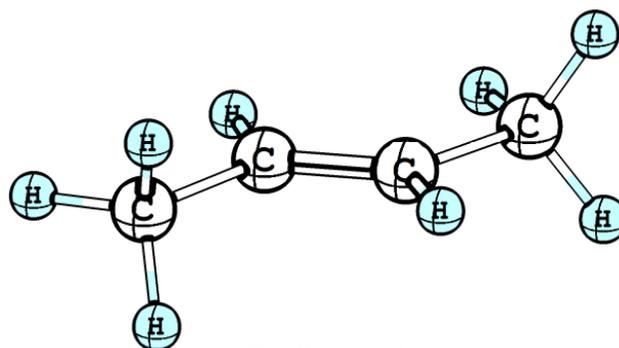
Propeno/propileno



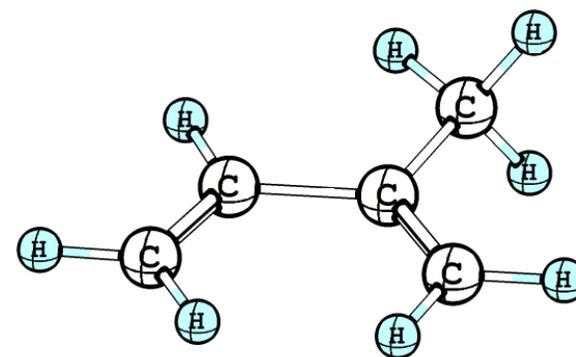
1-buteno



Z-2-buteno

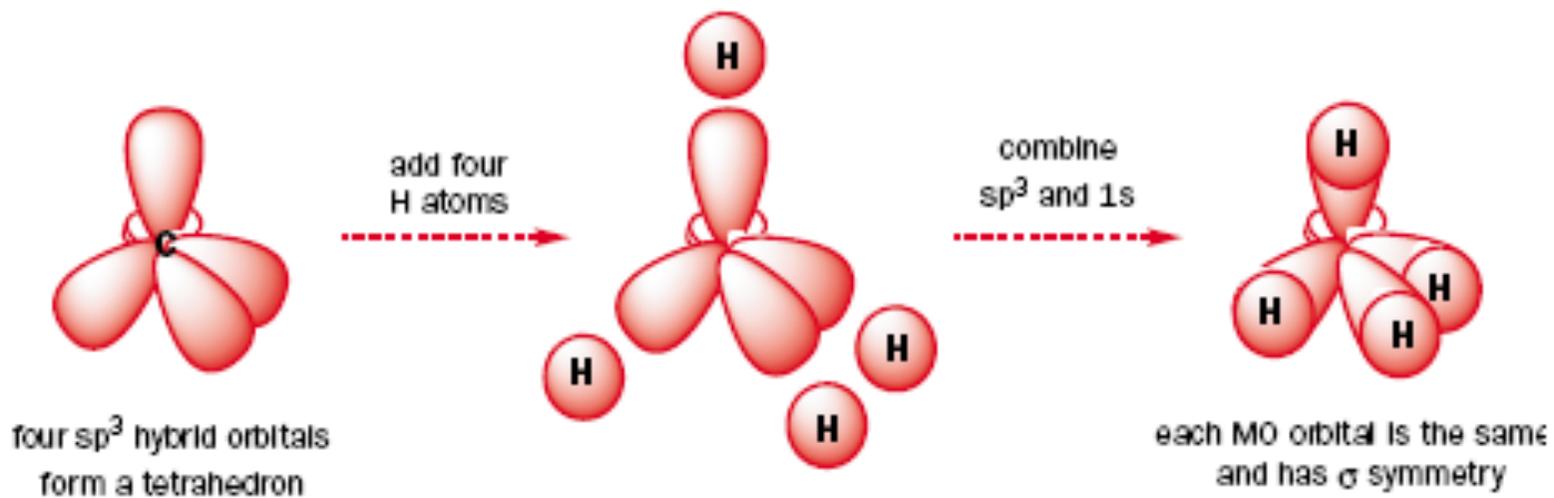
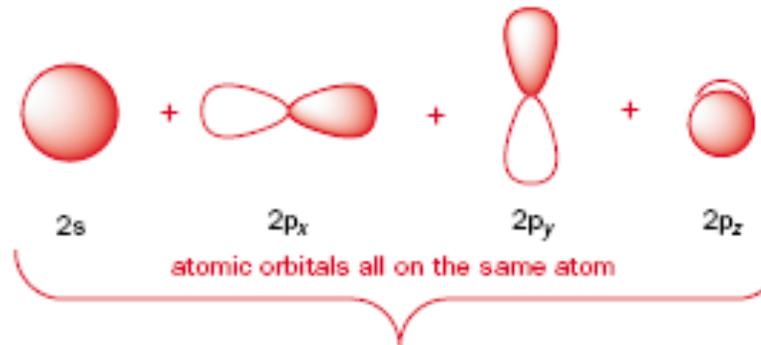


E-2-buteno

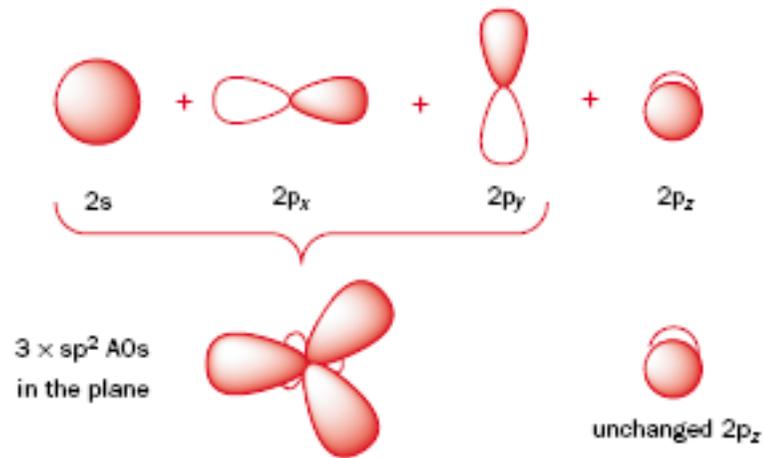


Isopreno

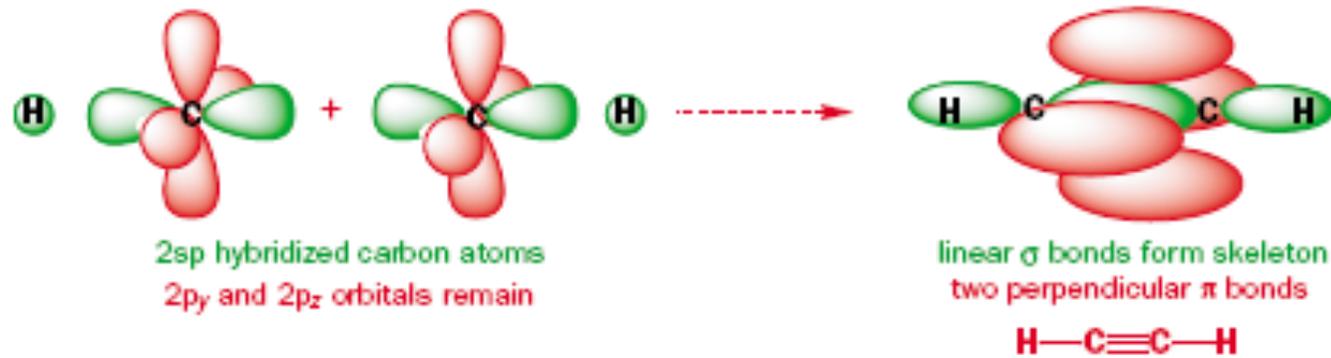
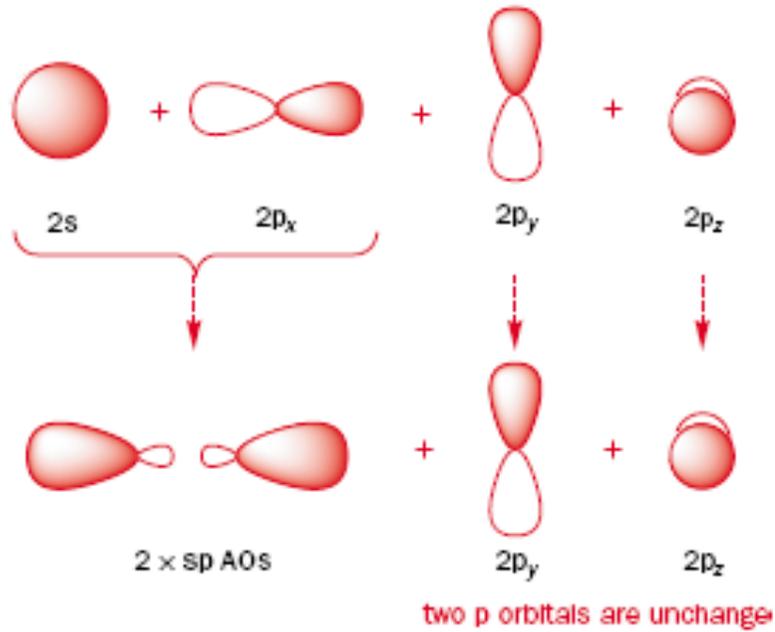
Hibridização sp^3



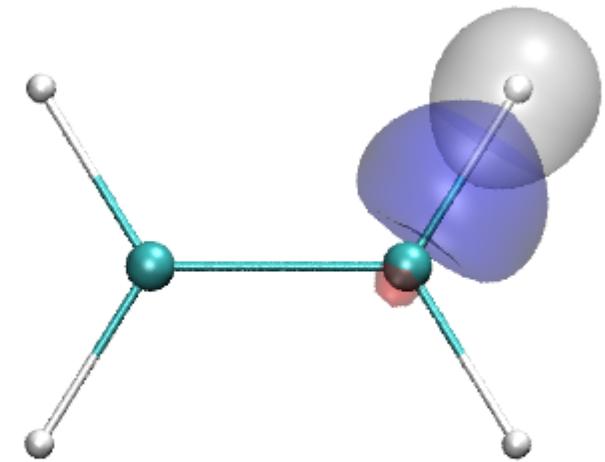
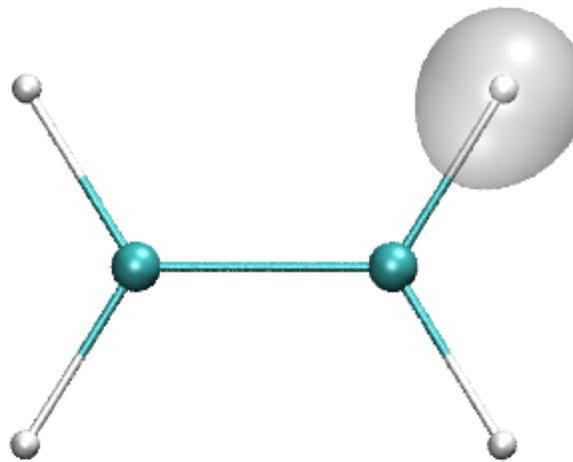
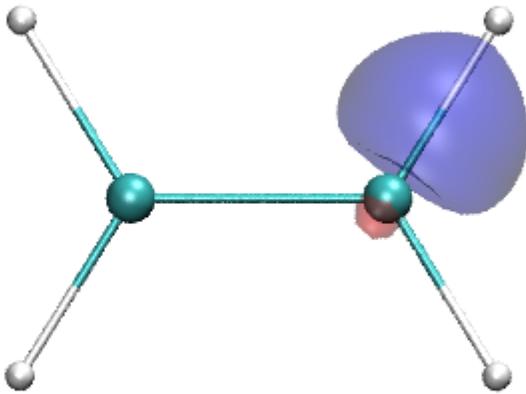
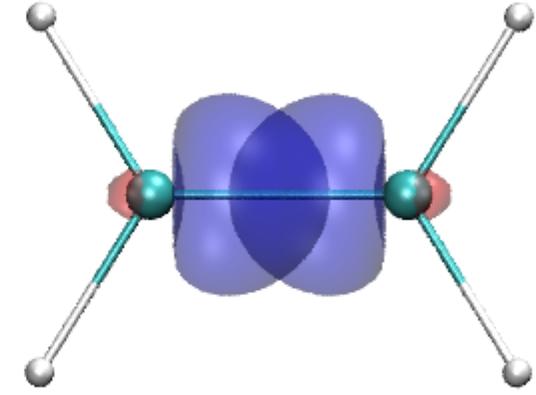
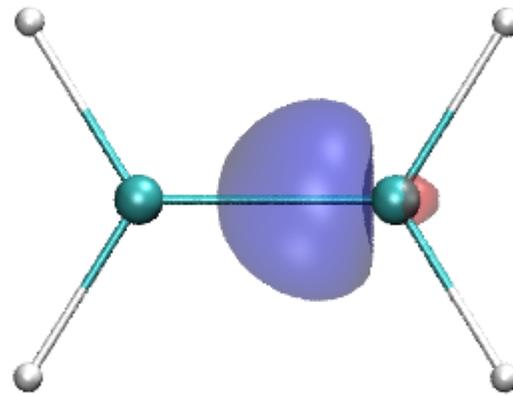
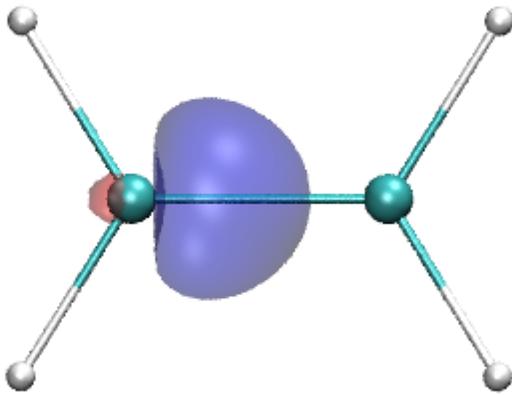
Hibridização sp^2



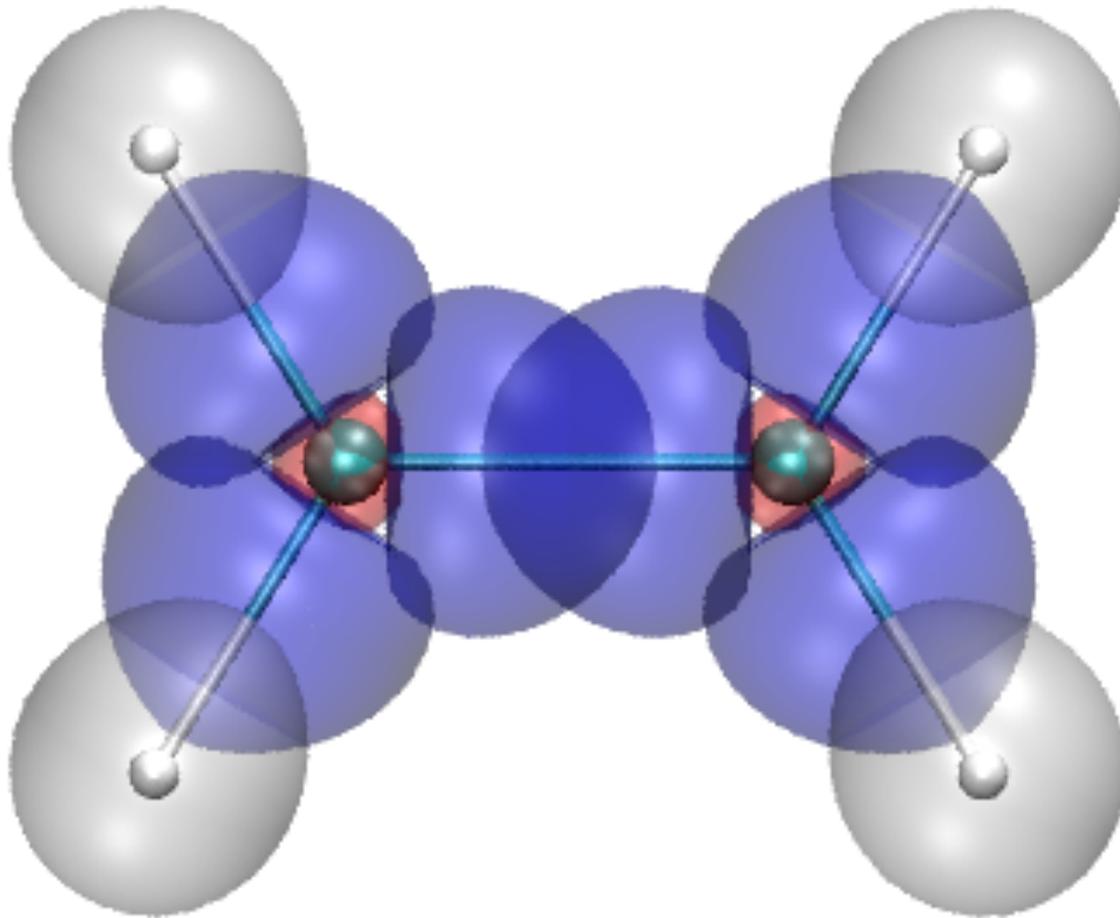
Hibridização sp



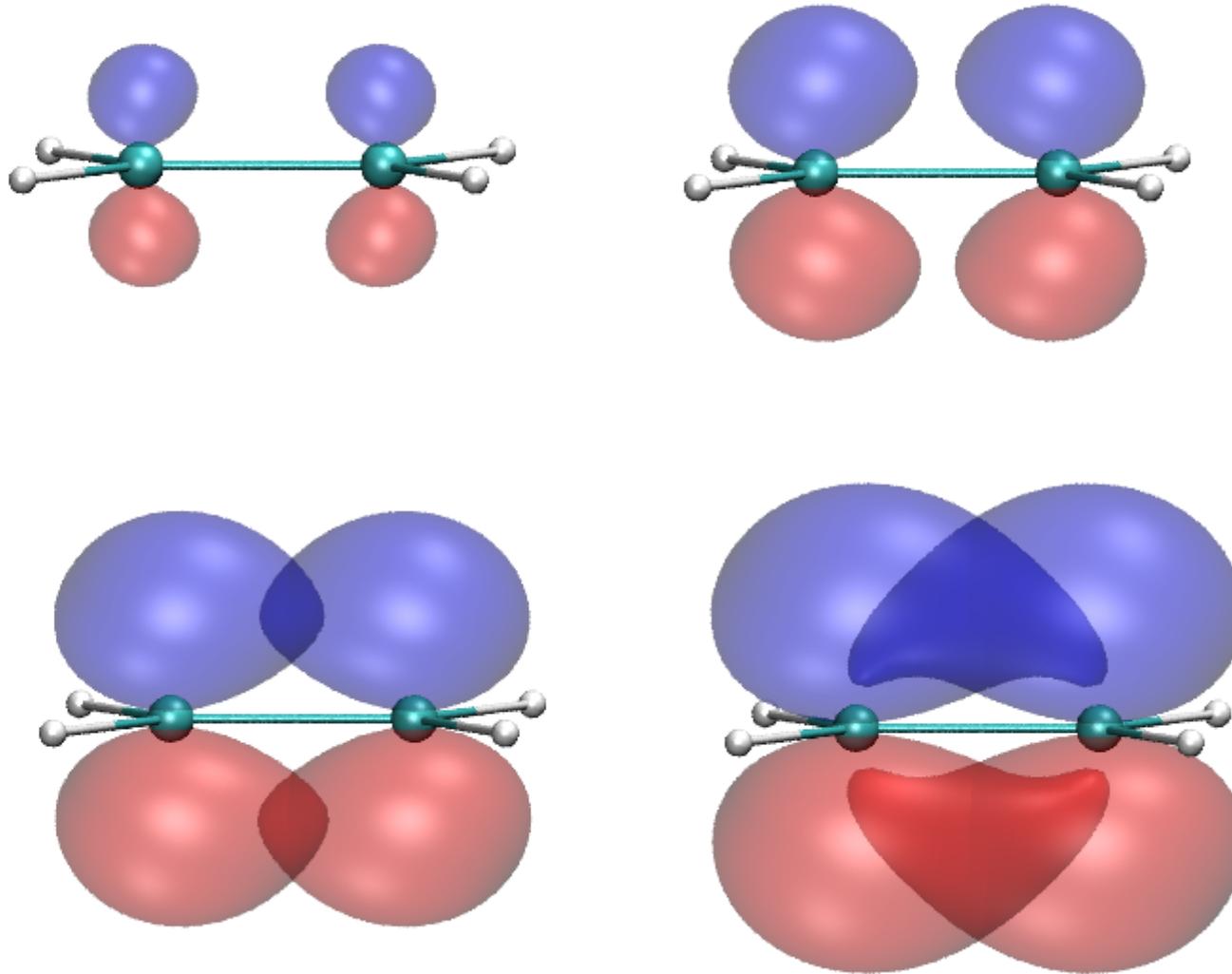
Orbitais VB para o C_2H_4

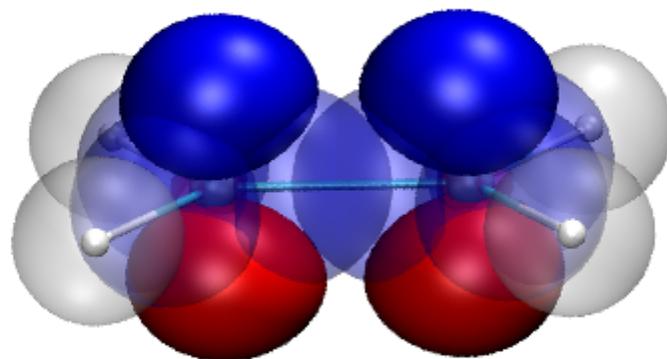
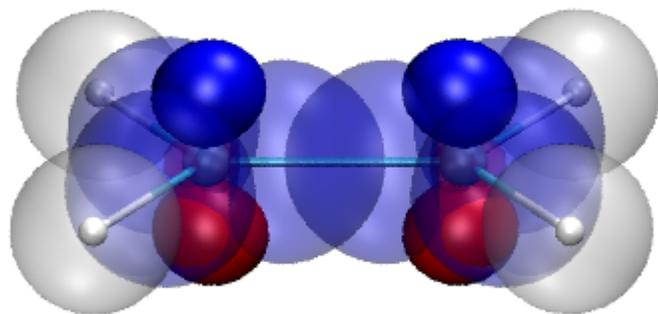
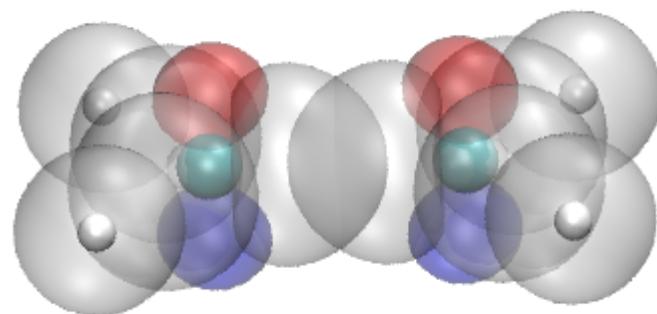
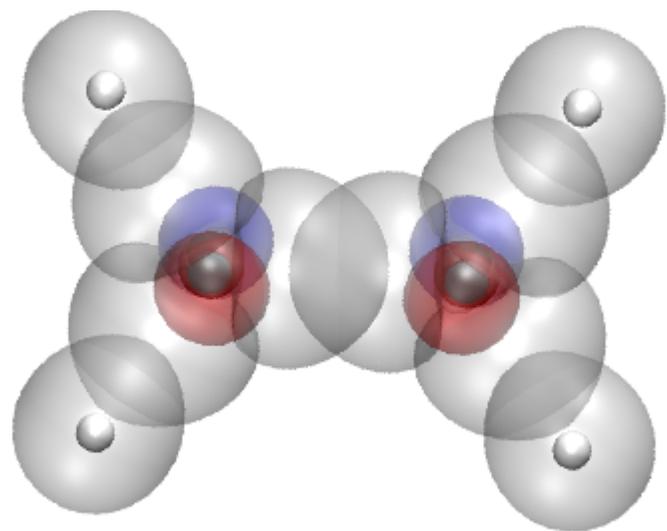


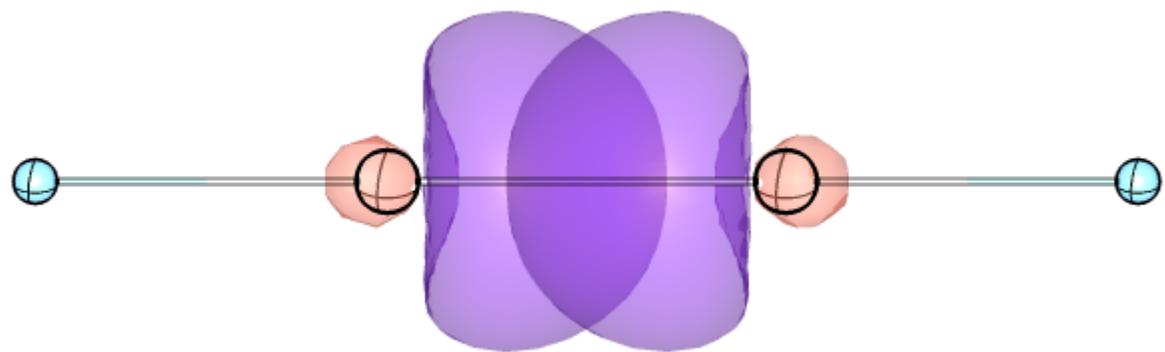
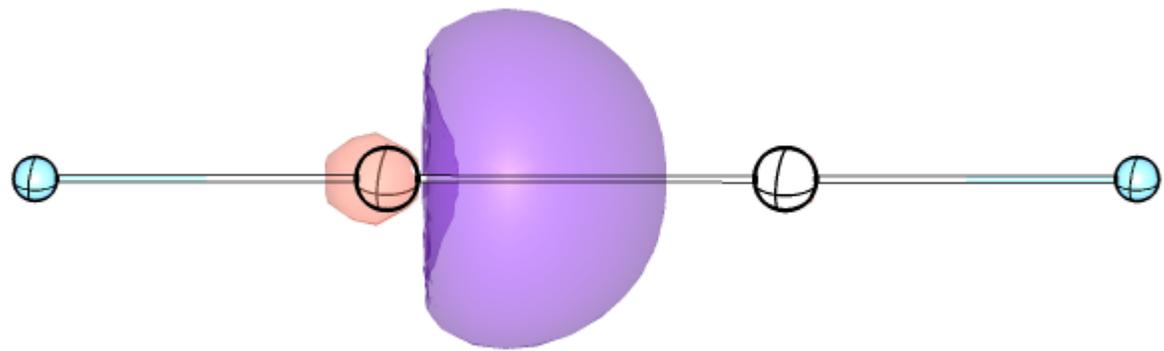
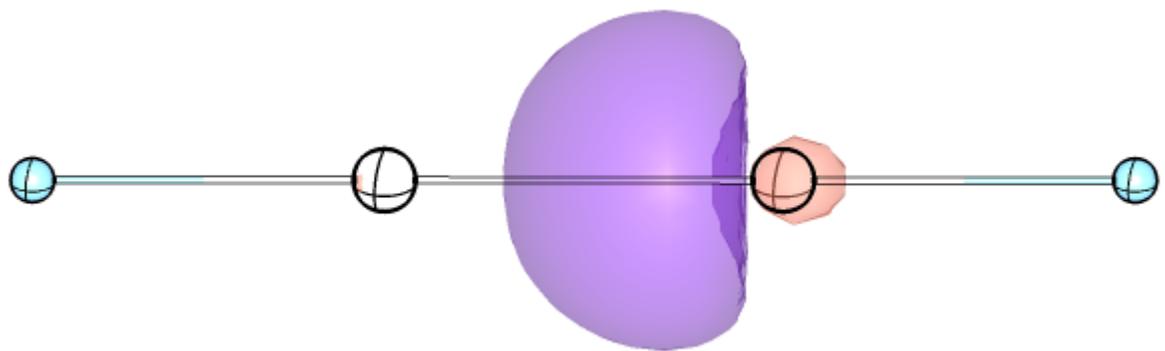
Orbitais VB para o C_2H_4 (sistema sigma)

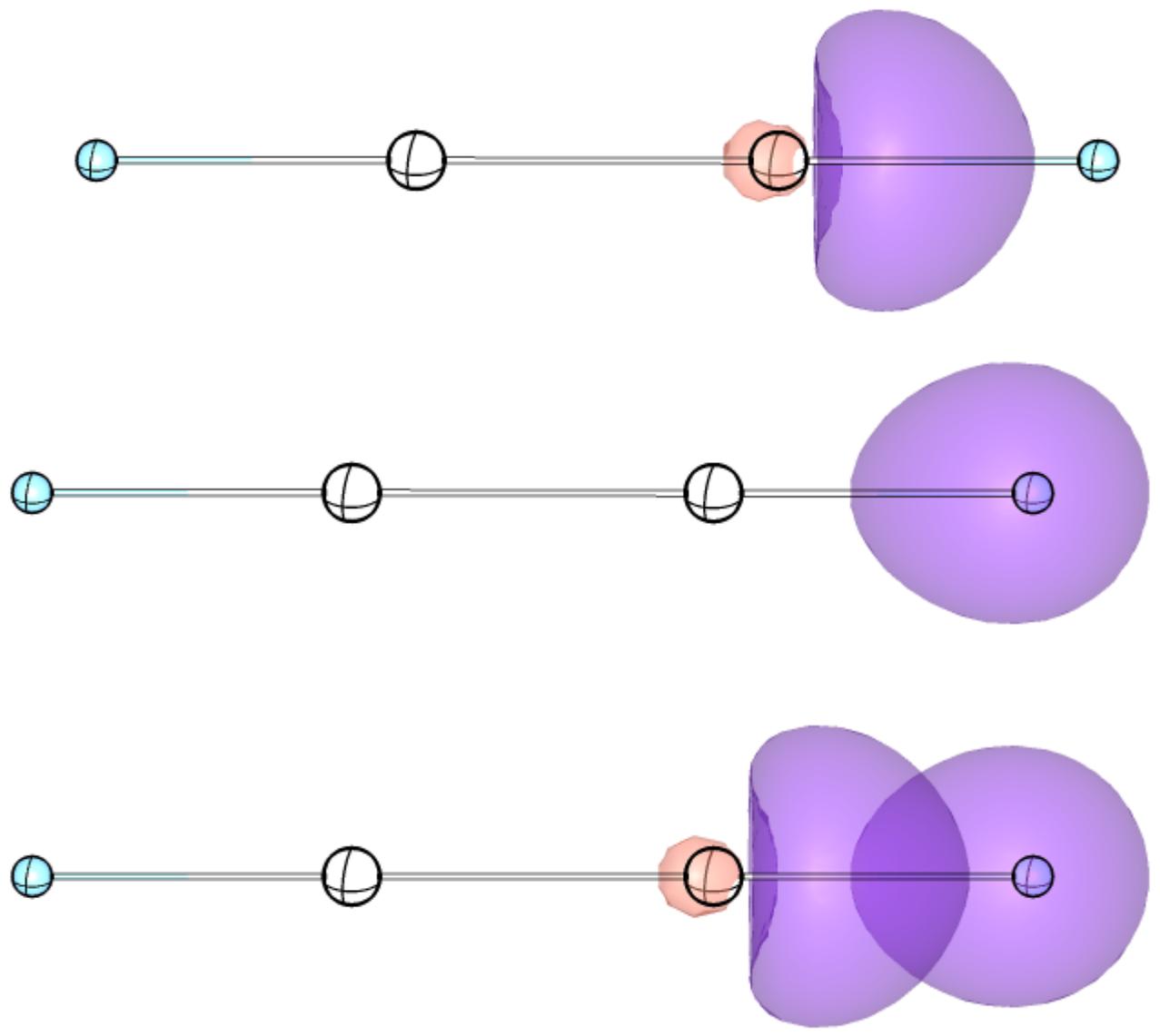


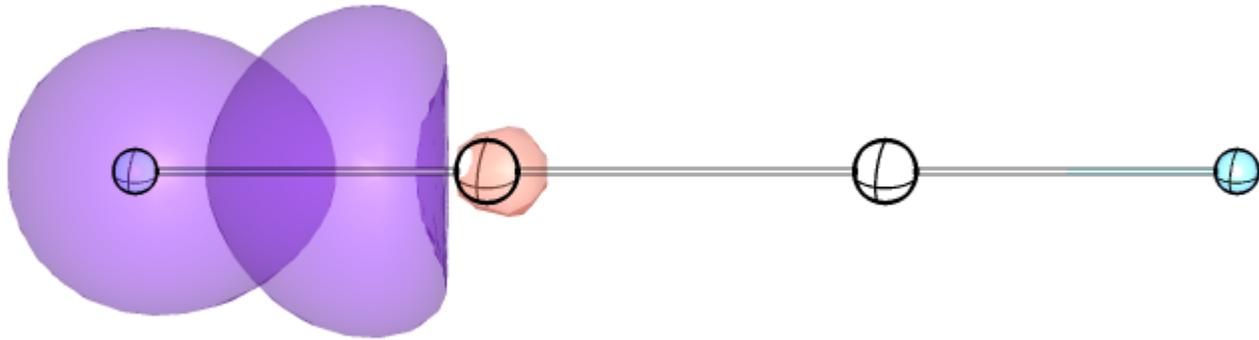
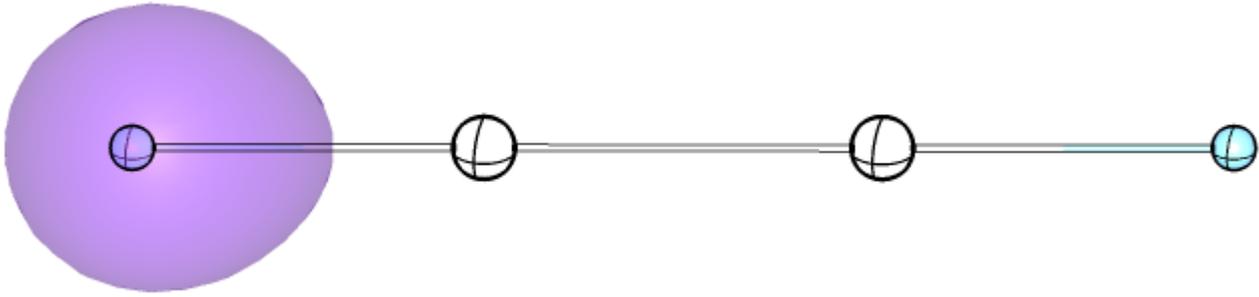
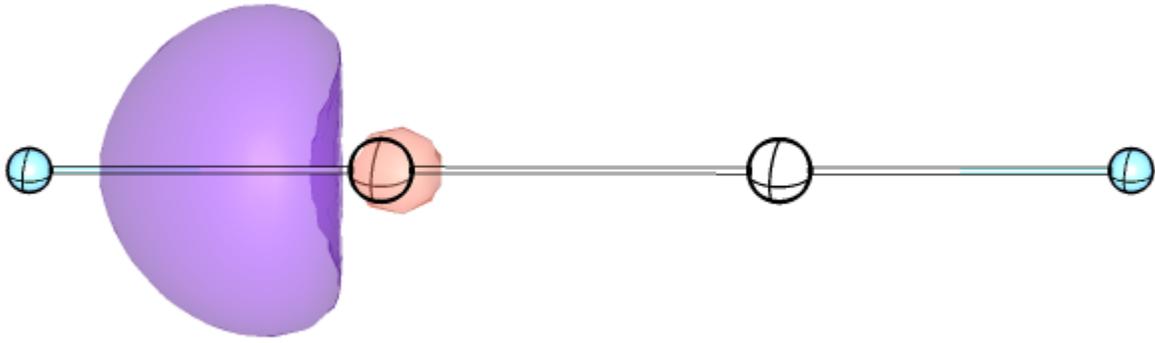
Orbitais VB para o C_2H_4 (sistema pi)

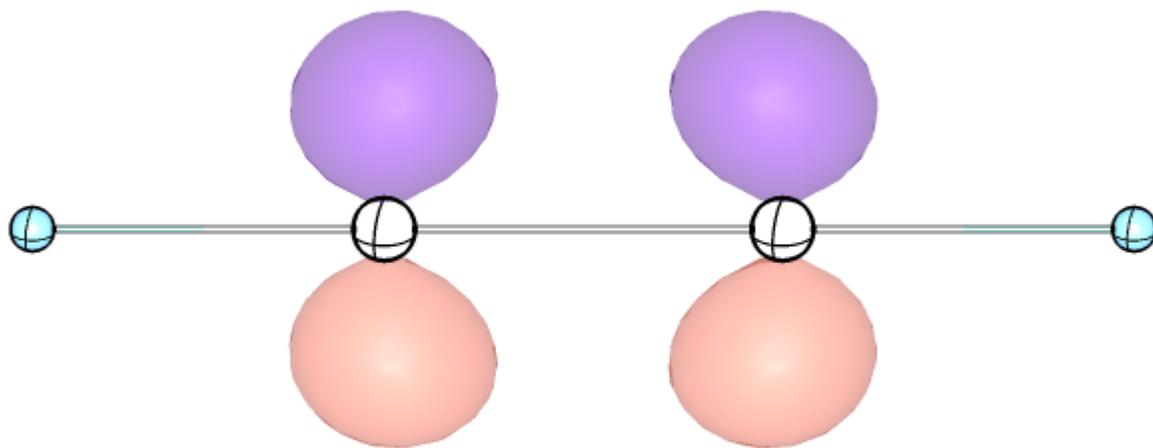
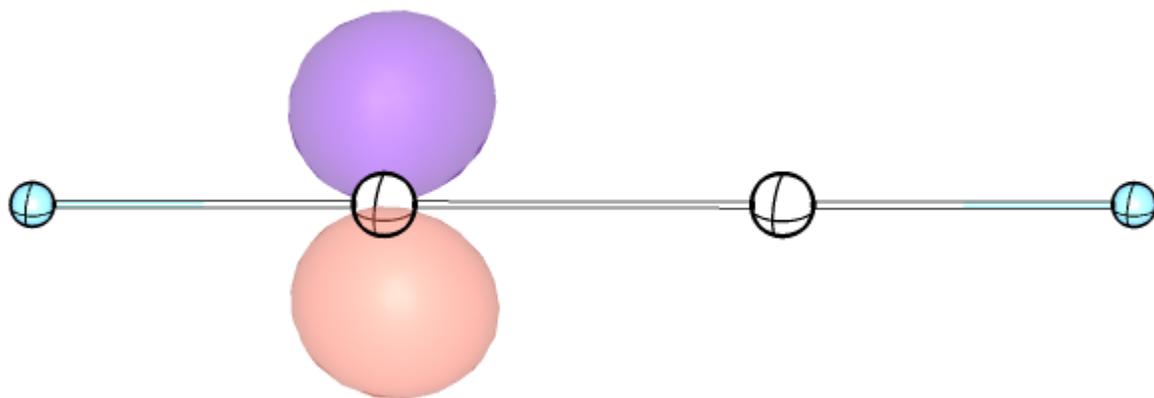
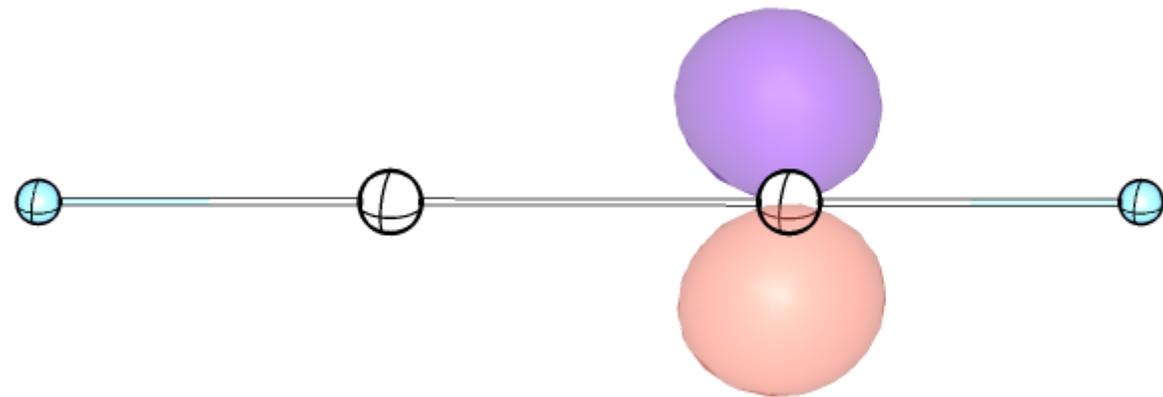


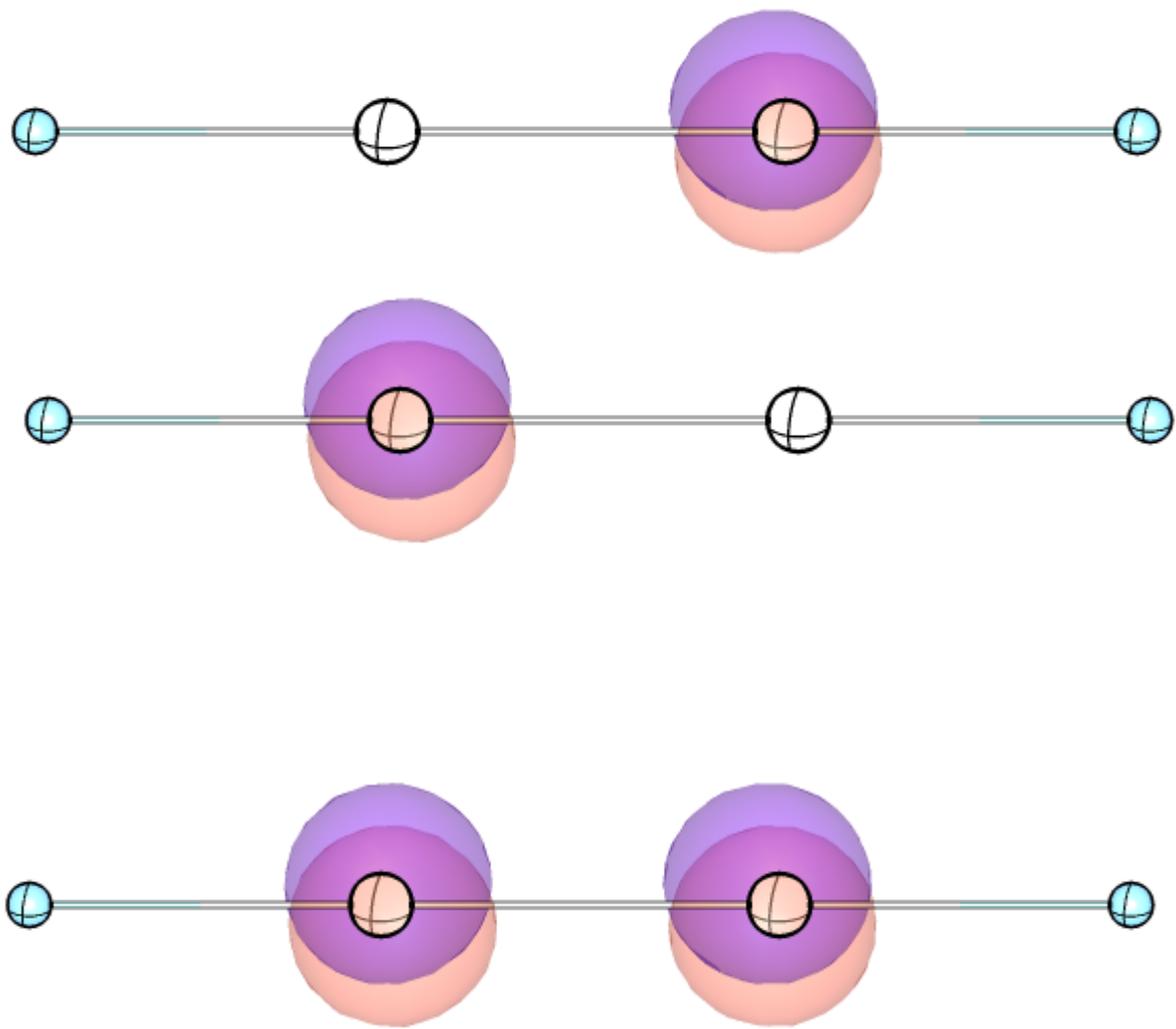


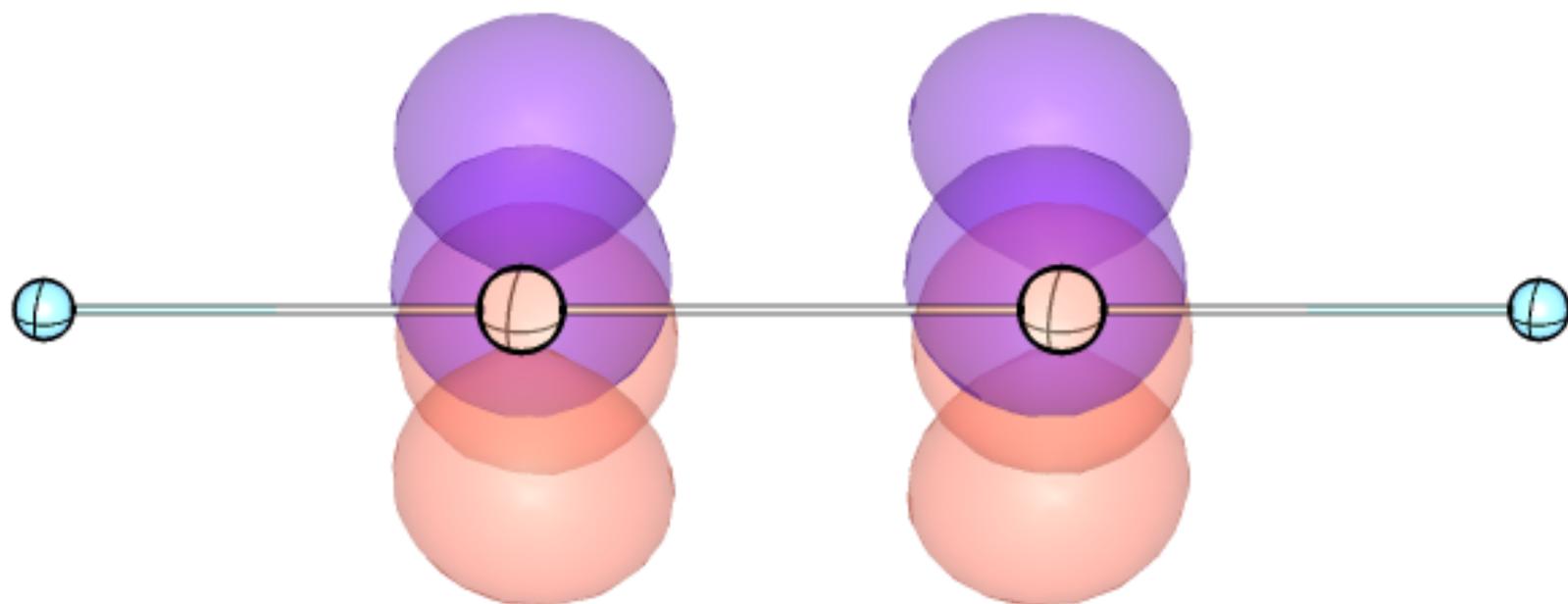
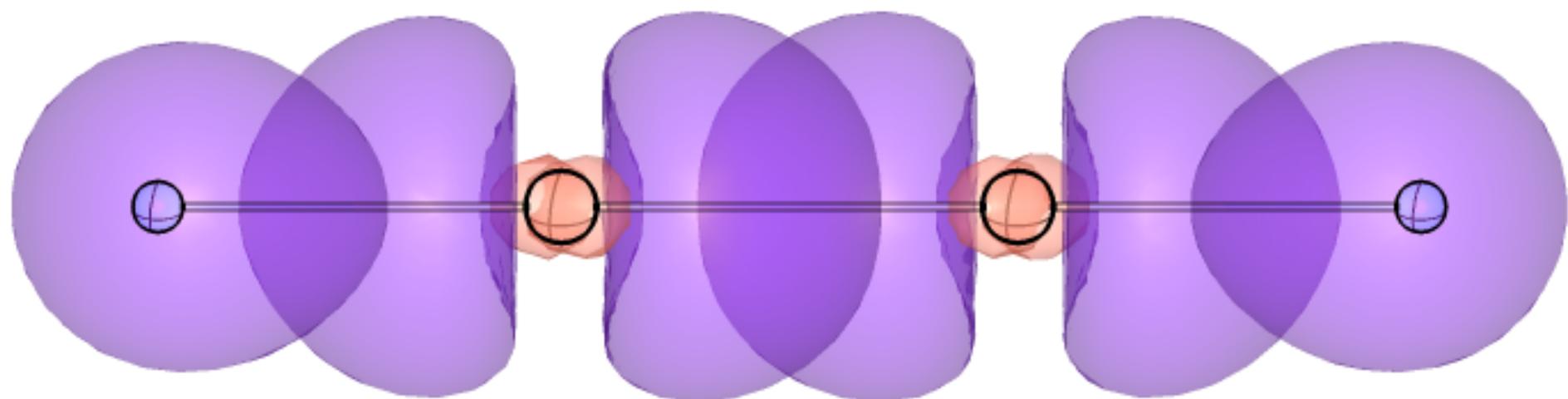


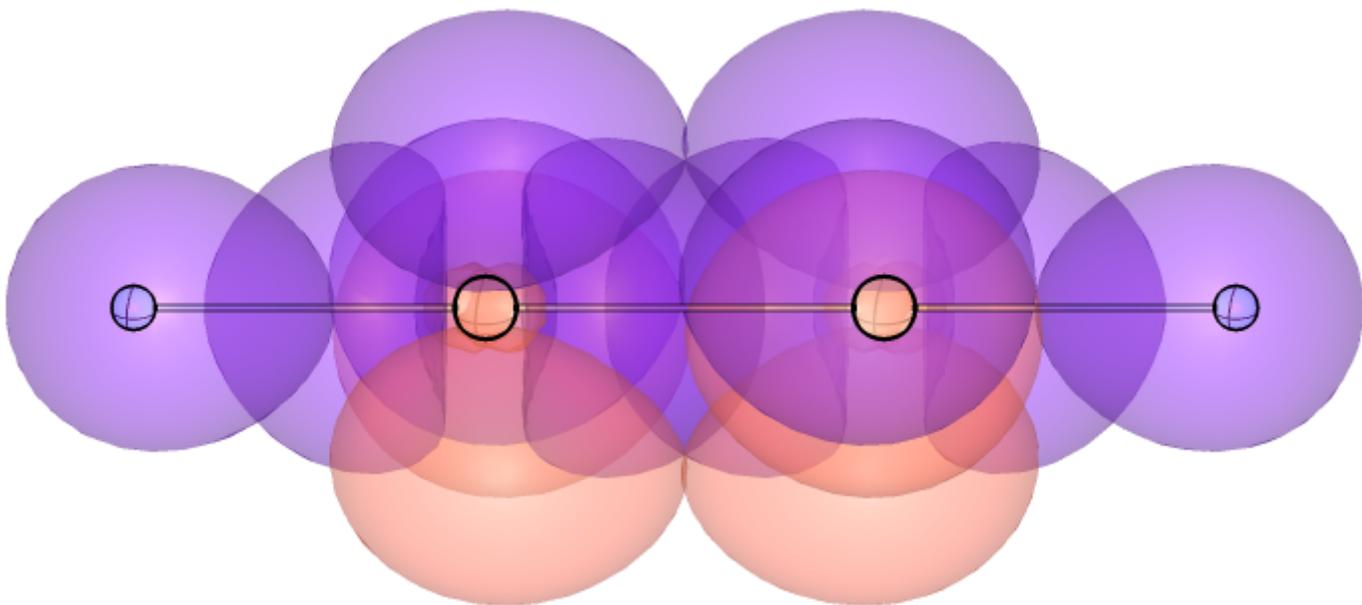
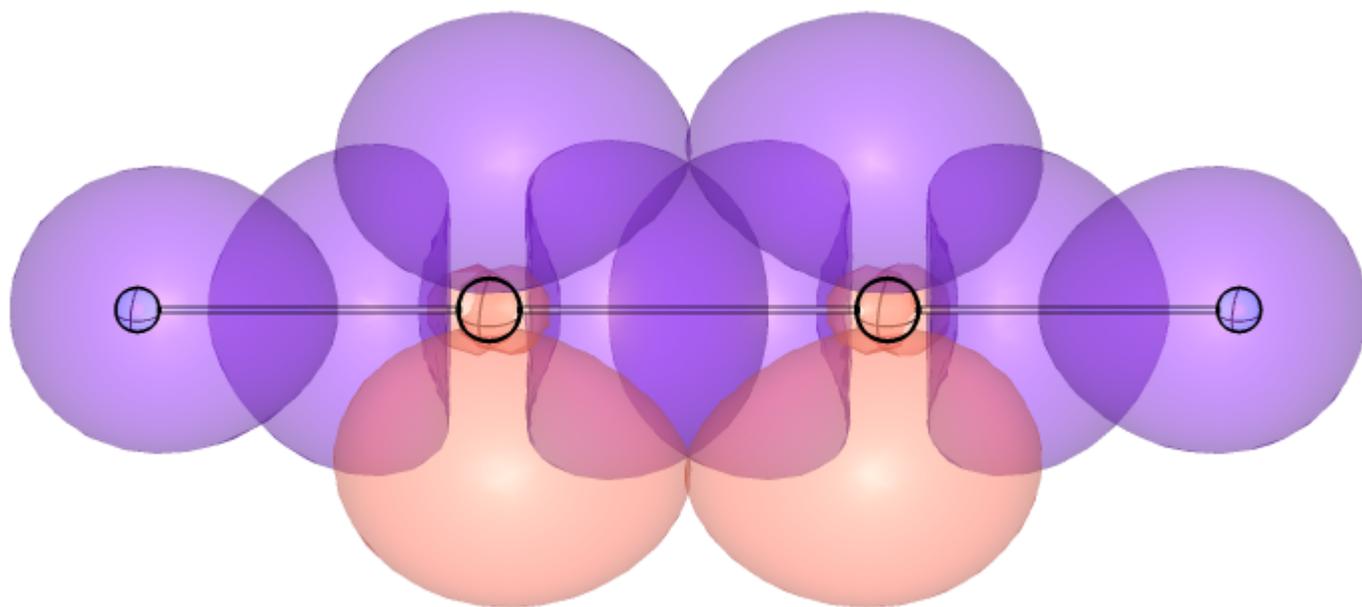


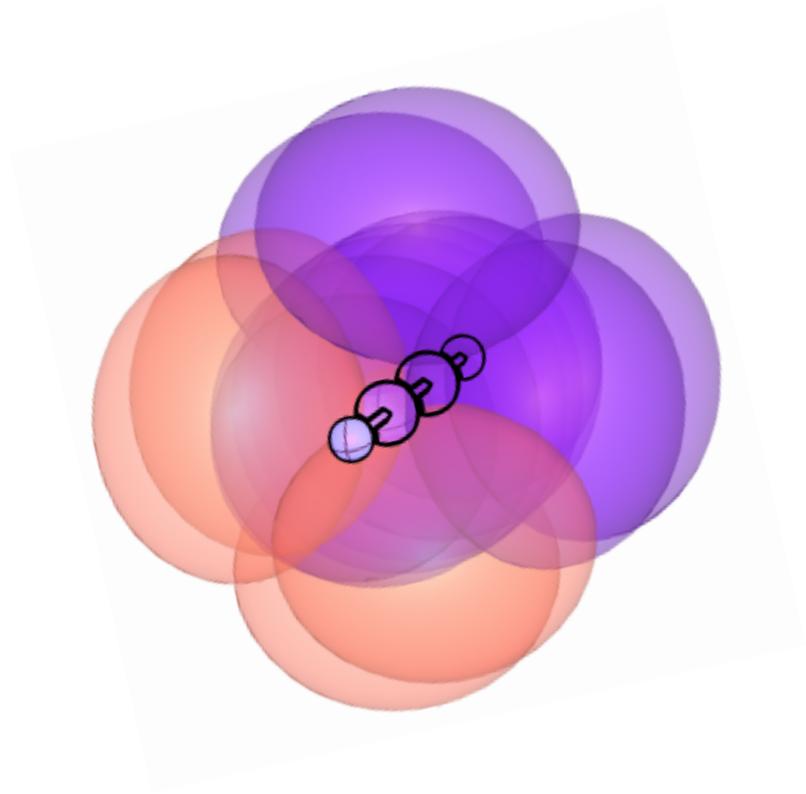








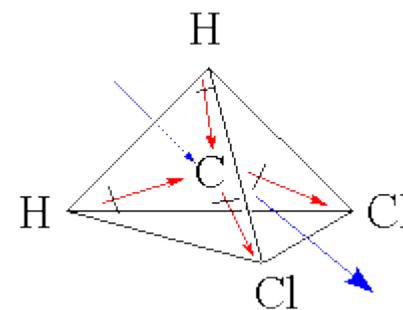
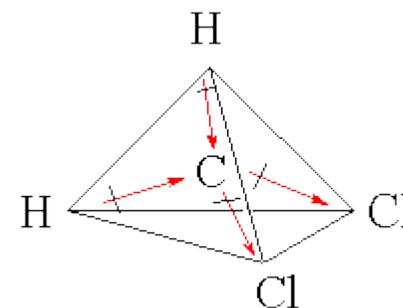
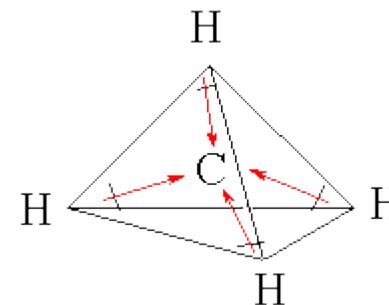
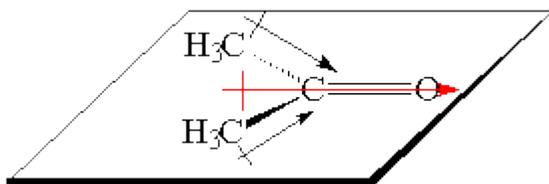
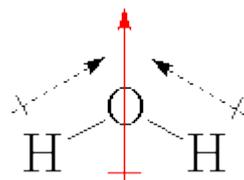
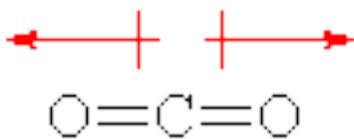




Noções de simetria

Composto	P.E. (°C)	P.M.
Água	100	18
Metano	-165	16
Etano	-88	30
Propano	-42	
Butano	-0,5	
Pentano	36	
isobutano	-7	58
Etanol	78	46
Diclorometano	40	85
Clorofórmio	62	127
Tetracloroeto de carbono	77	156
hexano	69	86

Noções de simetria



Noções de simetria

Elementos de simetria molecular

Os principais elementos de simetria molecular são o plano, o eixo e o centro. As moléculas que apresentam pelo menos um desses elementos são simétricas e, conseqüentemente, não têm atividade ótica, ou seja, não desviam o plano da luz polarizada.

No entanto, moléculas que apresentam apenas o eixo de simetria (não possuem plano nem centro de simetria) podem apresentar atividade ótica. Estas moléculas são ditas dissimétricas.

As moléculas que não apresentam nenhum desses elementos de simetria são assimétricas e ditas opticamente ativas, pois têm atividade ótica.

Noções de simetria

- Operação de simetria: é um movimento que mantém a molécula como a imagem original
- Elementos de simetria: são os elementos onde aplicamos a operação de simetria. São 5 ao todo: identidade, eixo, plano, centro de inversão e eixo impróprio

Noções de simetria

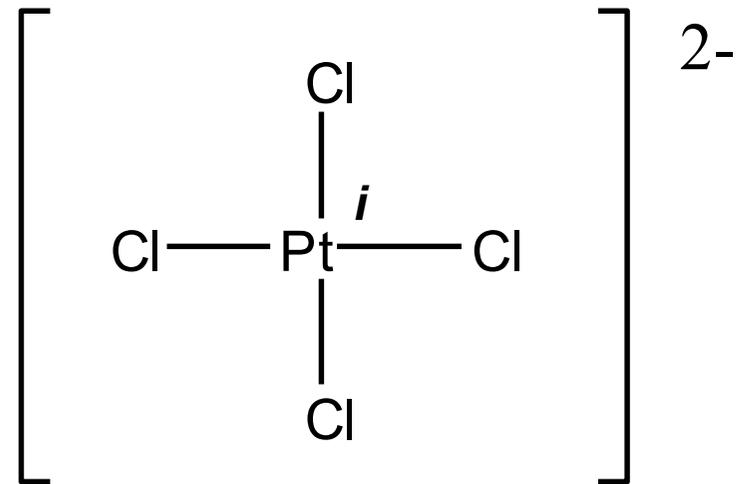
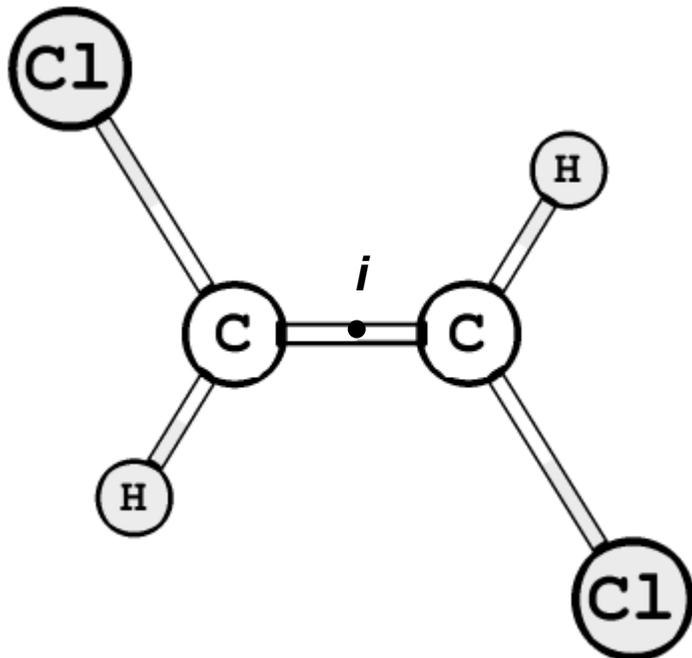
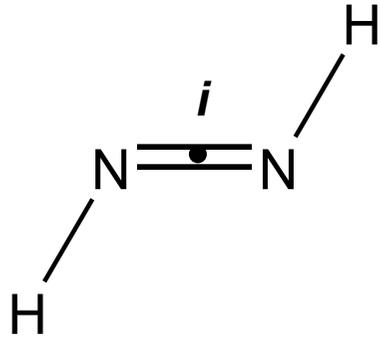
Elementos de simetria molecular

1. Identidade (E)
2. Centro de simetria (centro de inversão) (i)
3. Eixo de simetria (eixo de rotação) (C_n)
4. Plano de simetria (σ)
5. Eixo de rotação-reflexão (eixo rotacional impróprio) (S_n)

1. Operação identidade (E)

- a molécula permanece inalterada

2. Centro de simetria (centro de inversão) (*i*)



3. Eixo de simetria (eixo de rotação) (C_n)

- Eixo de simetria

⇒ H_2O

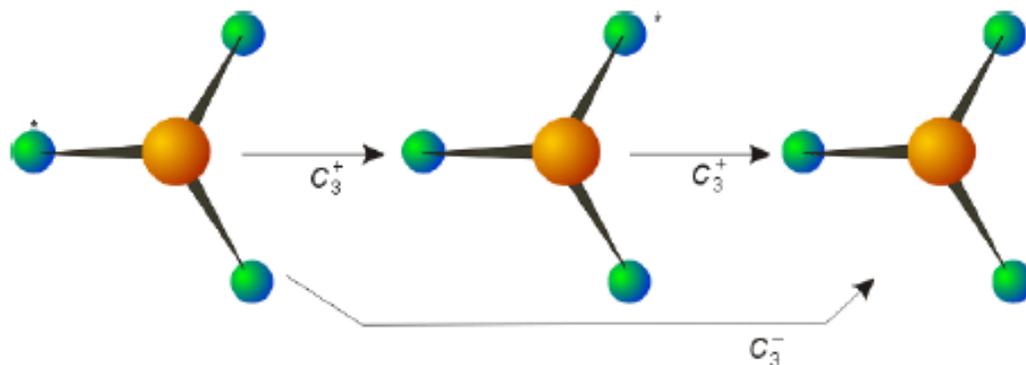
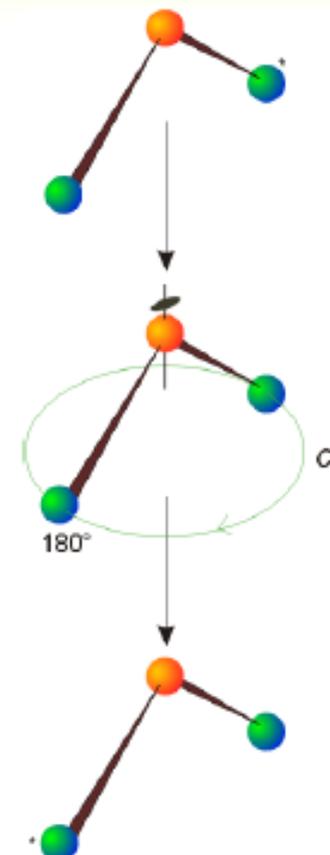
* 180° , $n=2$

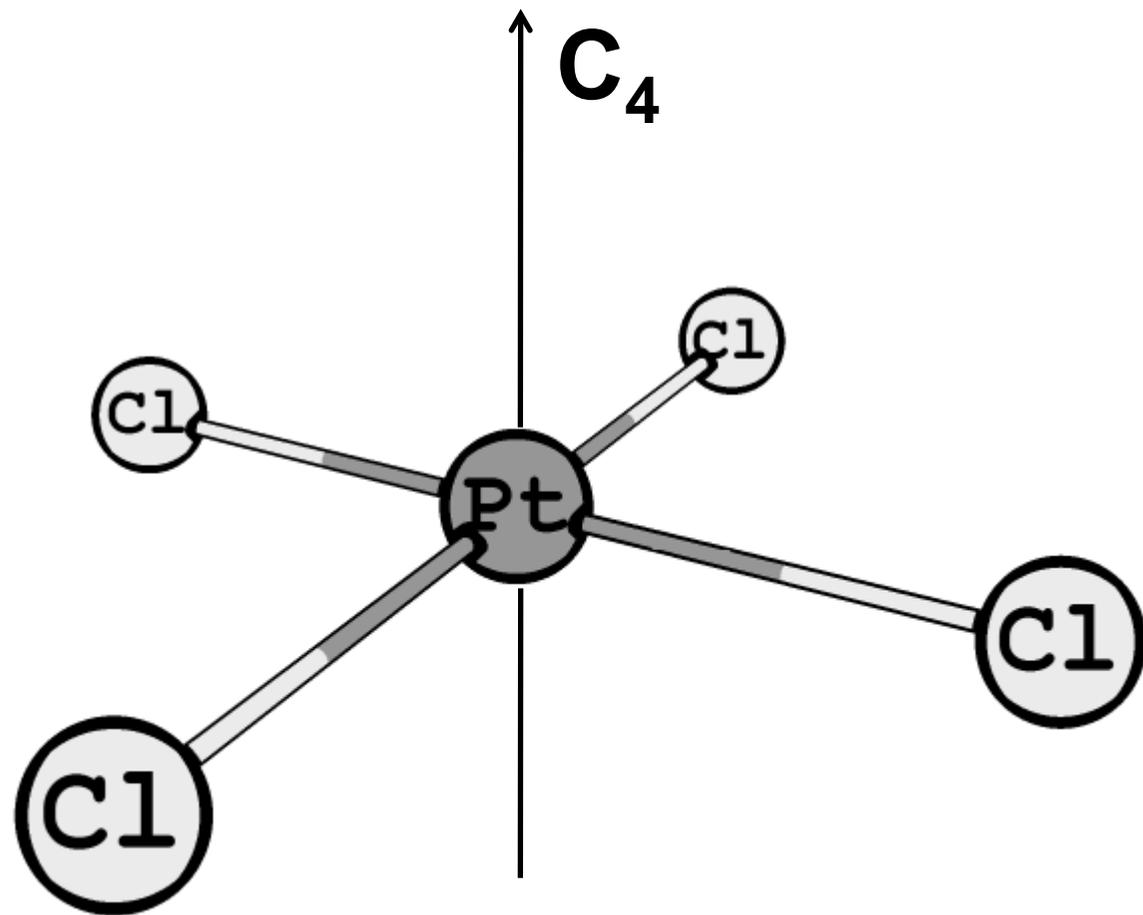
* C_2

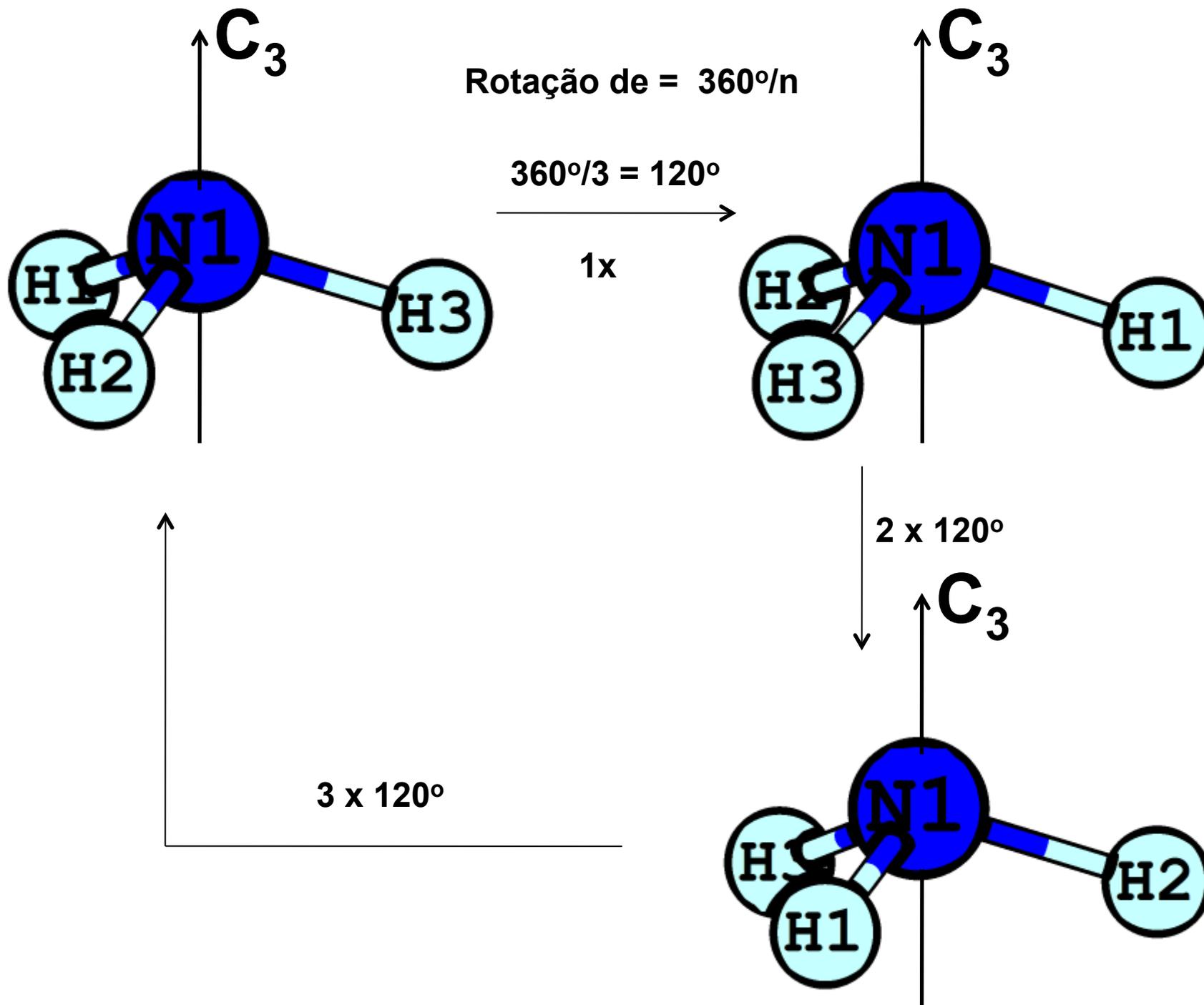
⇒ NH_3

* 120° , $n=3$

* C_3

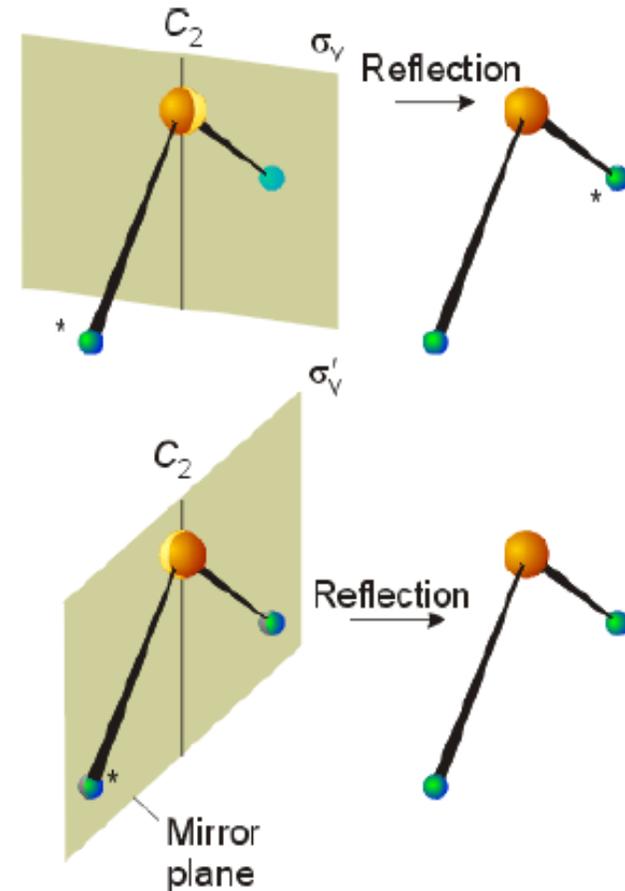
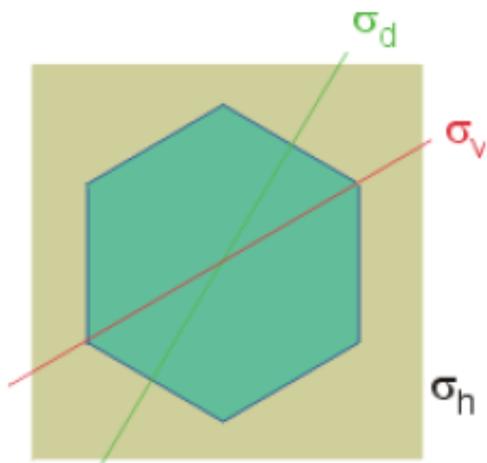






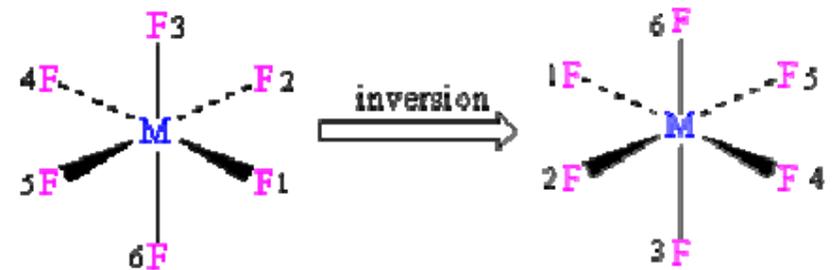
4. Plano de simetria (σ)

- Plano de simetria
- A molécula pode ter diferentes planos de simetria....

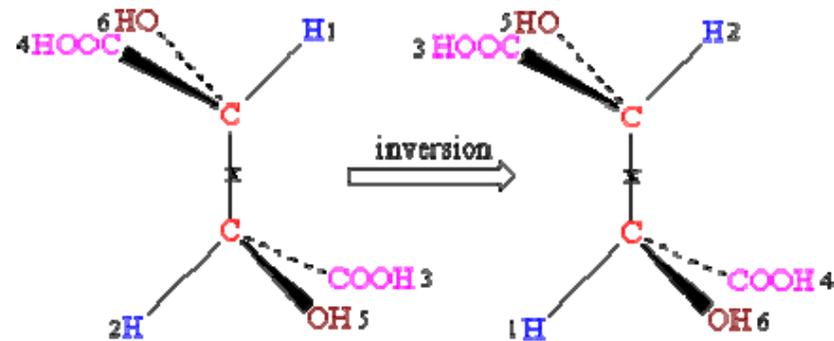
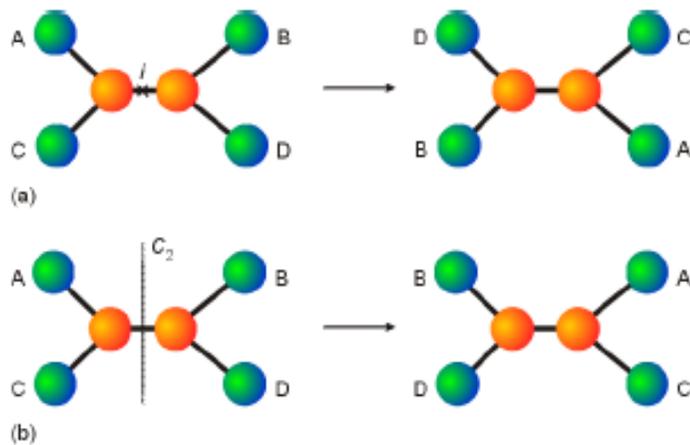


Noções de simetria

- Inversão

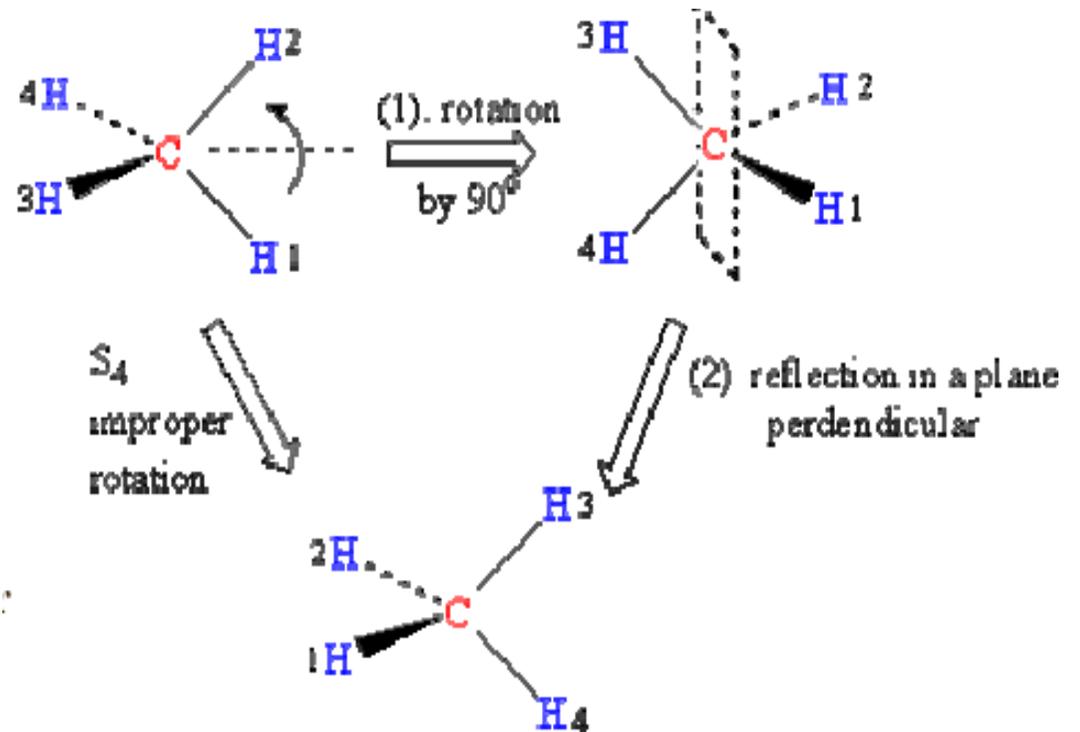


- Importante diferenciar de C_2 e i



5. Eixo de rotação-reflexão (eixo rotacional impróprio) (S_n)

- Inversão imprópria
- Consiste de duas operações separadas: rotação em um eixo e depois reflexão em um plano.



Grupos de ponto

- Sistema Internacional (Hermann-Maugin)

- C_1 , C_i , C_s
- C_n , C_{nv} , C_{nh}
- D_n , D_{nh} , D_{nd}
- S_n
- T_h , T_d
- O_h

Mais usado para moléculas

- Schoenflies (cristais)

Mais usado para cristais

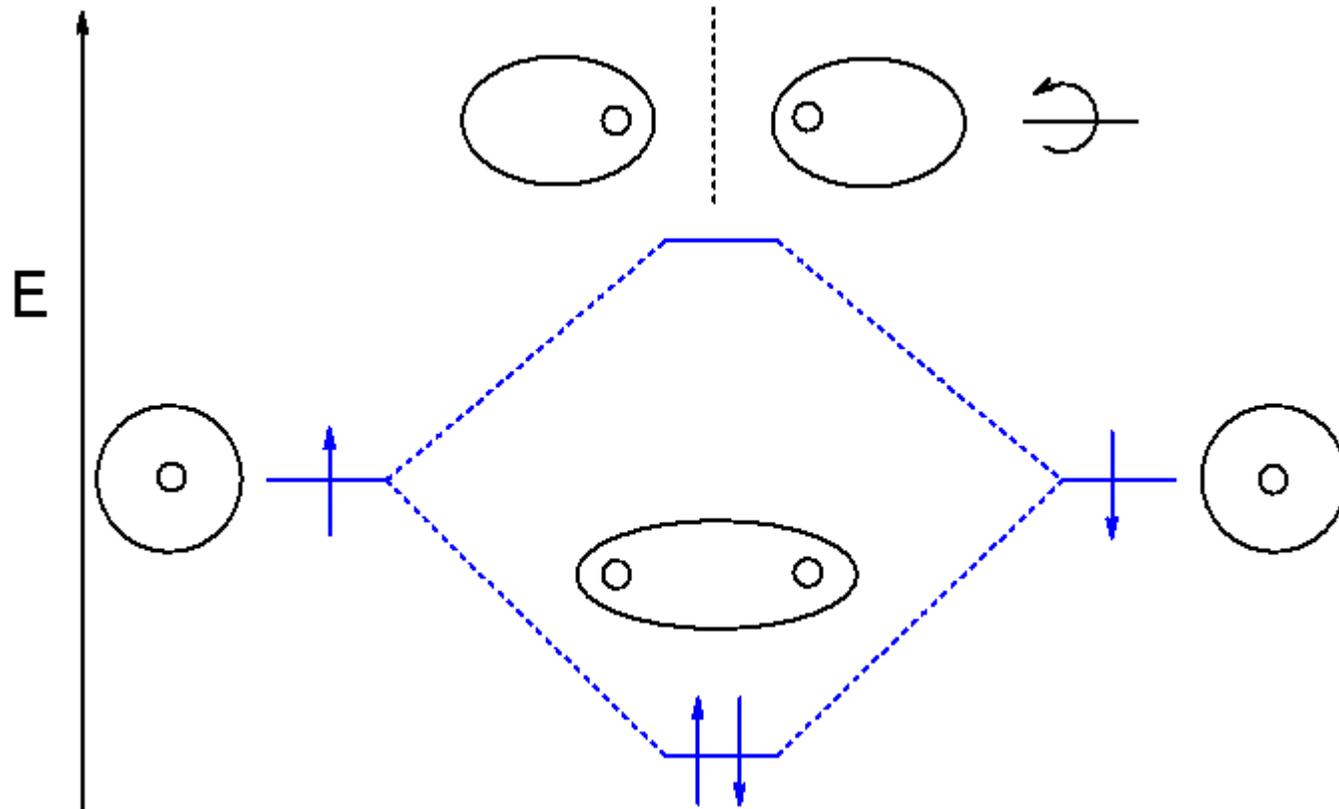
Teoria dos Orbitais Moleculares (MO)

- Mulliken

- Não há lugar na teoria MO para conceitos clássicos tais como valência ou ligação química
- “O fato de que os elétrons de valência quase sempre ocorram em pares em moléculas saturadas não parece ter conexão fundamental com a existência de estabilidade molecular... Um entendimento mais claro da estrutura molecular pode ser obtido abandonando-se a idéia de átomos ou íons ligados por força de valência e adotando o ponto de vista molecular, que considera a molécula individualmente como composta de núcleos e elétrons”

Robert Mulliken.

MO: H₂



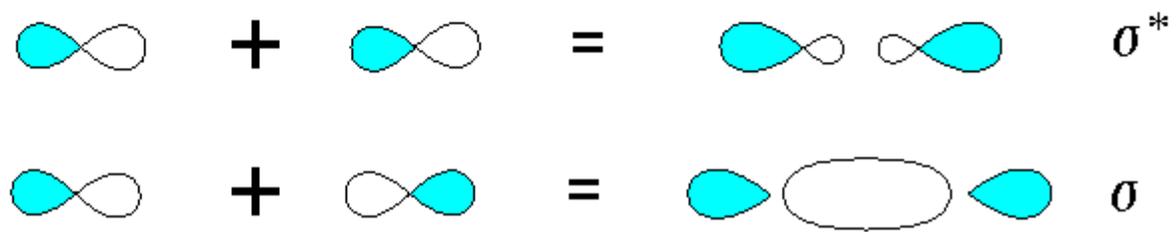
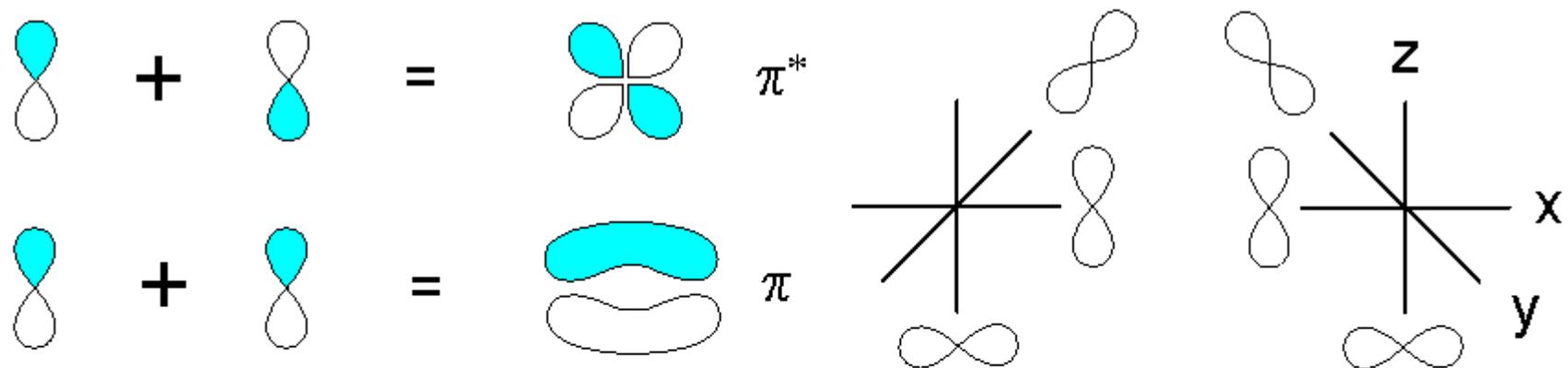
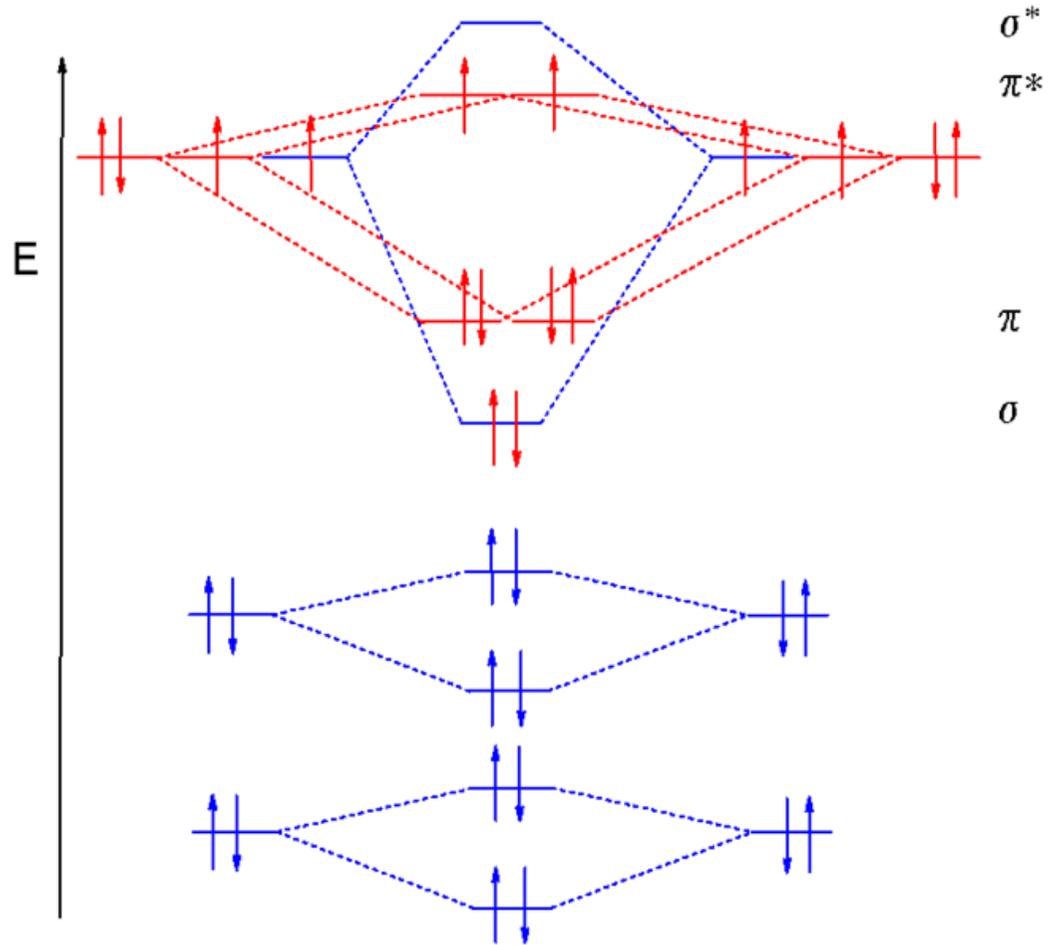
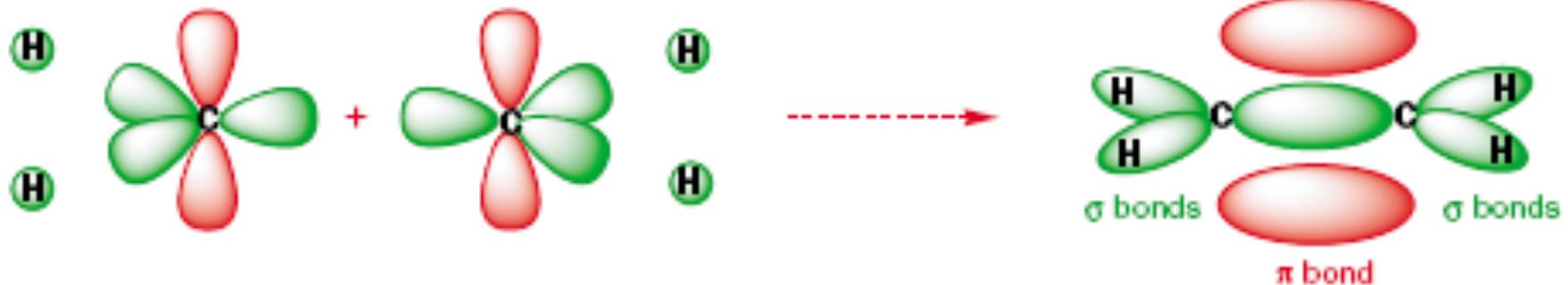
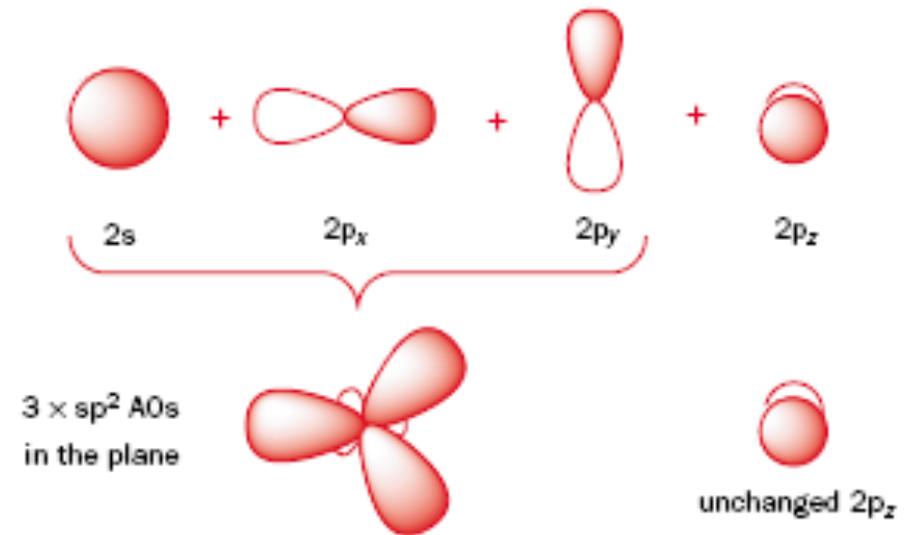


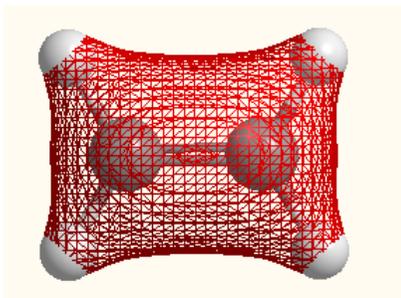
Diagrama MO para o O_2



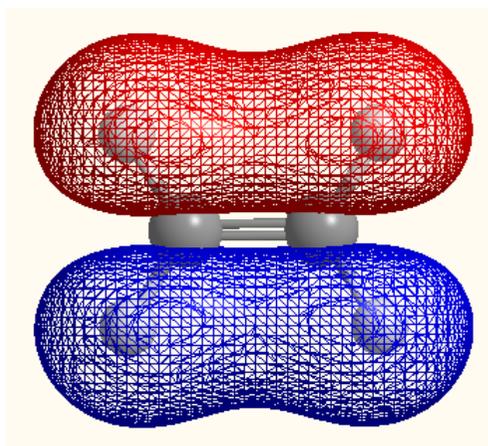
Orbitais Moleculares

- Uma das formas matemáticas de estudar mundo microscópico
- N orb. Atômicos \rightarrow N Orb. Mol.
- Ex.: Etileno: 12 OA

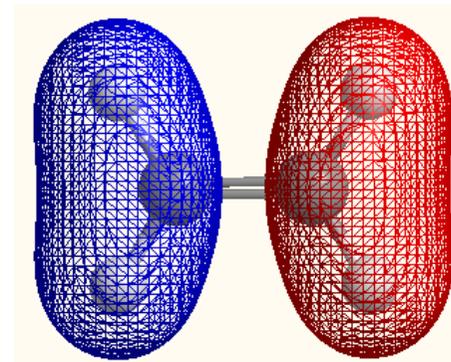




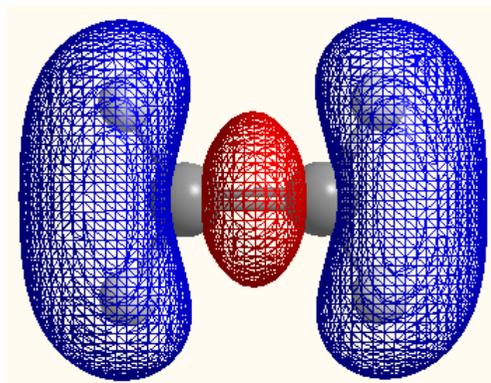
HOMO-5 (N=1)
-33.00 eV



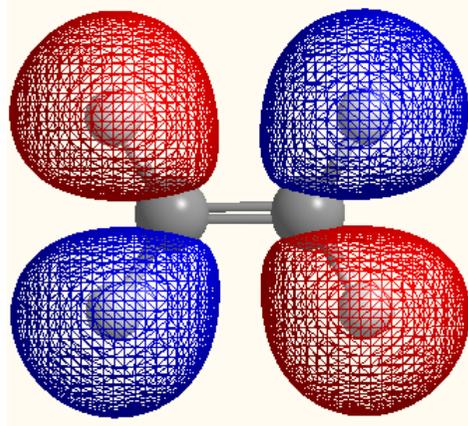
HOMO-4 (N=2)
-21.77 eV



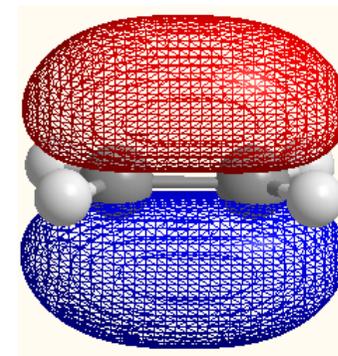
HOMO-3 (N=3)
-15.77 eV



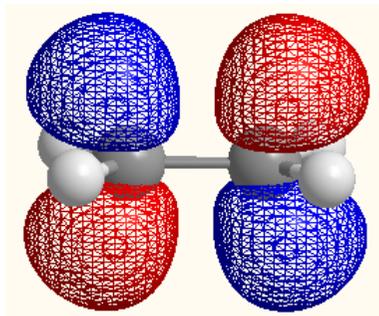
HOMO-2 (N=4)
-14.12 eV



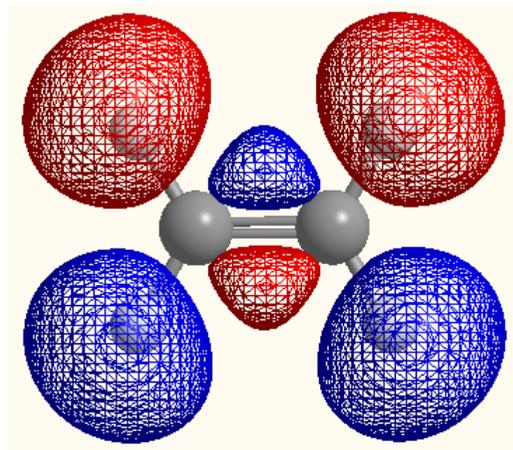
HOMO-1 (N=5)
-11.94 eV



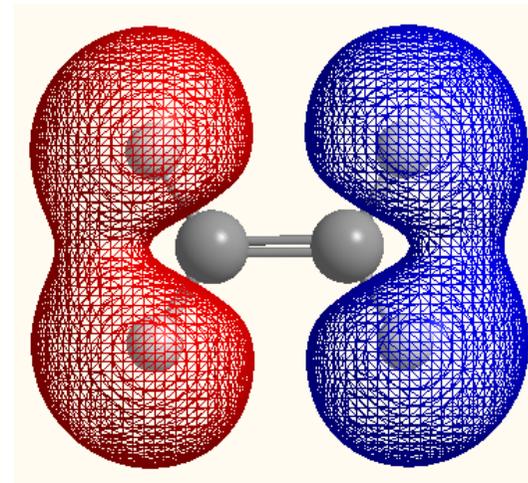
HOMO (N=6)
-10.46 eV



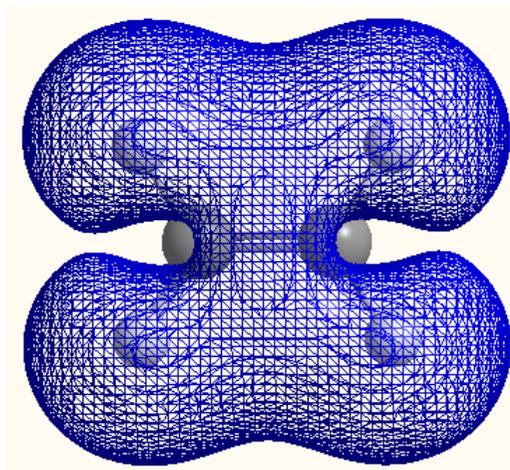
LUMO (N=7)
1.39 eV



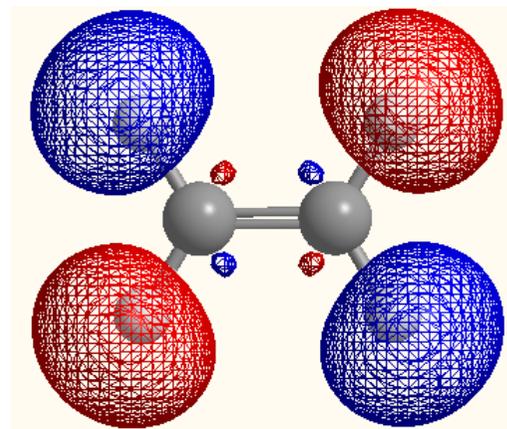
LUMO+1 (N=8)
4.10 eV



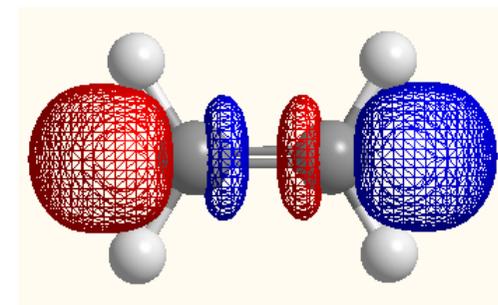
LUMO+2 (N=9)
4.35 eV



LUMO+3 (N=10)
4.98 eV



LUMO+4 (N=11)
5.59 eV



LUMO+5 (N=12)
5.73 eV

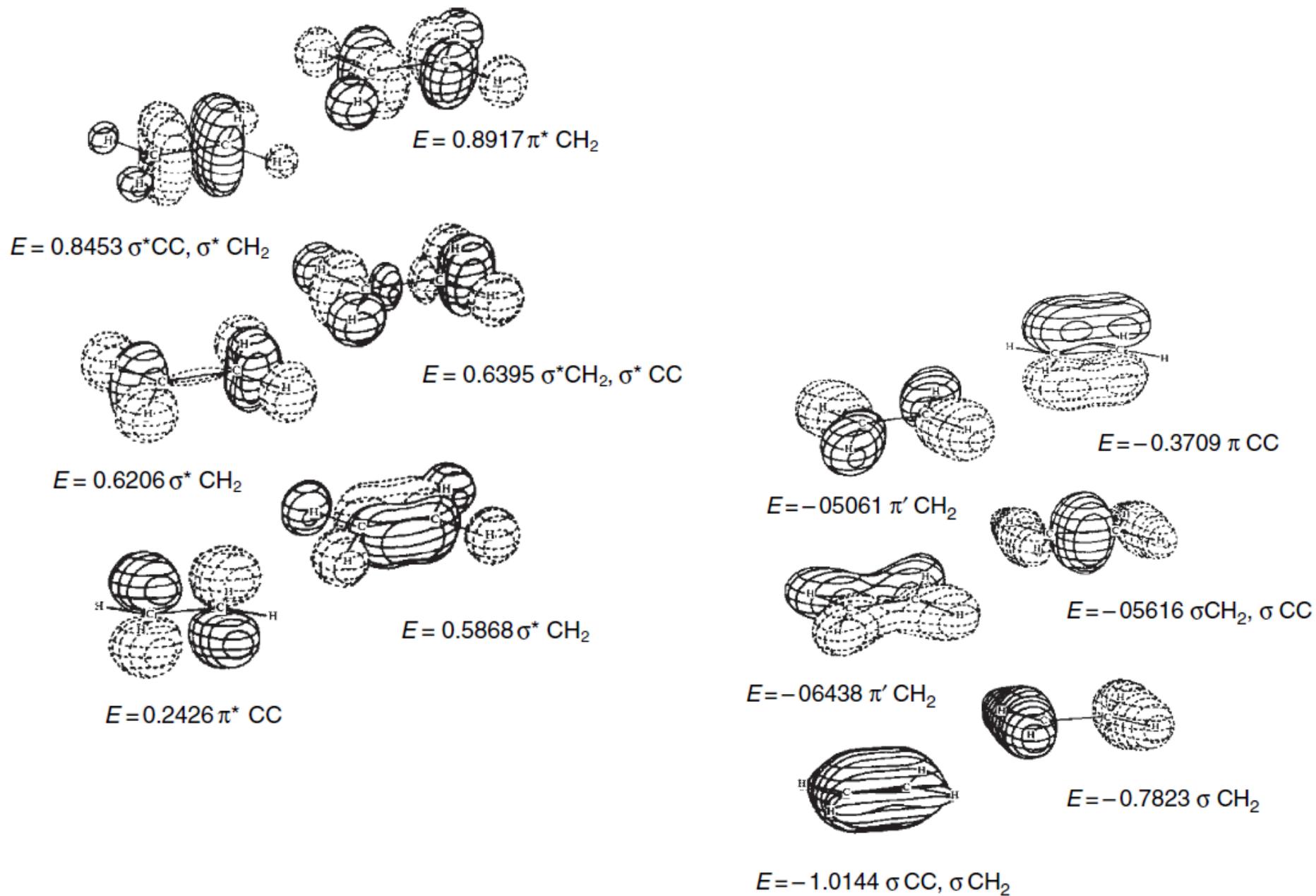


Fig. 1.18. Pictorial representation of ethene MOs. Reproduced with permission from W. L. Jorgensen and L. Salem, *The Organic Chemist's Book of Orbitals*, Academic Press, New York, 1973.

Aproximações e hipóteses

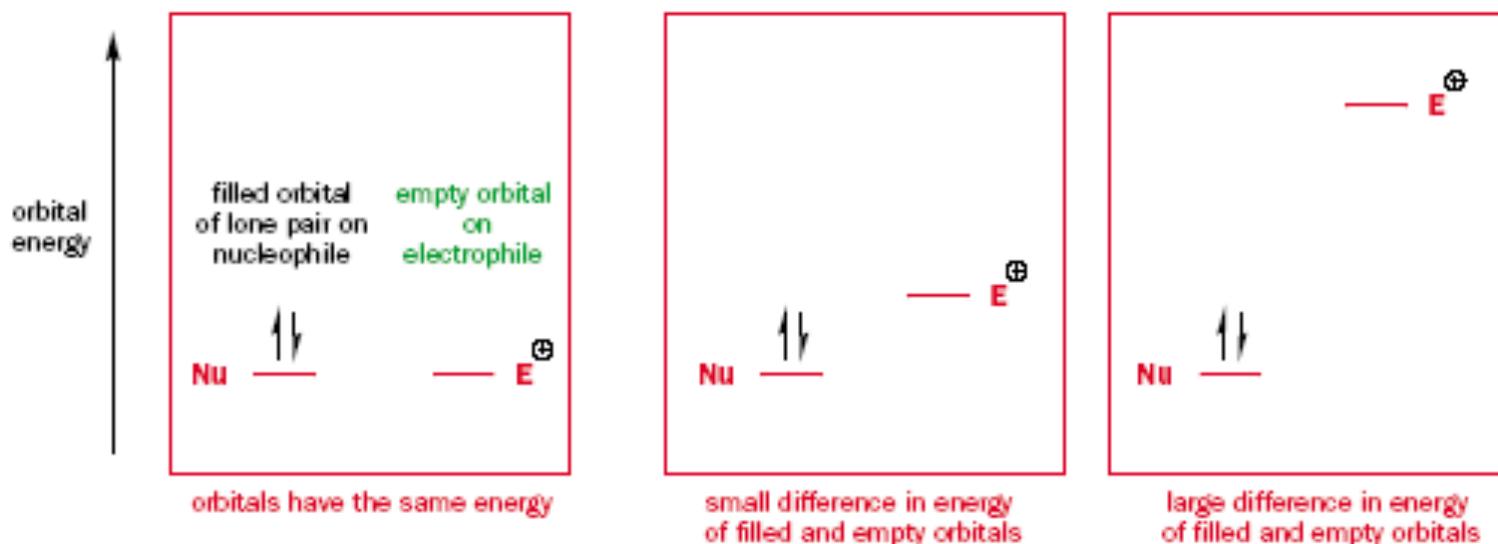
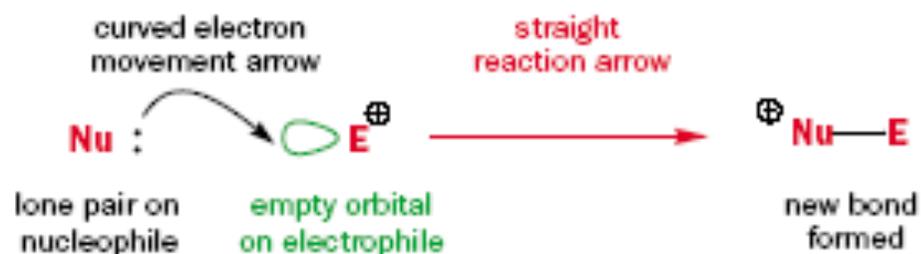
1. Aproximação de Born-Oppenheimer é inerentemente assumida no modelo
2. Efeitos relativísticos são completamente negligenciados
3. A solução variacional é assumida ser uma combinação linear de um número finito de funções de bases, que usualmente são ortogonais. O conjunto de bases é considerado aproximadamente completo.
4. Cada energia descrita é assumida ser descrita por um único determinante de Slater
5. Aproximação do campo médio. Desvios dessa hipótese (correlação eletrônica) é completamente negligenciada.

Remontagem da Função de onda total a partir dos “orbitais”

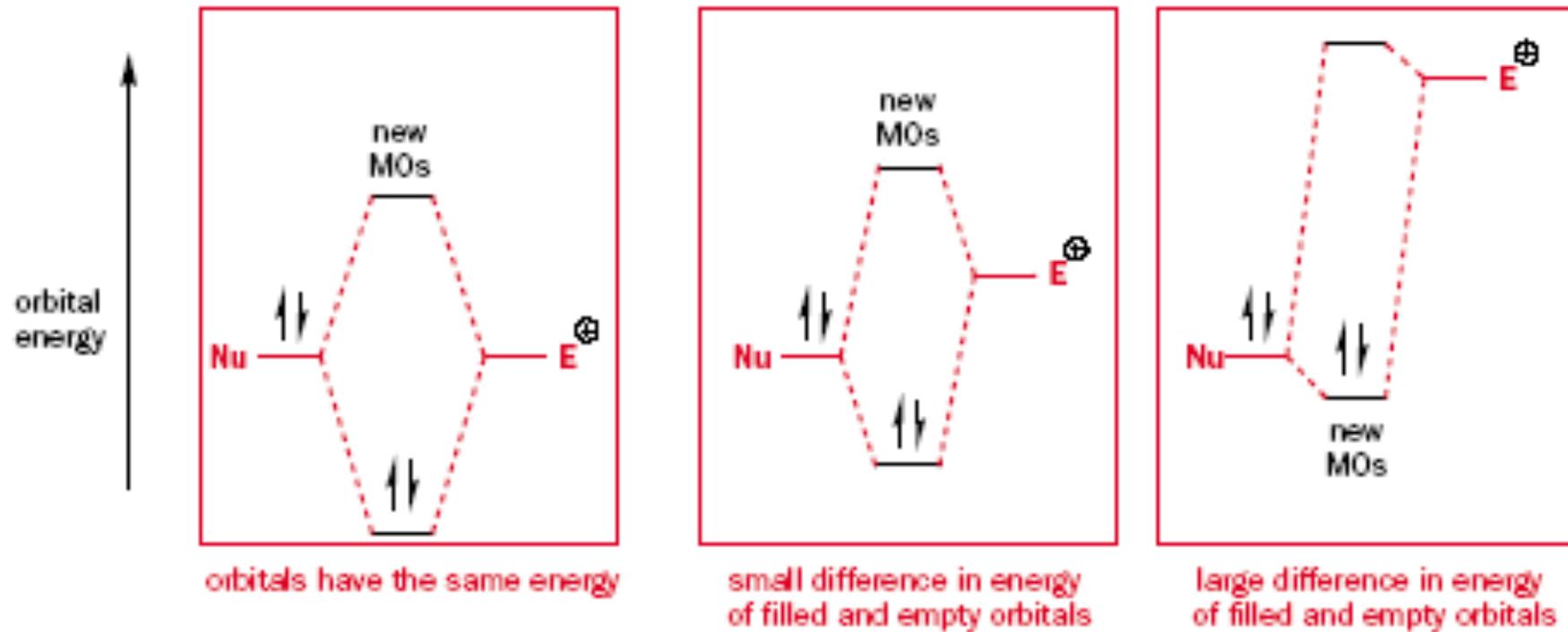
- Briga até hoje...
- Teoria de ligação de valência (Valence Bond - **VB**)
- Teoria dos Orbitais Moleculares (Molecular Orbitals – **MO**)

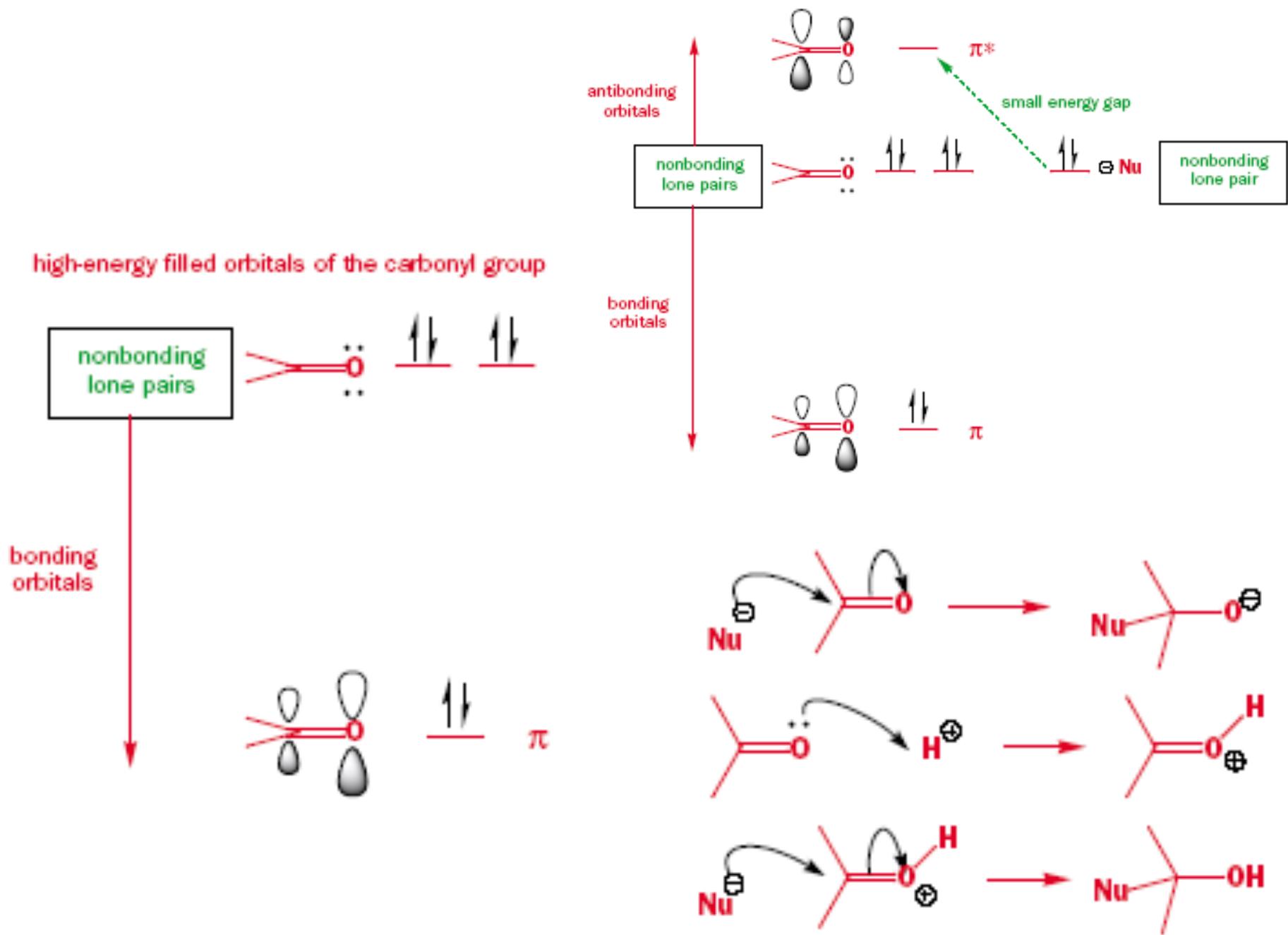
Mecanismos de Reação

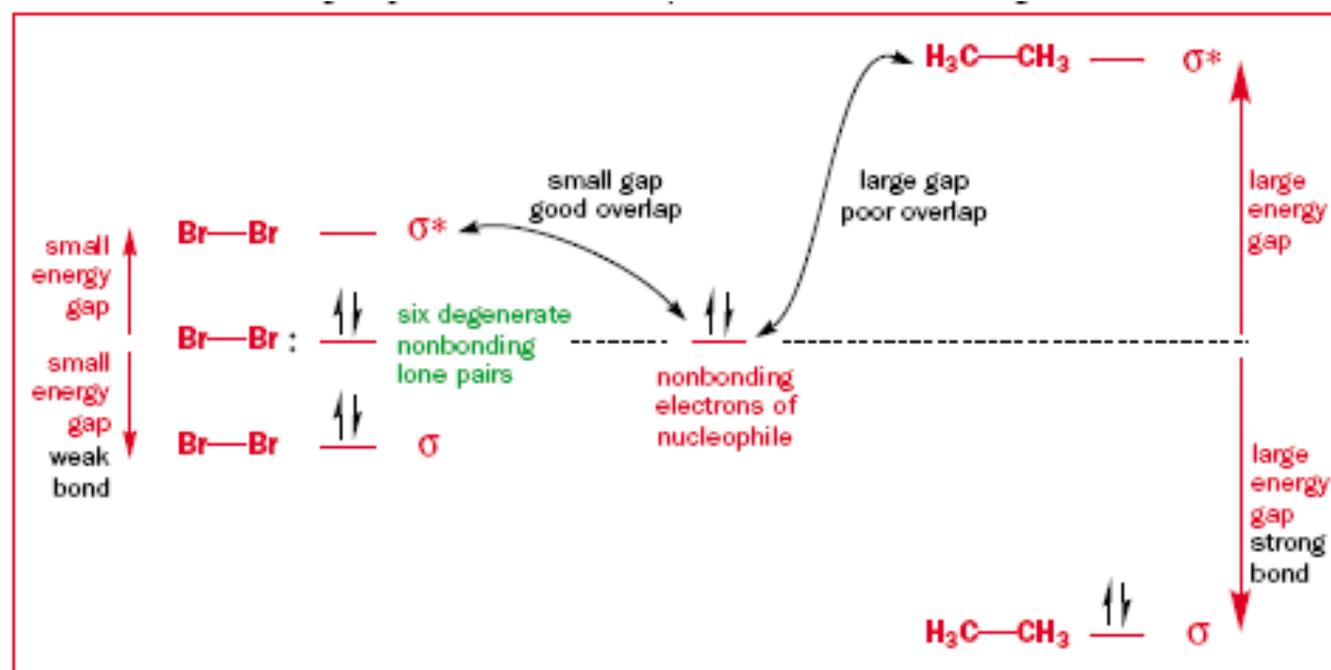
- Nucleófilos: Doam par de elétrons
- Eletrófilos: Aceitam par de elétrons



Proximidade Orbitais: HOMO e LUMO







A guide to drawing mechanisms with curly arrows

- 1 Draw out the reagents as clear structures following the guidelines in Chapter 2. Check that you understand what the reagents and the solvent are under the conditions of the reaction, for example, if the reaction is in a base, will one of the compounds exist as an anion?
- 2 Inspect the starting materials and the products and assess what has happened in the reaction. What new bonds have been formed? What bonds have been broken? Has anything been added or removed? Have any bonds moved around the molecule?
- 3 Identify the nucleophilic centres in all the reactant molecules and decide which is the most nucleophilic. Then identify the electrophiles present and again decide which is the most electrophilic
- 4 If the combination of these two centres appears to lead to the product, draw the reactants, complete with charges, so as to position the nucleophilic and electrophilic centres within bonding distance ensuring that the angle of attack of the nucleophile is more or less consistent with the orbitals involved
- 5 Draw a curly arrow from the nucleophile to the electrophile. It must start on the filled orbital or negative charge (show this clearly by just touching the bond or charge) and finish on the empty orbital (show this clearly by the position of the head). You may consider a 'push' or a 'pull' mechanism at this stage
- 6 Consider whether any atom that has been changed now has too many bonds; if so one of them must be broken to avoid a ridiculous structure. Select a bond to break. Draw a curly arrow from the centre of the chosen bond, the filled orbital, and terminate it in a suitable place
- 7 Write out the structures of the products specified by the curly arrows. Break the bonds that are the sources of the arrows and make those that are the targets. Consider the effect on the charges on individual atoms and check that the overall charge is not changed. Once you have drawn the curly arrows, the structure of the products is already decided and there is no room for any further decisions. Just write what the curly arrows tell you. If the structure is wrong, then the curly arrows were wrong so go back and change them
- 8 Repeat stages 5–7 as required to produce a stable product

Espécies Reativas

- Espécies com Orbitais Vazios: Eletrófilos
- Espécies com Orbitais Semipreenchidos:
Radicais Livres
- Espécies com Pares de Elétrons Isolados:
Nucleófilos

Nucleófilos: Tipos de Pares Eletrônicos e Basicidade de Lewis

- Pares de elétrons

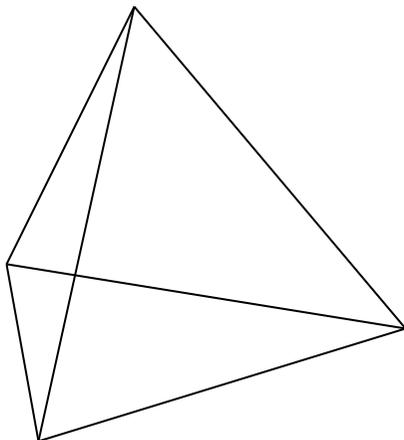
σ

π

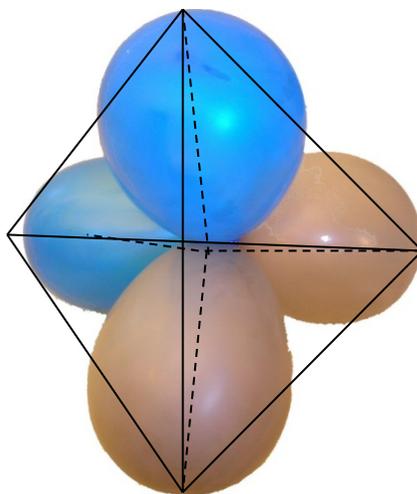
n

- Ordem de Basicidade

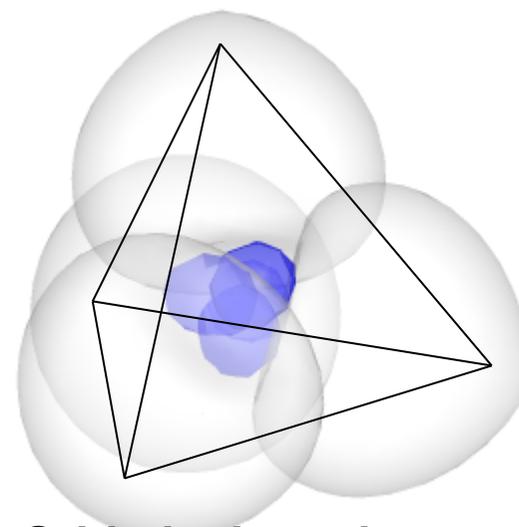
$n > \pi > \sigma$



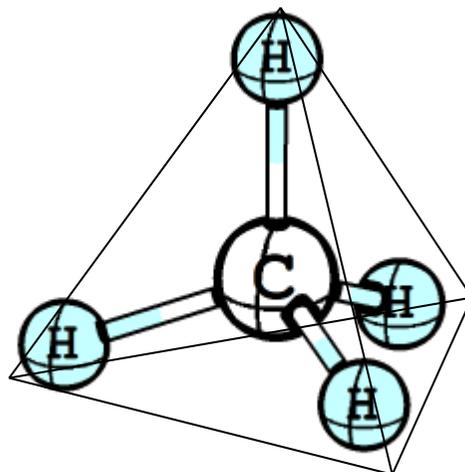
tetraedro



**Bolas de aniversário
(arranjo tetraédrico)**

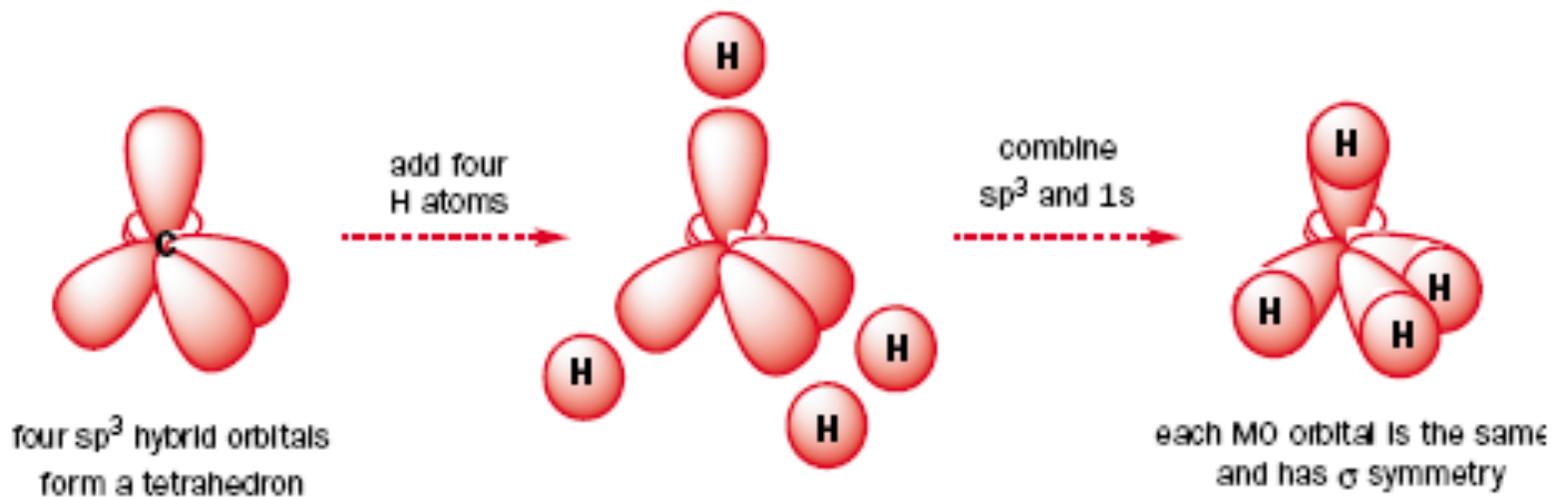
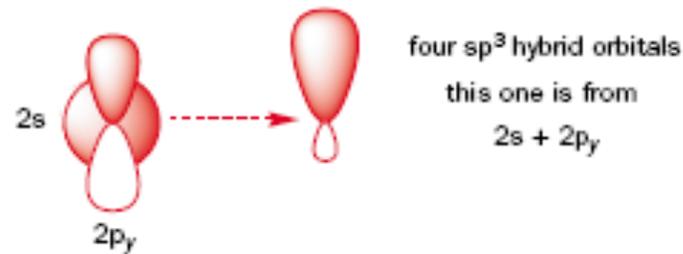
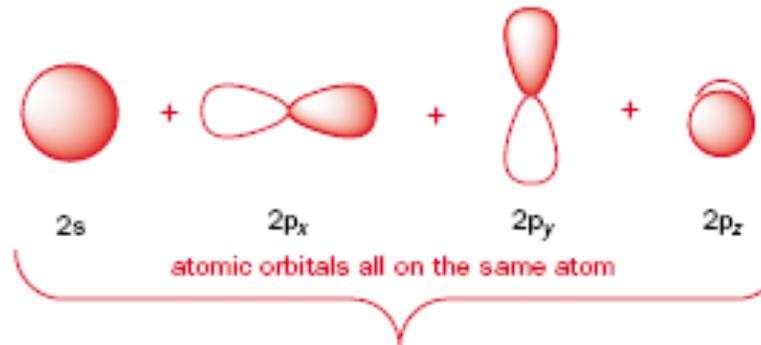


**Orbitais do carbono
(arranjo tetraédrico)**

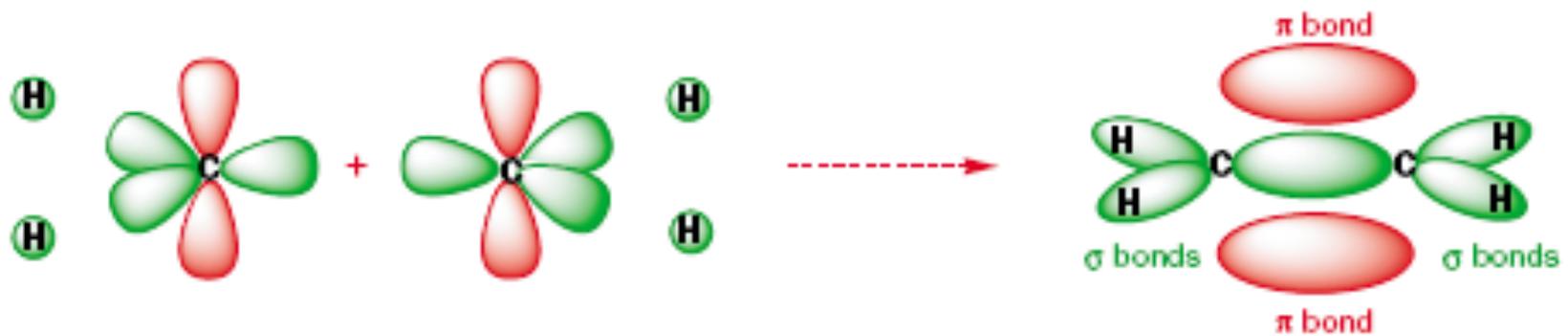
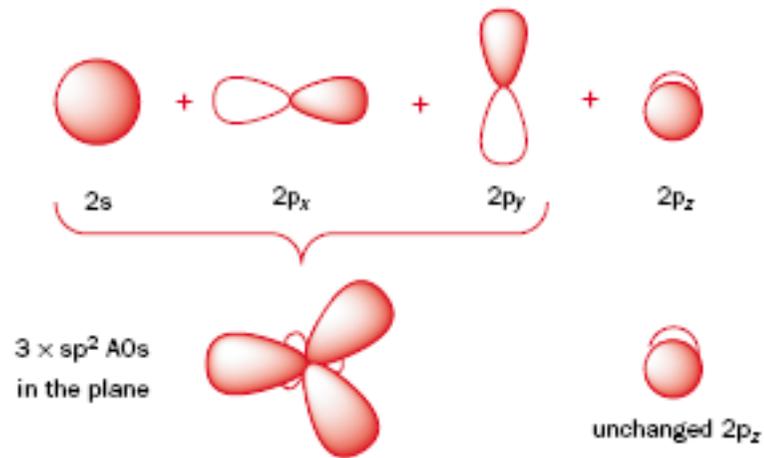


**Metano dentro
em um tetraedro**

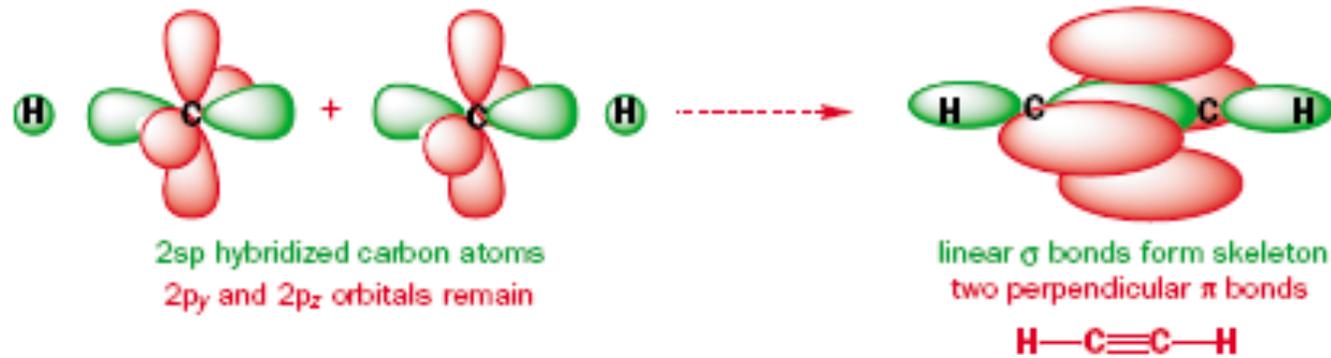
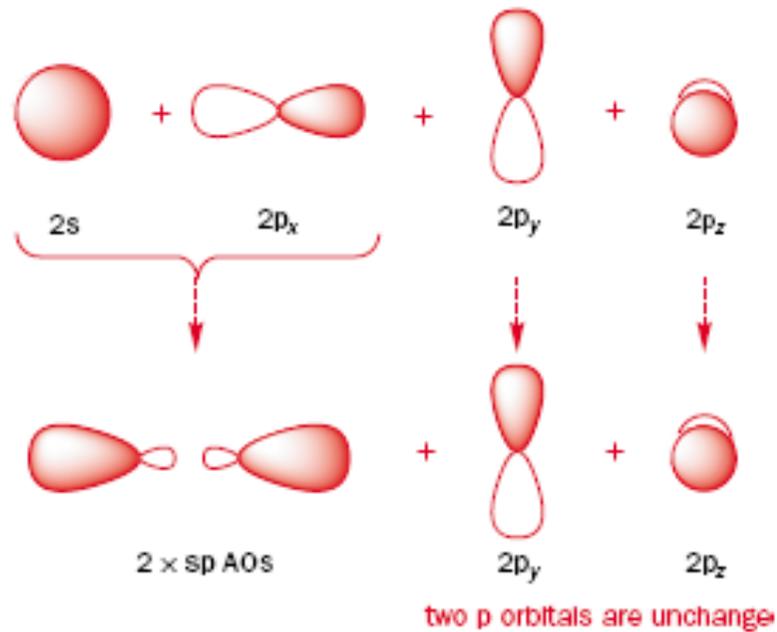
Hibridização sp^3



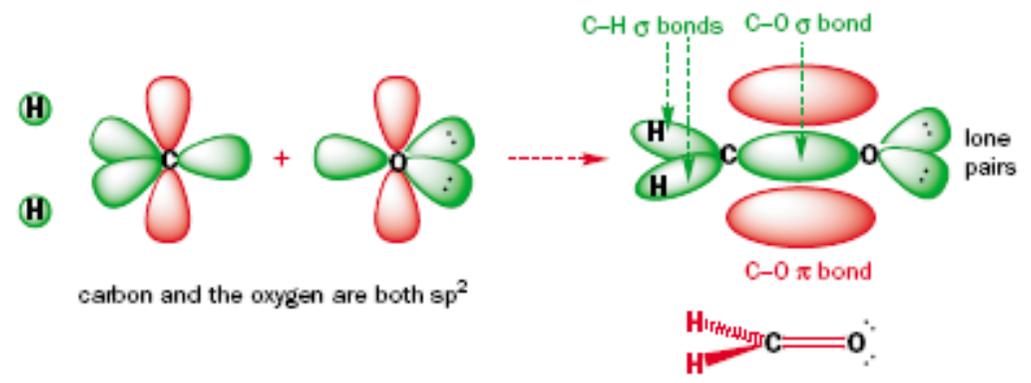
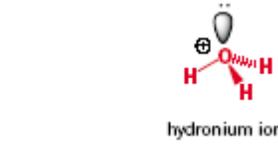
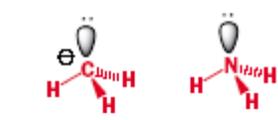
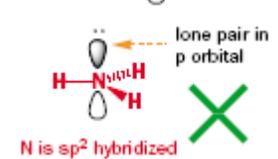
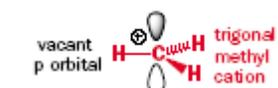
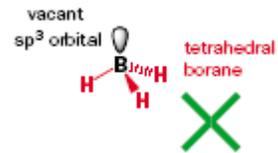
Hibridização sp^2



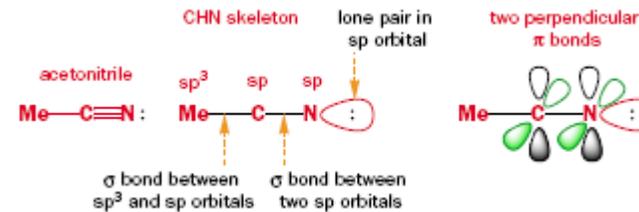
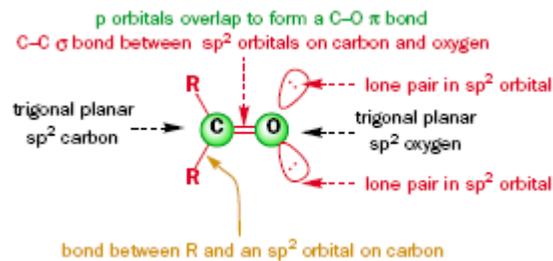
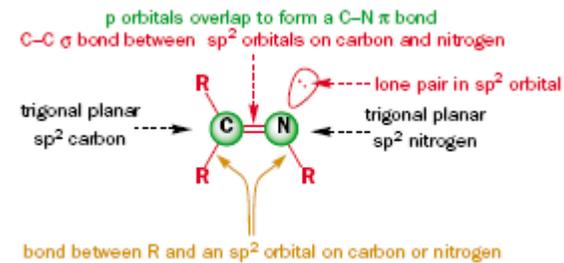
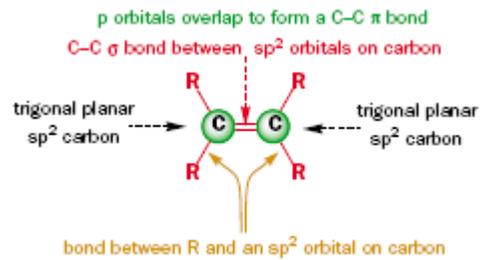
Hibridização sp

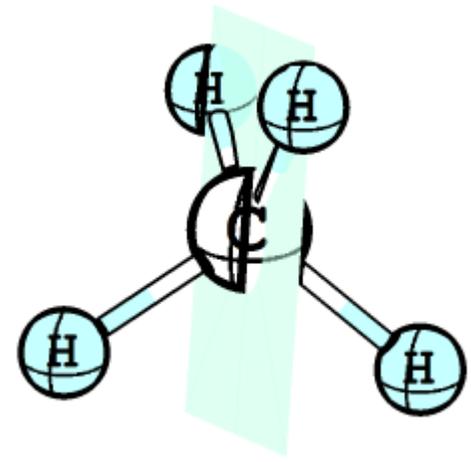
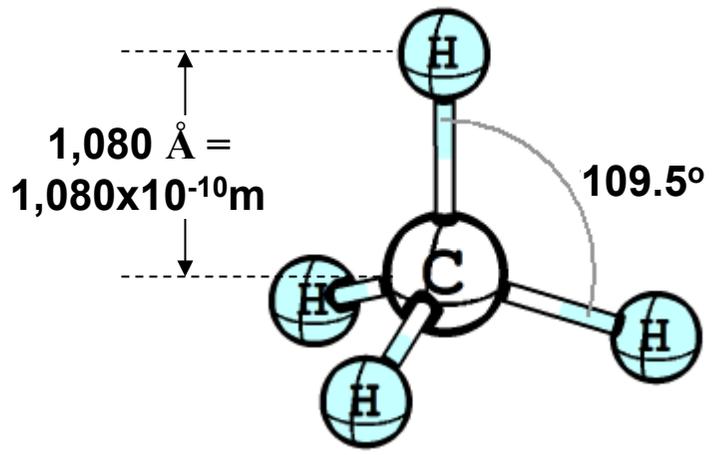


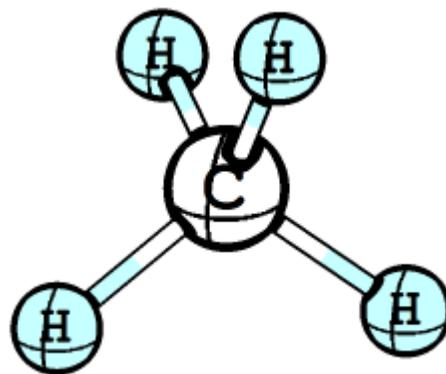
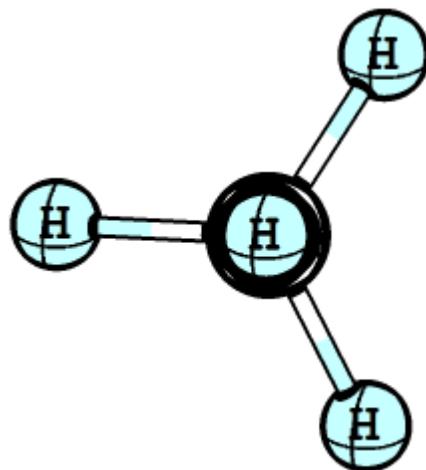
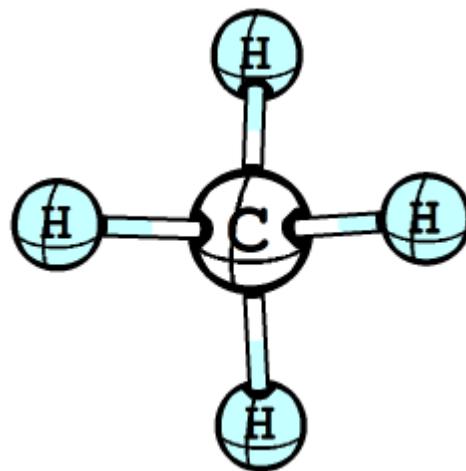
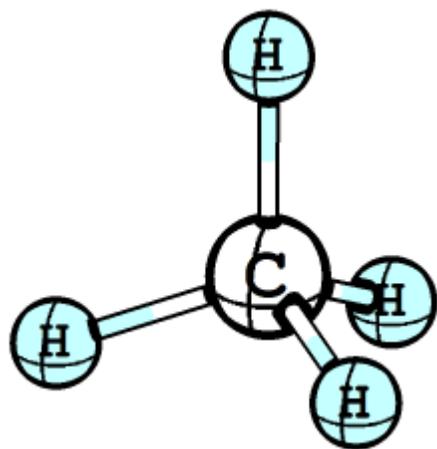
VSEPR

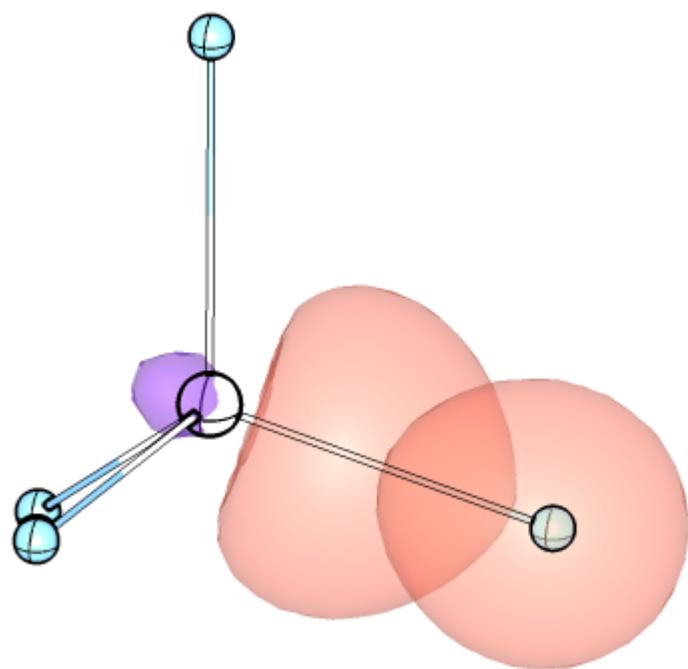
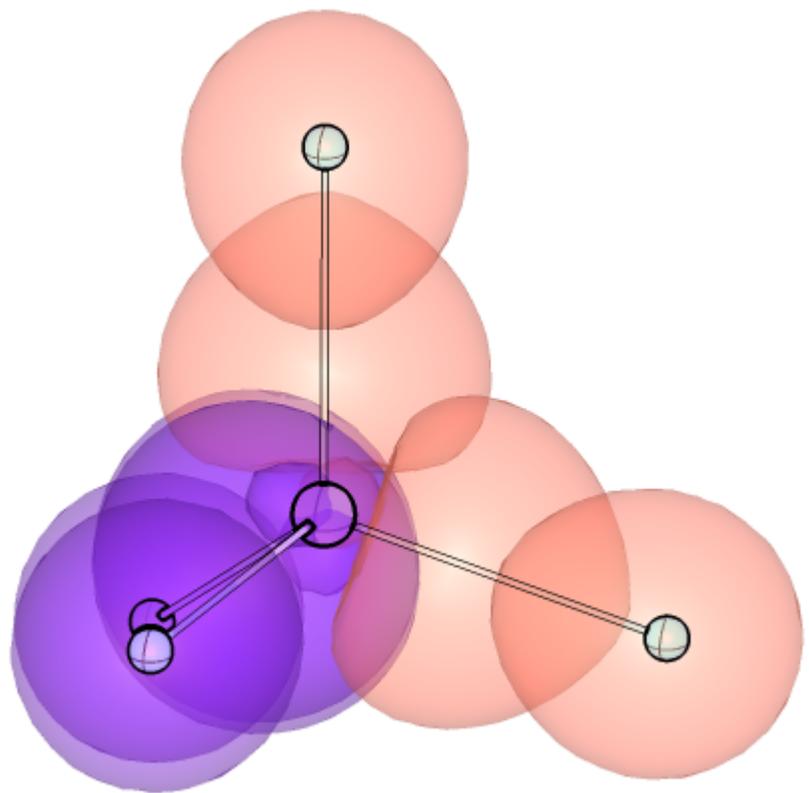


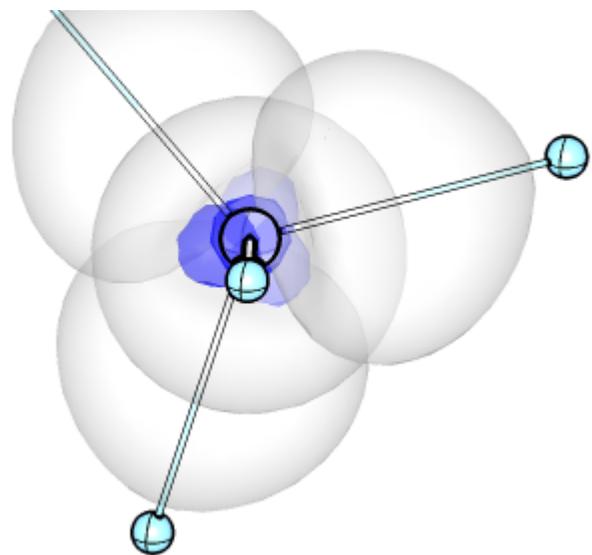
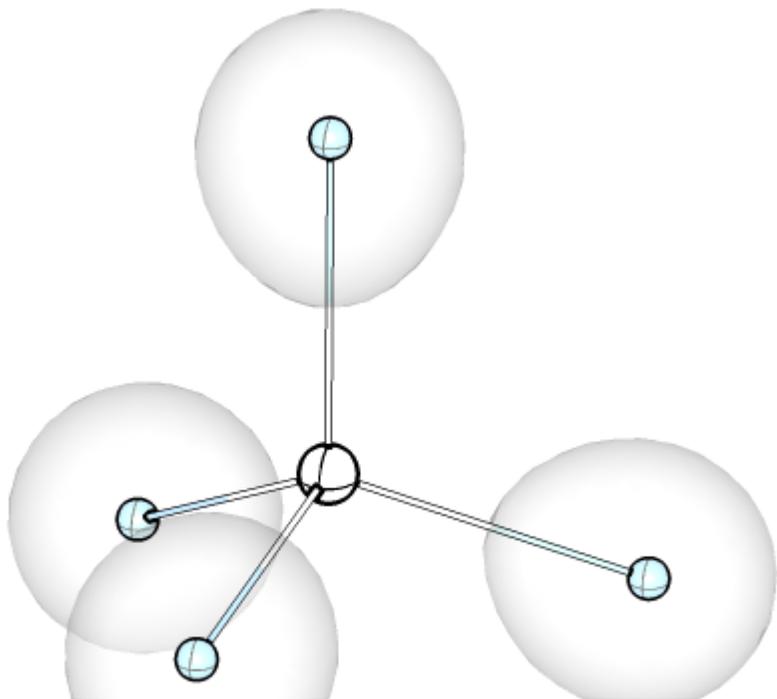
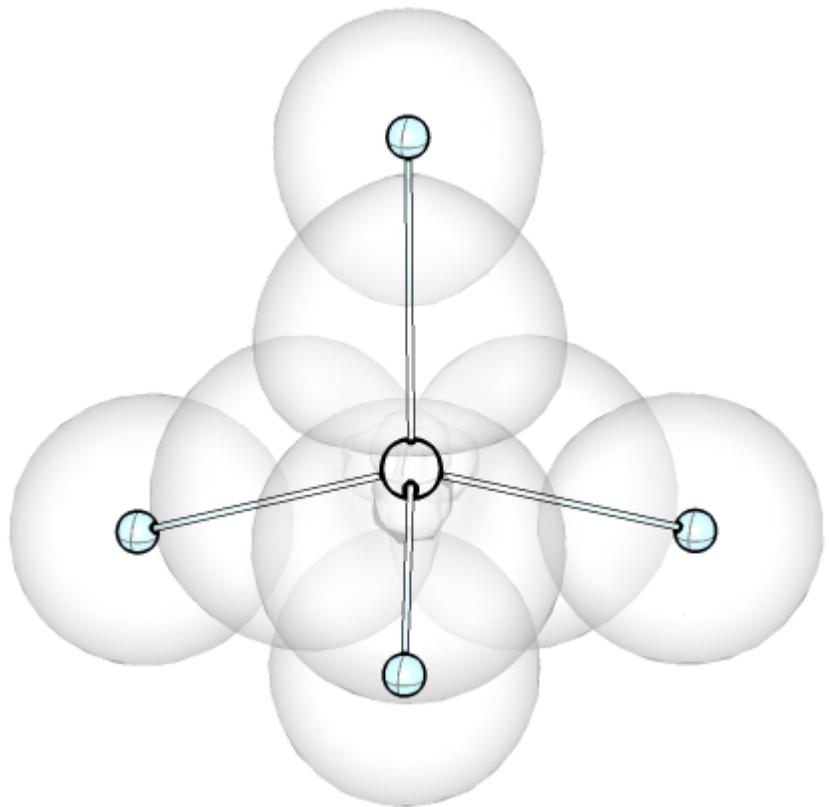
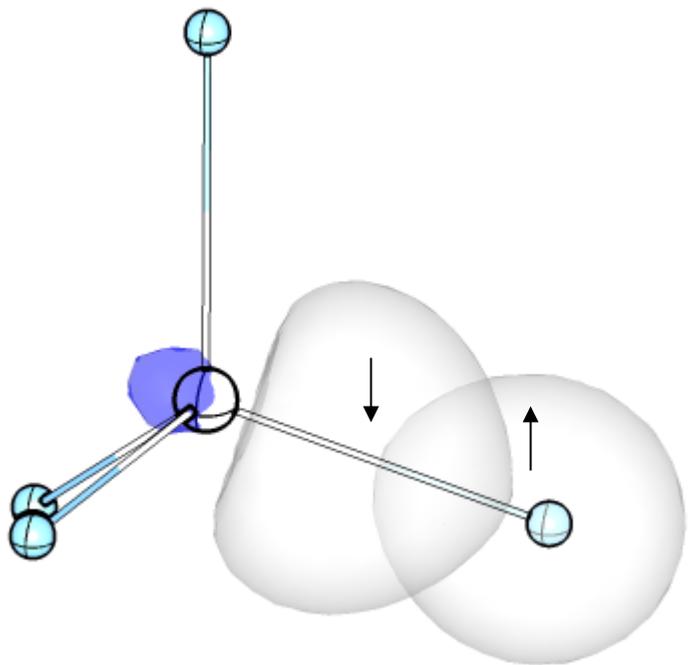
Construindo Moléculas

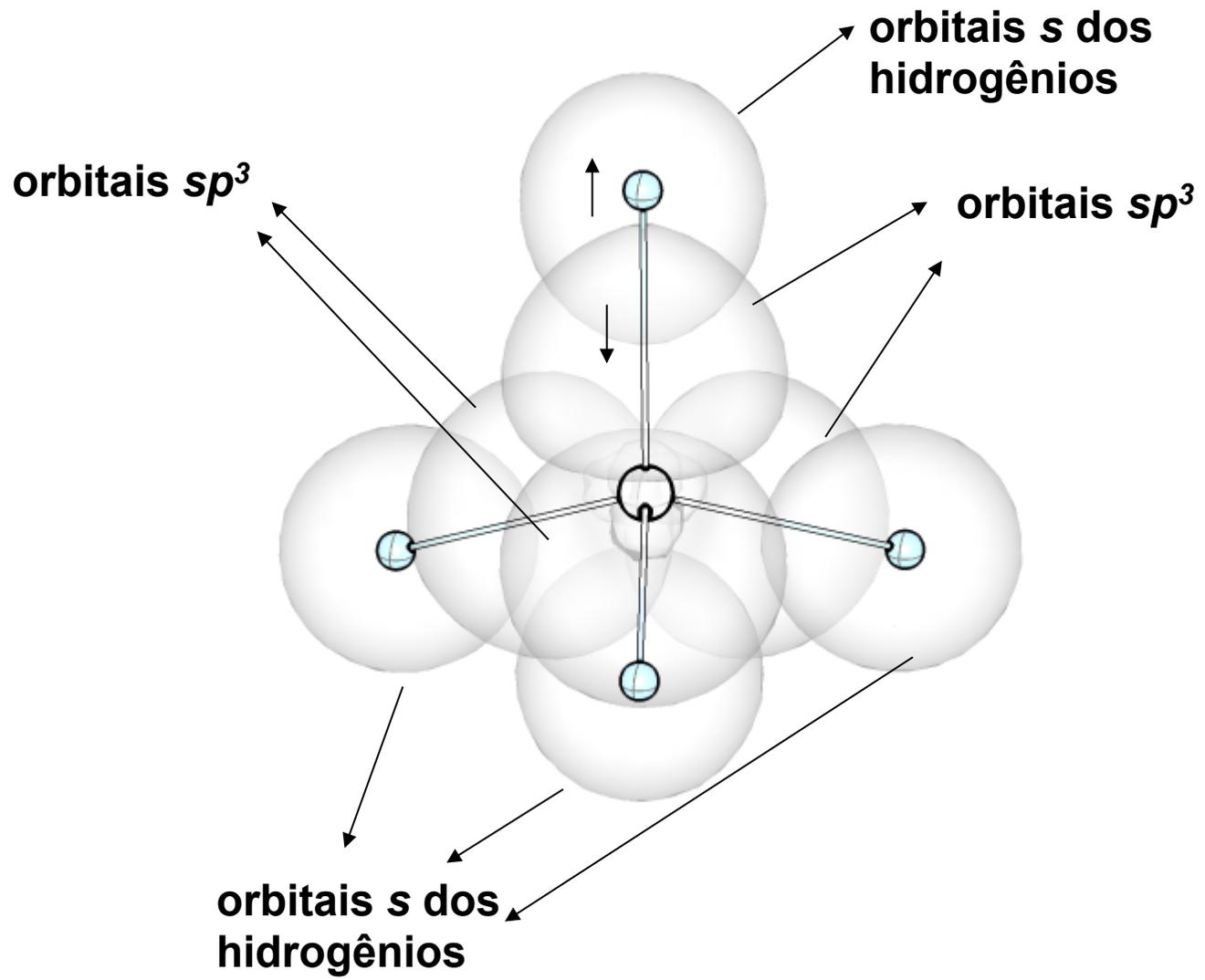


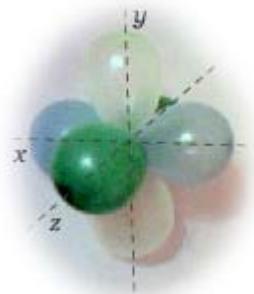
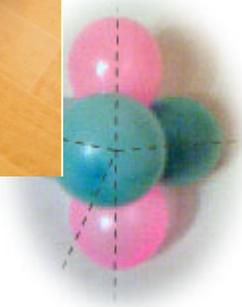
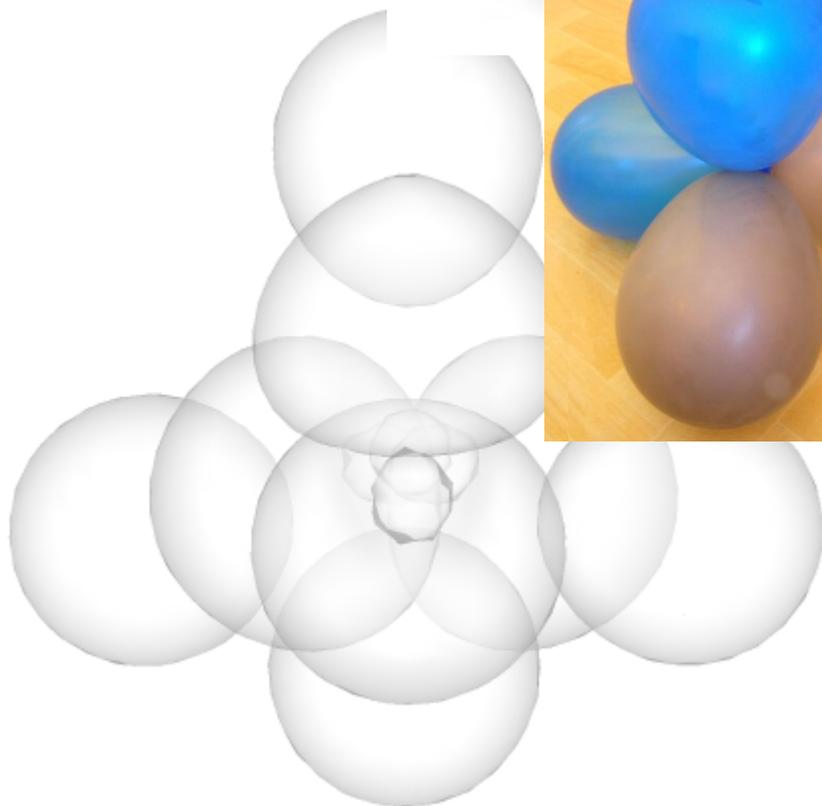
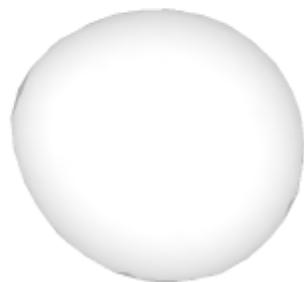
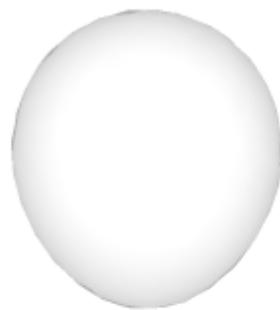
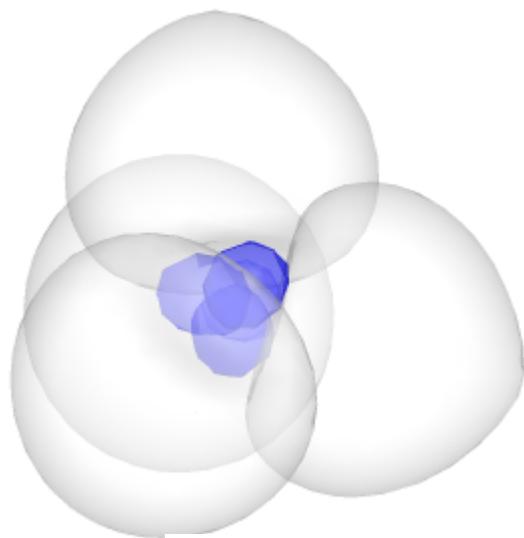


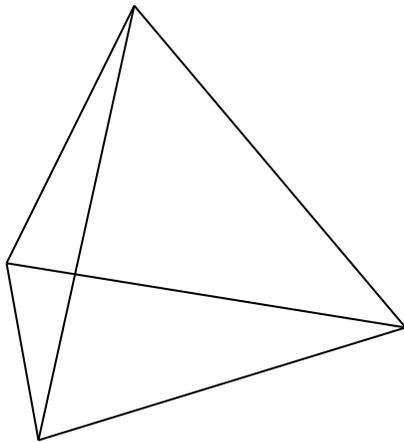




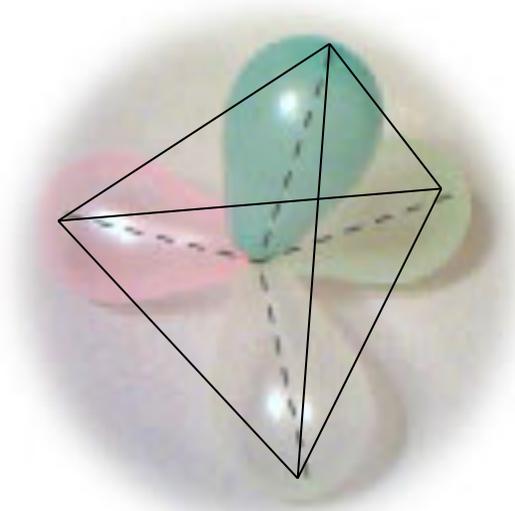




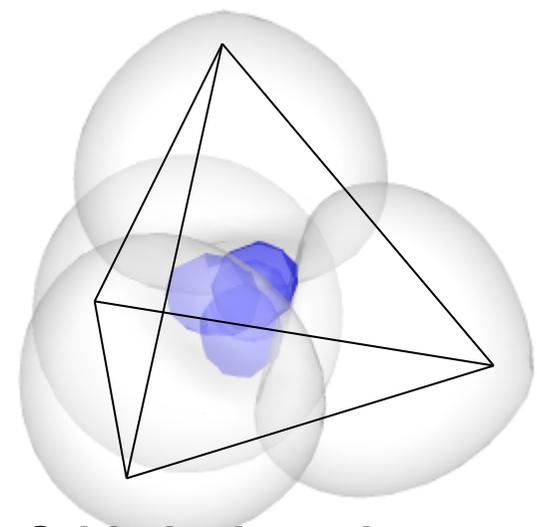




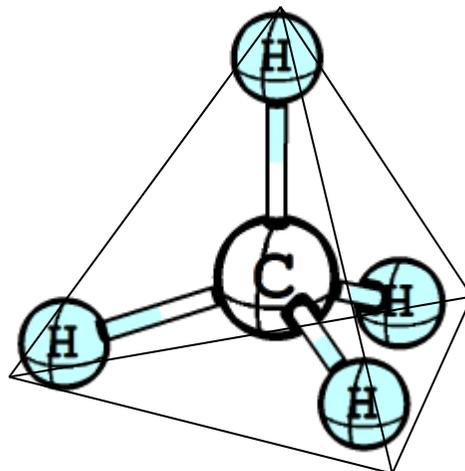
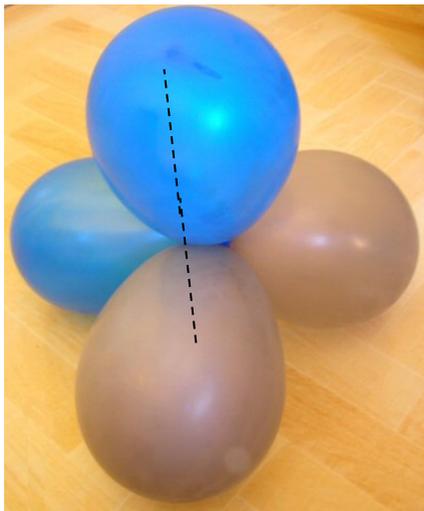
tetraedro



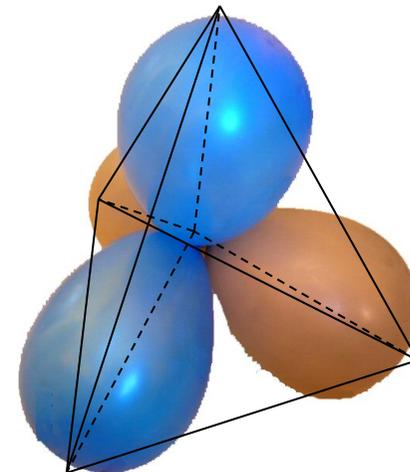
**Bolas de aniversário
(arranjo tetraédrico)**

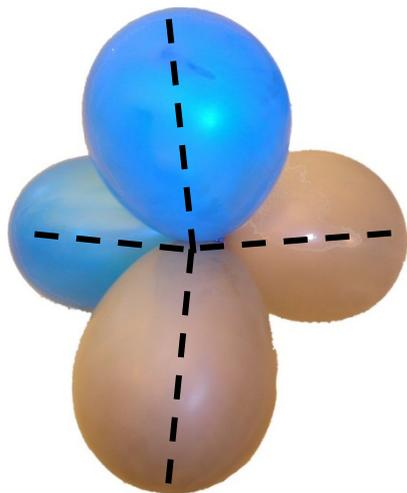
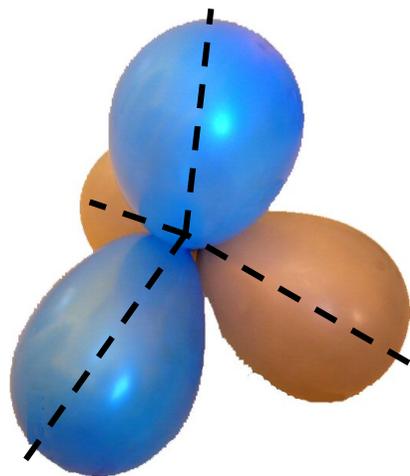
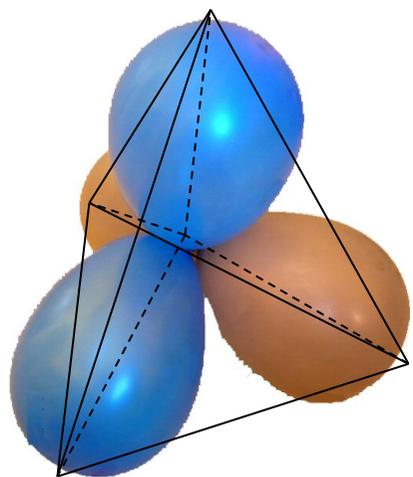


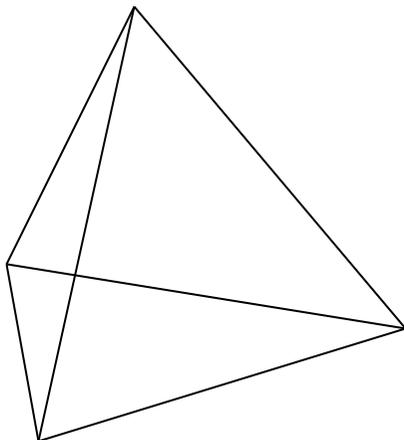
**Orbitais do carbono
(arranjo tetraédrico)**



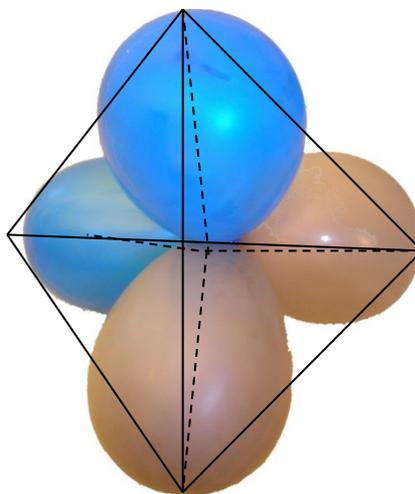
**Metano dentro
em um tetraedro**



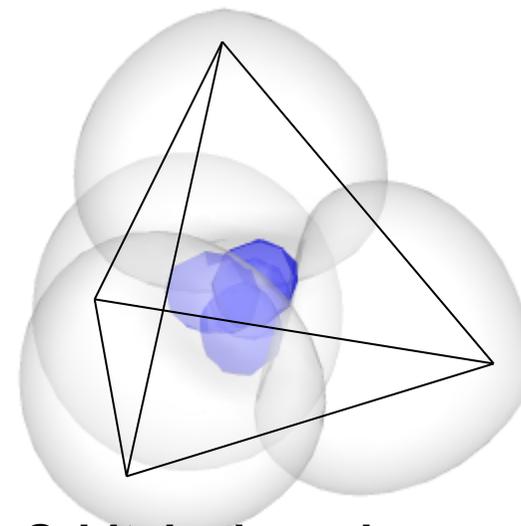




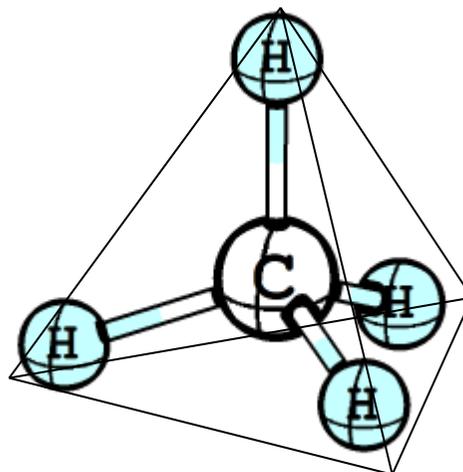
tetraedro



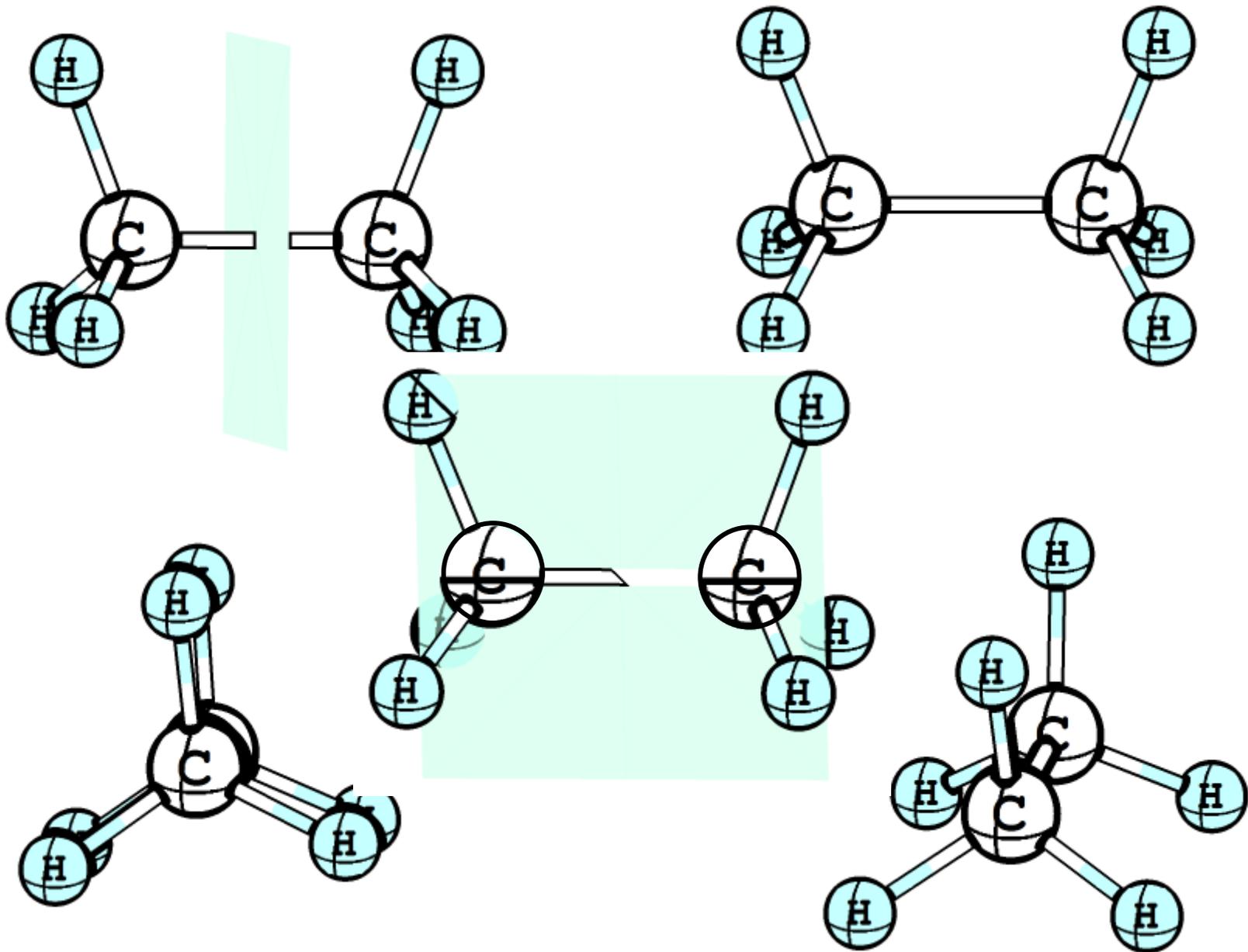
**Bolas de aniversário
(arranjo tetraédrico)**

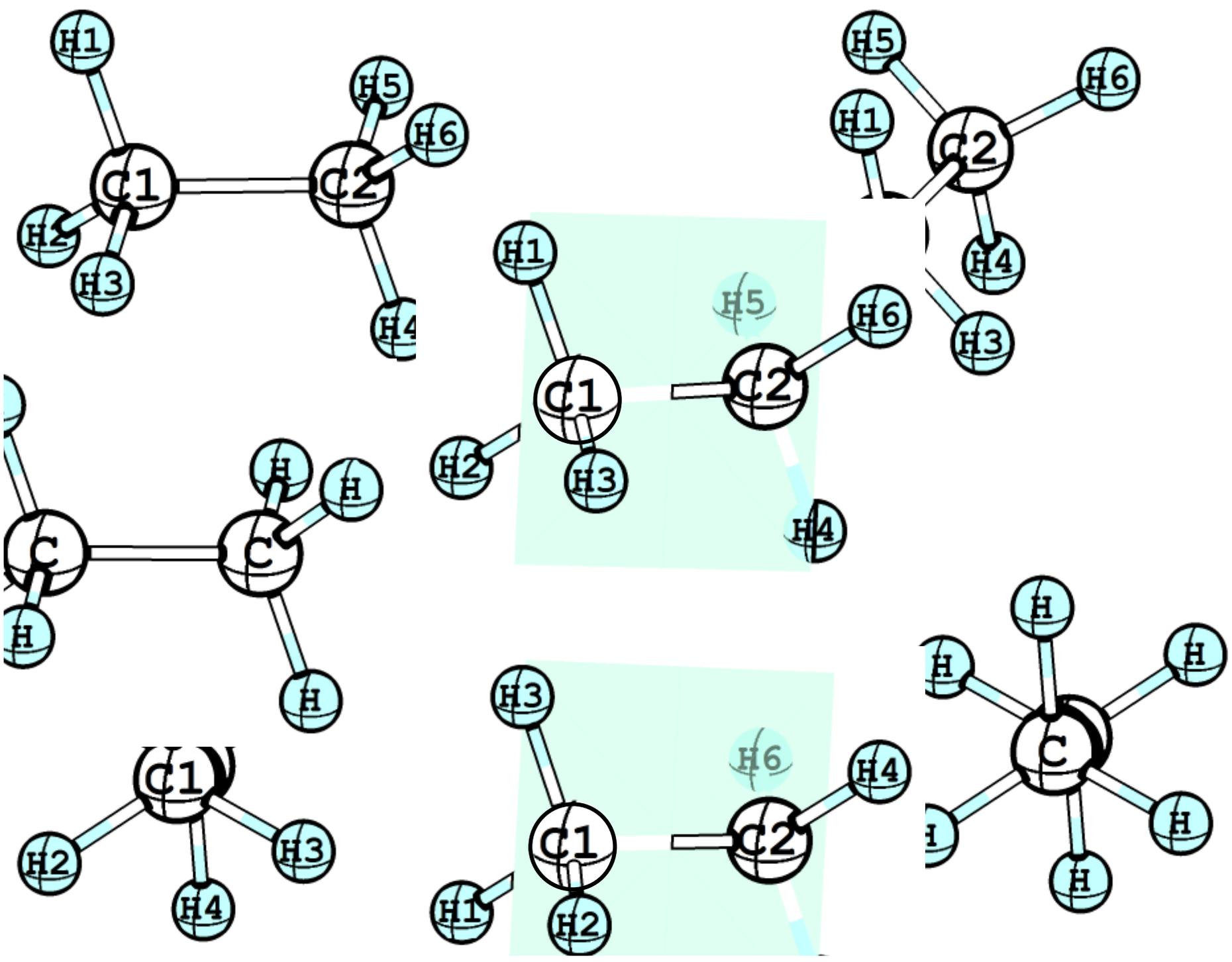


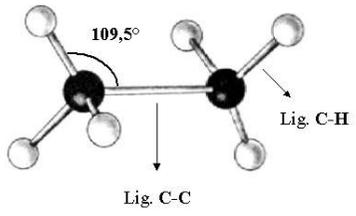
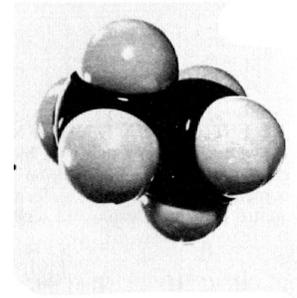
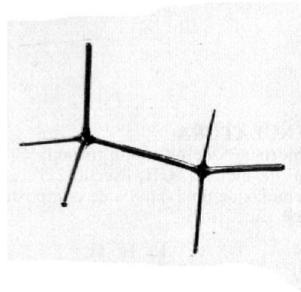
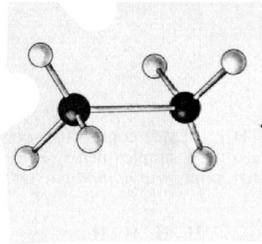
**Orbitais do carbono
(arranjo tetraédrico)**

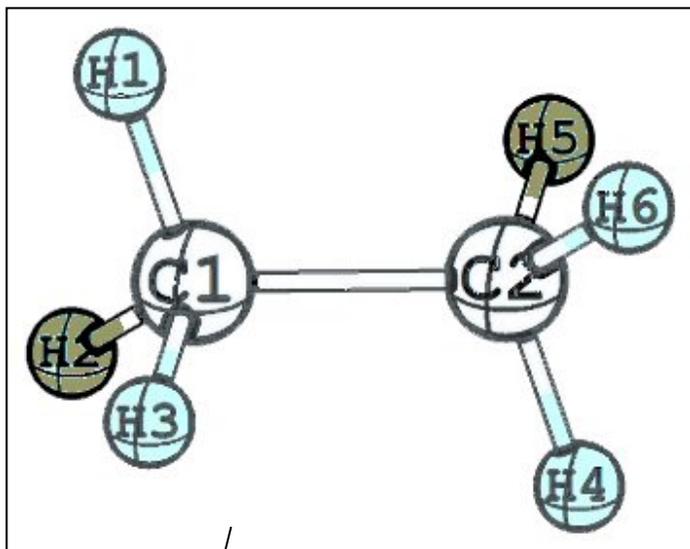


**Metano dentro
em um tetraedro**

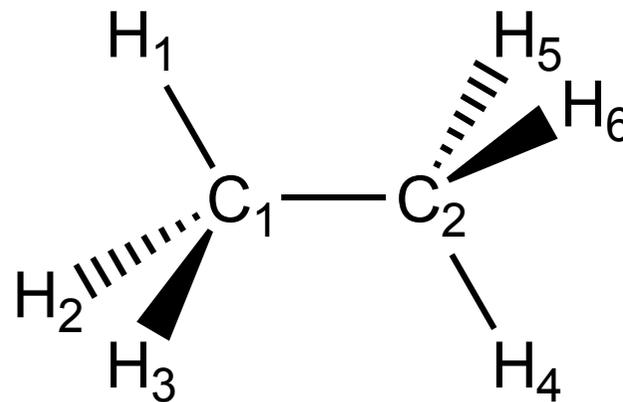


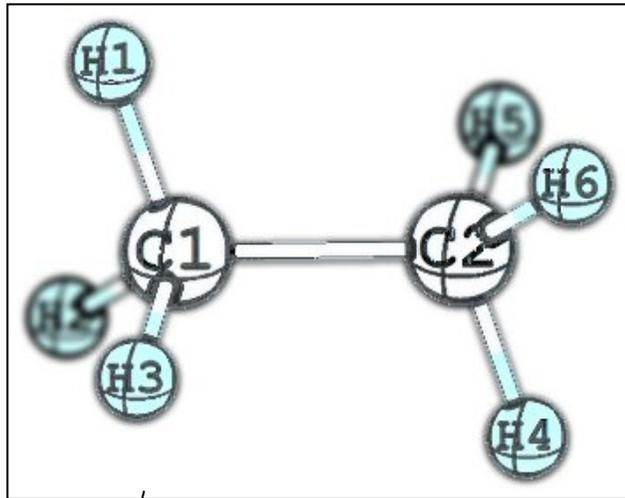




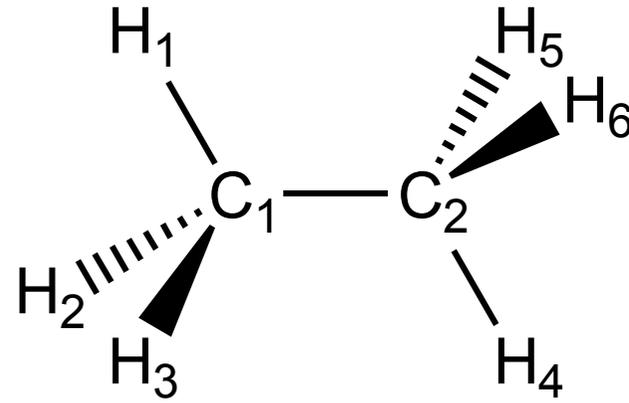


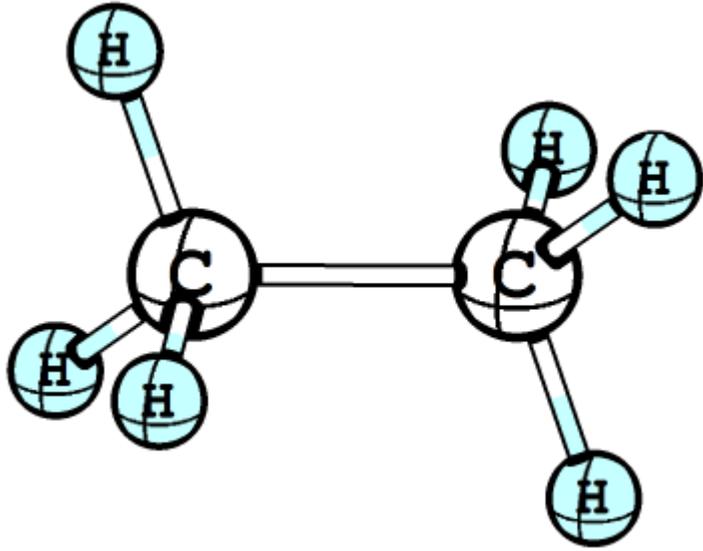
Plano definido
pelos átomos
H1-C1-C2-H4
(Plano A)



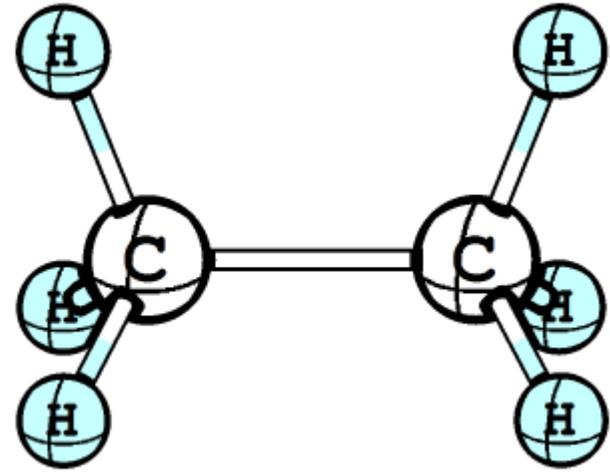


**Plano definido
pelos átomos
H1-C1-C2-H4
(Plano A)**

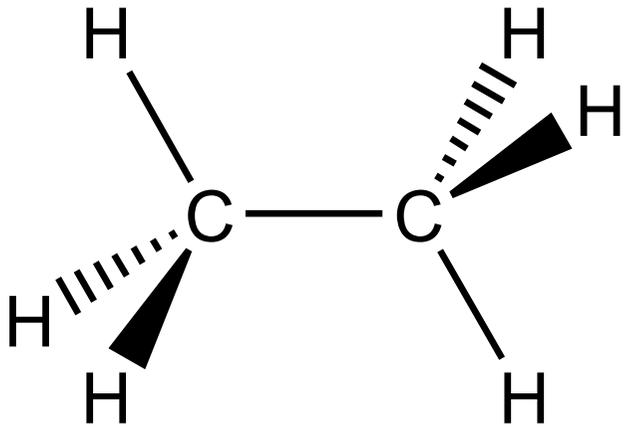




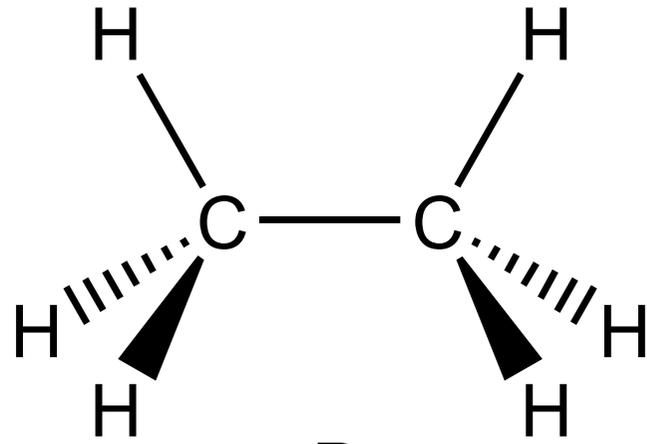
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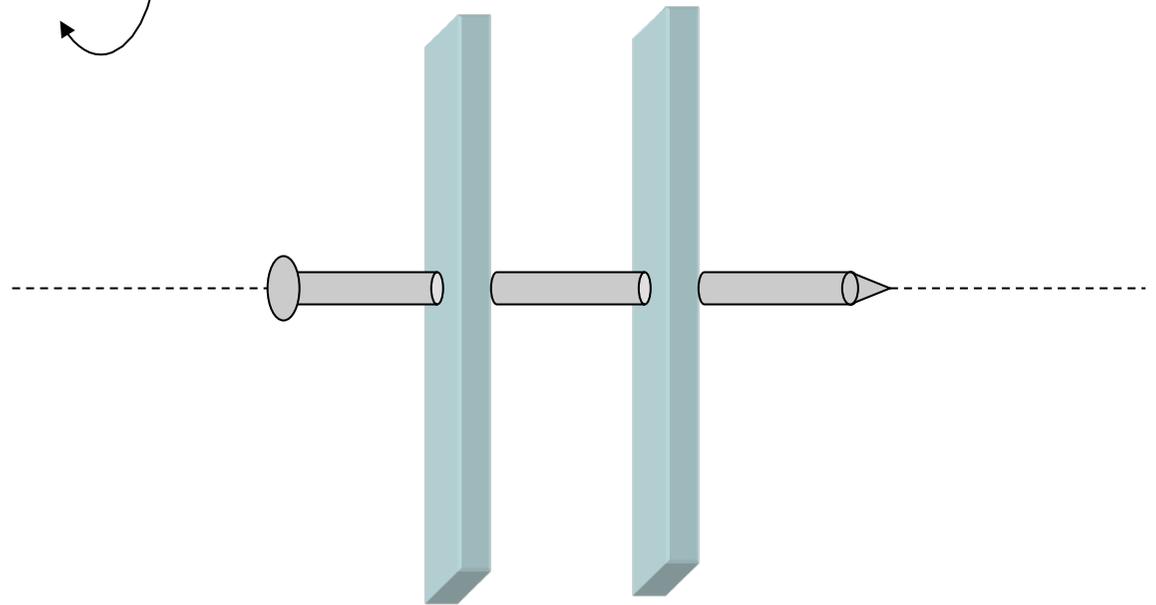
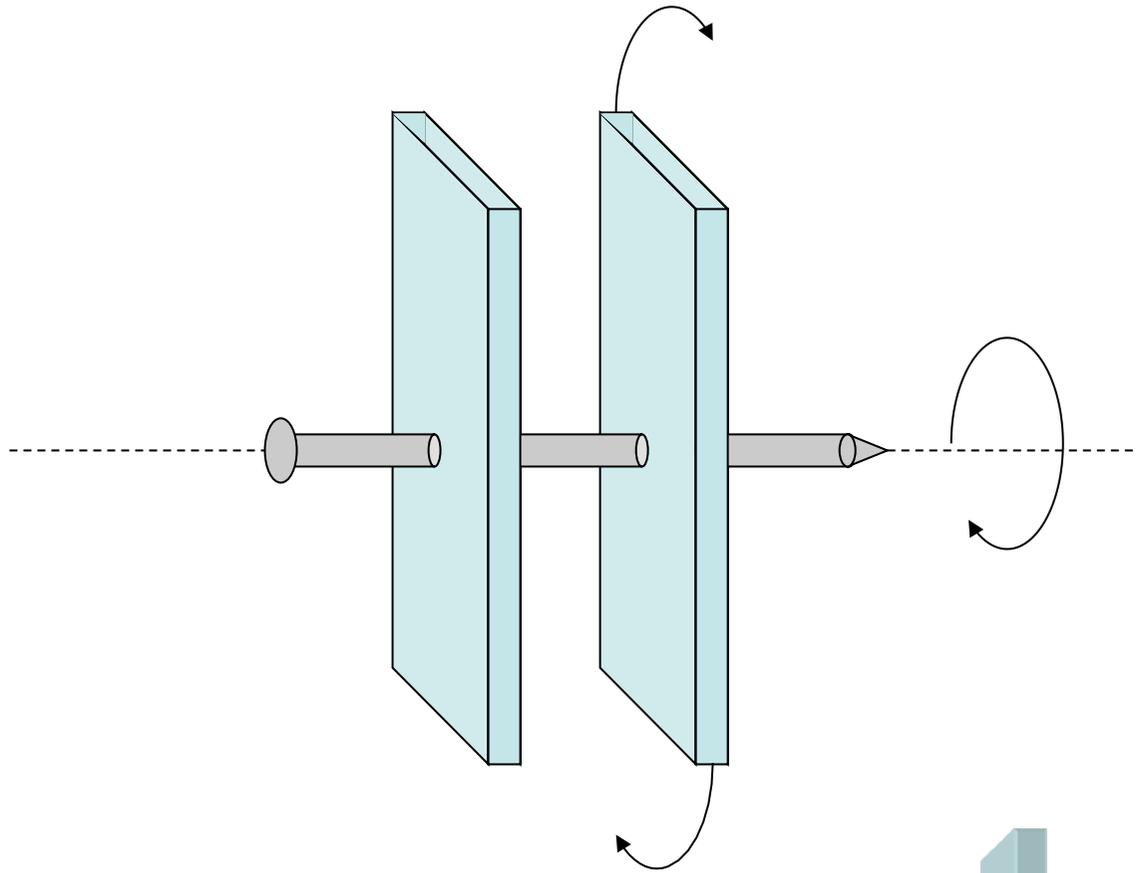
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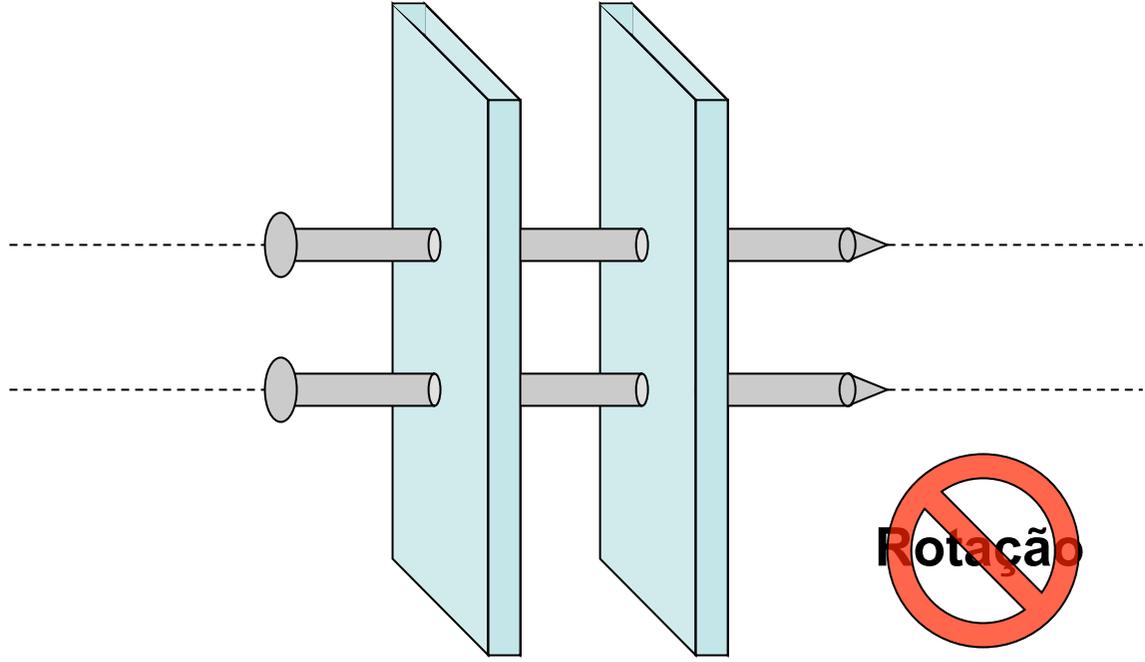


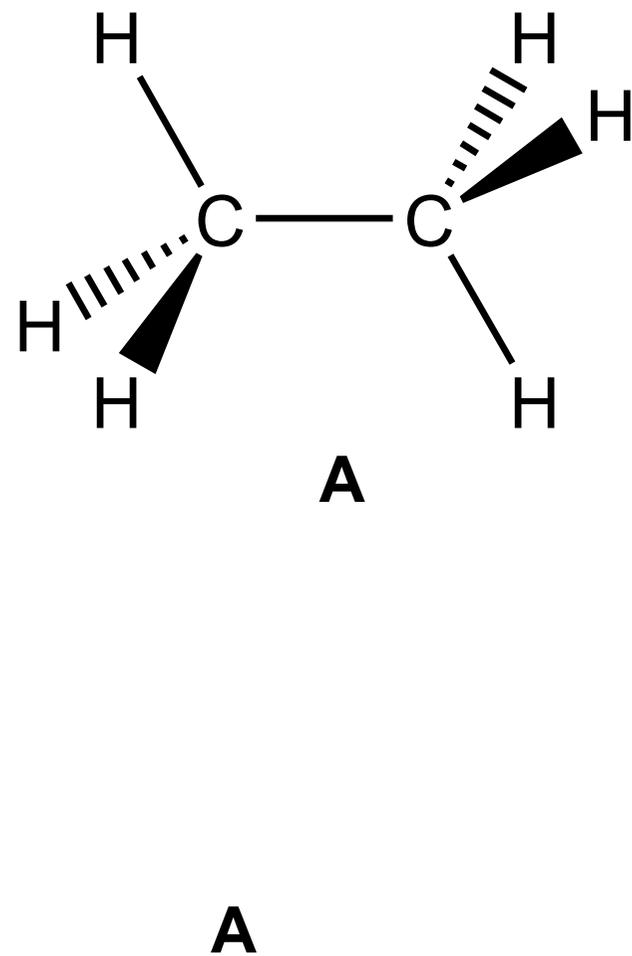
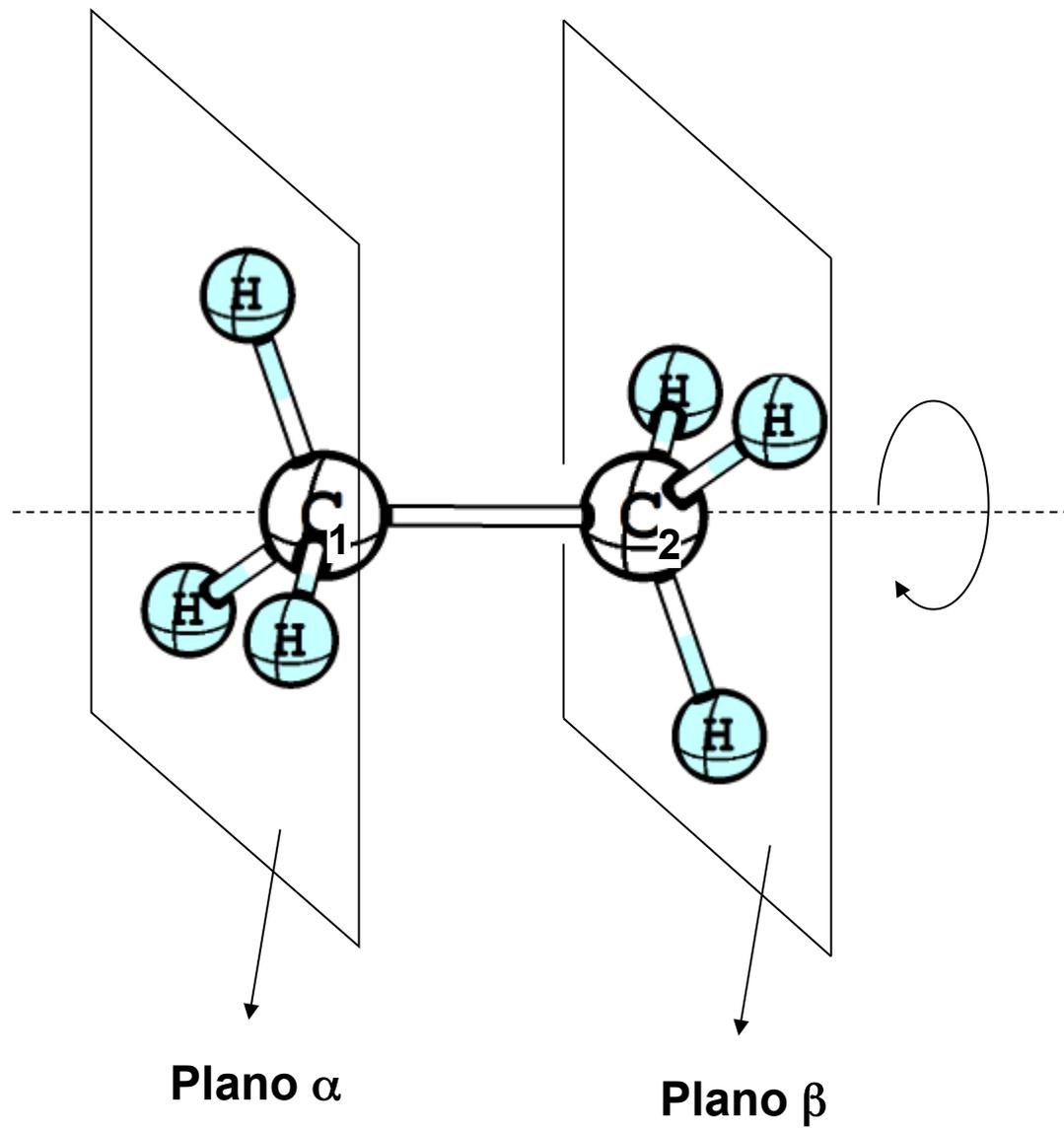
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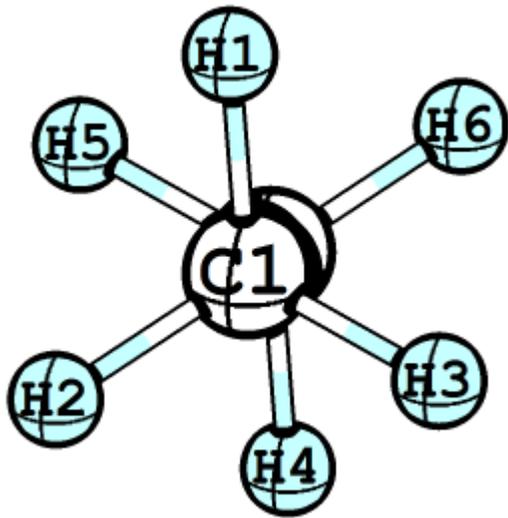
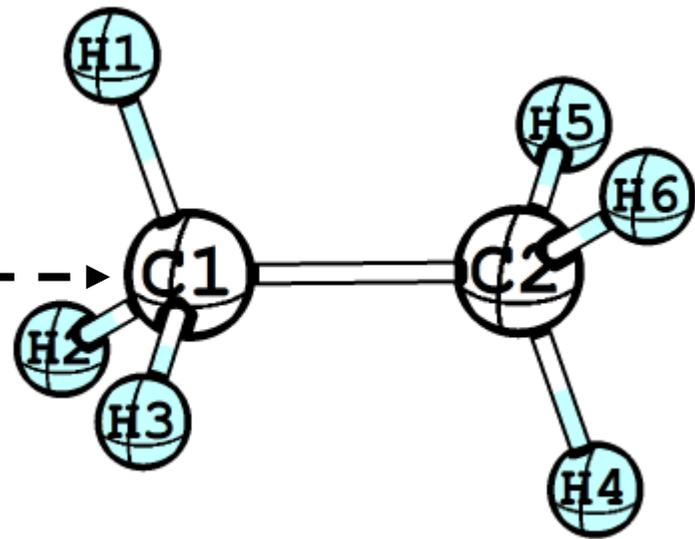


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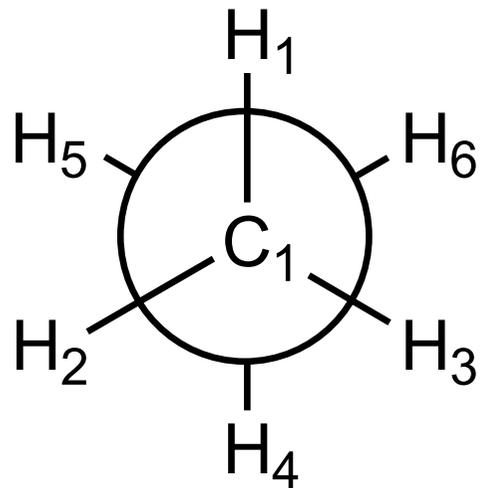




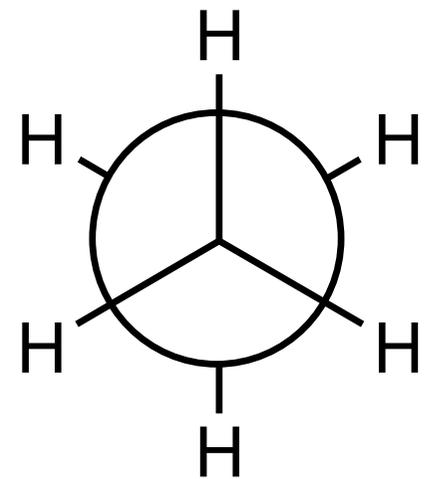




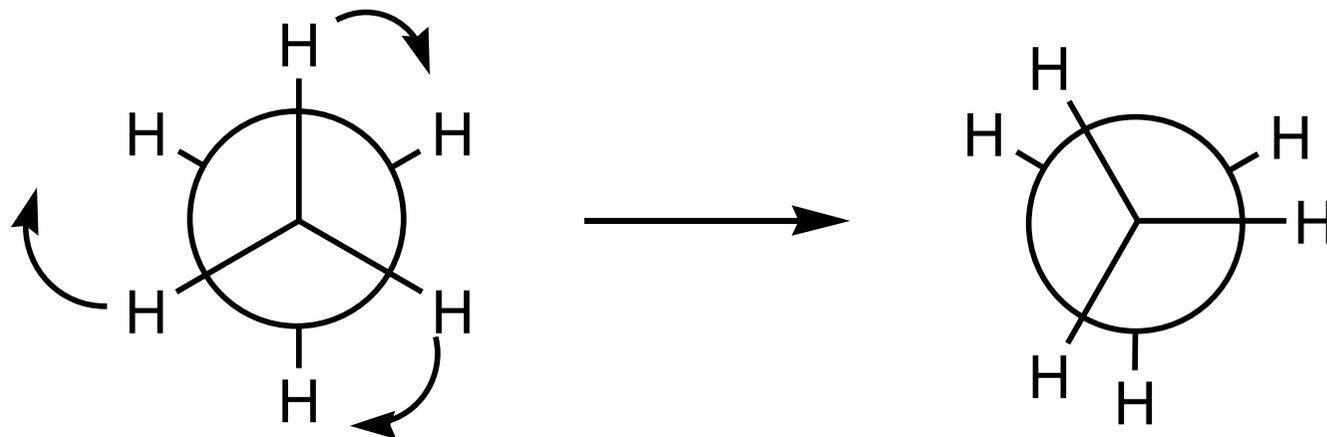
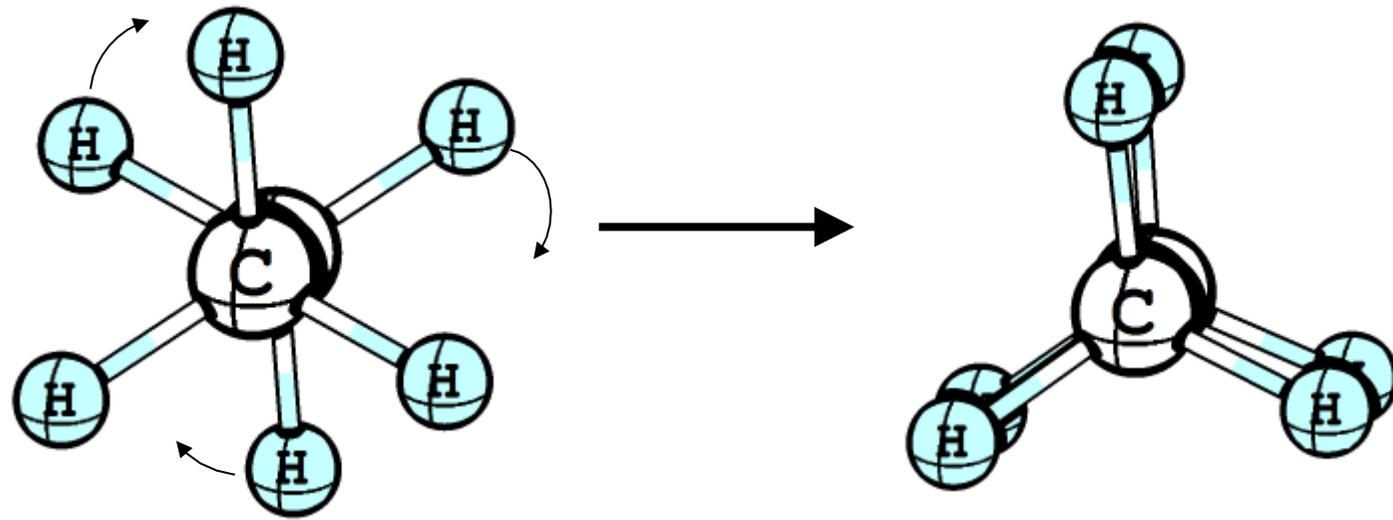
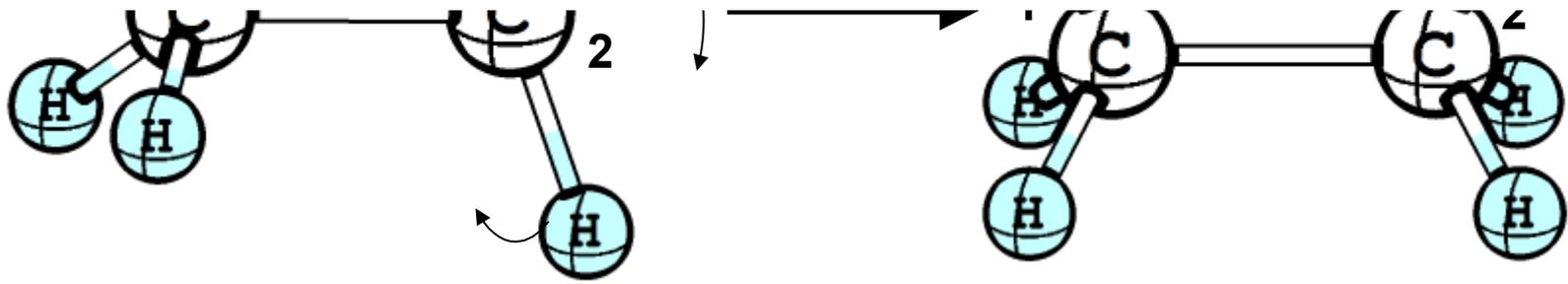
Visão do cientista

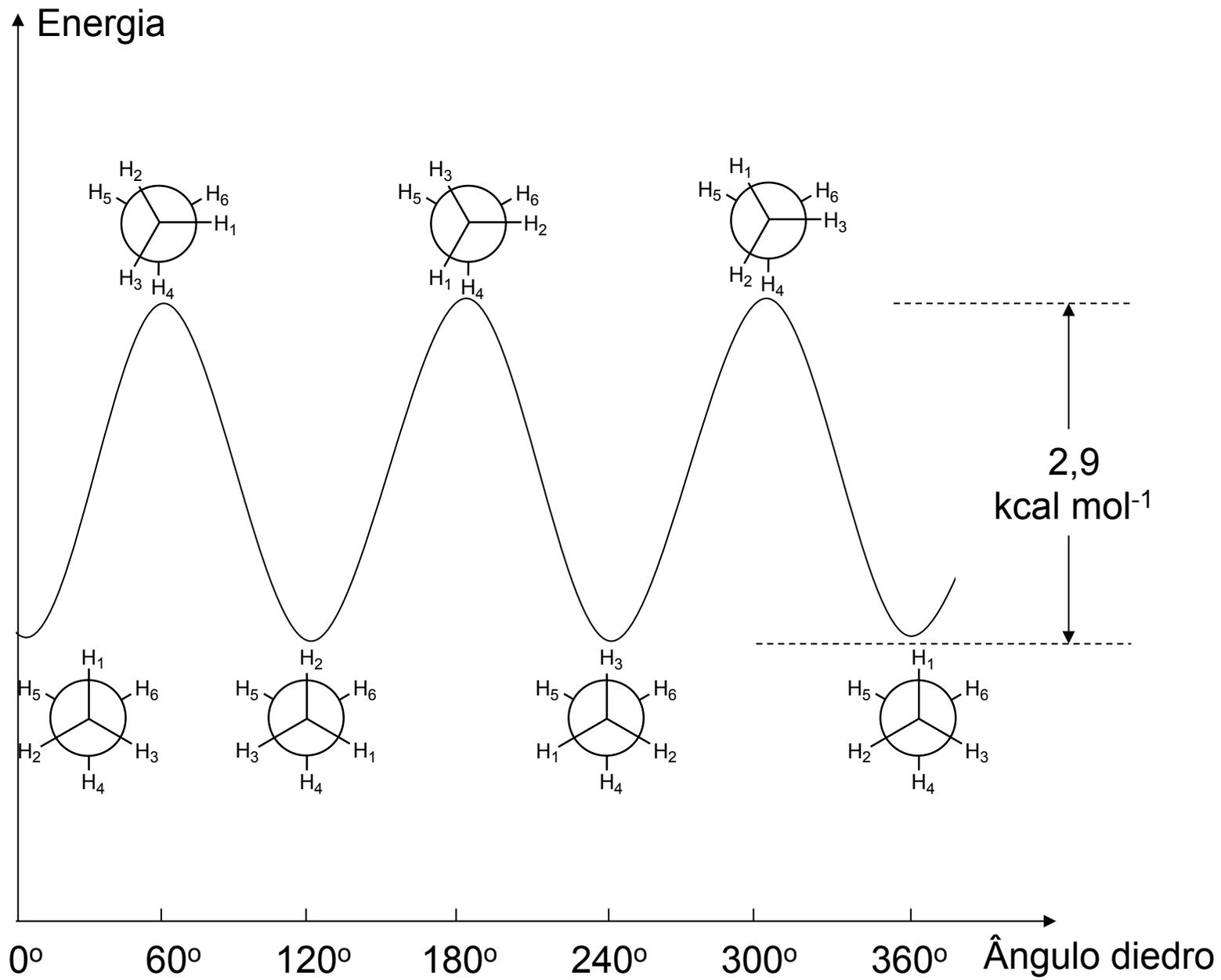


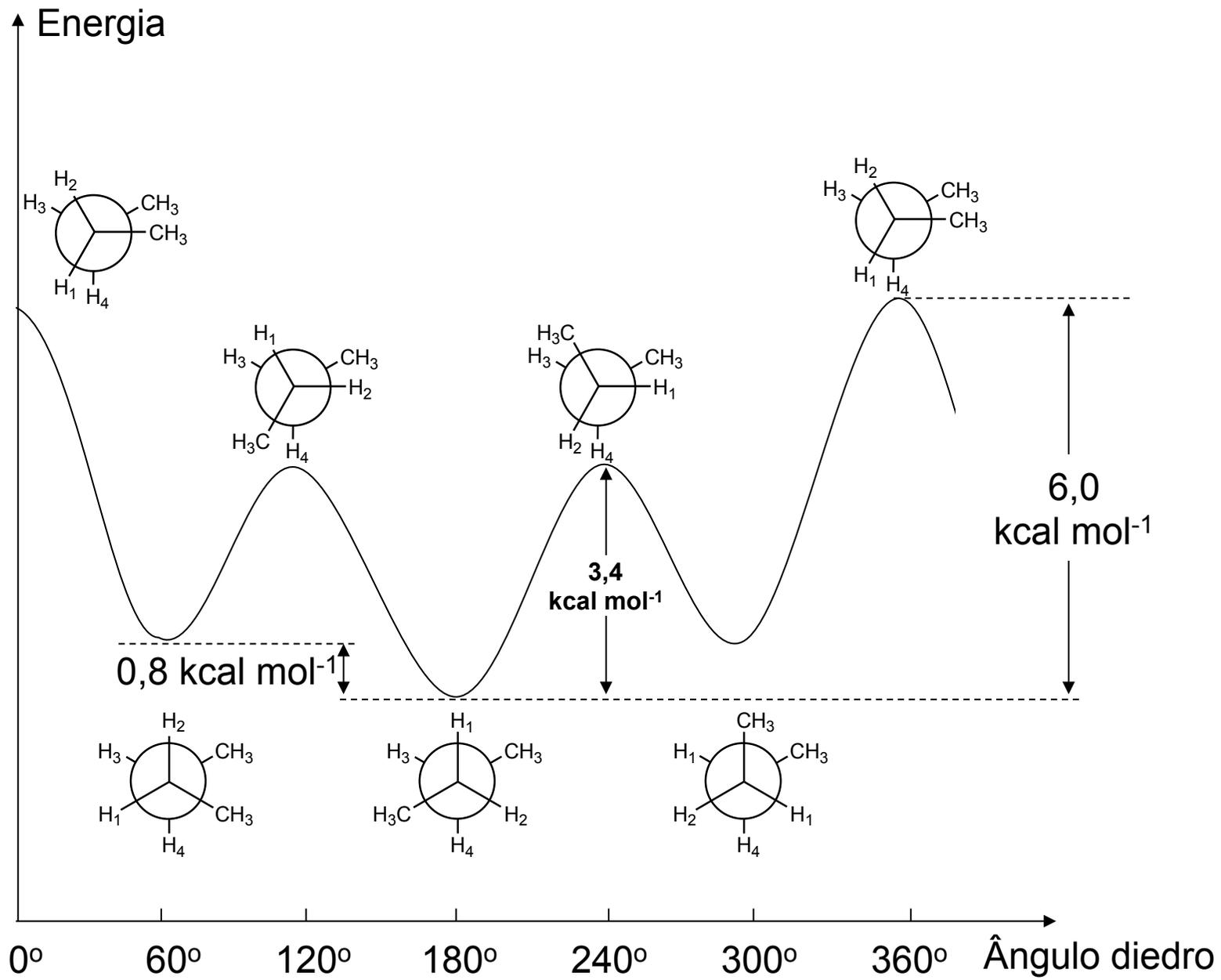
Projeção de Newman

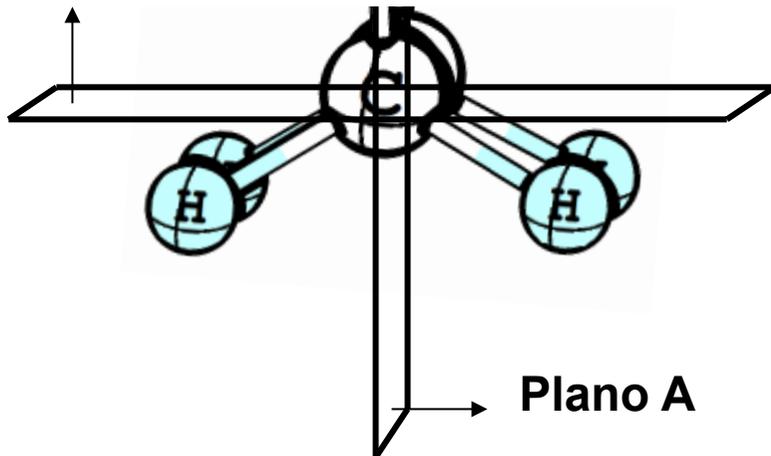


Projeção de Newman convencional

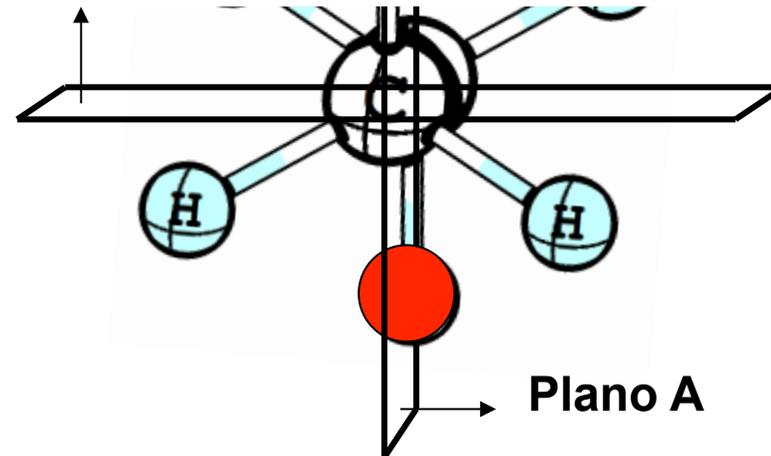




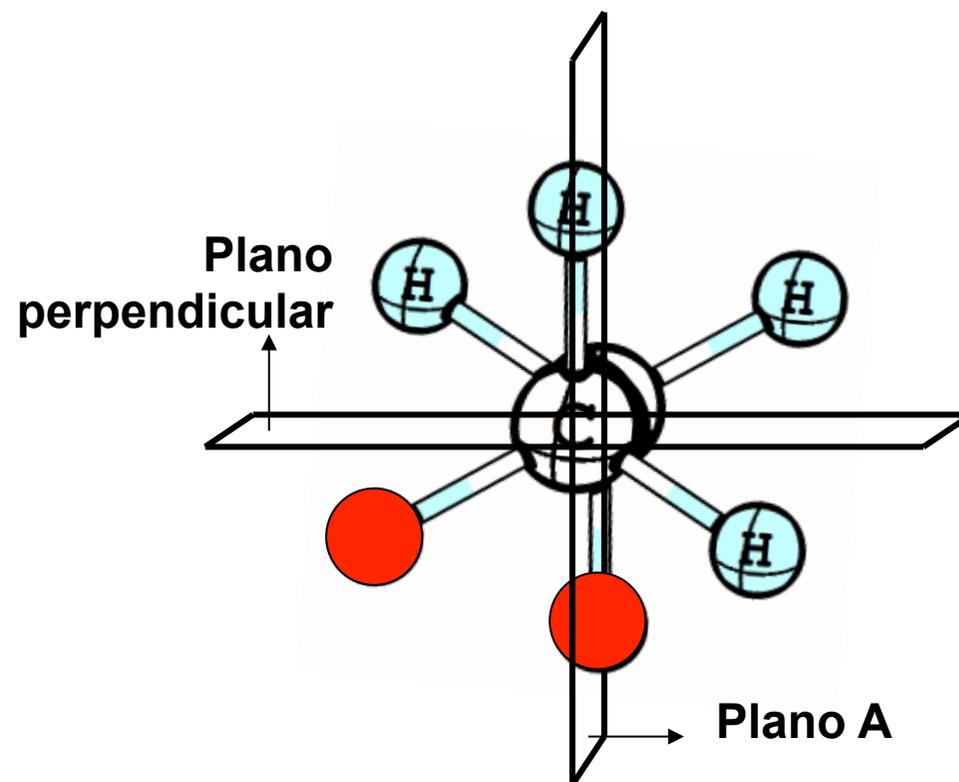
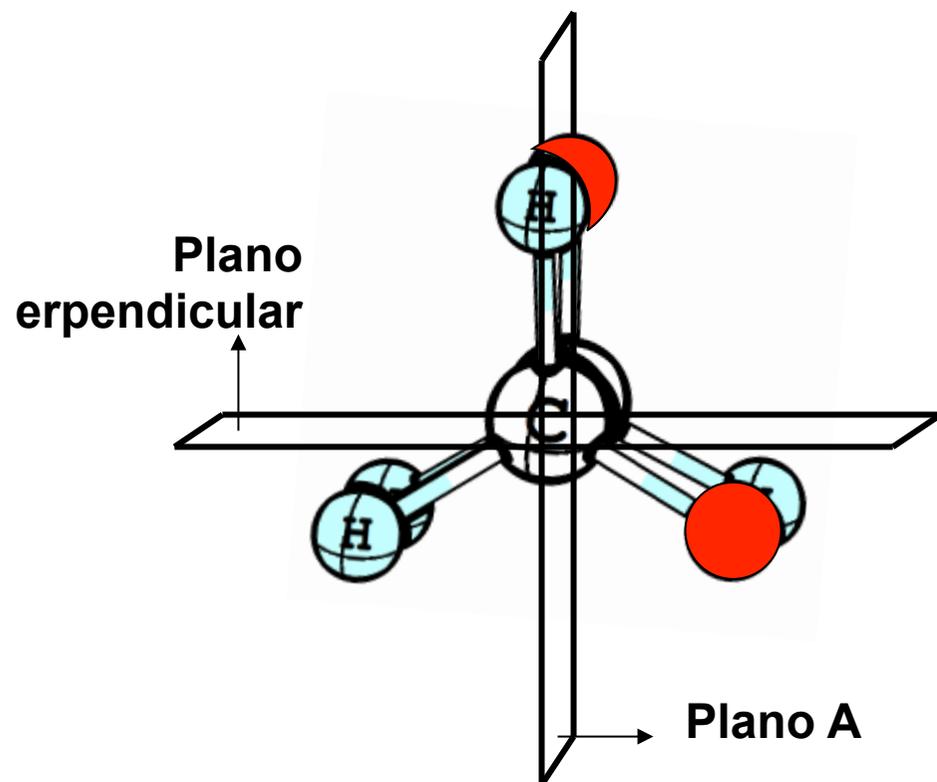


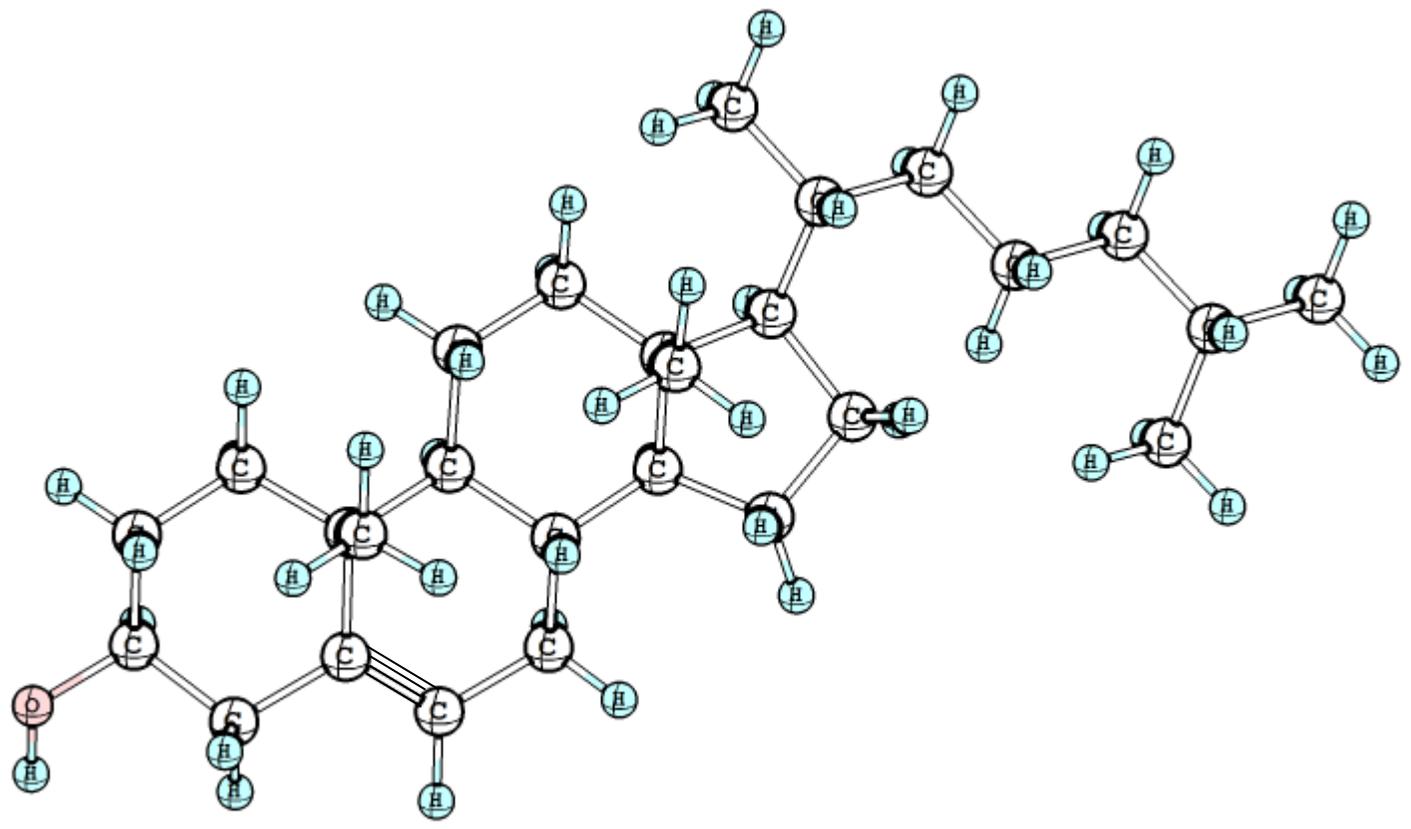


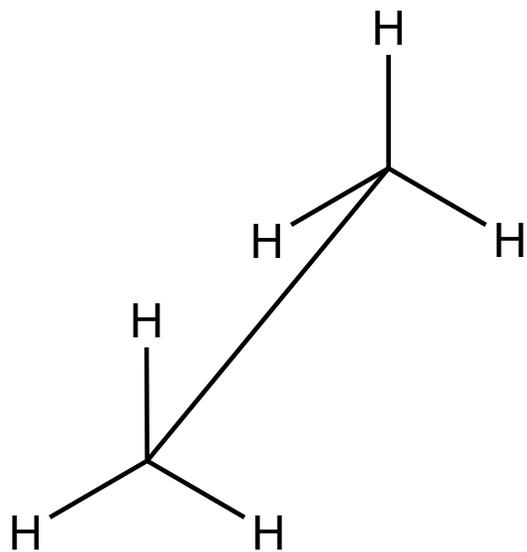
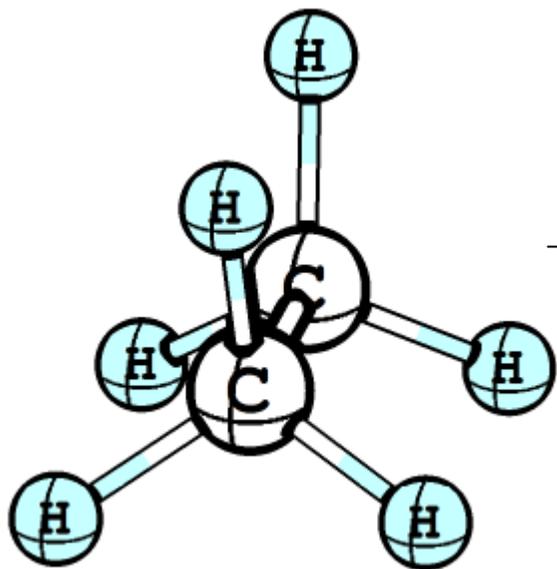
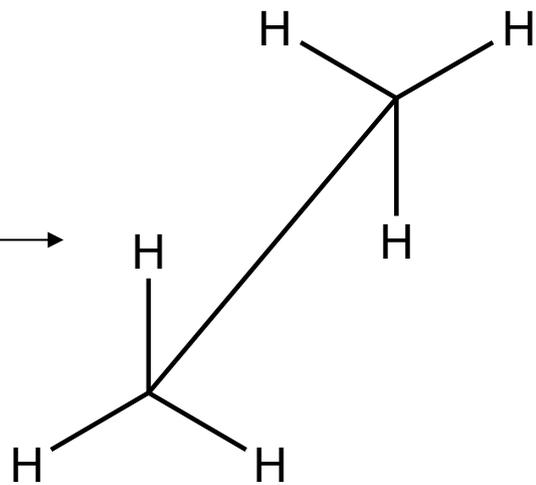
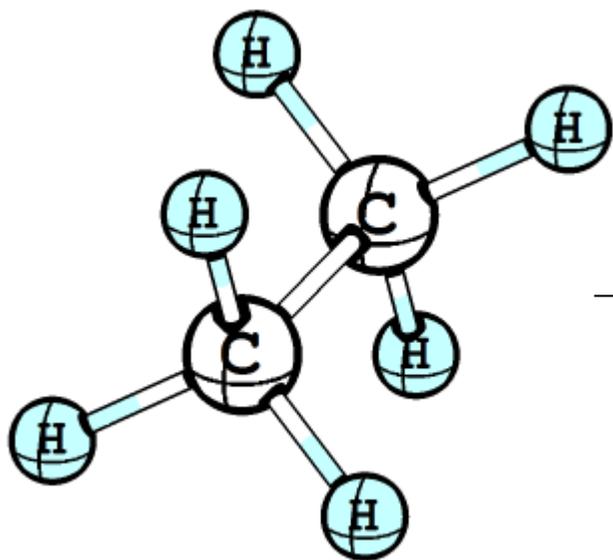
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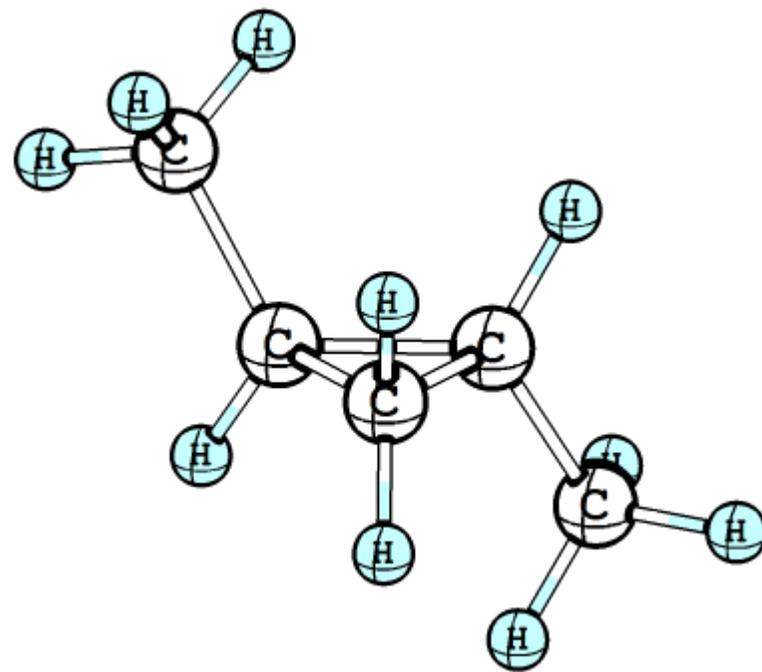
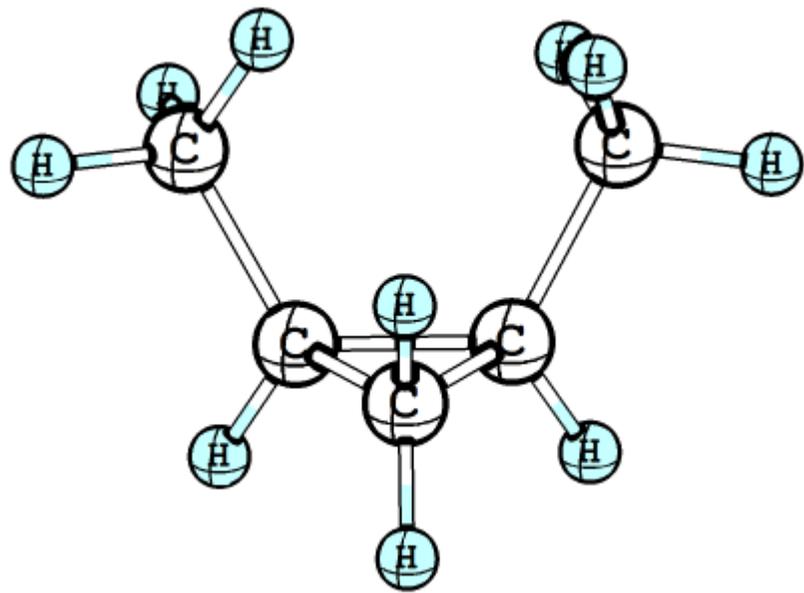


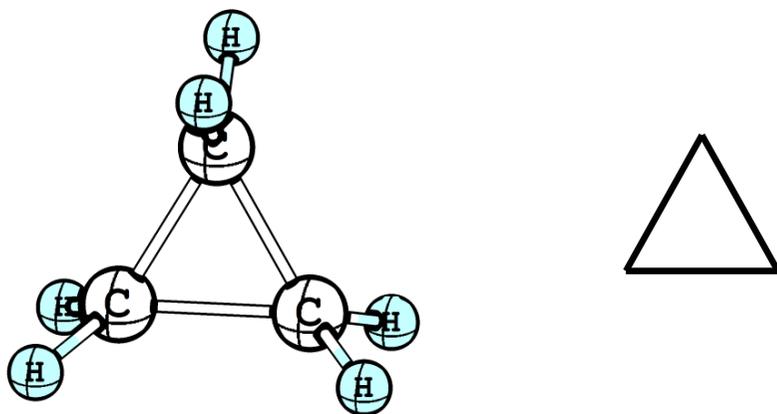
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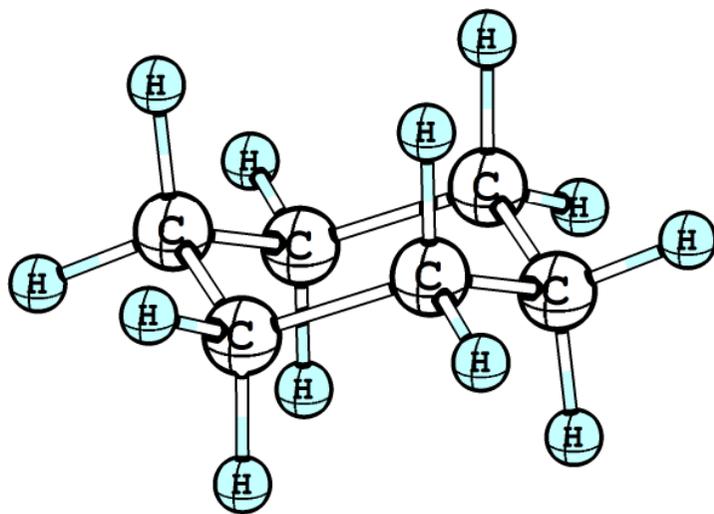




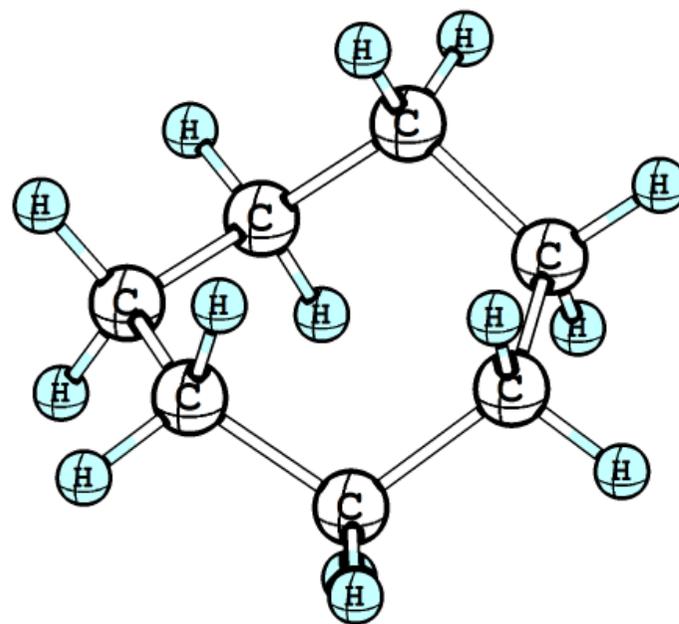




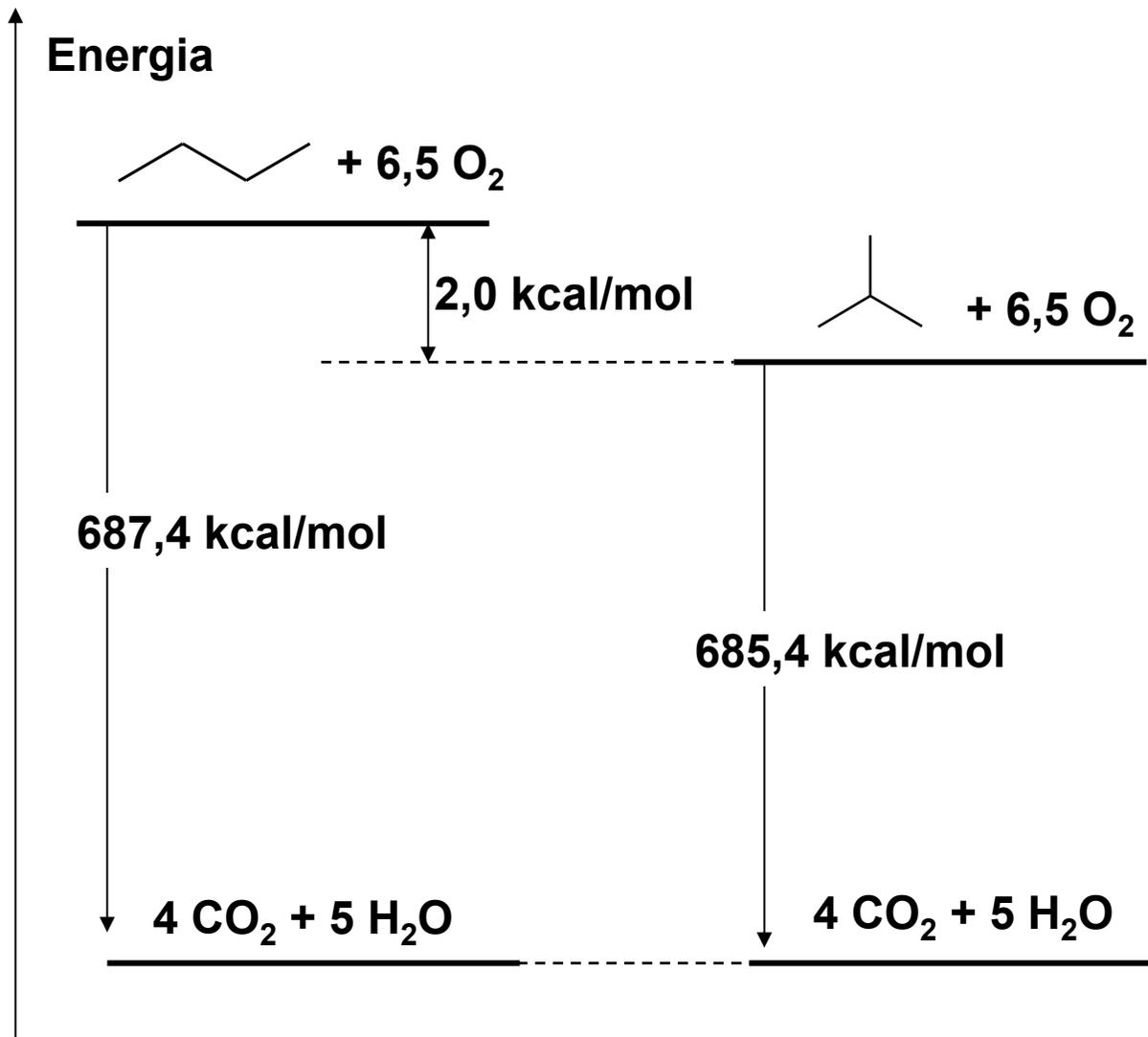
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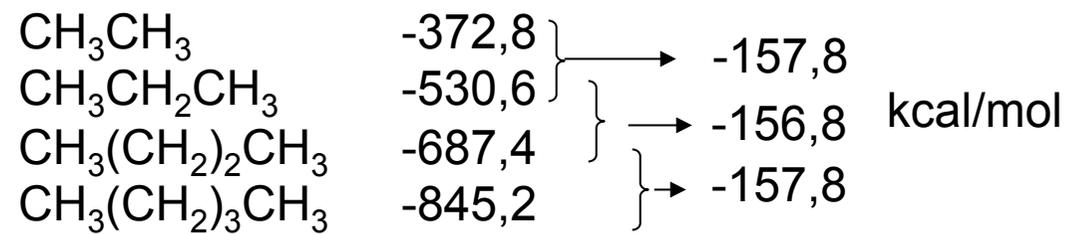


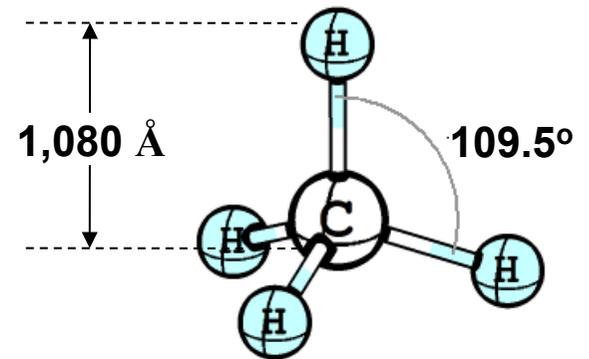
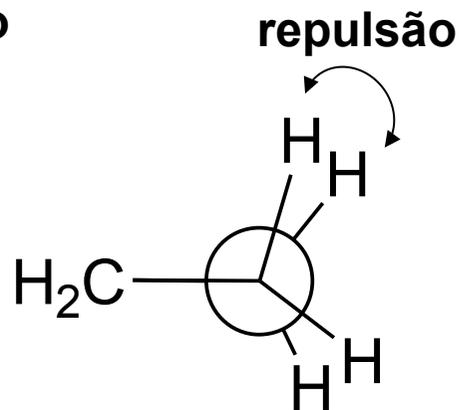
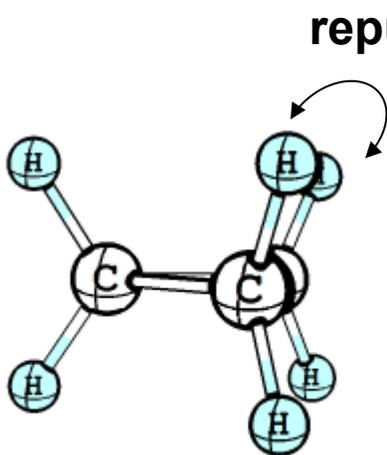
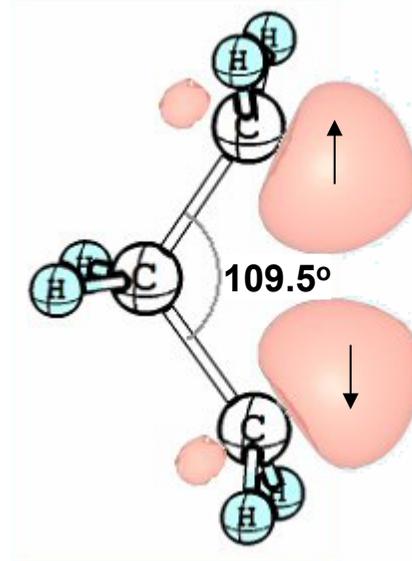
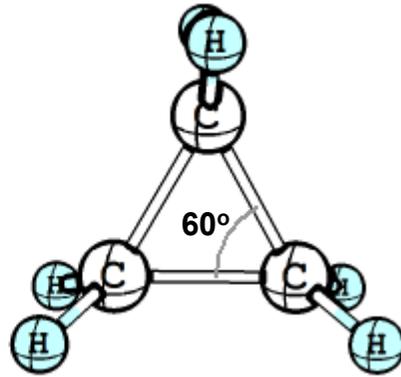
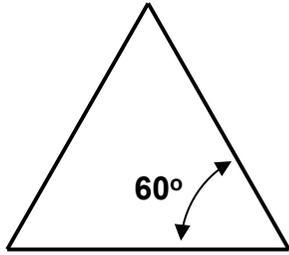
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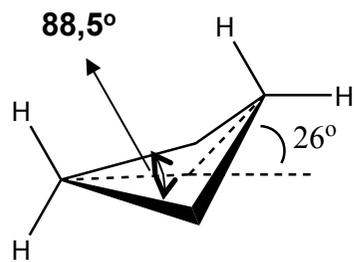
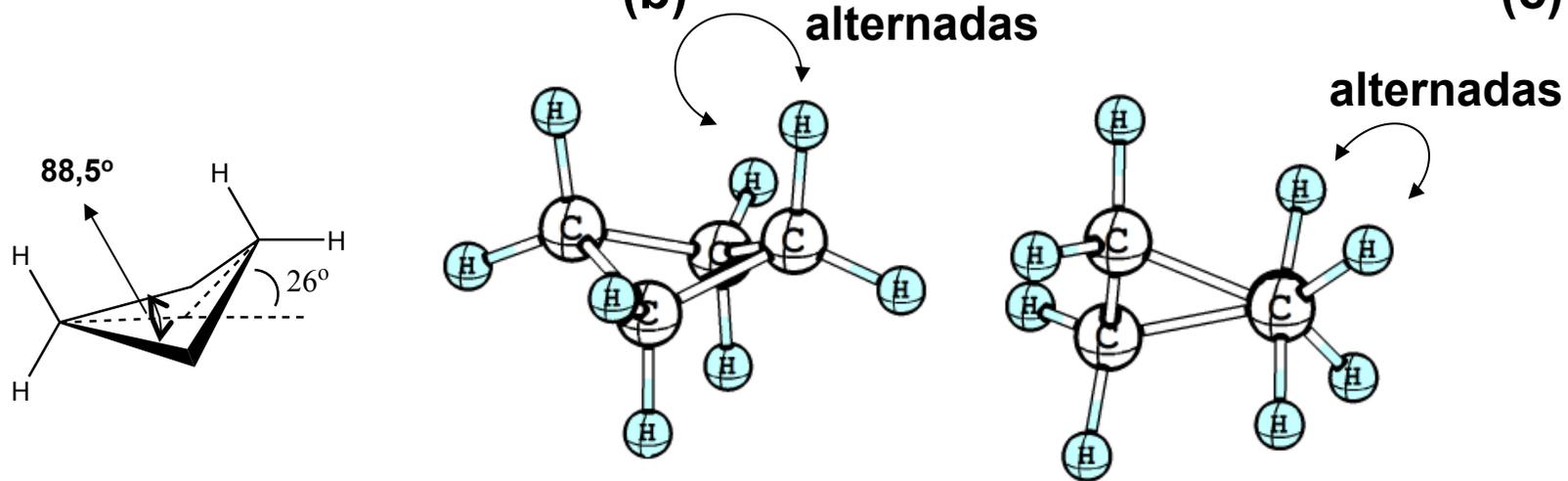
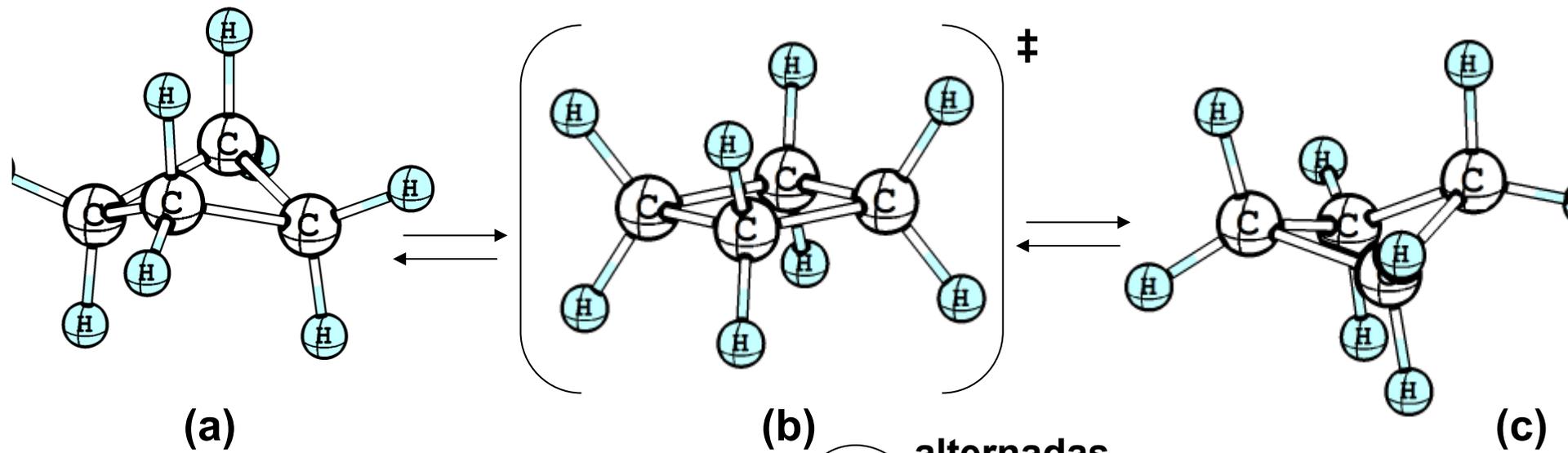


Ciclo-heptano

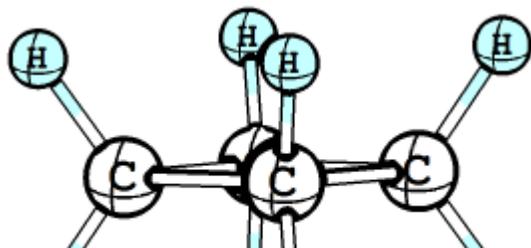


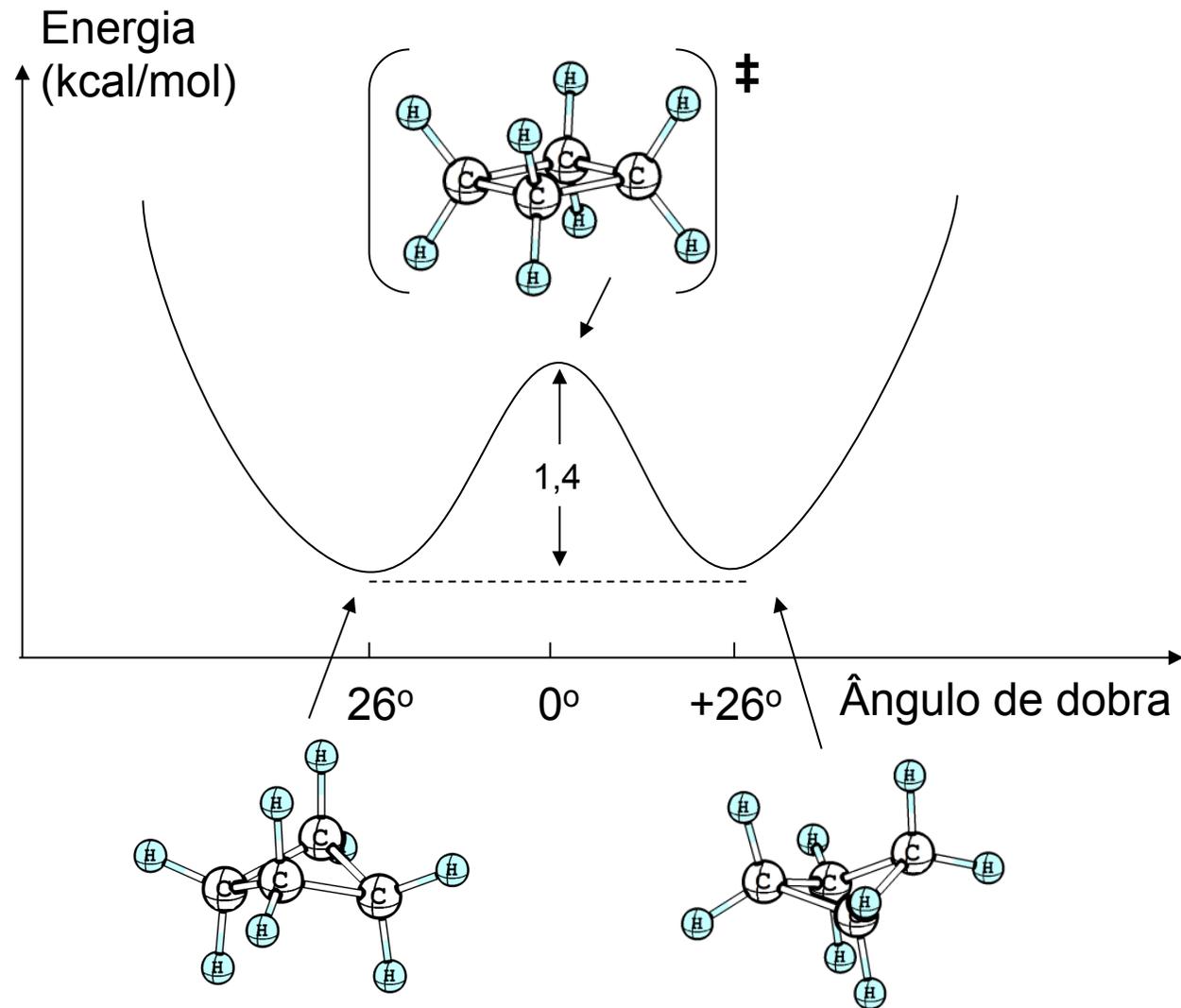


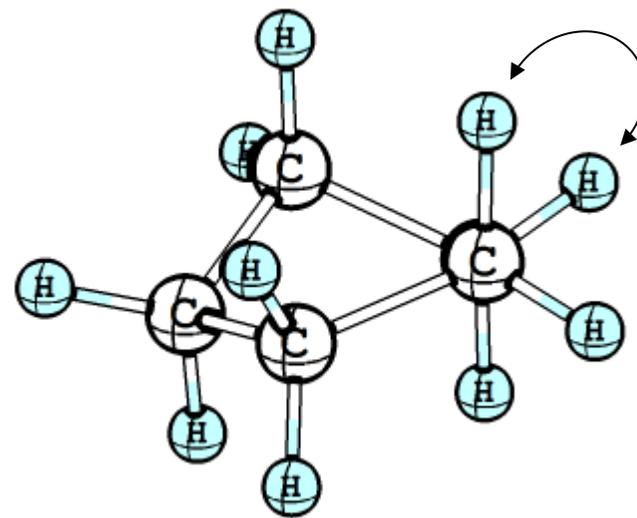
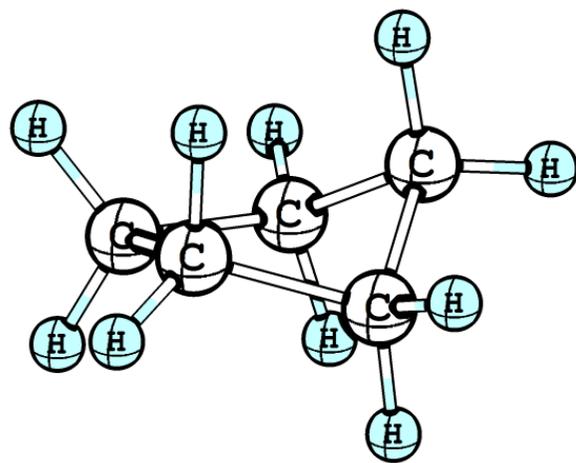




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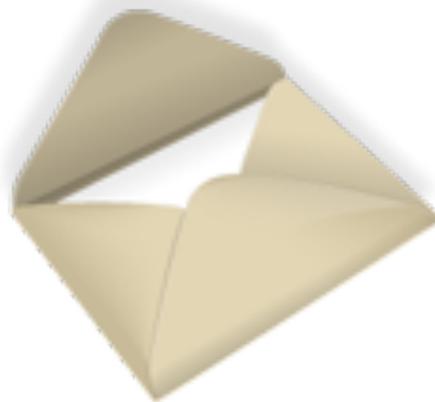
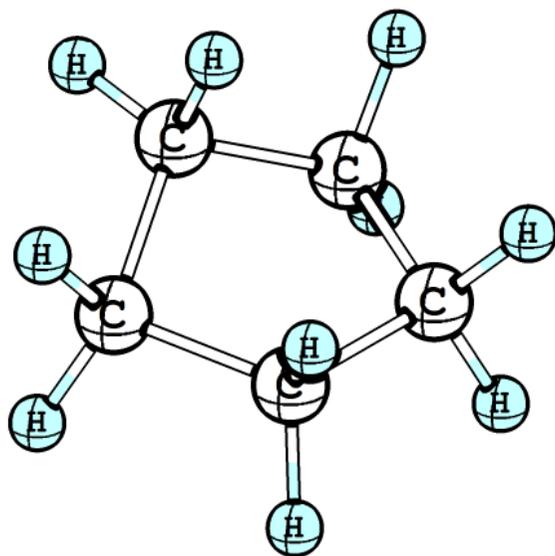




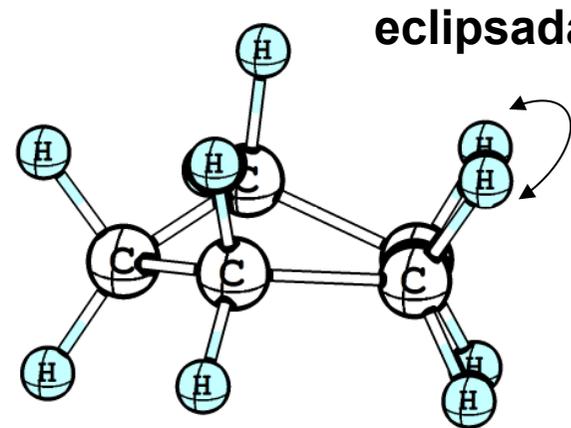


perfeitamente
alternadas

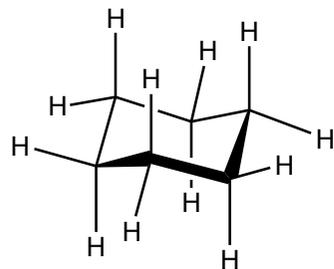
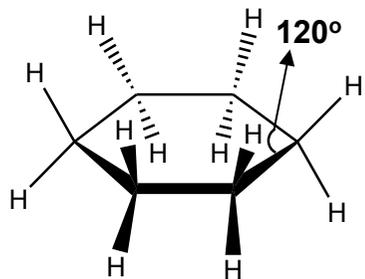
**Ciclopentano
(conformação meia-cadeira)**



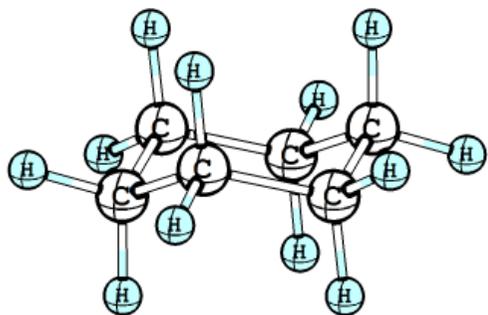
Ciclopentano



eclipsadas



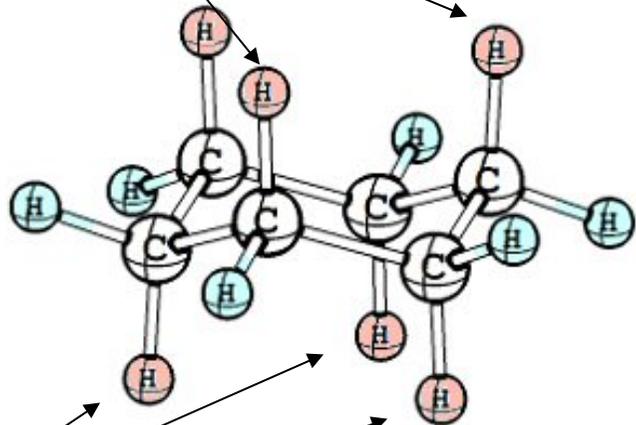
**conformação
cadeira**



**conformação
cadeira**

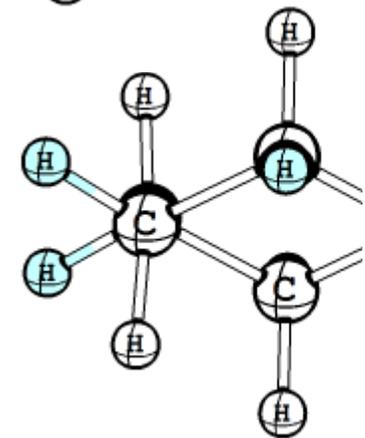
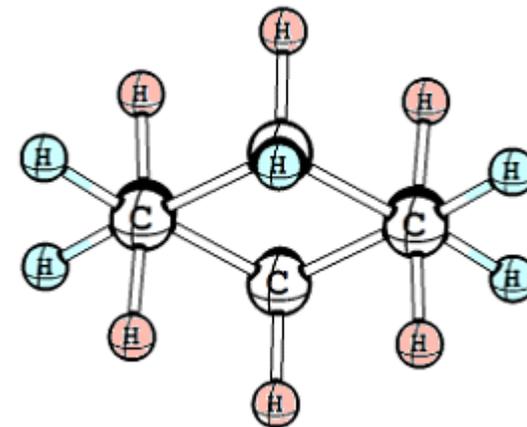
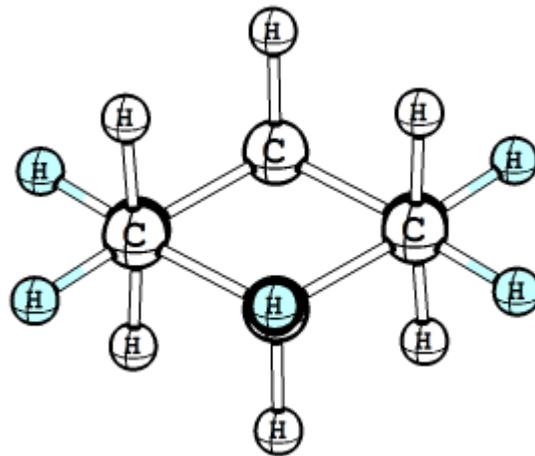


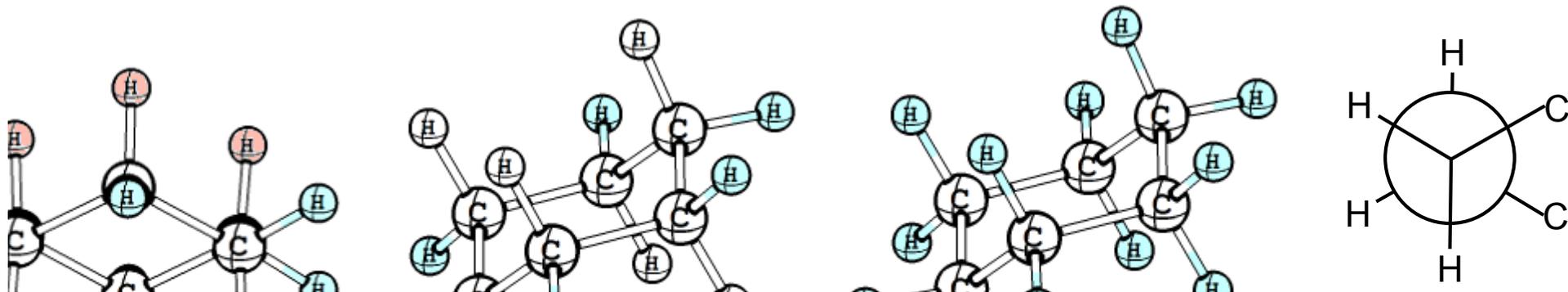
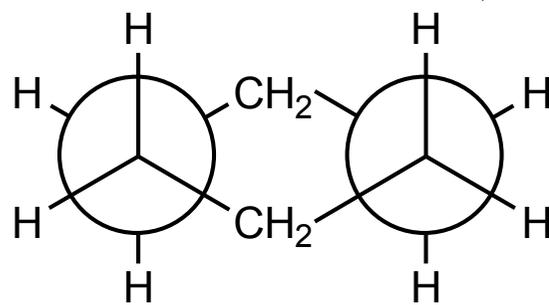
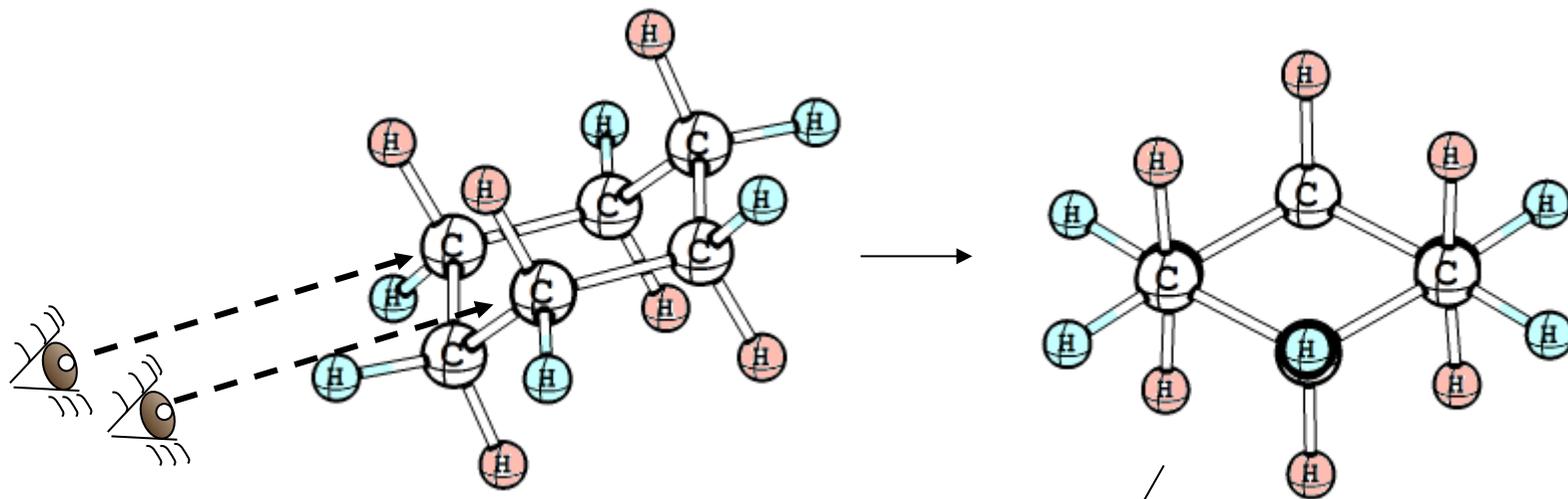
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axiais

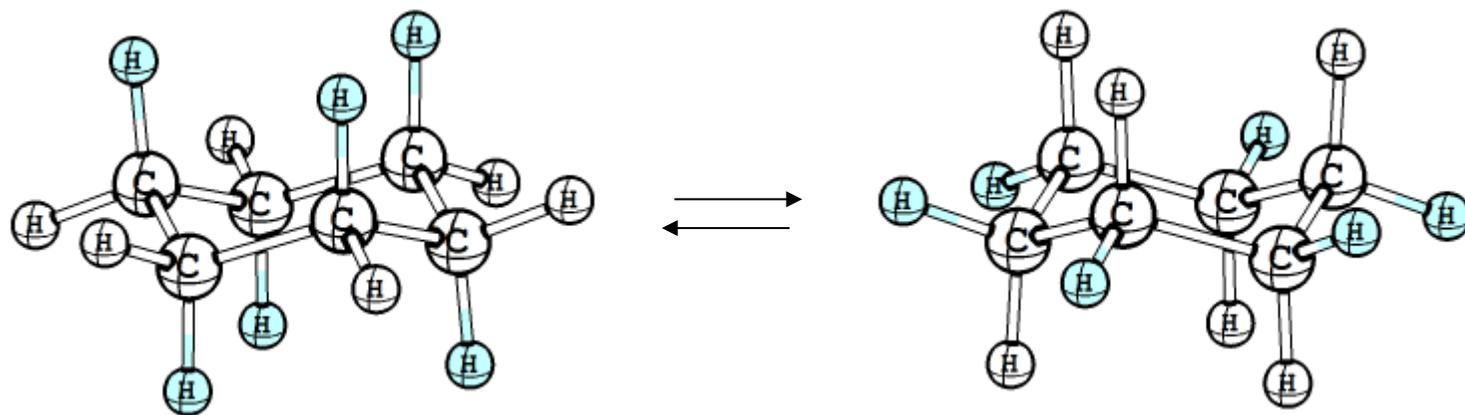


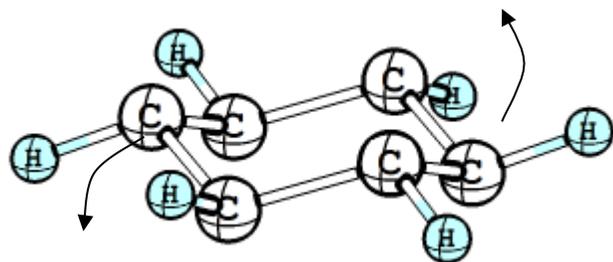
posições
equatoriais

posições
axiais

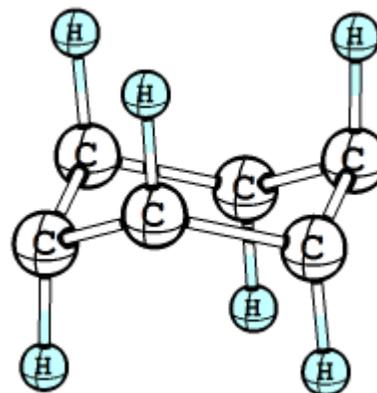
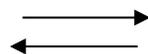




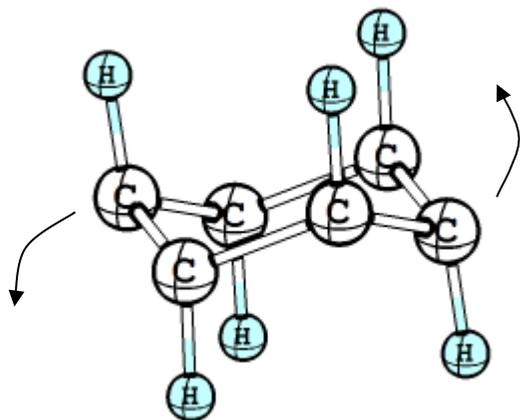




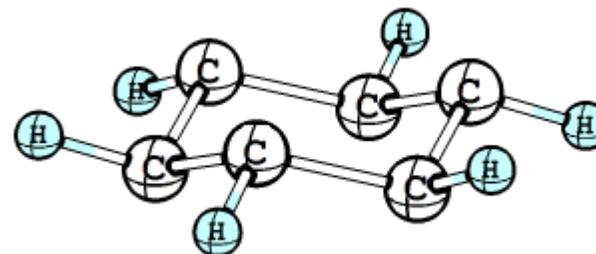
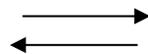
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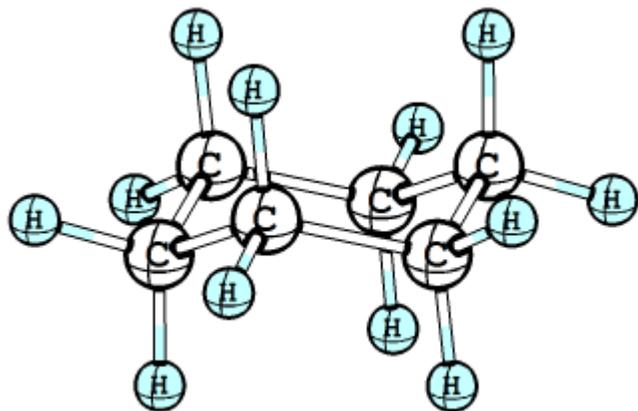
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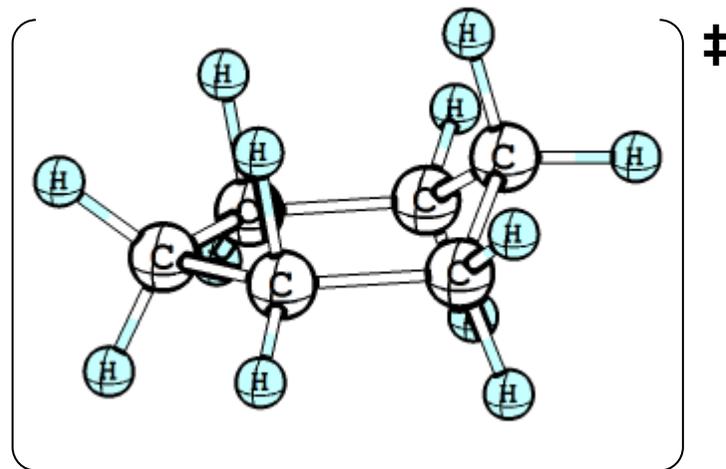
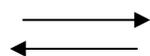
posições axiais



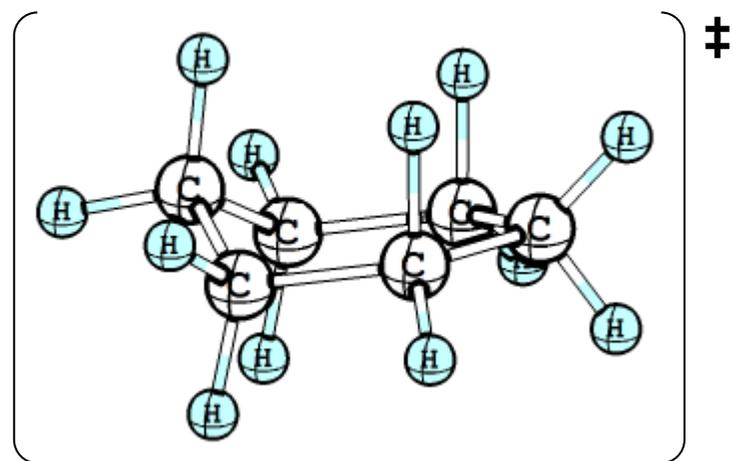
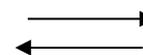
posições equatoriais



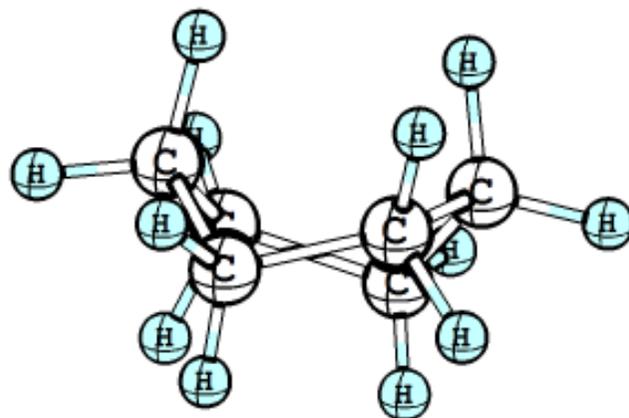
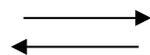
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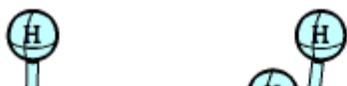
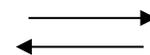
meia-cadeira A

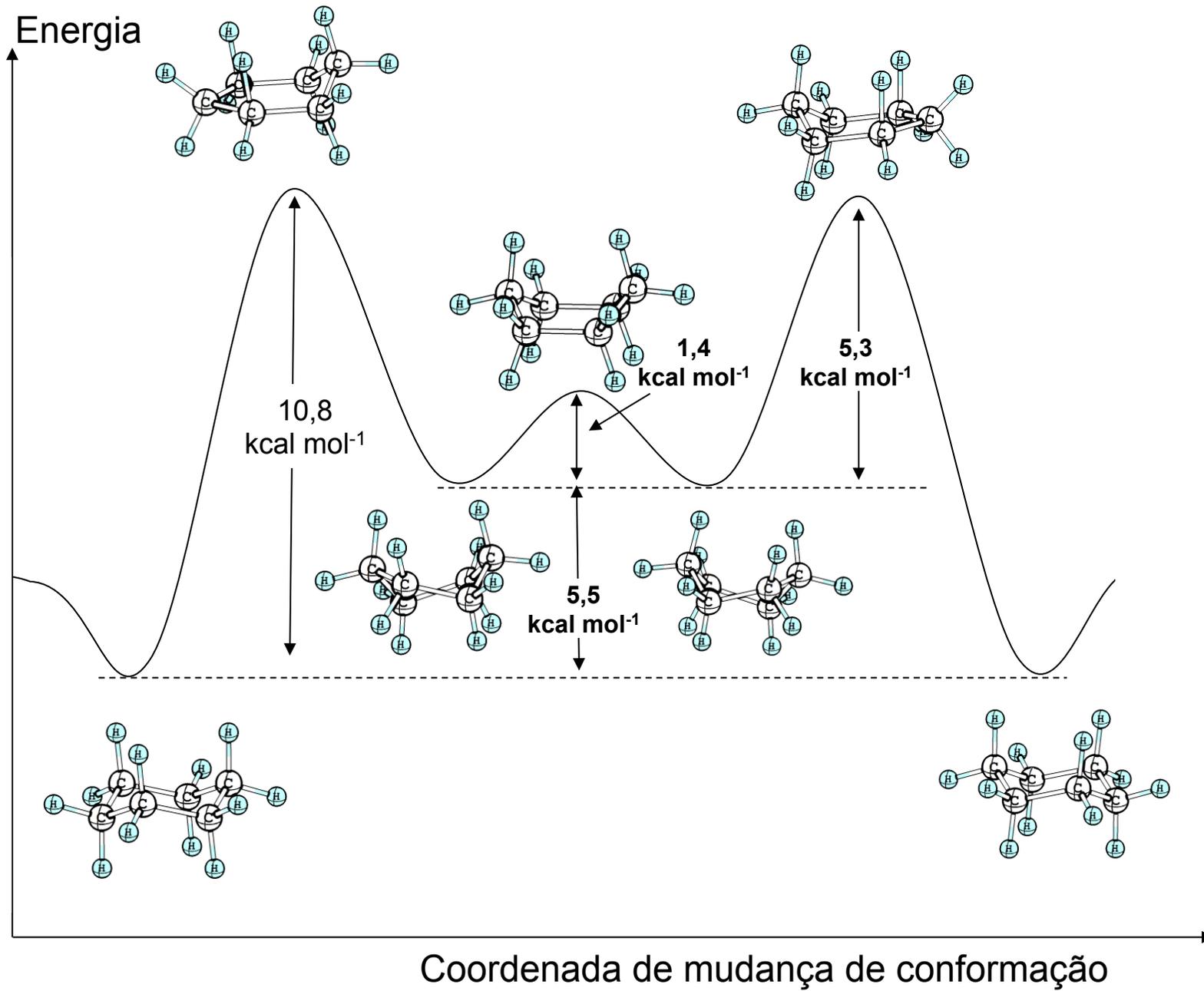


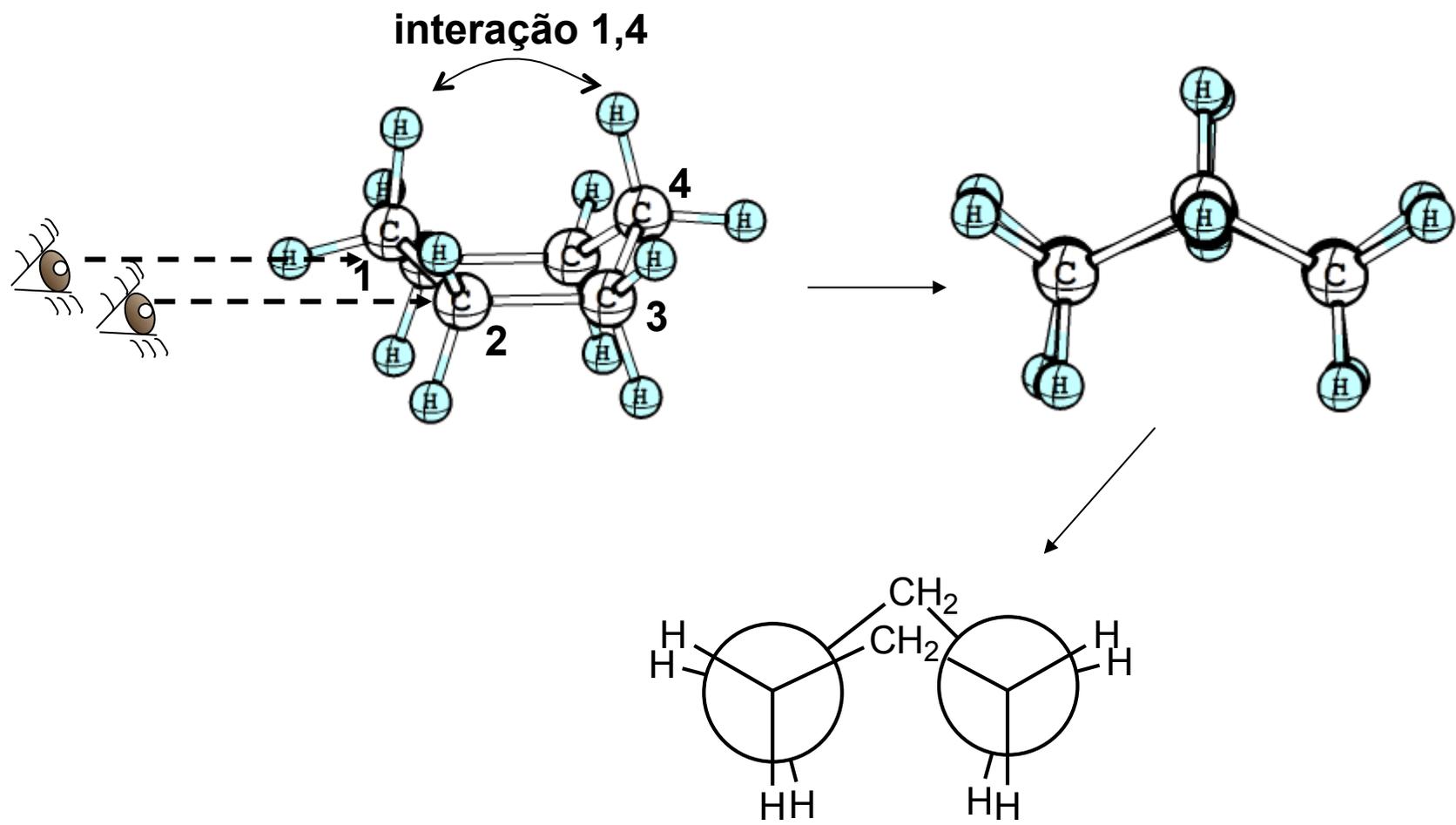
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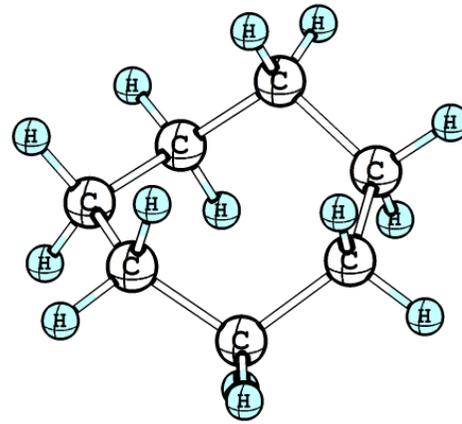
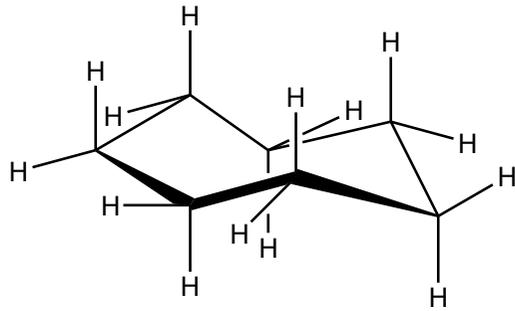


bote torcido B

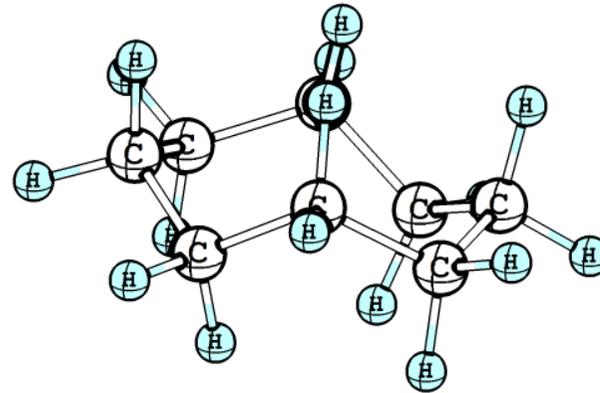
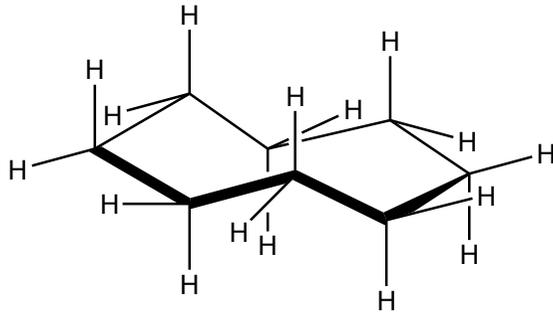




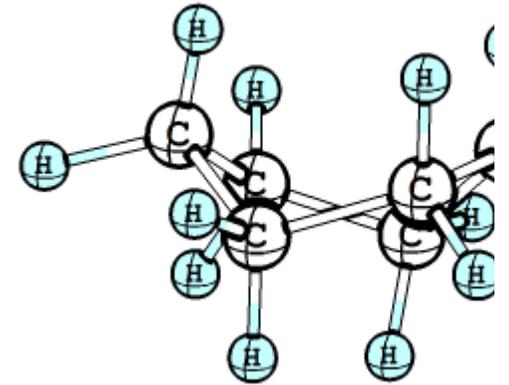
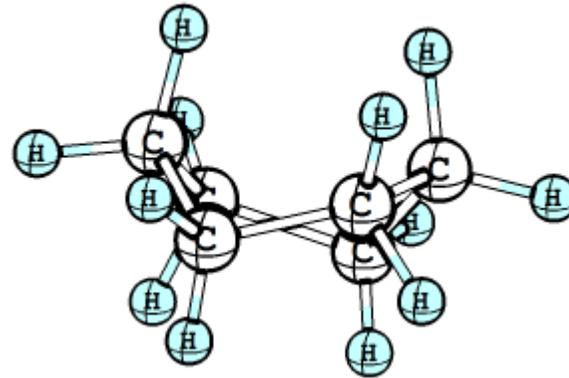
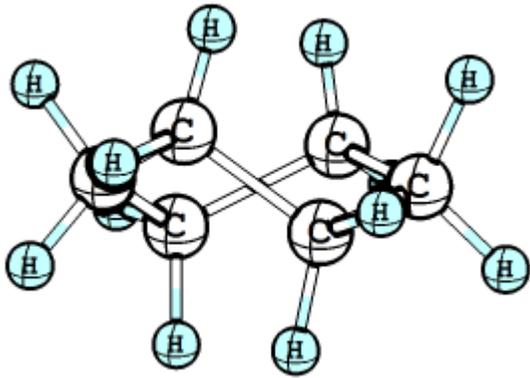
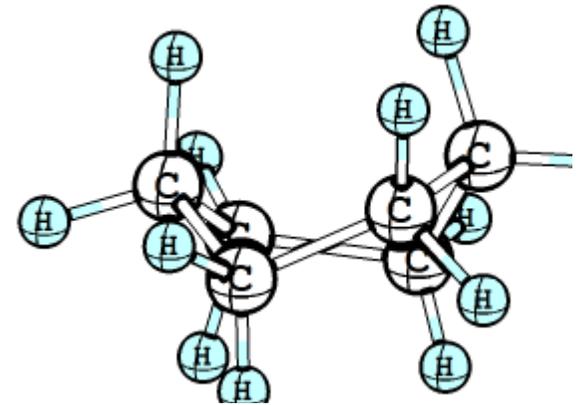
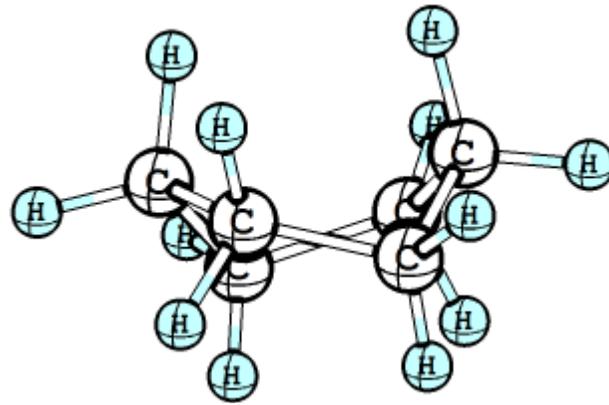
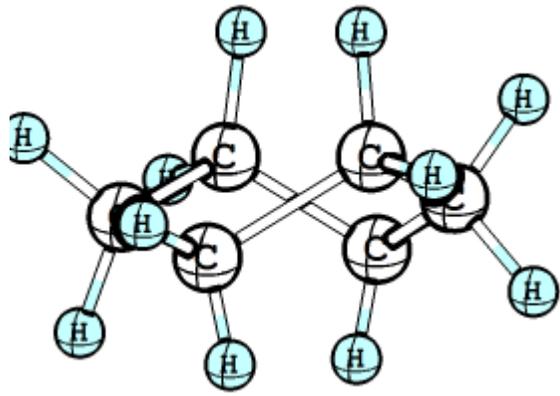


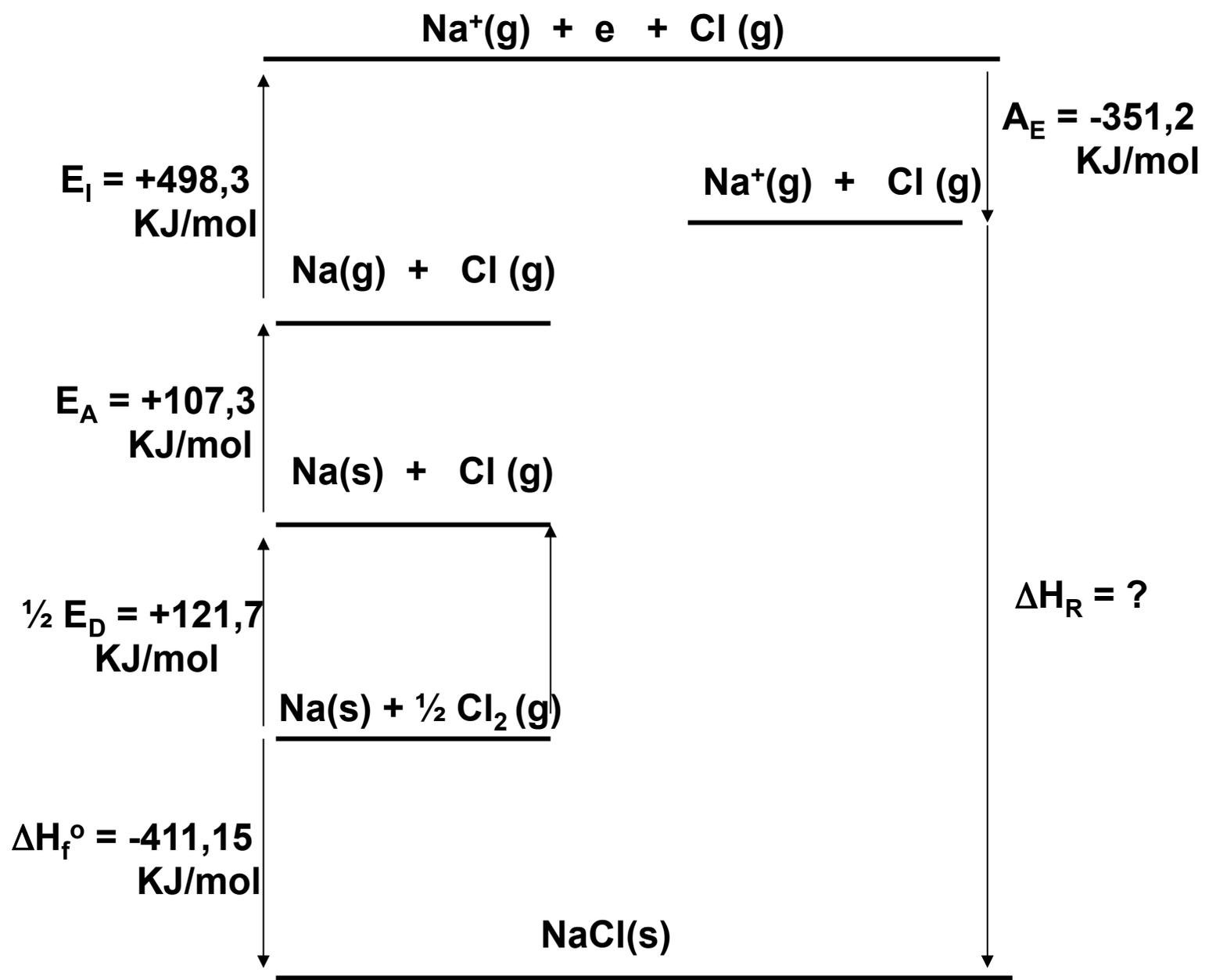


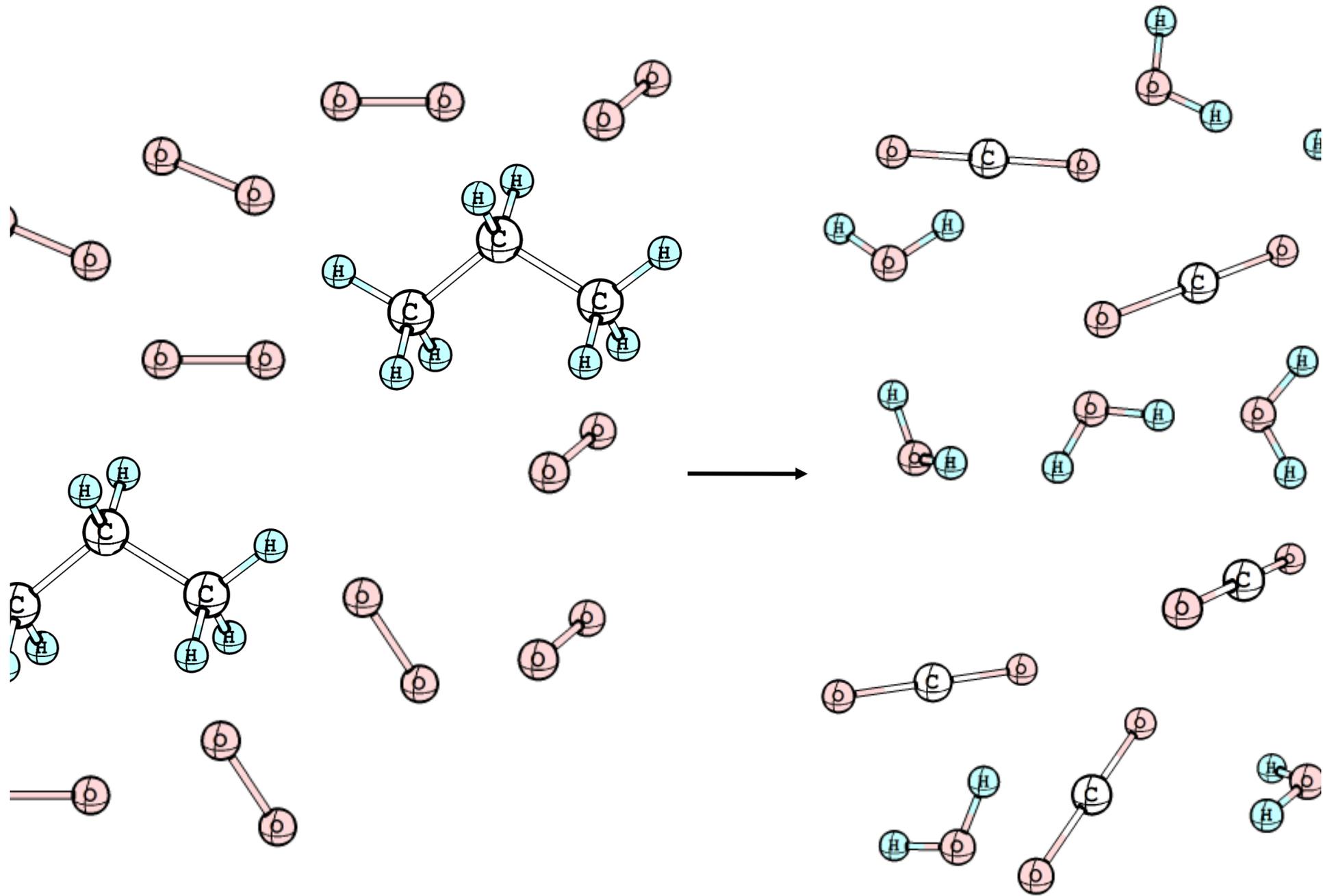
ciclo-heptano



ciclo-octano







Reagentes

Produtos

Fundamentos de Química Orgânica

Módulo 1

1- Grupos funcionais

- Análise da estrutura dos principais grupos funcionais da Química Orgânica com base na Teoria da Ligação de Valência e na Teoria do Orbital Molecular.
- Estudo das propriedades físicas das moléculas orgânicas.
- Modelagem Molecular e o estudo das propriedades químicas dos principais grupos funcionais da Química Orgânica.

2- Ácidos e Bases ; Nucleófilos e Eletrófilos

- Principais teóricas usadas para explicar as propriedades ácido/base.
- Escalas de acides/basicidade e o efeito do solvente.
- Paralelos e diferenças entre acides, basicidade, eletrofilicidade e nucleofilicidade.
- A termodinâmica e a direção da reação ácido/base.

3- Reações de Substituição Nucleofílica

- Revisão de estereoquímica.
- Introdução à cinética química.
- Reações SN2 e E2 em Carbono sp^3 .
- Reações SN1 e E1.
- Reações SN2 e E2 em Carbono sp^2 .
- Uso de reações de SN em síntese orgânica.
- Exemplos de reações de SN na natureza.

4- Reações de Substâncias Aromáticas, Olefinas e Acetilenos

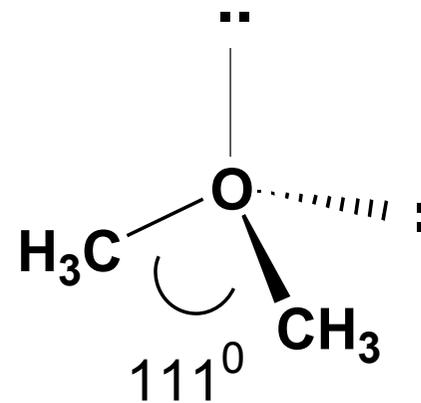
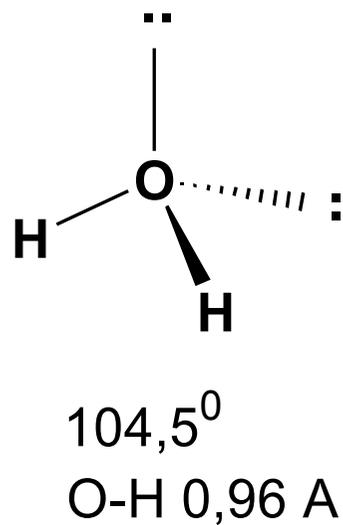
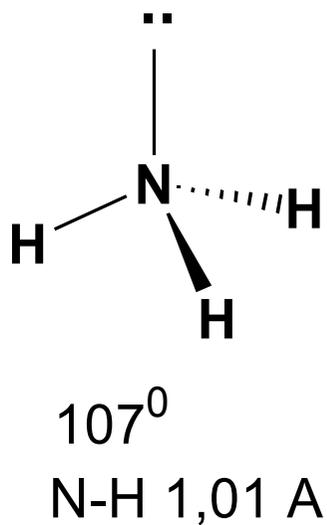
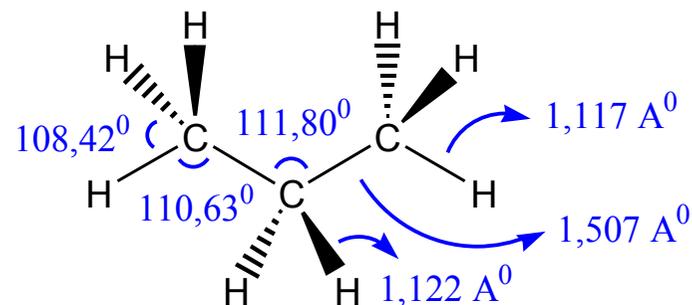
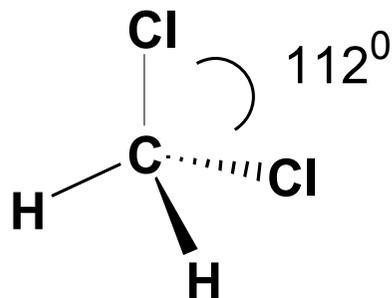
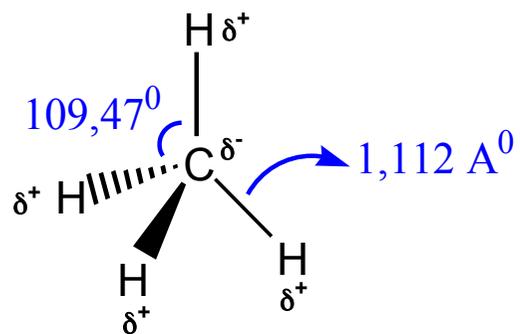
- **Aromaticidade.**
- **Substituição eletrofílica versus adição eletrofílica.**
- **Substituições eletrofílicas aromáticas; aplicações em síntese.**
- **Adições eletrofílicas a olefinas e acetilenos; aplicações em síntese.**
- **Substituições nucleofílicas aromáticas.**

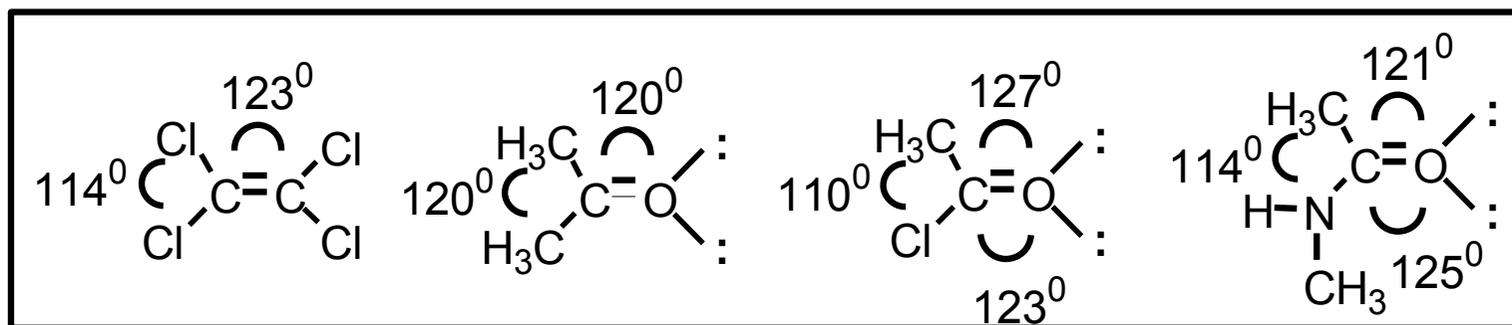
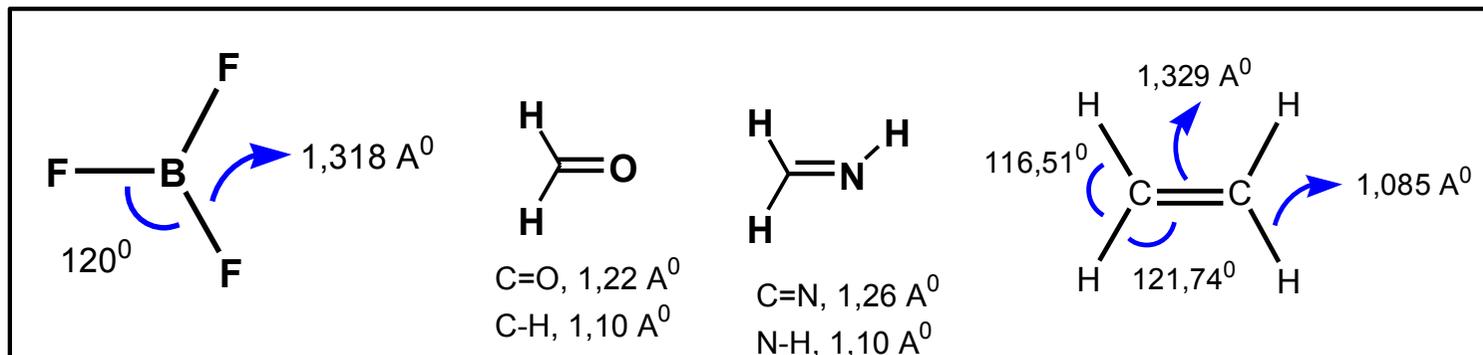
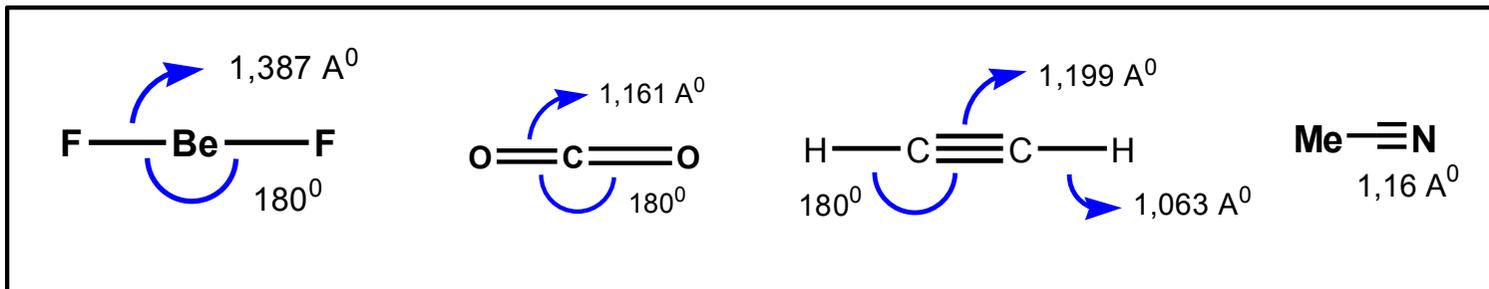
Módulo 2

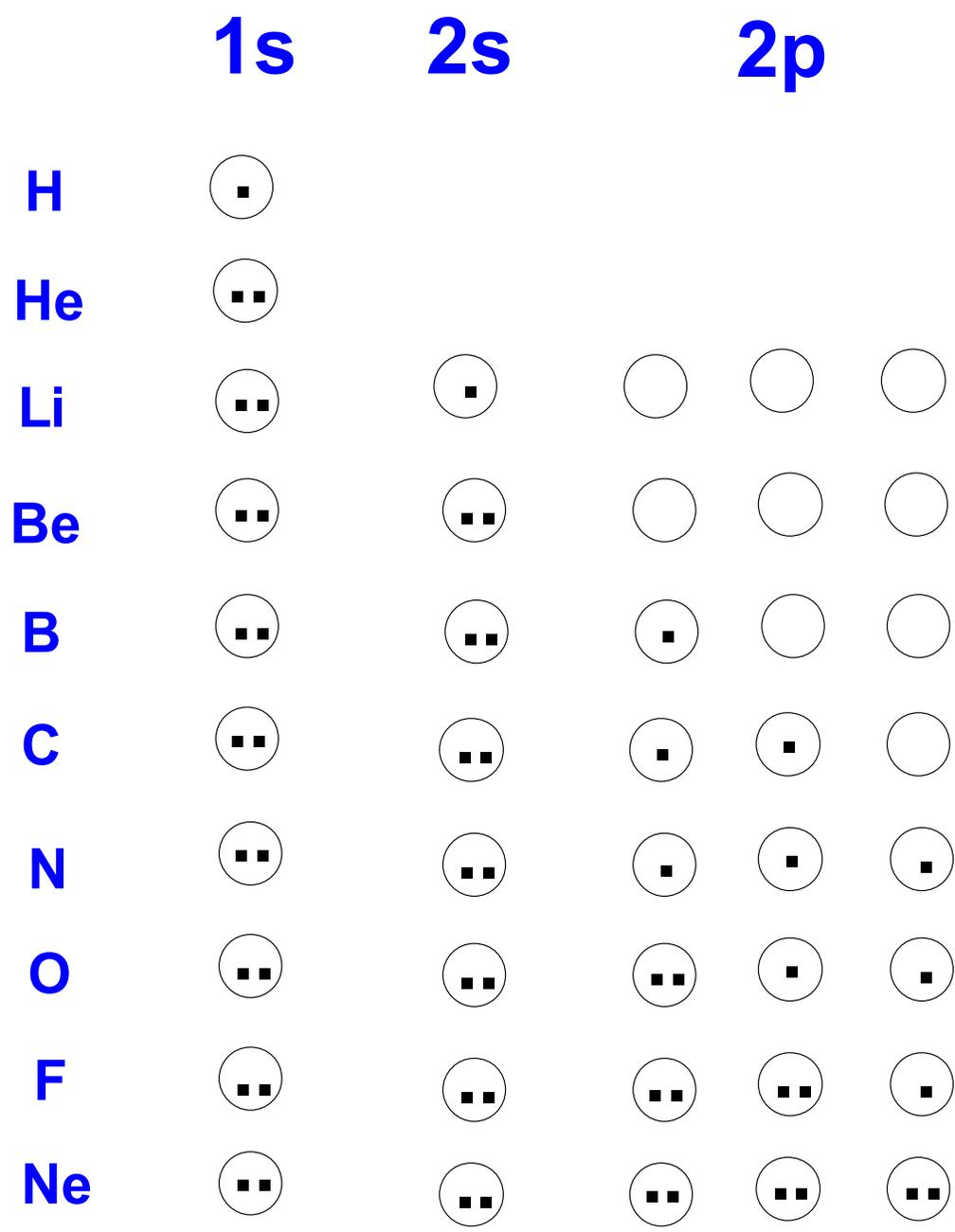
módulo 2 será construído em função da demanda dos participantes do curso ou em função de interesses específicos da empresa.

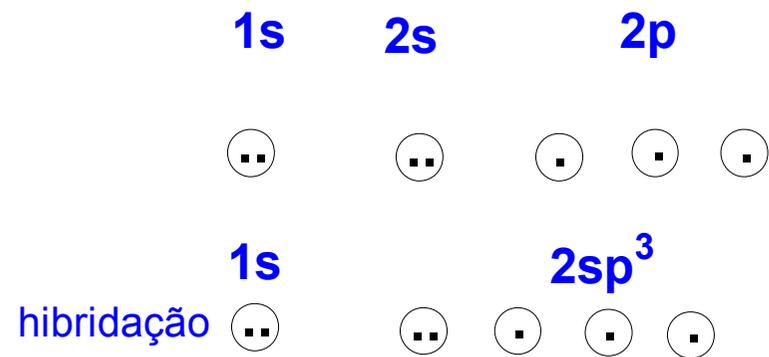
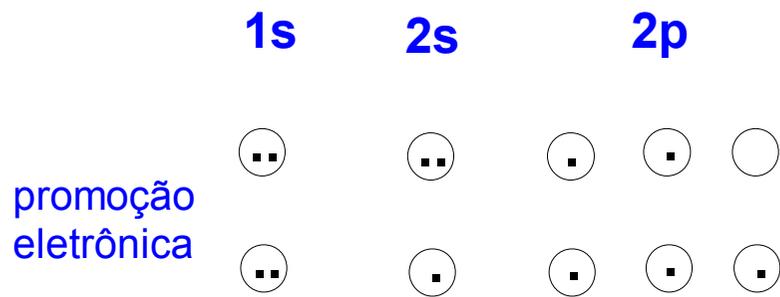
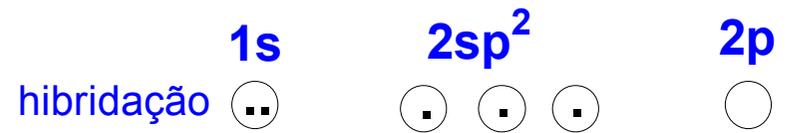
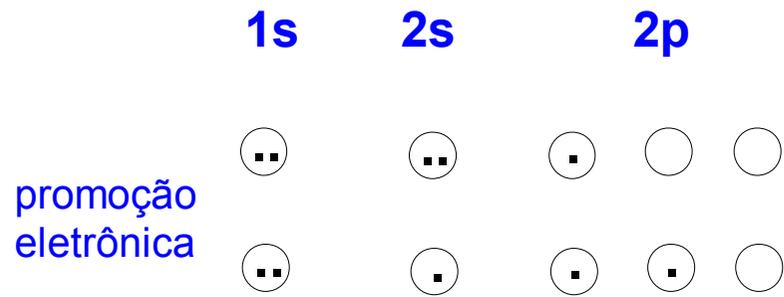
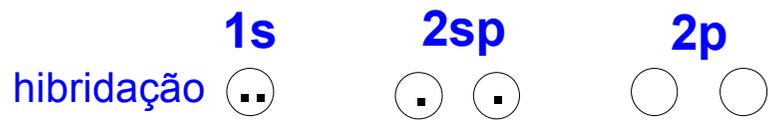
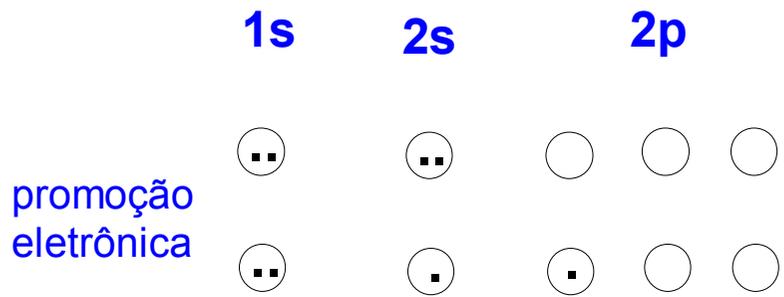
Principais Grupos Funcionais da Química Orgânica

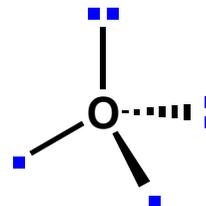
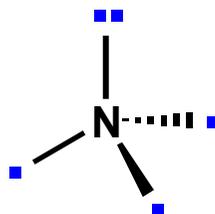
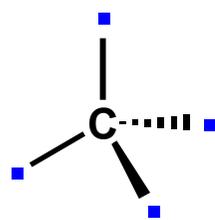
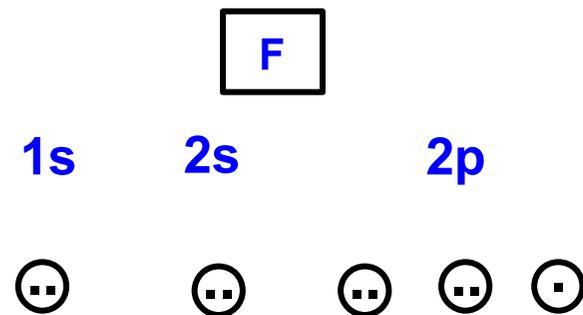
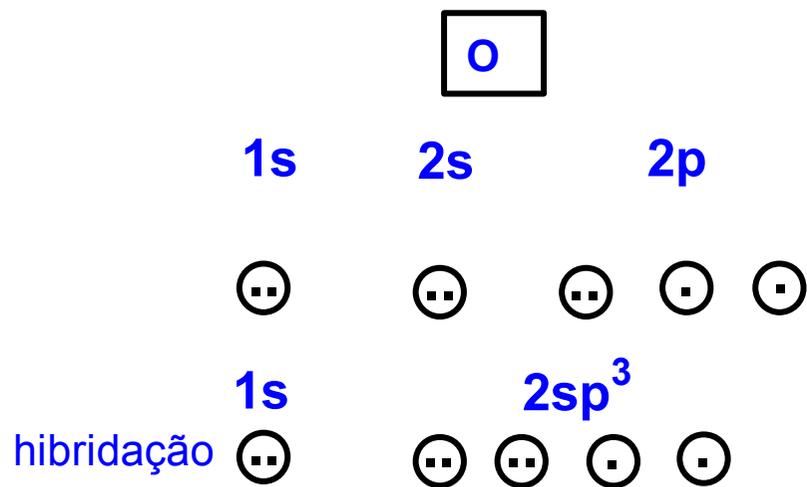
Ângulos e comprimentos de ligação, a partir de cálculos semi-empíricos AM1

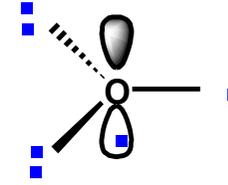
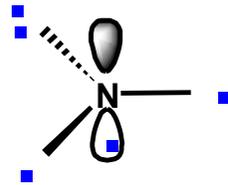
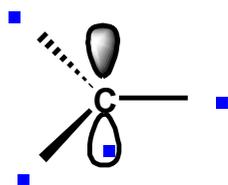
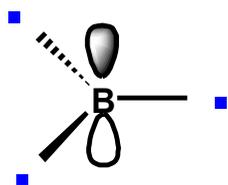
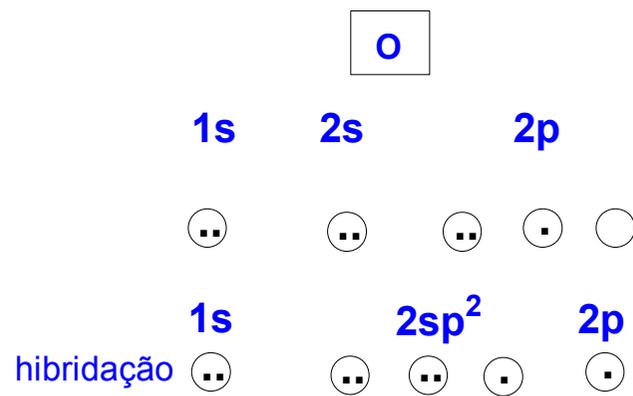
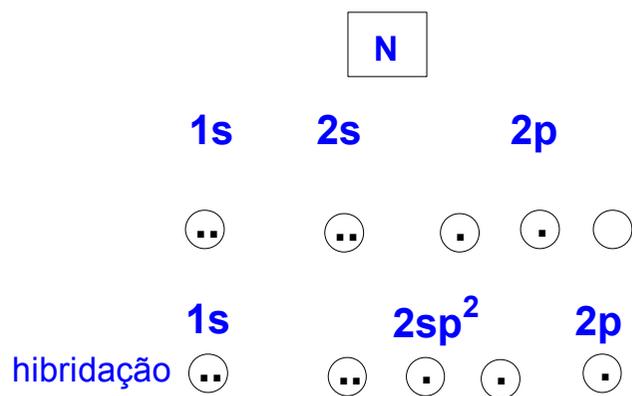












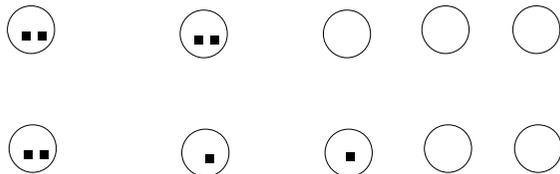
Be

1s

2s

2p

promoção eletrônica



1s

2sp

2p

hibridação



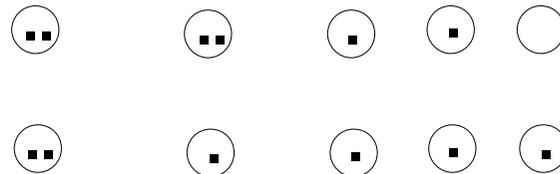
C

1s

2s

2p

promoção eletrônica



1s

2sp

2p

hibridação

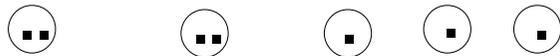


N

1s

2s

2p

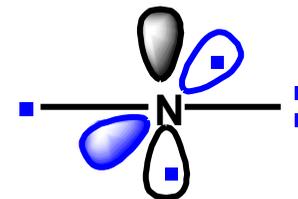
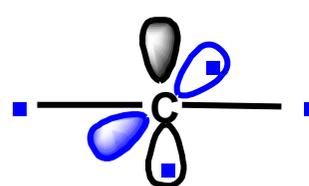
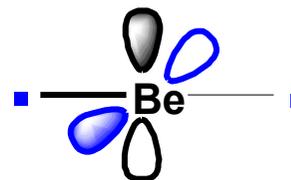


1s

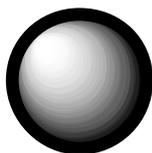
2sp

2p

hibridação



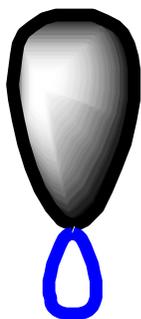
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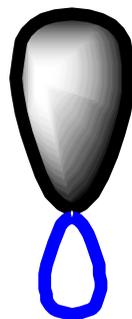
p



sp³



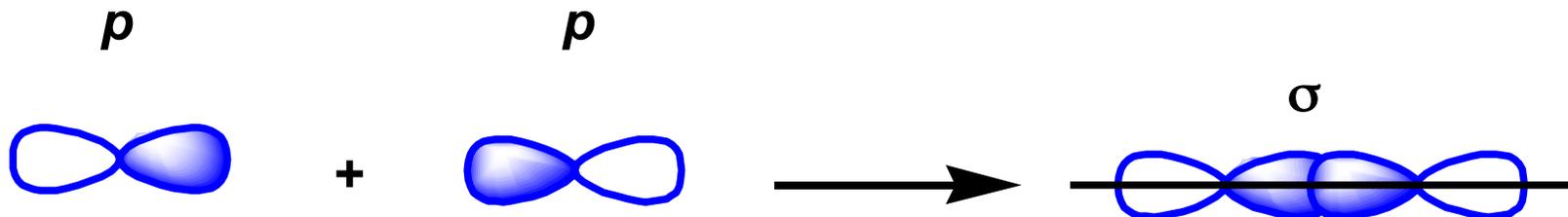
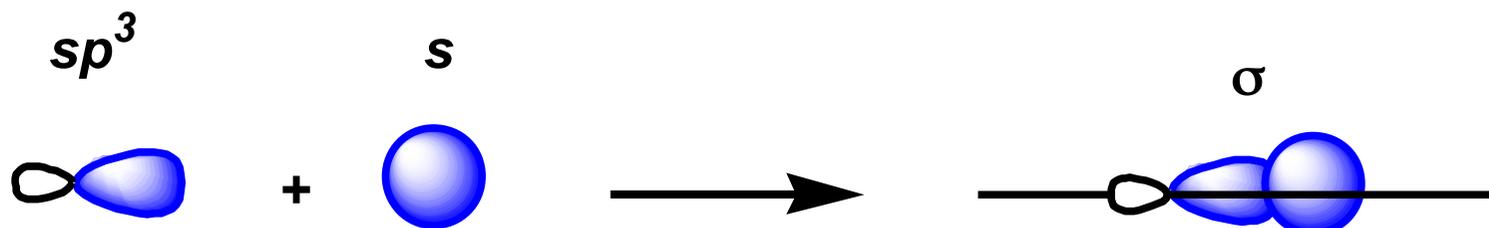
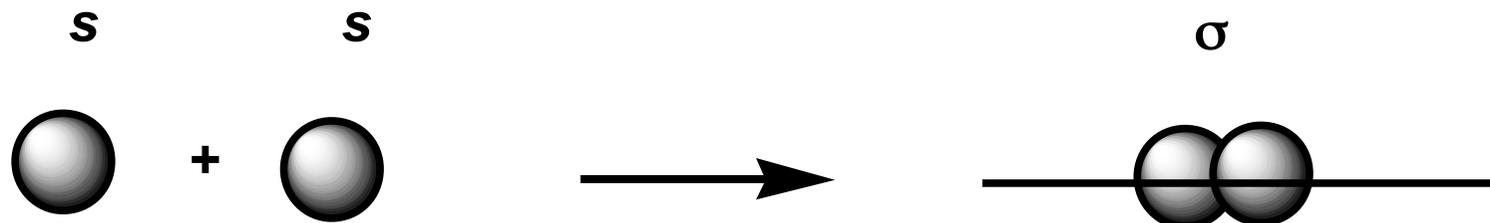
sp²

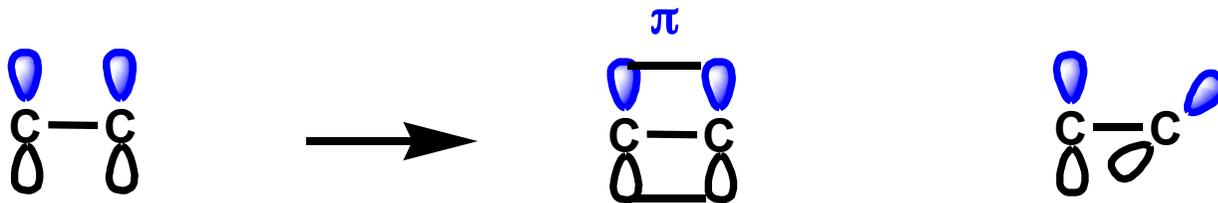


sp



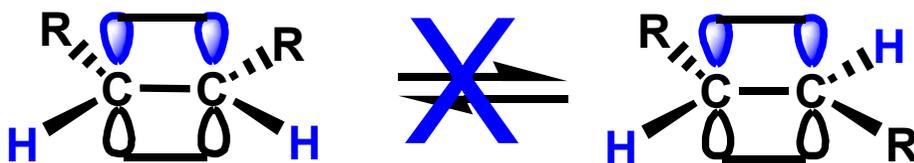
Ligação σ : simetria em relação ao eixo que contem os átomos





A ligação π não tem simetria ao redor do eixo que une os núcleos.

Orbitais p ortogonais: ausência de interação construtiva.



Isomeria *E* e *Z*
(*cis* e *trans*)

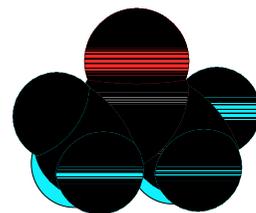
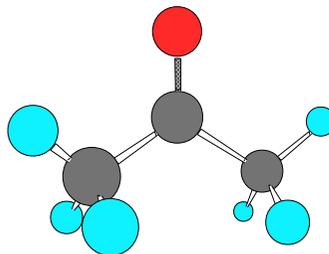
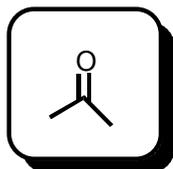
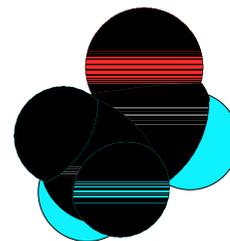
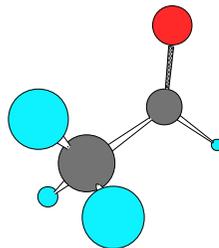
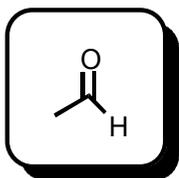
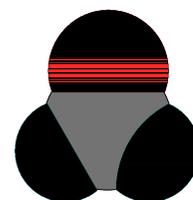
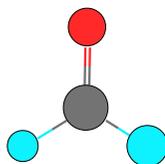
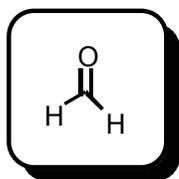
Representações para o formaldeído, acetaldeído, acetona e iminas (*E* e *Z*) do acetaldeído com a amônia

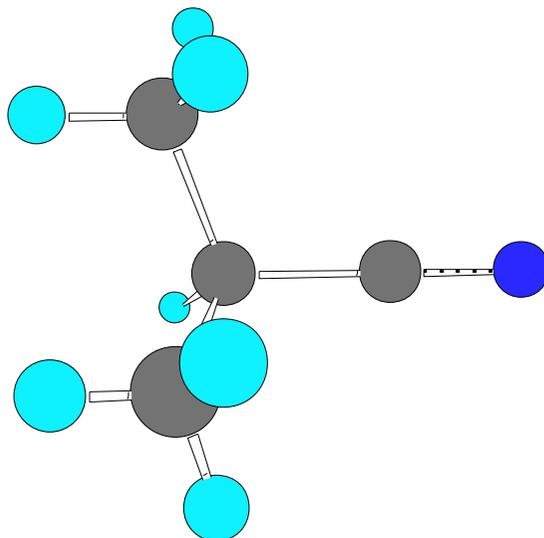
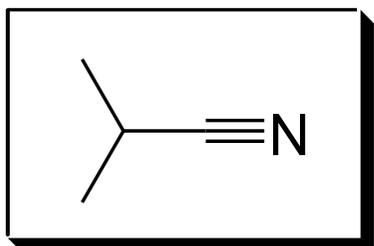
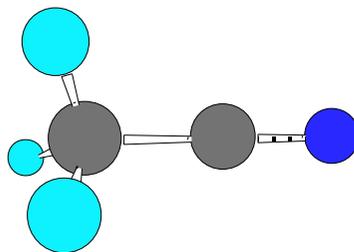
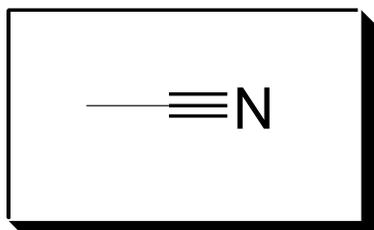
Representações em traços

Representações Tridimensionais

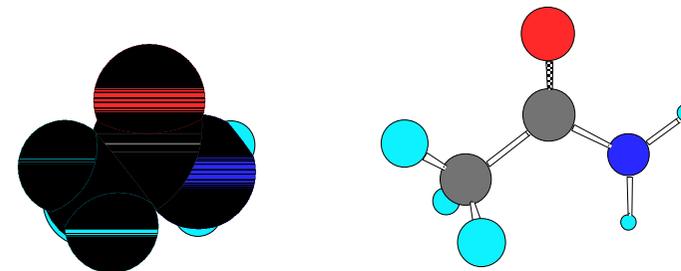
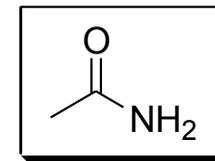
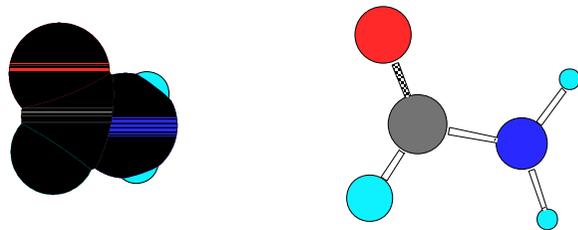
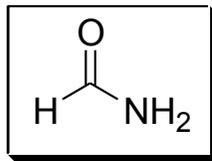
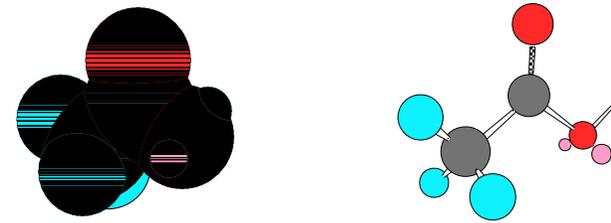
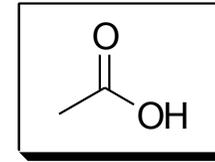
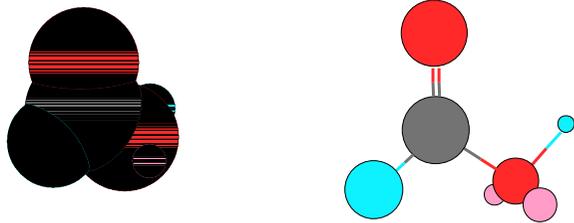
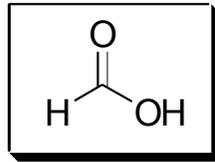
"Ball and Stick"

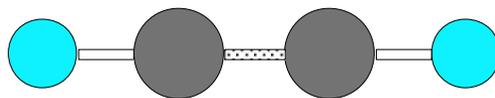
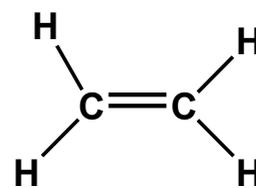
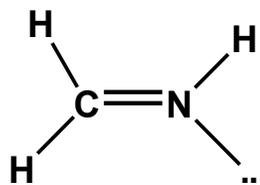
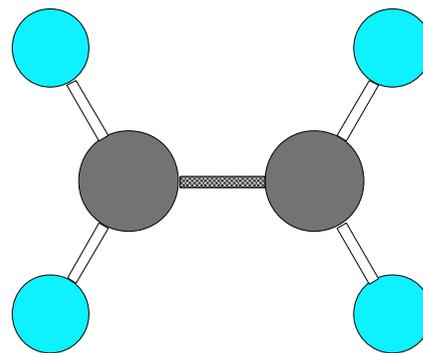
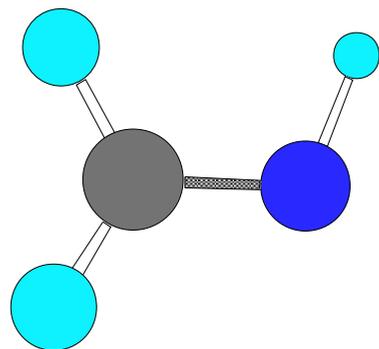
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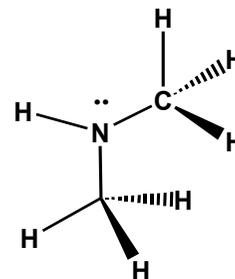
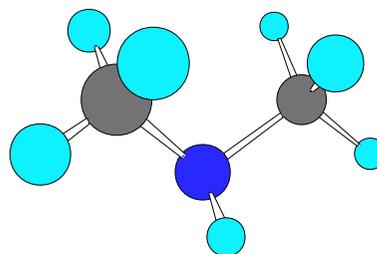
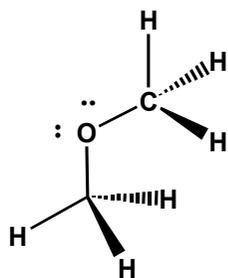
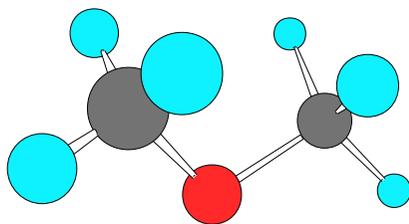
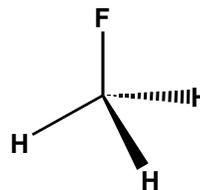
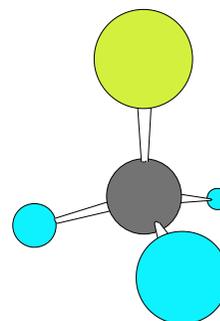
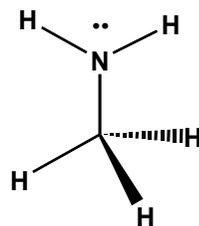
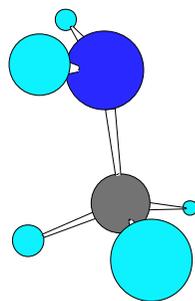
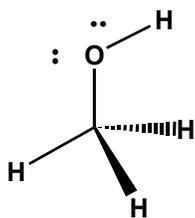
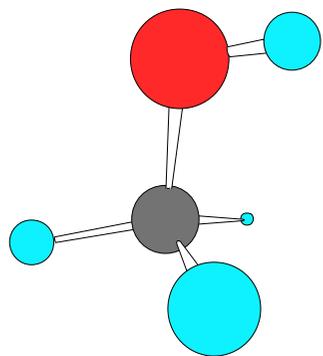


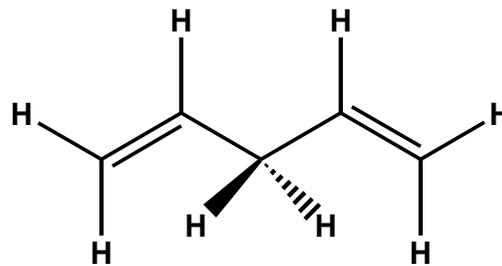
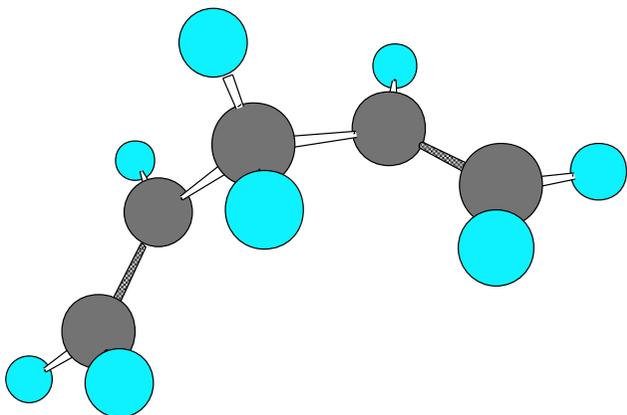
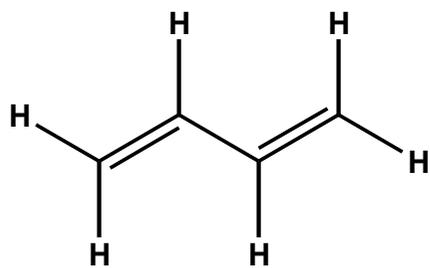
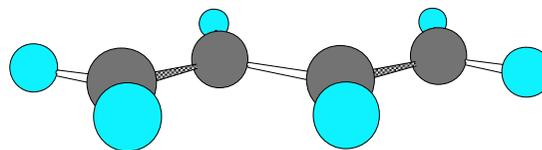
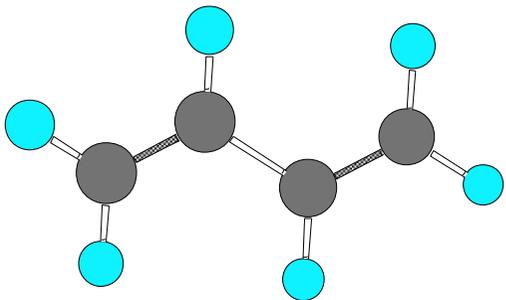


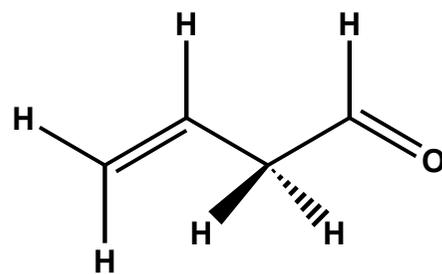
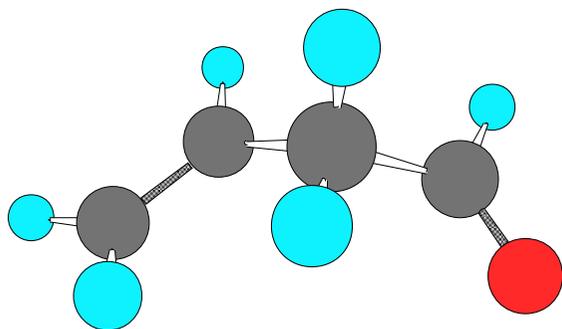
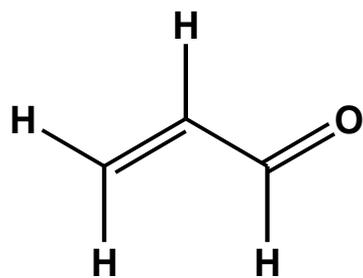
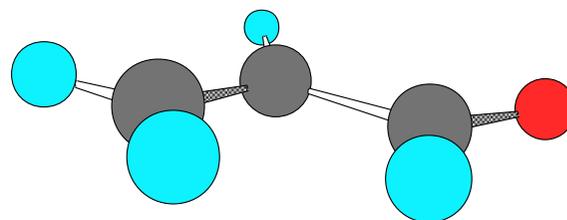
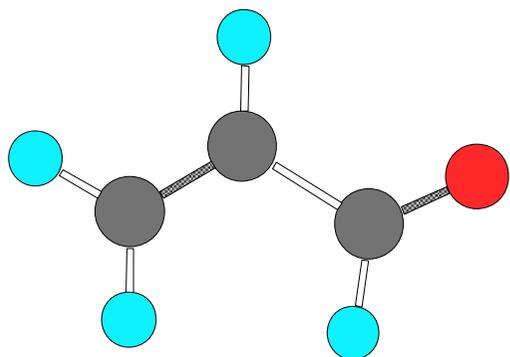
Representações do tipo "space filling" e "ball and stick" para o ácido fórmico, ácido acético, formamida e acetamida

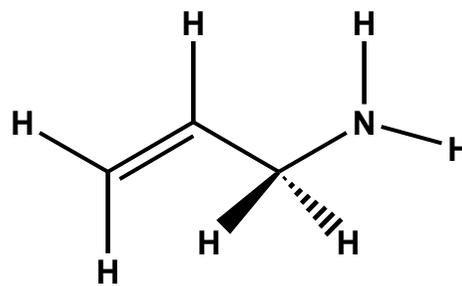
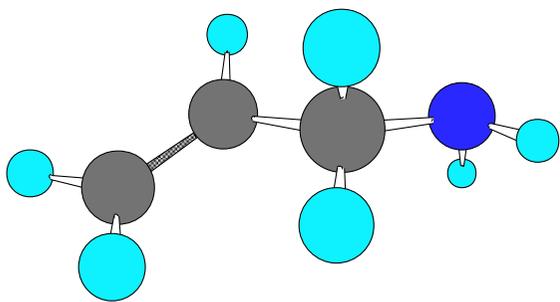
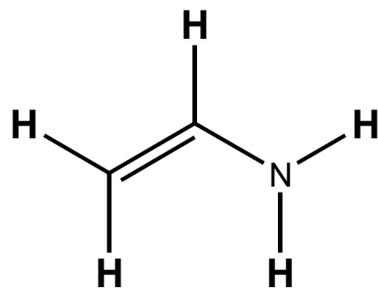
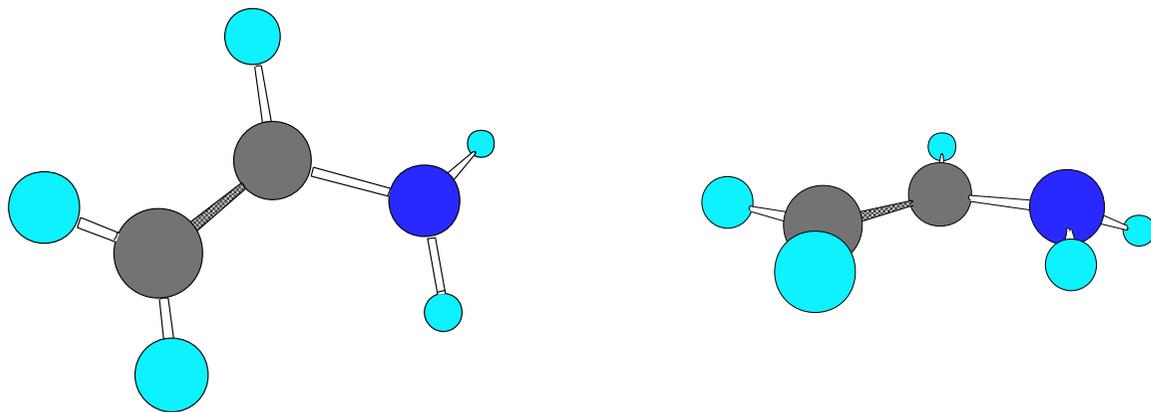












Estrutura das moléculas Orgânicas

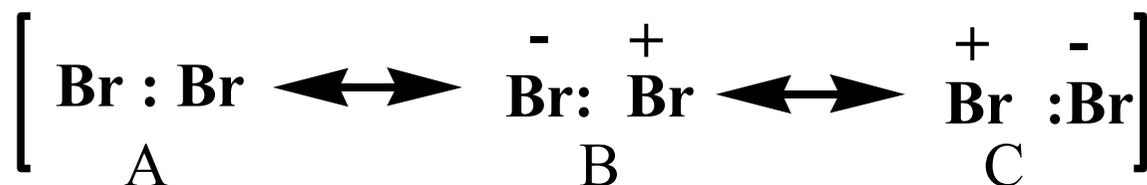
Teoria da Ligação de Valência

Teoria do Orbital Molecular

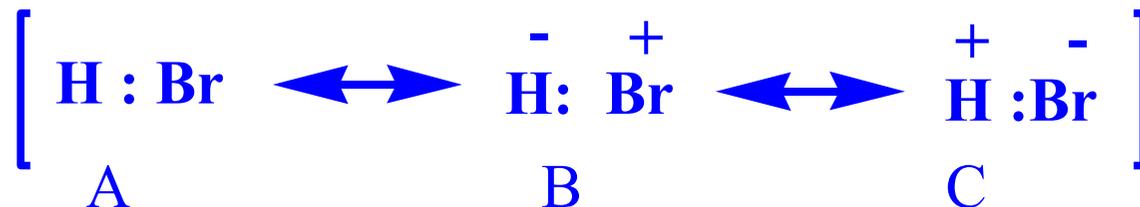
Teoria da Ligação de Valência

A média ponderada da contribuição das diversas estruturas de Lewis que podem ser representadas para a molécula.

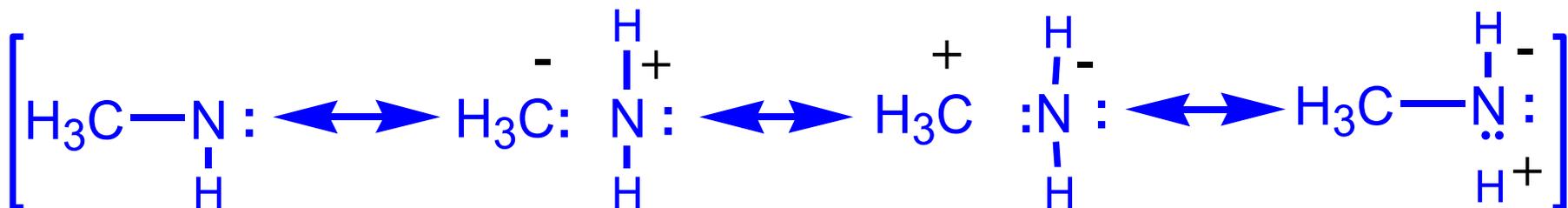
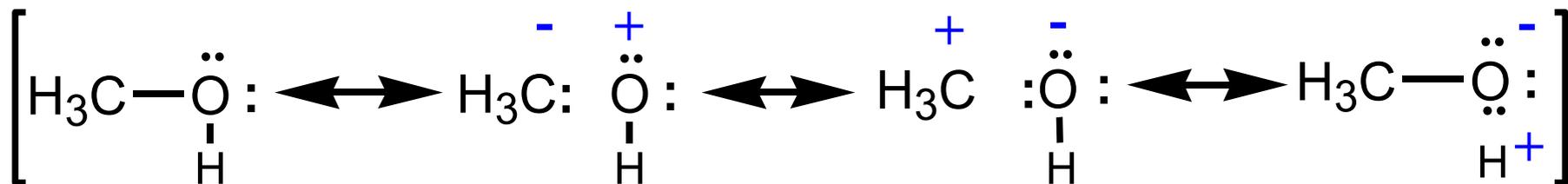
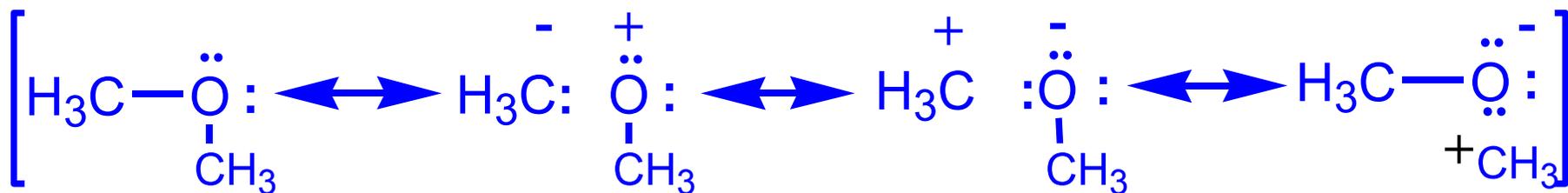
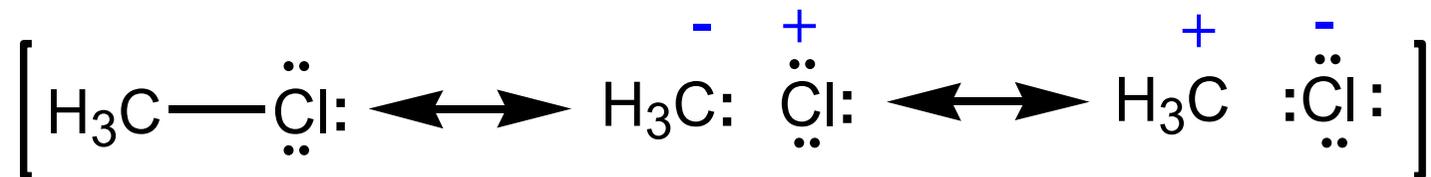
Híbridos de Ressonância



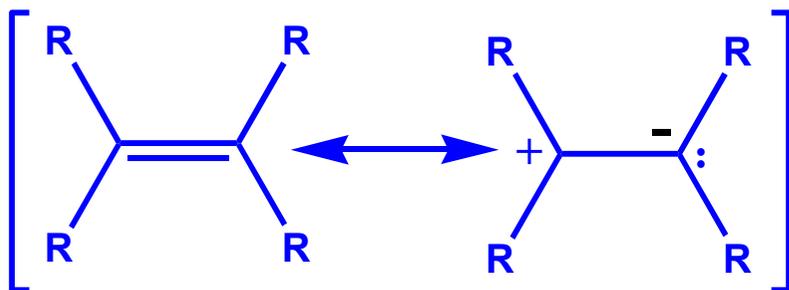
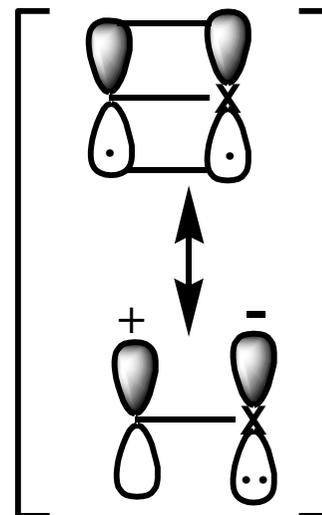
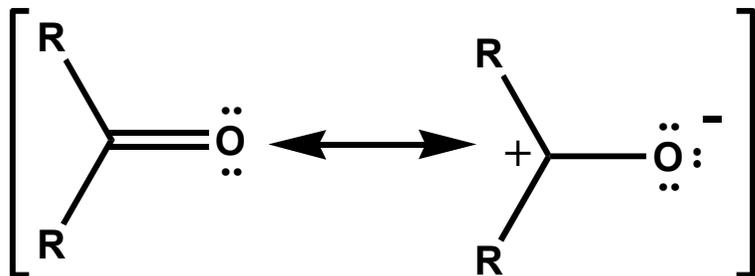
$$\Psi_{\text{Br}_2} = \Psi_{\text{A}} + \Psi_{\text{B}} + \Psi_{\text{C}}$$



$$\Psi_{\text{Br}_2} = \Psi_{\text{A}} + \Psi_{\text{B}} + \Psi_{\text{C}}$$

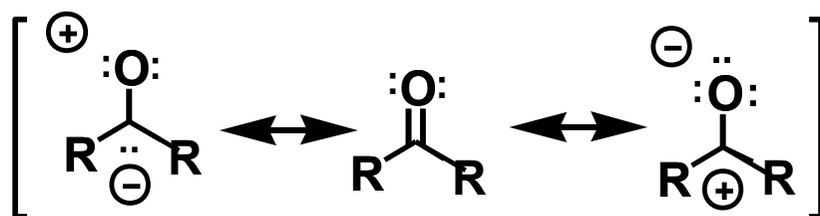


Elétrons n e π possuem maior mobilidade do que elétrons σ .



A contribuição das estruturas canônicas depende da diferença de eletronegatividade entre os átomos envolvidos.

As Ligações $\pi_{C=O}$ e $\pi_{C=C}$ Segundo o Método da Teoria de Valência



aldeídos e cetonas

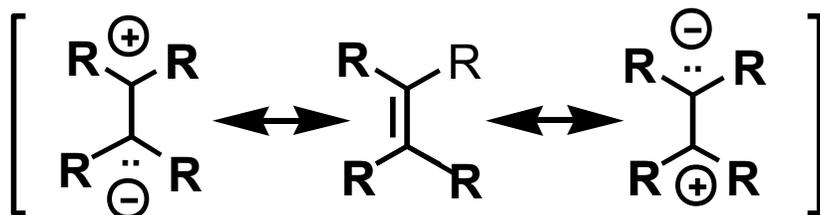
A

B

C

$$\Psi_{C=O} = C_A \Psi_A + C_B \Psi_B + C_C \Psi_C$$

$$C_B > C_C \gg C_A \sim 0$$



olefinas

A'

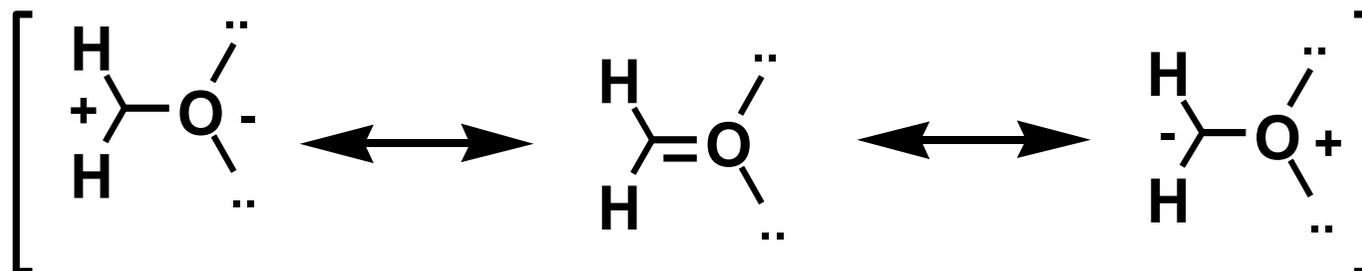
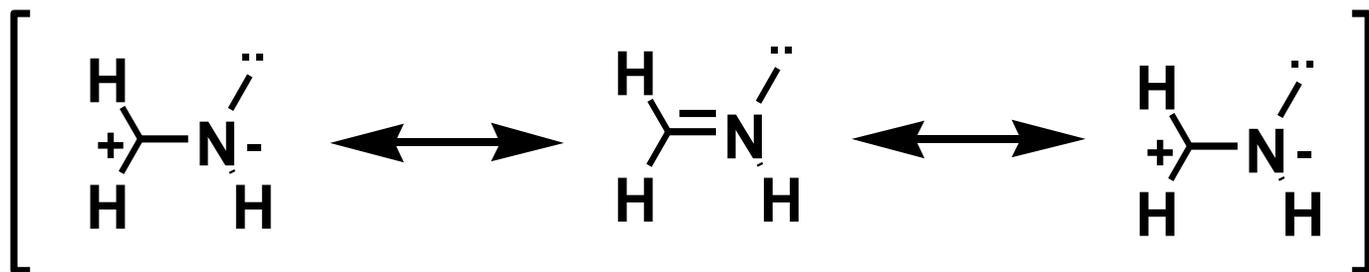
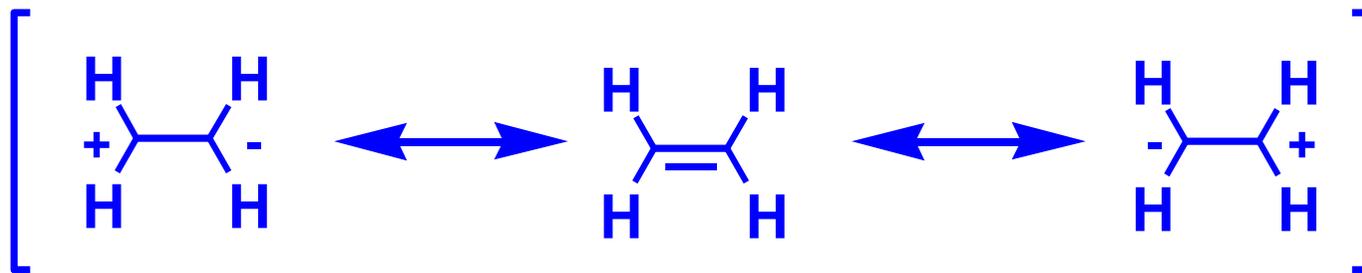
B'

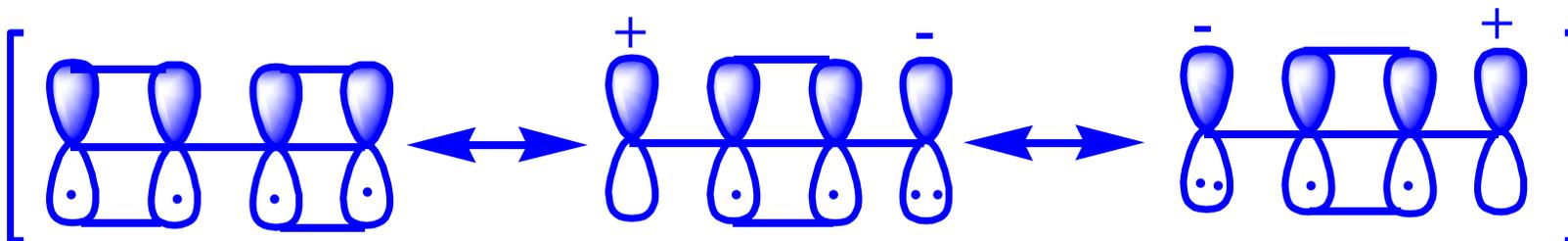
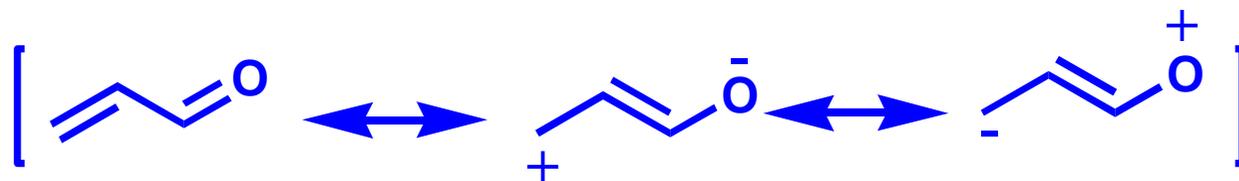
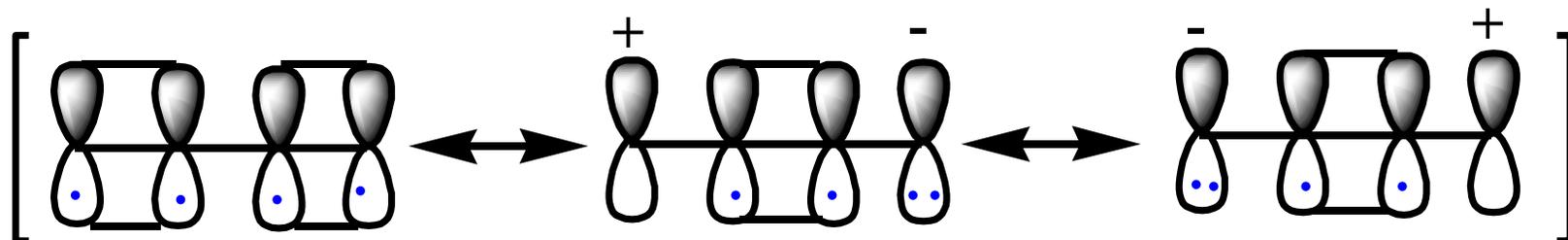
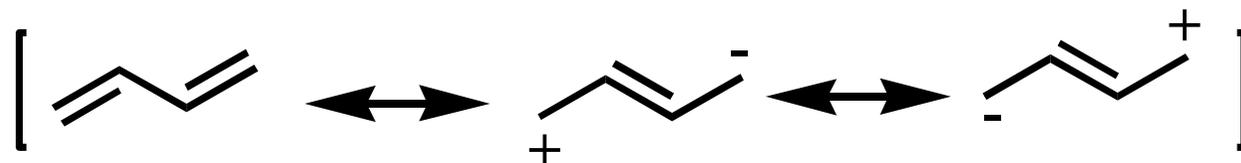
C'

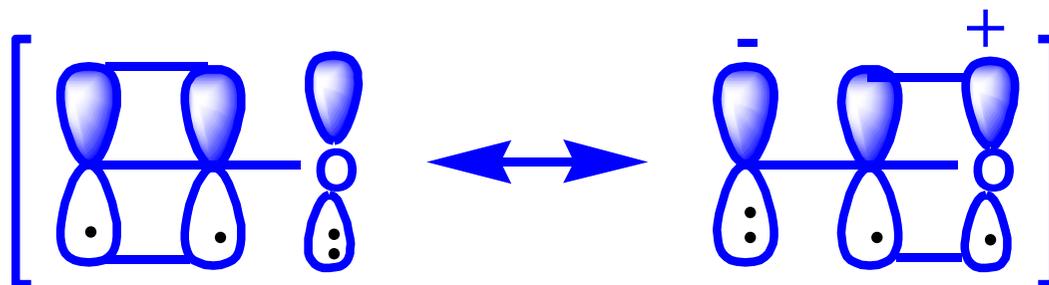
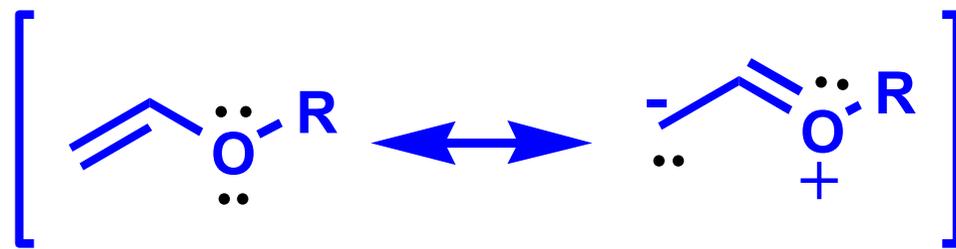
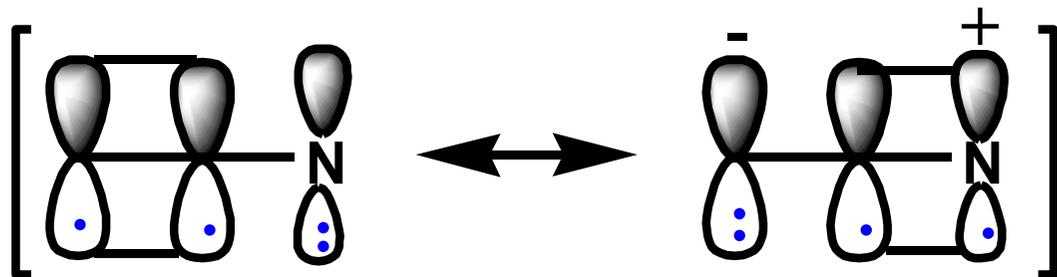
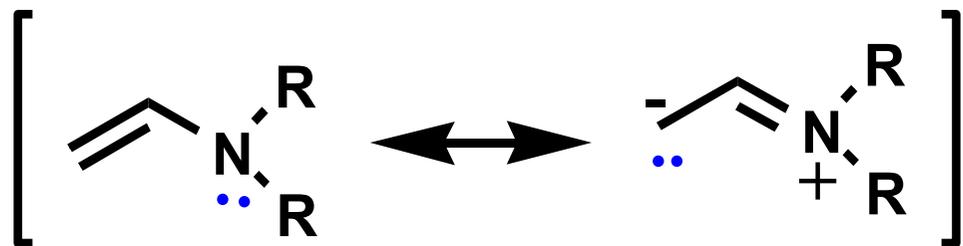
$$\Psi_{C=C} = C_{A'} \Psi_{A'} + C_{B'} \Psi_{B'} + C_{C'} \Psi_{C'}$$

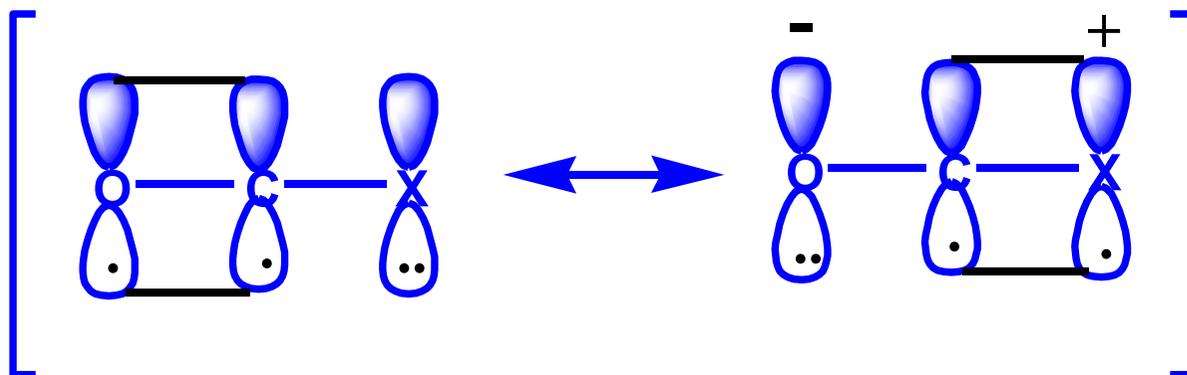
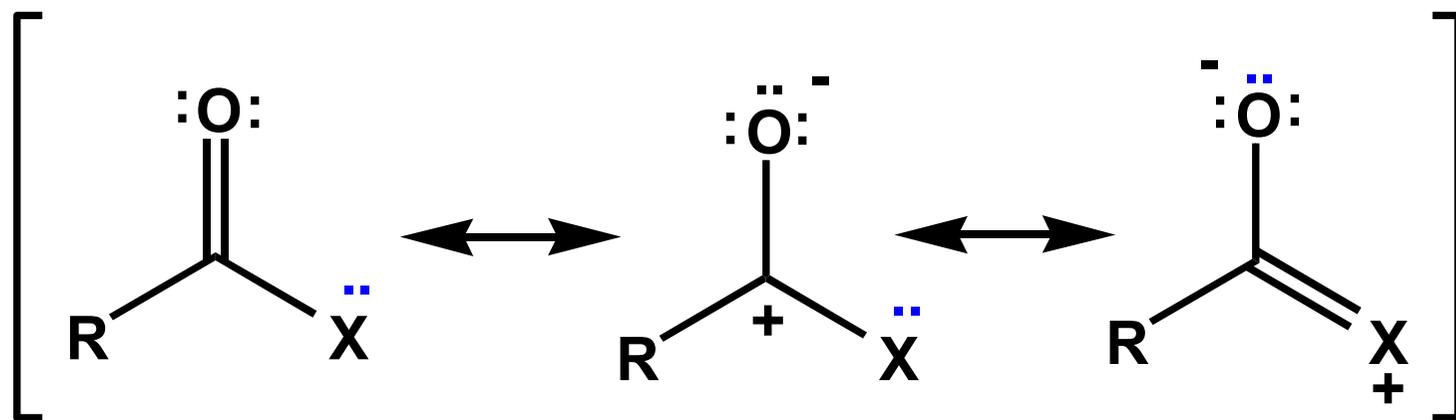
$$C_{B'} \gg C_{C'} = C_{A'} \sim 0$$

Teoria da Ligação de Valência

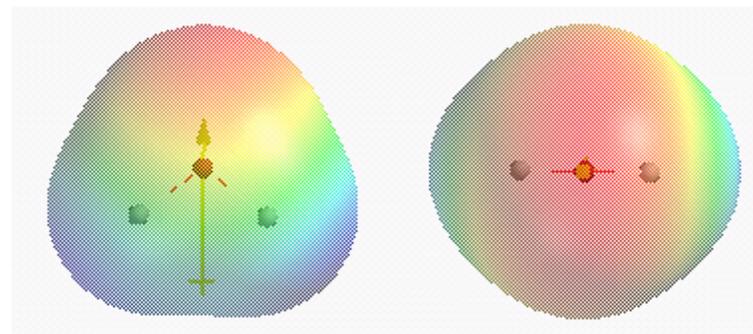
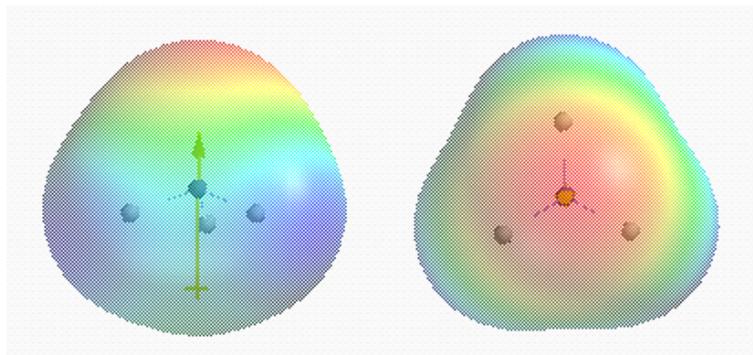
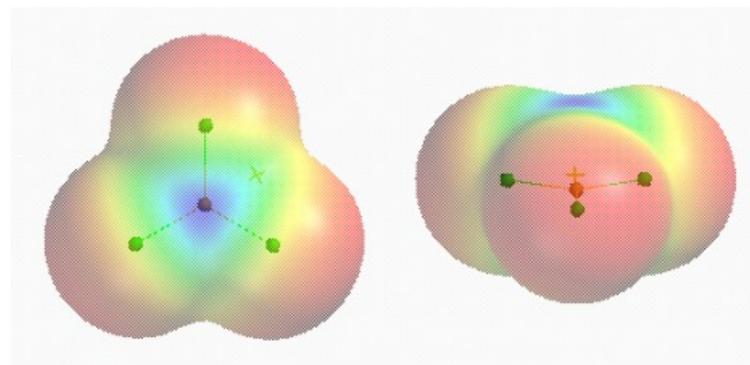
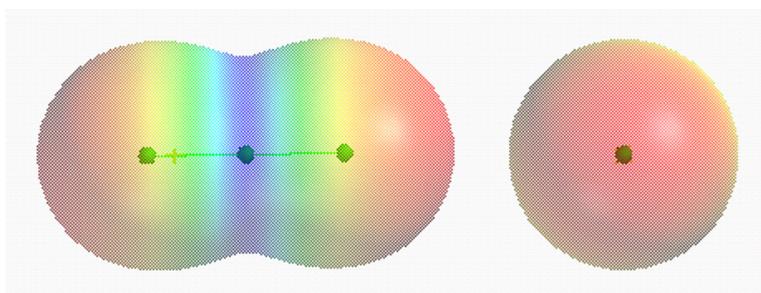


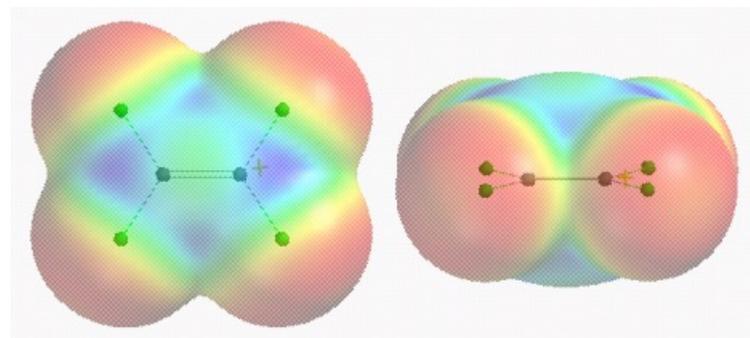
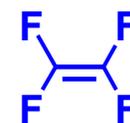
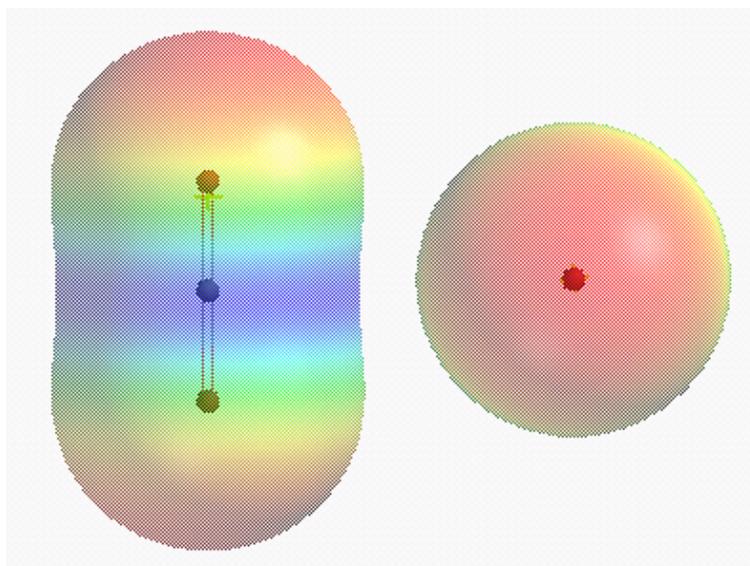
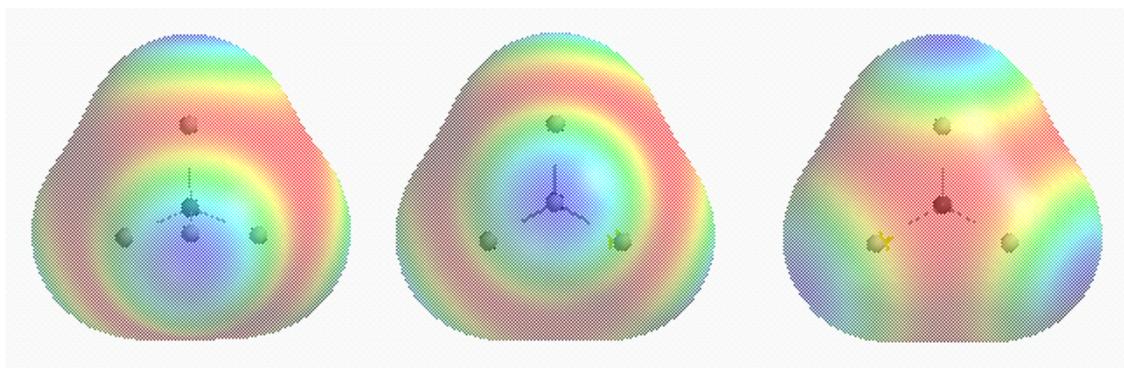
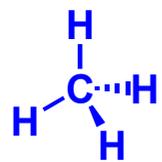


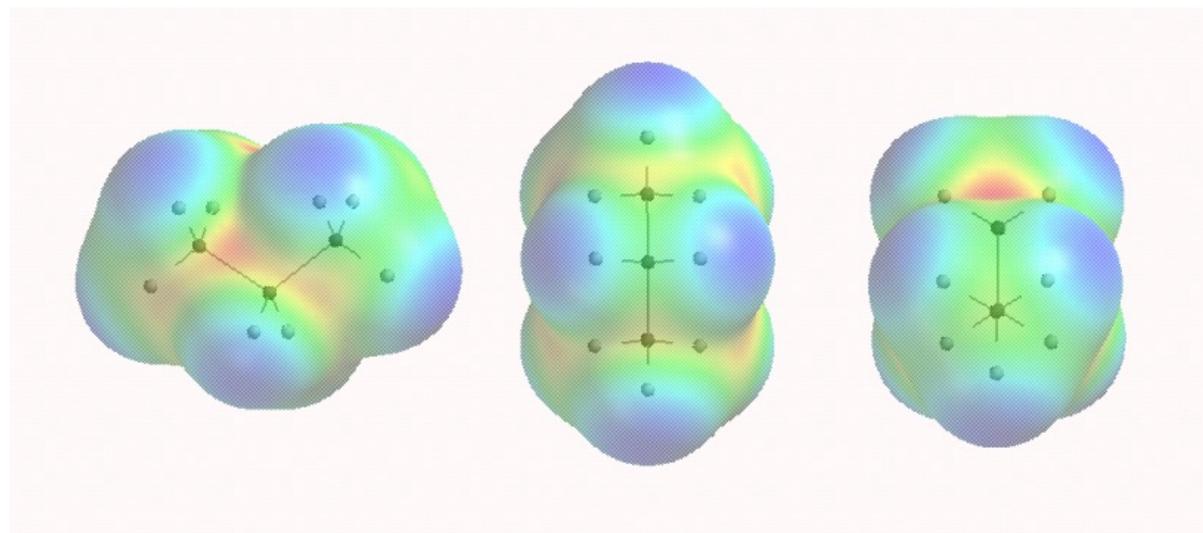


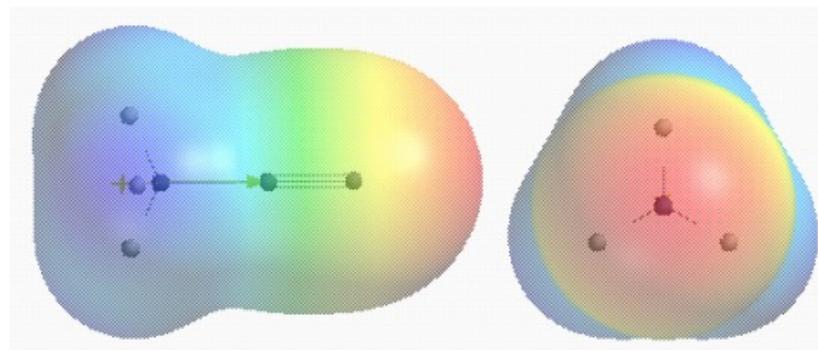
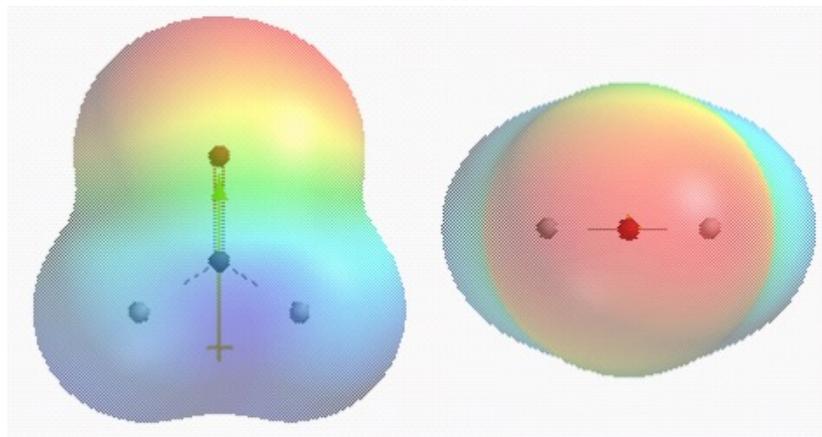
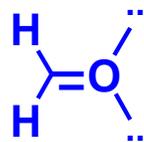
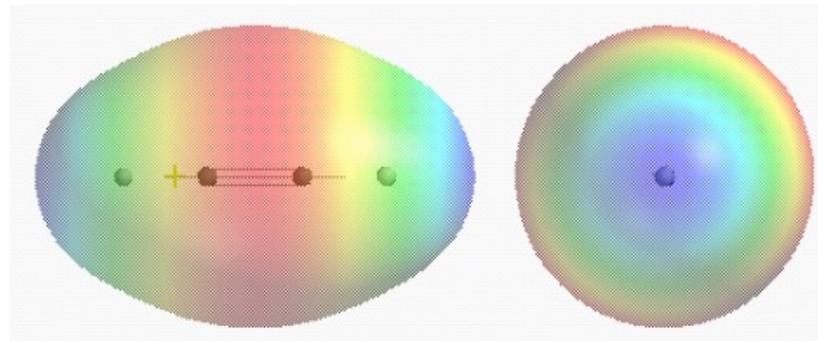
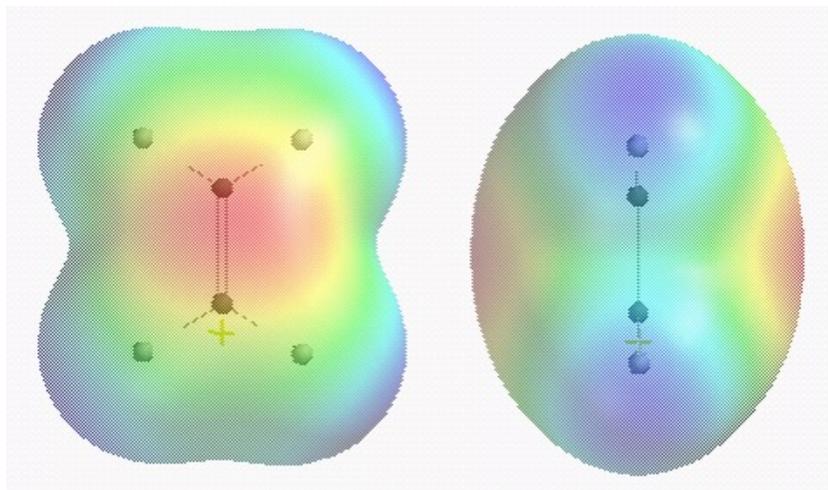
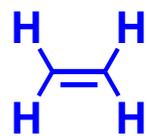


Mapas de Potencial Eletrostático (AM1)









Teoria do Orbital Molecular

Orbitais Moleculares e Reatividade Química

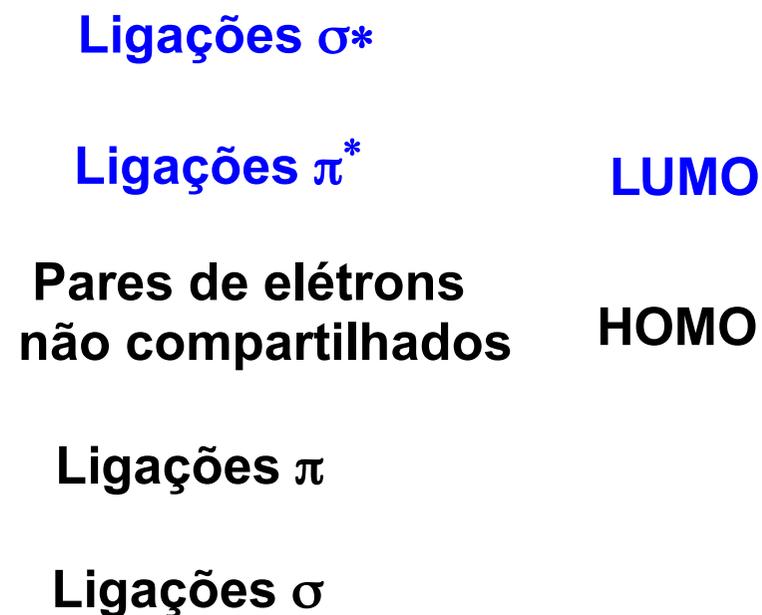
Enquanto que a estabilidade termodinâmica de espécies químicas está associada com a energia de todos os seus orbitais moleculares preenchidos, a reatividade química depende, em grande extensão, mas não exclusivamente, da energia de seus orbitais de fronteira.

Por exemplo, a medida que nucleófilos aproximam-se e colidem com eletrófilos, três tipos principais de interações ocorrem:

- 1- Os orbitais ocupados de uma espécie repelem os orbitais ocupados da outra e a energia envolvida nesta interação de natureza antiligante contribui em grande parte para a energia de ativação da adição nucleofílica,
- 2- Espécies iônicas ou com cargas parciais opostas sofrem atração eletrostática enquanto que as espécies iônicas ou com cargas parciais idênticas sofrem repulsão eletrostática e estes efeitos devem ser consideradas quando a reação envolve ions ou moléculas polares,
- 3- O HOMO da espécie nucleofílica interage com o LUMO da espécie eletrofílica, para formar a nova ligação química.

LCAO LINEAR COMBINATION OF ATOMIC ORBITALS

Energia



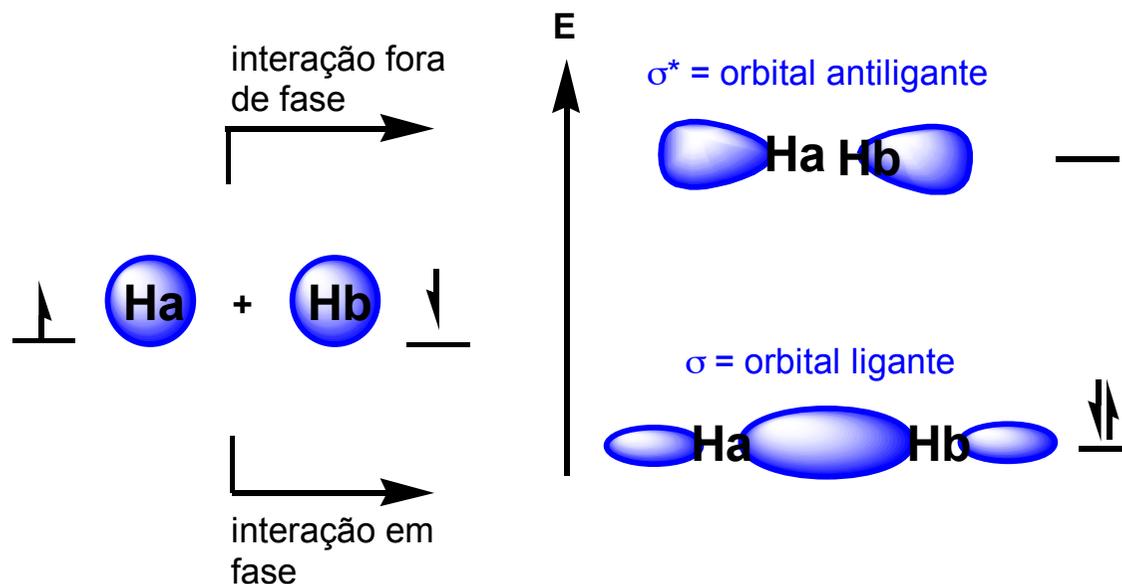
HOMO lowest unoccupied molecular orbital

LUMO highest occupied molecular orbital

O Tratamento Mecânico Quântico da Molécula do Hidrogênio

Nos anos 1920 desenvolveram-se duas descrições matemáticas para as ligações químicas, a Teoria do Orbital Molecular e a Teoria de Valência, que são aproximações para a solução da equação de Schöndinger.

Teoria do Orbital Molecular

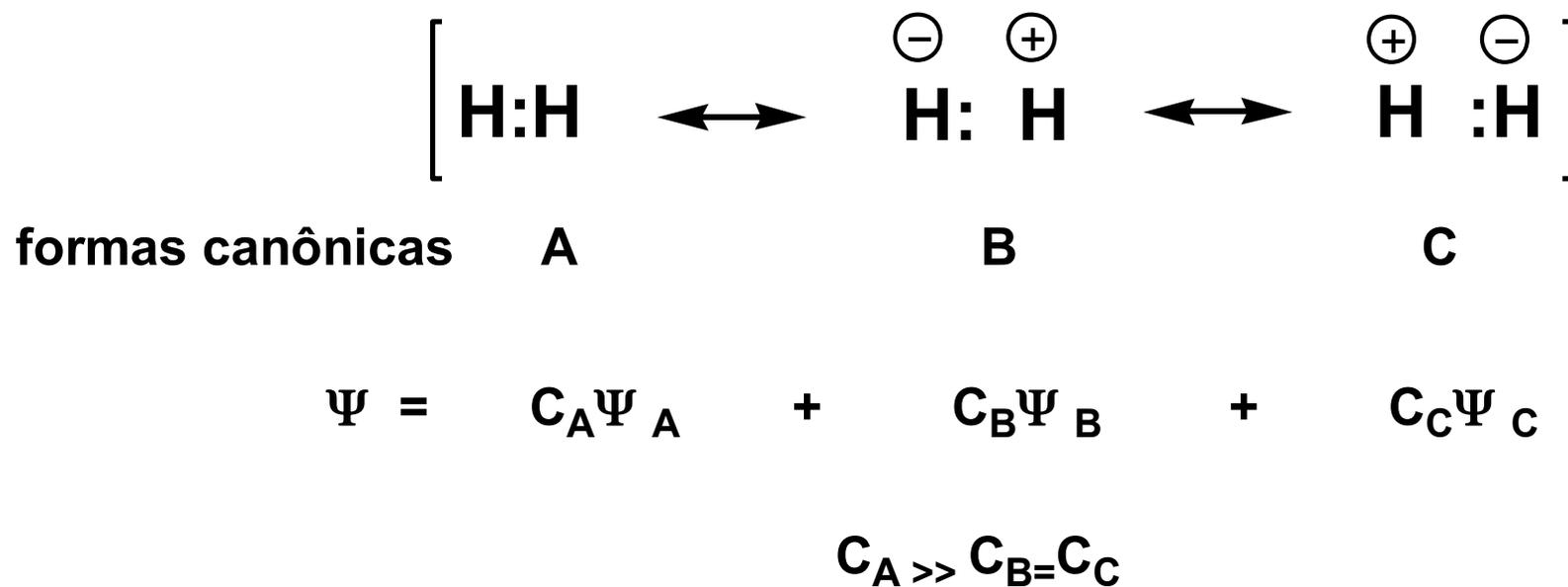


$$\Psi_{\sigma} = \Psi_1 + \Psi_2 \text{ (interação em fase)}$$

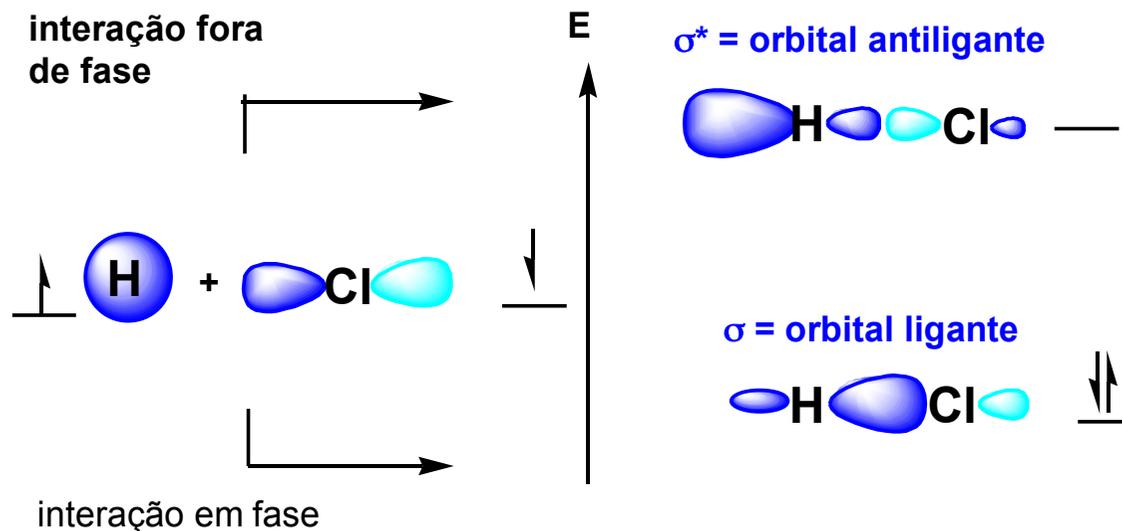
$$\Psi_{\sigma^*} = \Psi_1 - \Psi_2 \text{ (interação fora de fase)}$$

O Tratamento Mecânico Quântico da Molécula do Hidrogênio

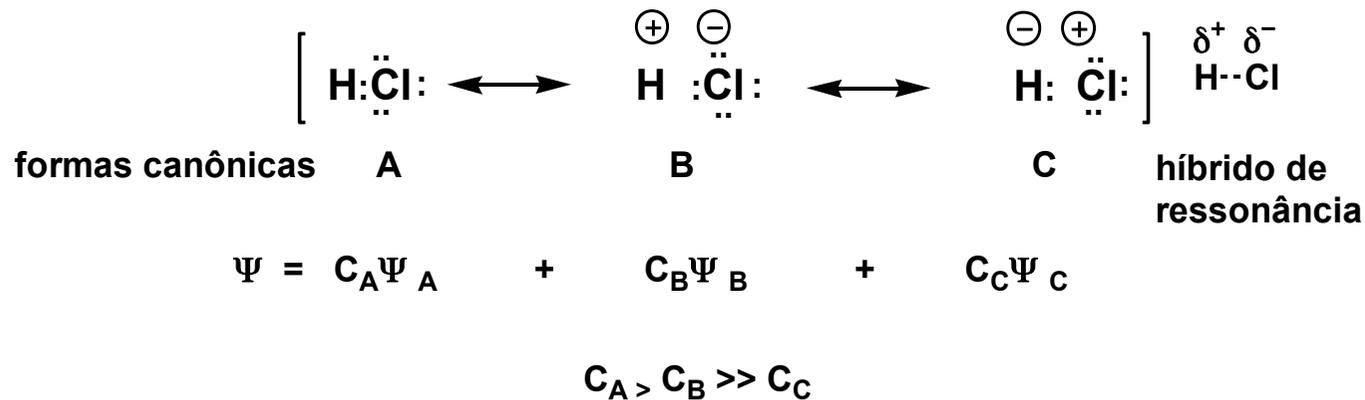
Teoria da Ligação de Valência



Molécula do HCl pelo Método do Orbital Molecular

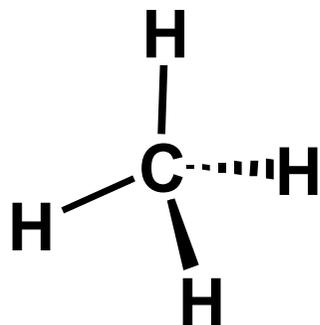


Molécula do HCl pelo Método da Teoria de Valência

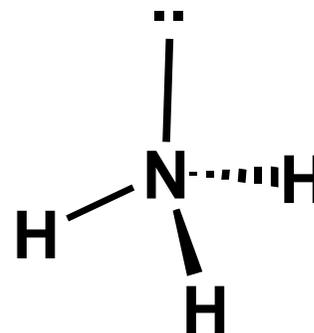


A contribuição da forma canônica B é mais importante neste caso, indicando que a ligação é polar.

Orbitais moleculares no metano e na amônia.

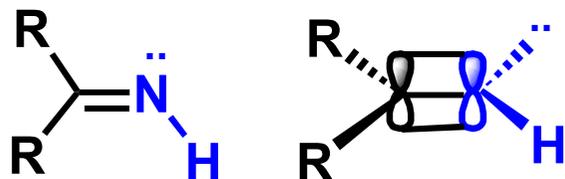


$\sigma^* 8$
 $\sigma^* 7$
 $\sigma^* 6$
 $\sigma^* 5$ **LUMO**
 $\sigma 4 \uparrow\downarrow$ **HOMO**
 $\sigma 3 \uparrow\downarrow$
 $\sigma 2 \uparrow\downarrow$
 $\sigma 1 \uparrow\downarrow$



$\sigma^* 6$
 $\sigma^* 5$
 $\sigma^* 4$ **LUMO**
 $n \uparrow\downarrow$ **HOMO**
 $\sigma 3 \uparrow\downarrow$
 $\sigma 2 \uparrow\downarrow$
 $\sigma 1 \uparrow\downarrow$

Orbitais moleculares em aldeídos, cetonas e iminas



σ^*8

σ^*7

σ^*6

σ^*5

π^* **LUMO**

n $\uparrow\downarrow$ **HOMO**

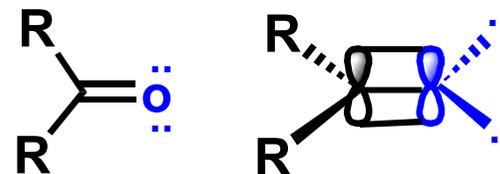
π $\uparrow\downarrow$

$\sigma4$ $\uparrow\downarrow$

$\sigma3$ $\uparrow\downarrow$

$\sigma2$ $\uparrow\downarrow$

$\sigma1$ $\uparrow\downarrow$



σ^*6

σ^*5

σ^*6

σ^*4

π^* **LUMO**

n $\uparrow\downarrow$ **HOMO**

n $\uparrow\downarrow$

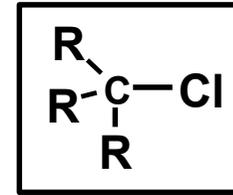
π $\uparrow\downarrow$

$\sigma3$ $\uparrow\downarrow$

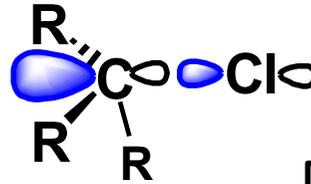
$\sigma2$ $\uparrow\downarrow$

$\sigma1$ $\uparrow\downarrow$

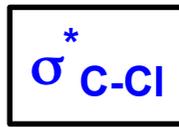
Orbitais Moleculares Ligantes e não-Ligantes
 σ e σ^* em Derivados Haçogendados



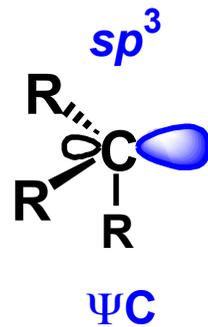
Orbital molecular σ^*



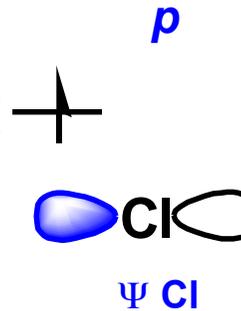
$$\Psi_C - \Psi_{Cl}$$



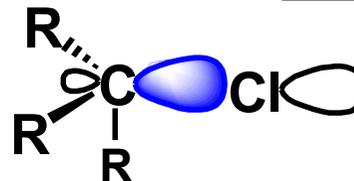
ENERGIA ↑



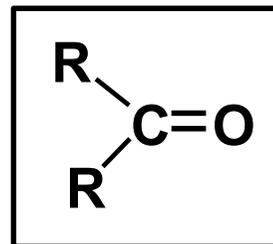
$$\Psi_C + \Psi_{Cl}$$



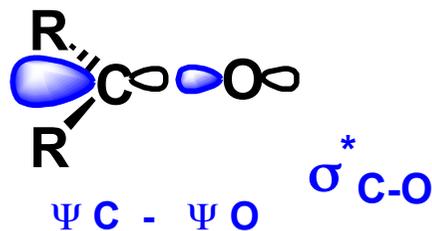
Orbital molecular σ



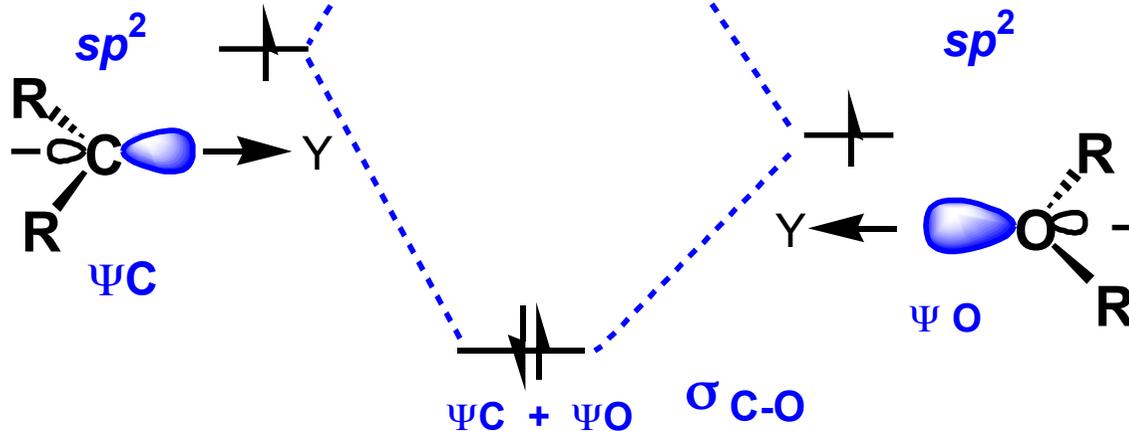
Orbitais Moleculares Ligantes e não-Ligantes
 σ e σ^* em Aldeídos e Cetonas



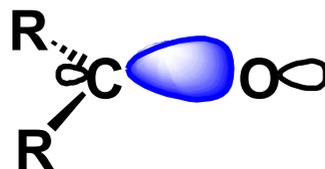
Orbital molecular σ^*



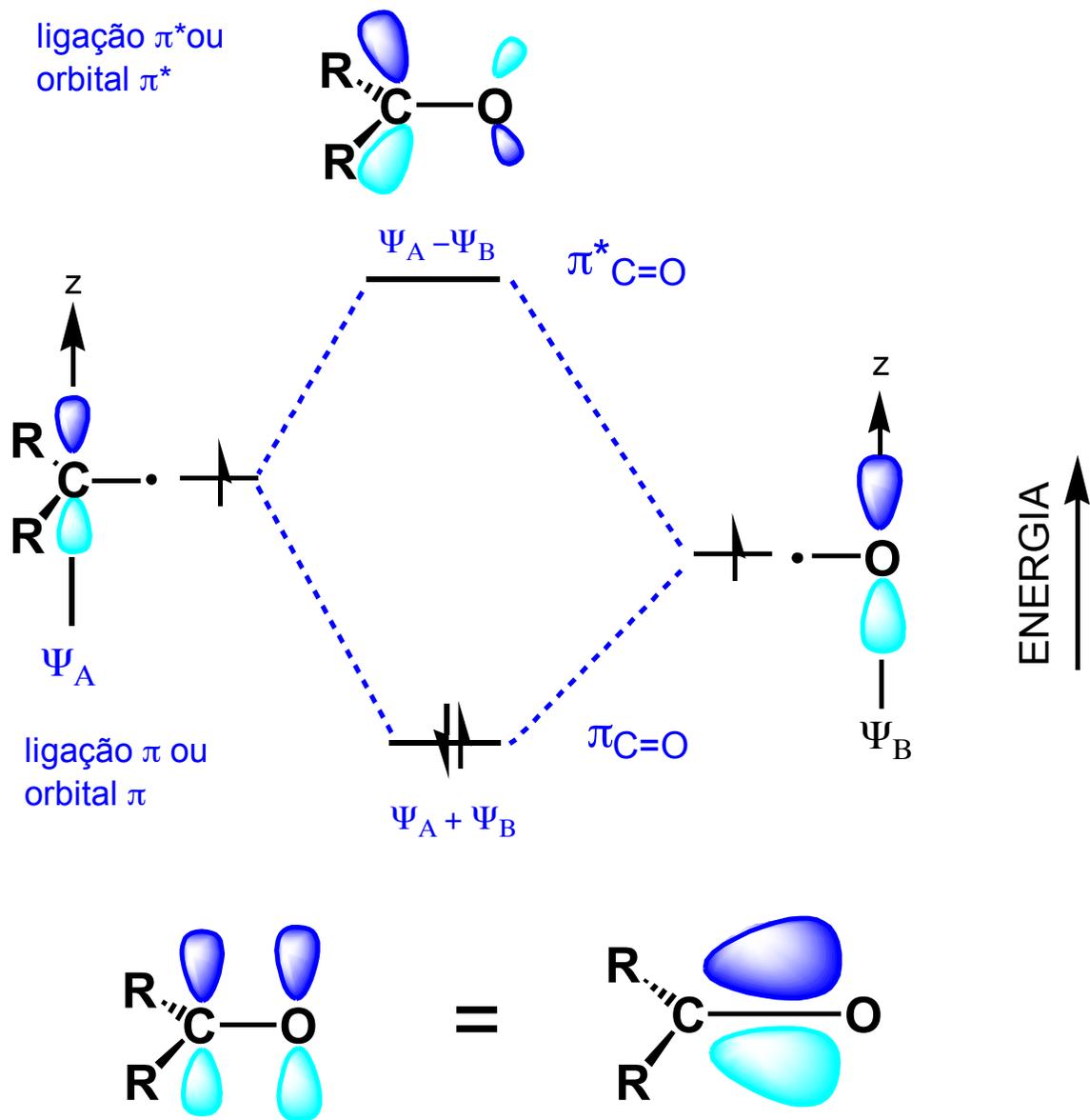
ENERGIA ↑



Orbital molecular σ



Orbitais Moleculares Ligante (π) e Antiligante (π^*) em Aldeídos e Cetona



Ácidos e Bases

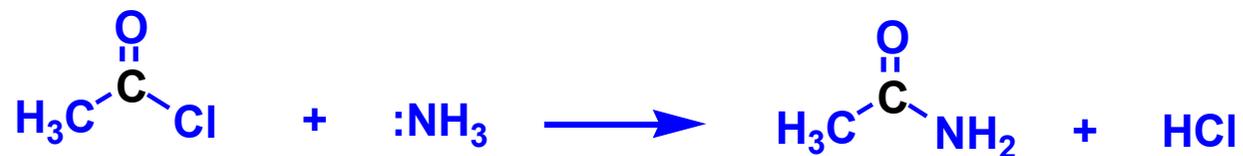
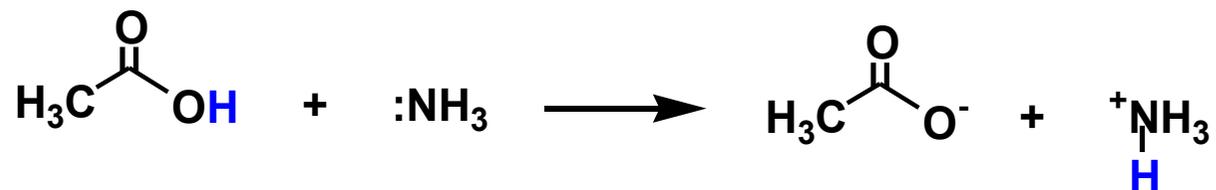
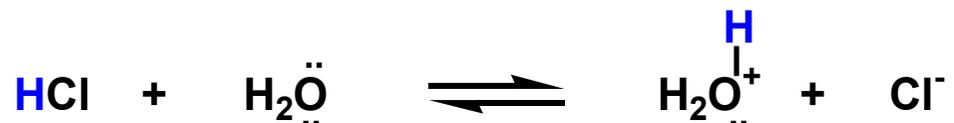
Eletrófilos e Nucleófilos

Ácidos e Eletrófilos

Aceitam um par de elétrons em uma reação química

Bases e Nucleófilos

Doam um par de elétrons em uma reação química



Acidez e Basicidade : Medidas termodinâmicas de afinidade pelo proton.

A posição do equilíbrio depende da estabilidade do ácido ou base conjugada, em geral espécies carregadas, e é fortemente afetada pelo solvente.

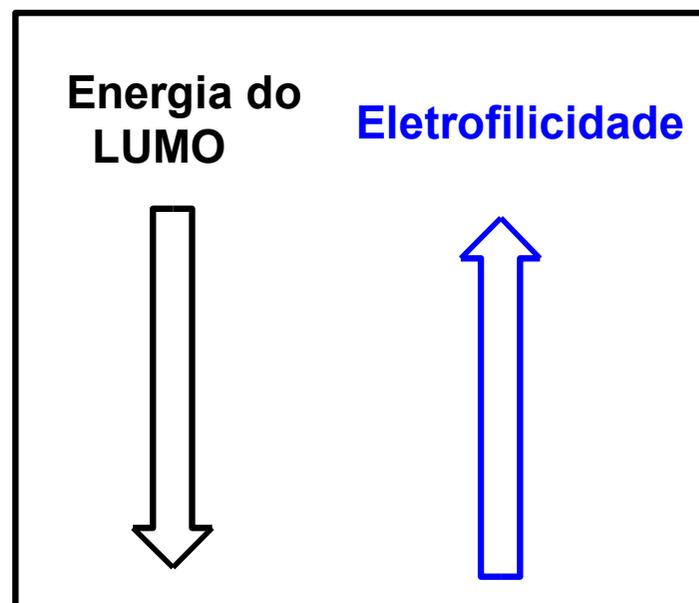
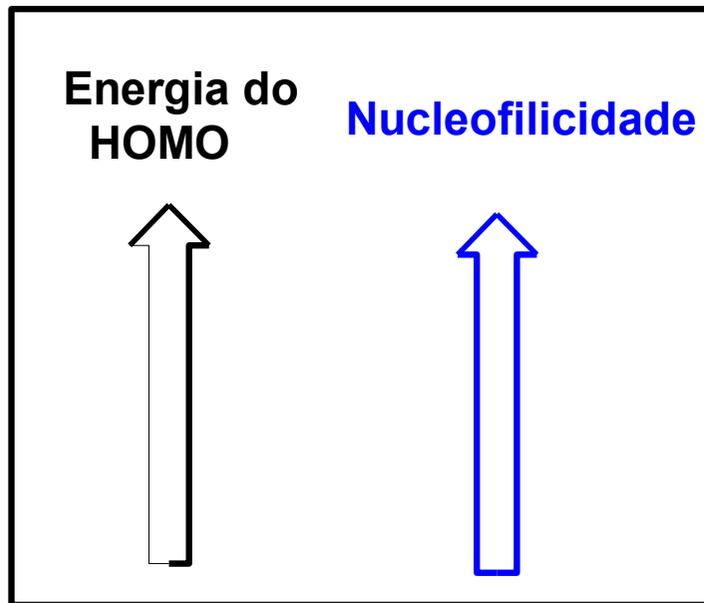
Eletrofilicidade e Nucleofilicidade : Medidas cinéticas de afinidade pelo carbono.

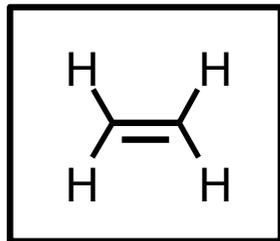
A velocidade depende dos orbitais de fronteira e, no caso de espécies carregadas, depende também do solvente.

Eletrofilicidade

e

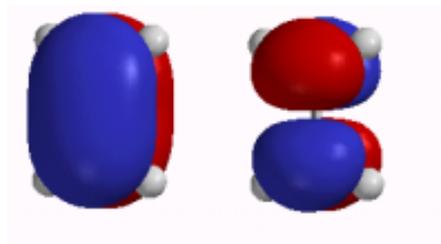
Nucleofilicidade





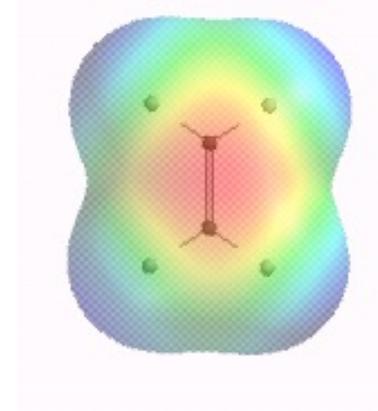
HOMO
Energia -10,55 eV

Coeficientes
C (+0,71)
C (+0,71)

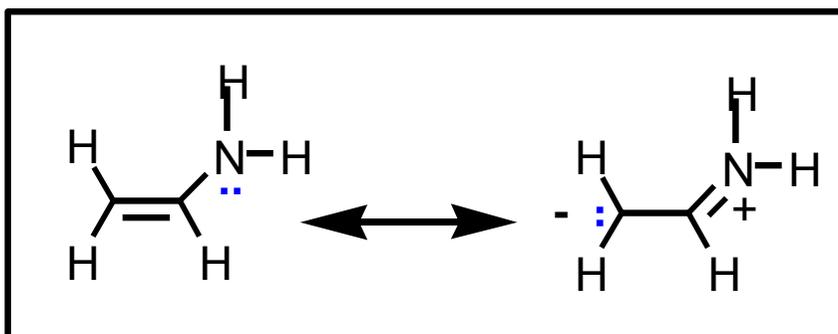


LUMO
Energia +1,44 eV

Coeficientes
C (+0,71)
C (-0,71)



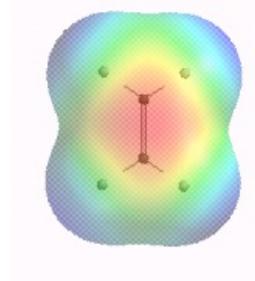
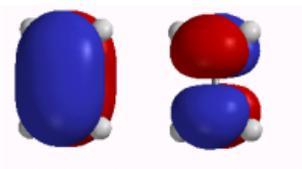
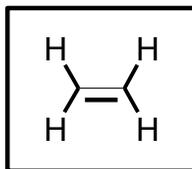
$\mu = 0$



HOMO
Energia -8,40 eV

Coeficientes

$C\alpha$	+0,69
C(N)	+0,37
N	-0,62



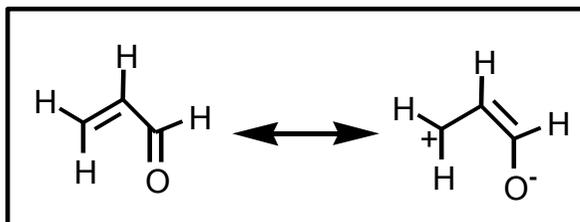
$$\mu = 0$$

HOMO
Energia -10,55 eV

LUMO
Energia +1,44 eV

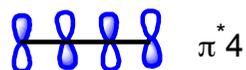
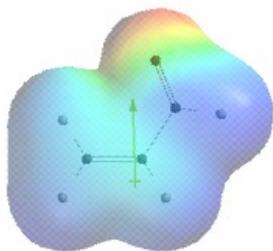
Coefficientes
C (+0,71)
C (+0,71)

Coefficientes
C (+0,71)
C (-0,71)

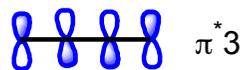


LUMO
Energia +0,05 eV

Coefficientes
O (+0,42)
C2 (-0,63)
C3 (-0,42)
C4 (+0,63)

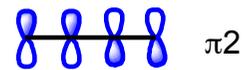


$\pi^* 4$

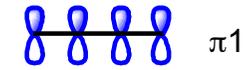


$\pi^* 3$

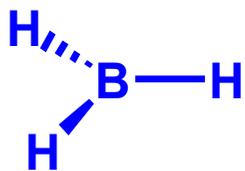
LUMO



$\pi 2$



$\pi 1$



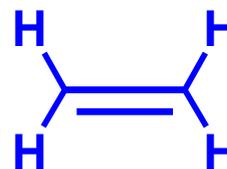
HOMO = -13.55560

LUMO = 1.01686

B (+1,22092)

H1 (+0,01234)

H2 (+0,01234) H3 (+0,01234)



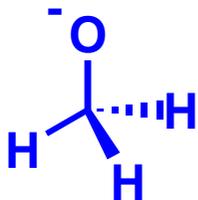
HOMO = -10,55

LUMO = 1.44

HOMO = -2.80472

C1 (-0,26192) H1 (-0,00581)

H2 (-0,46298) H3 (+0,46298) O1 (+1,21992)



LUMO = 6.05231

C1 (+4,61599)

H1 (-1,08561)

H2 (-1,08798)

H3 (-1,08798)

O1 (+0,83186)



HOMO = -0,57273

C1 (1,67087) H1 (-0,12015) H2 (-0,12258) H3 (-0,12258)



HOMO = -1,27401

N (1,29502) H1 (+0,0302) H2 (+0,0302)



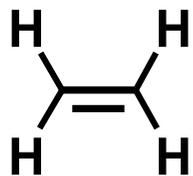
HOMO = -2,86661

O1 (+1,28958) H1 (+0,03501)



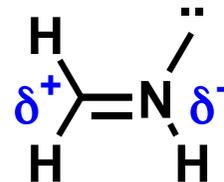
HOMO = -4,82645

F (+1,86366)



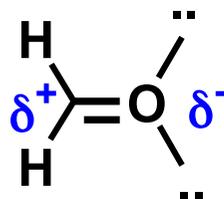
LUMO 2,29

HOMO -10,22



LUMO 1,31

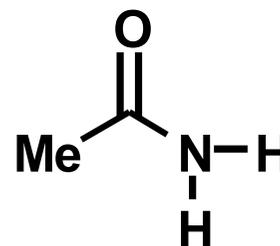
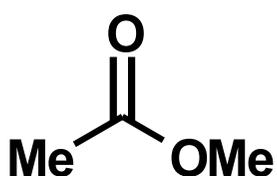
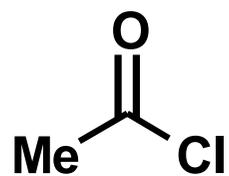
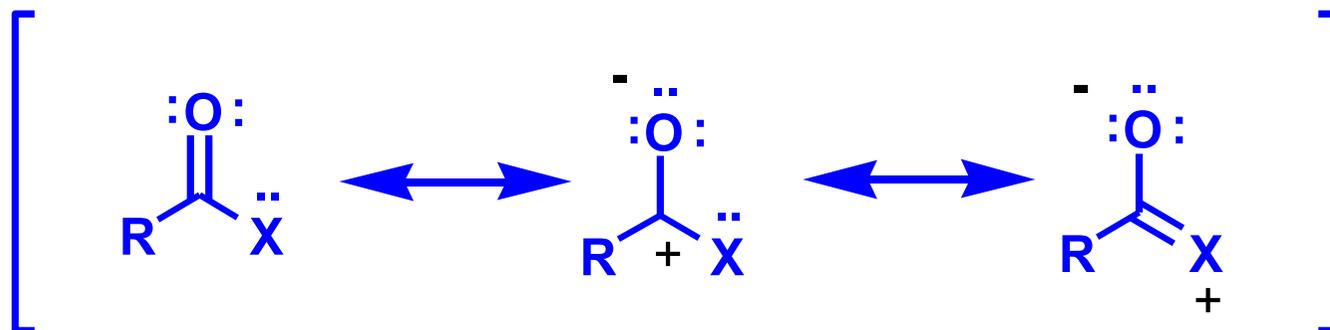
HOMO -10,55



LUMO 0,79

HOMO -12,10

Contribuição das formas canônicas dependem da eletronegatividade de X e de seu volume.



LUMO

+0,19

+1,10

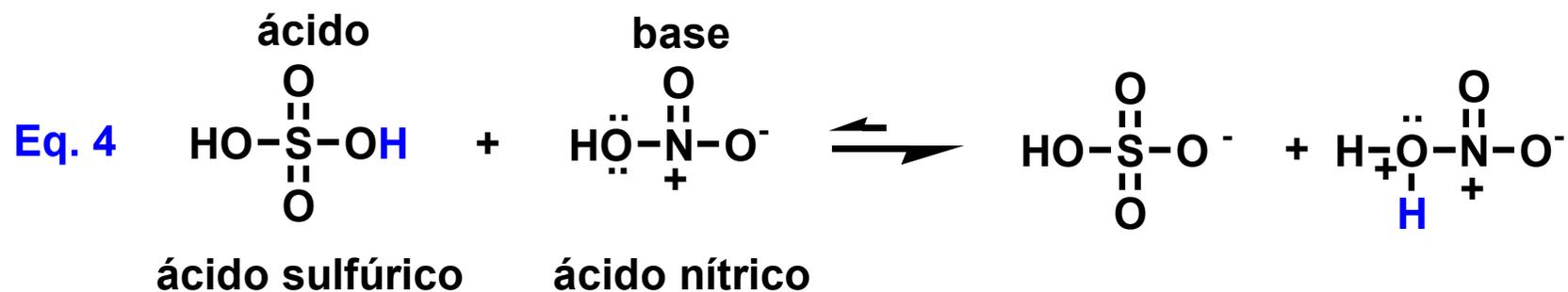
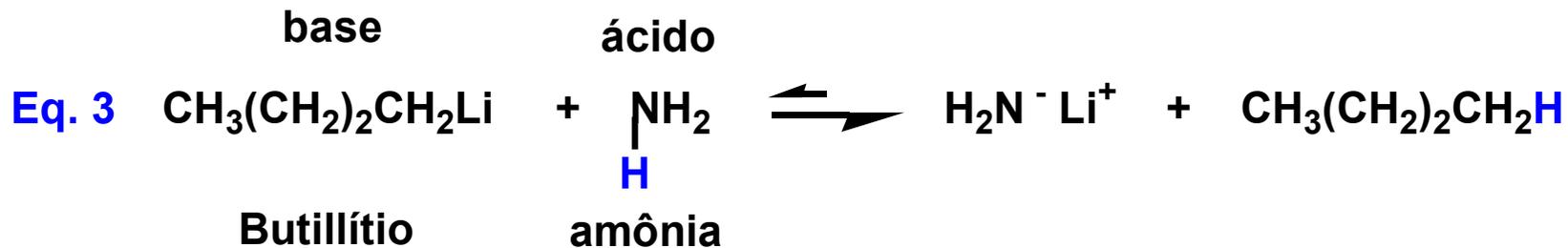
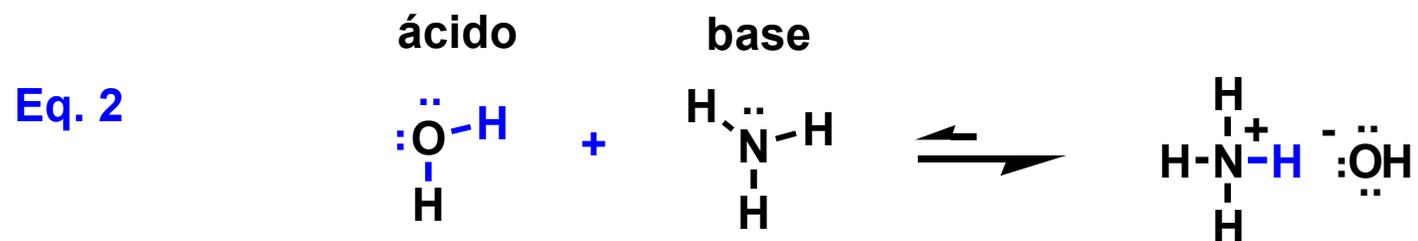
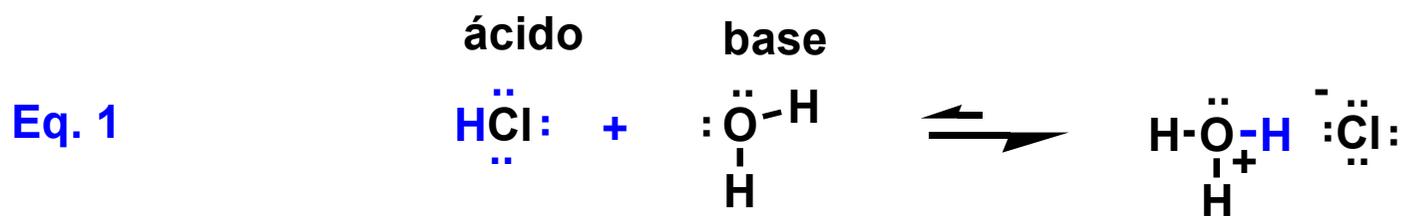
+1,44

Ácidos e Bases

Ácido de Lewis: uma espécie aceptora de elétrons.

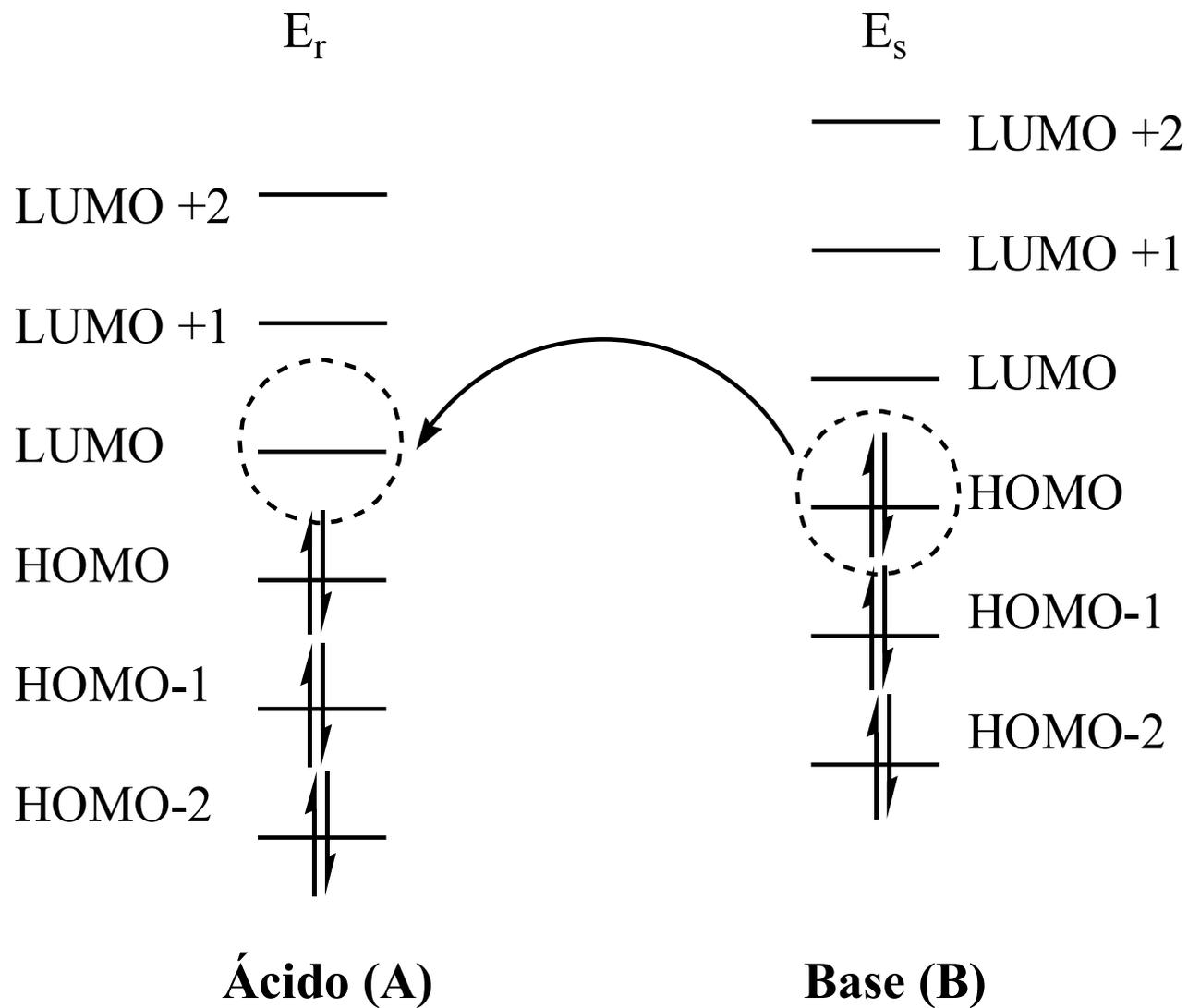
Base de Lewis: uma espécie doadora de elétrons.

Exemplos de reações ácido-base

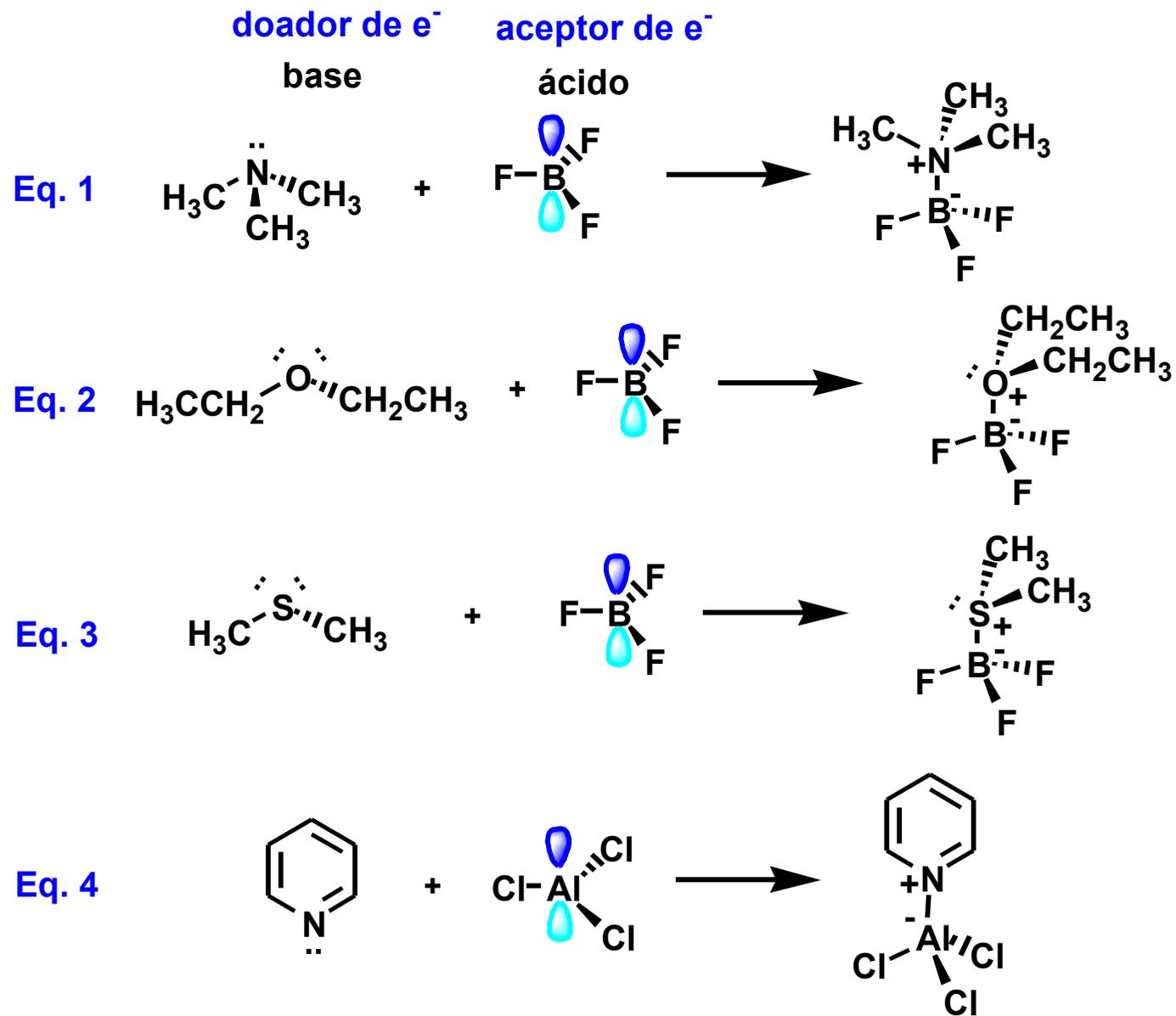


Potencial de ionização
PI = -E do HOMO

Afinidade eletrônica (AE) = -E do LUMO



Alguns ácidos de Lewis e suas reações com espécies doadoras de elétrons



Seletividade de ácidos de Lewis frente a bases

Ácidos Duros e Moles : A Teoria de Pearson

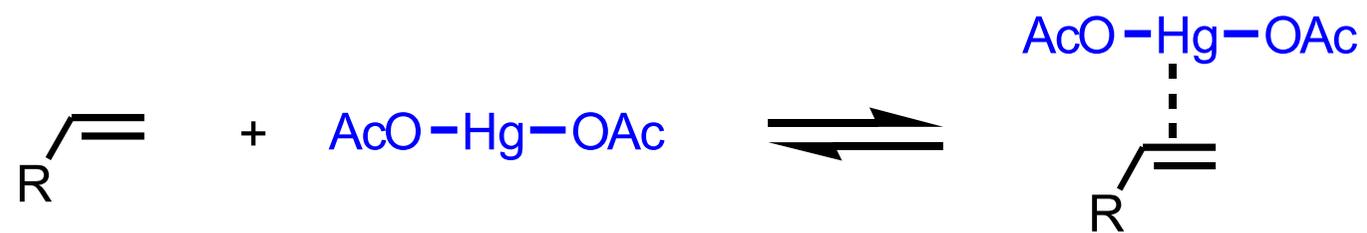
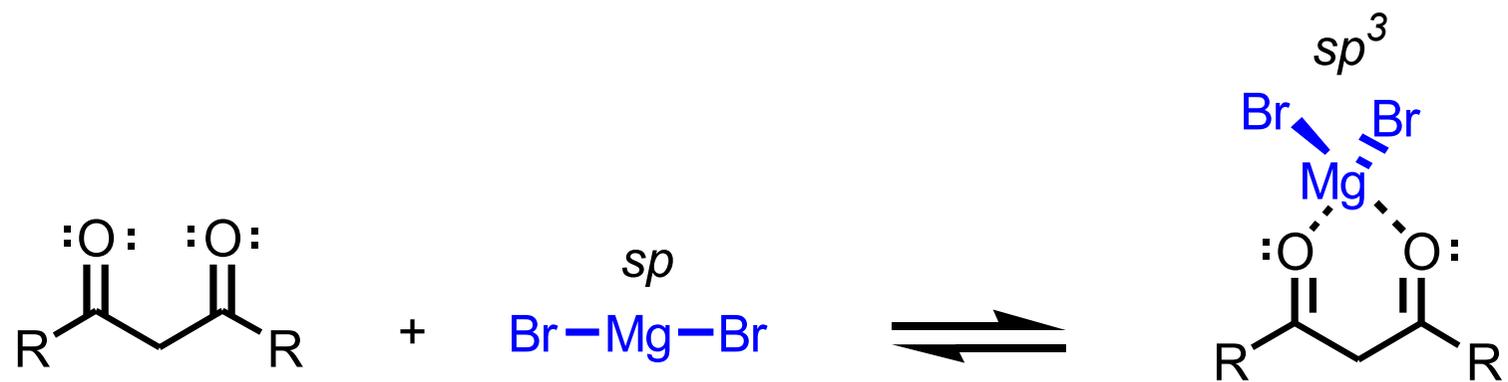


Figura 1.1 Algumas bases de Lewis moles, segundo a teoria de Pearson

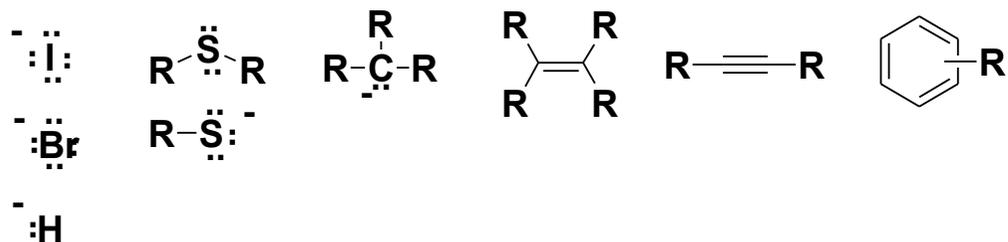


Figura 1.2 Algumas bases de Lewis duras

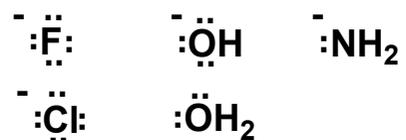


Figura 1.3 Alguns ácidos de Lewis duros

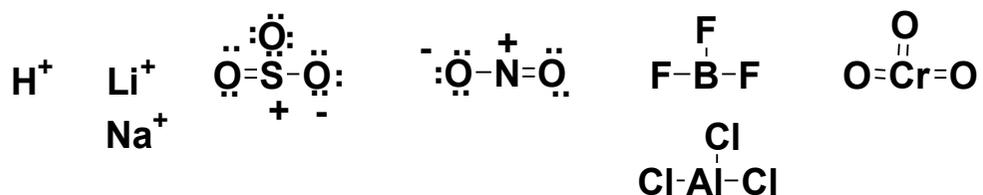


Figura 1.4 Alguns ácidos de Lewis moles

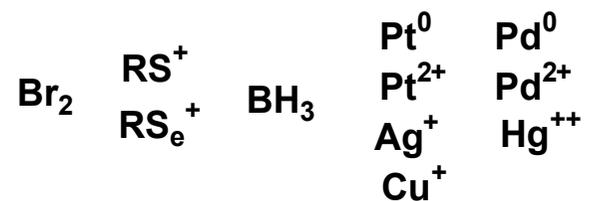
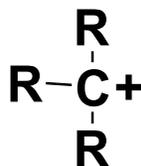
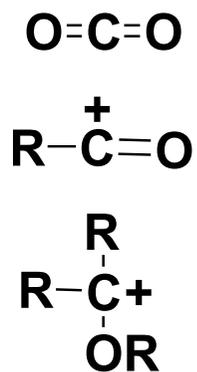
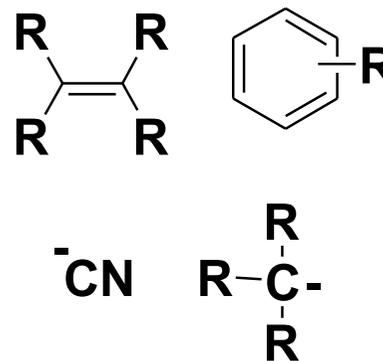


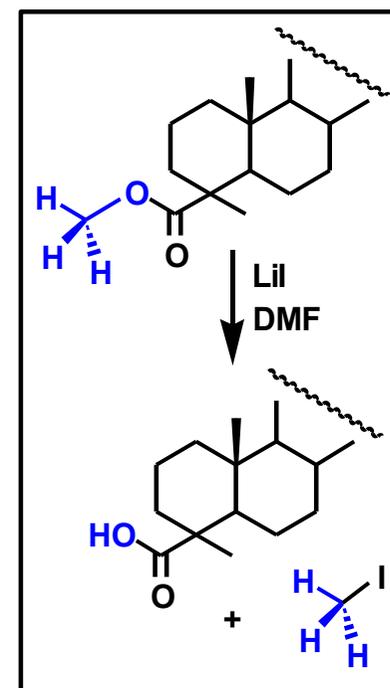
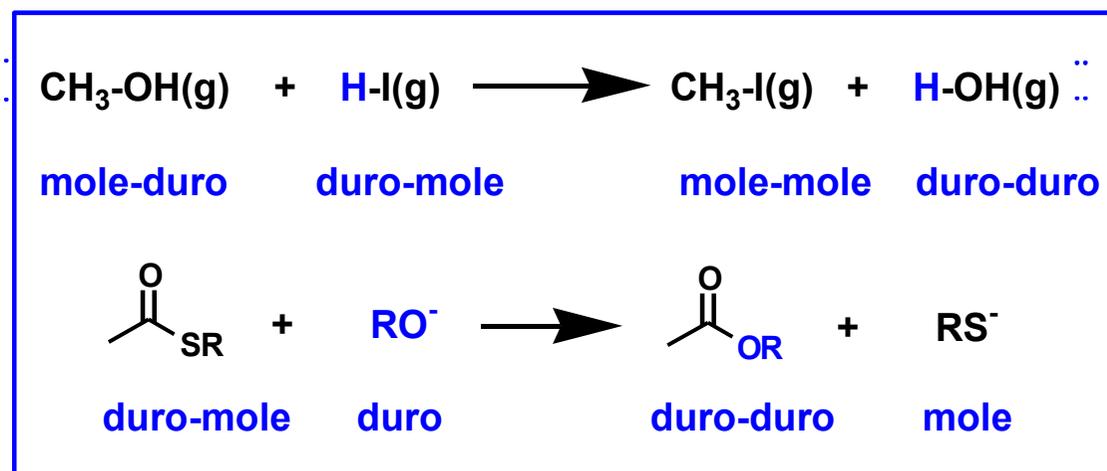
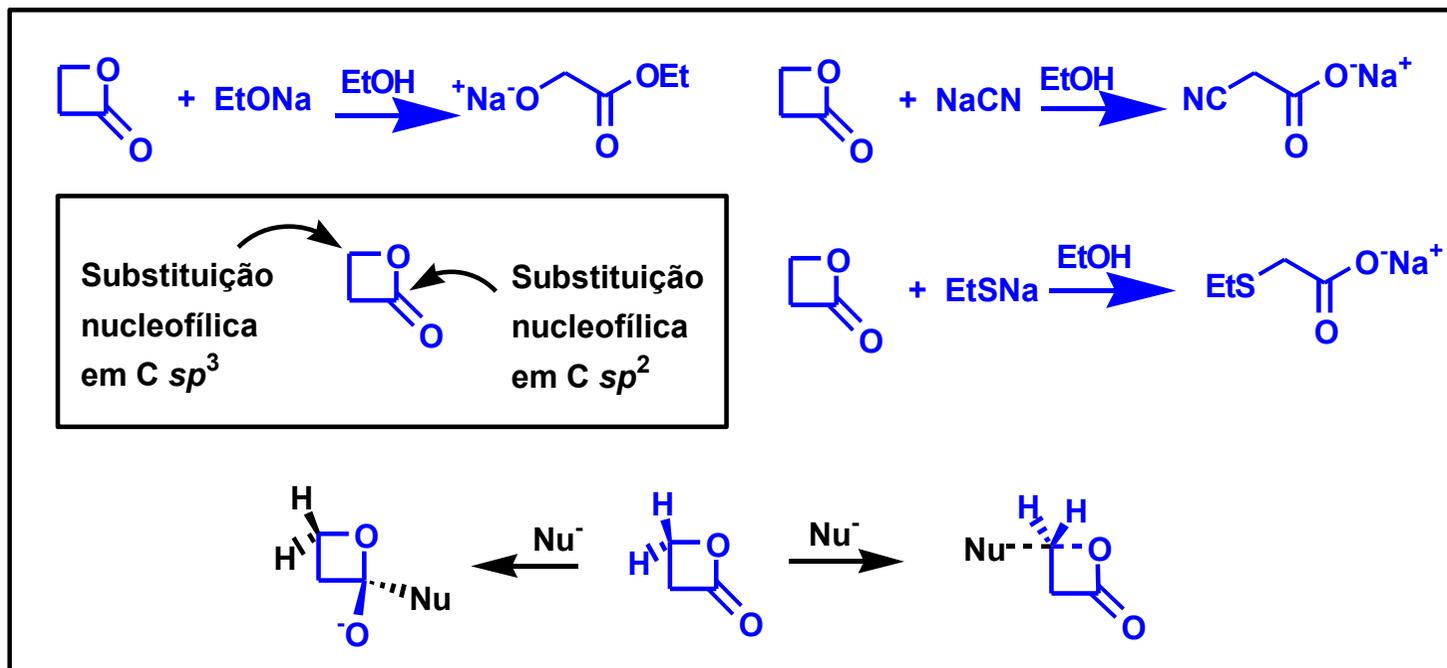
Figura 1.5 Substâncias e íons onde o carbono funciona como ácido ou base de Lewis

ácidos duros ácidos intermediários



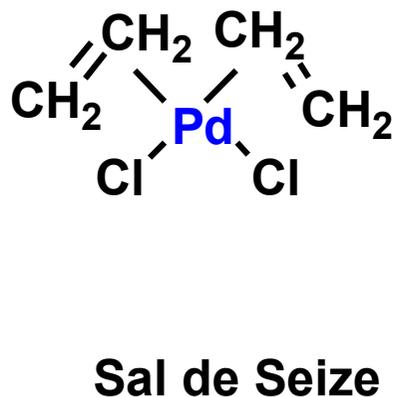
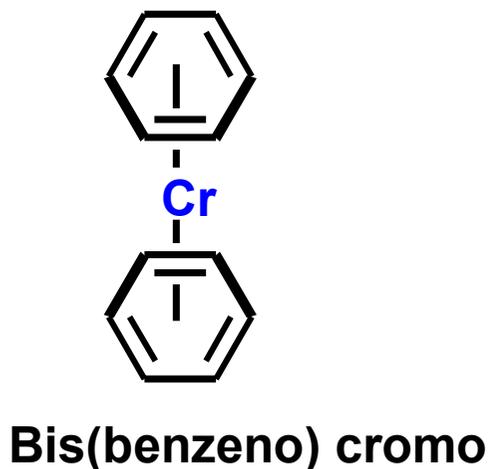
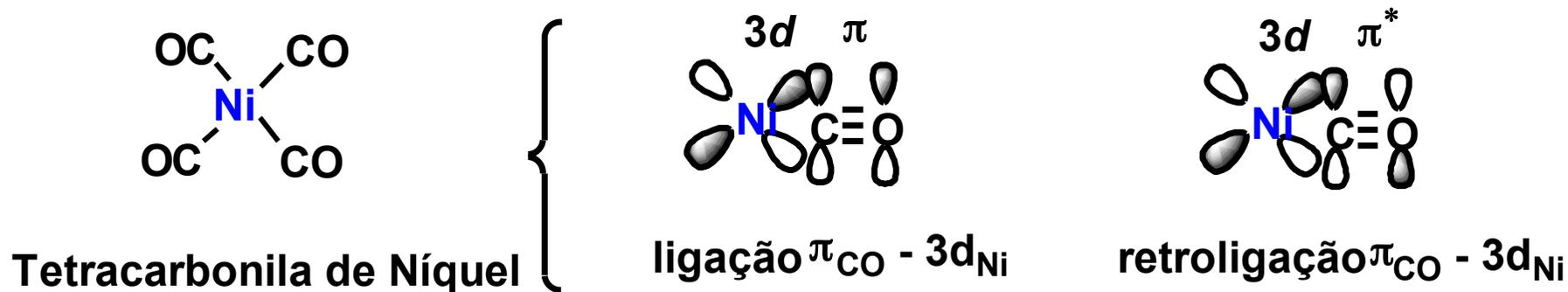
base moles







Organometálicos: Interação ácido-base netre os ligantes e os metais



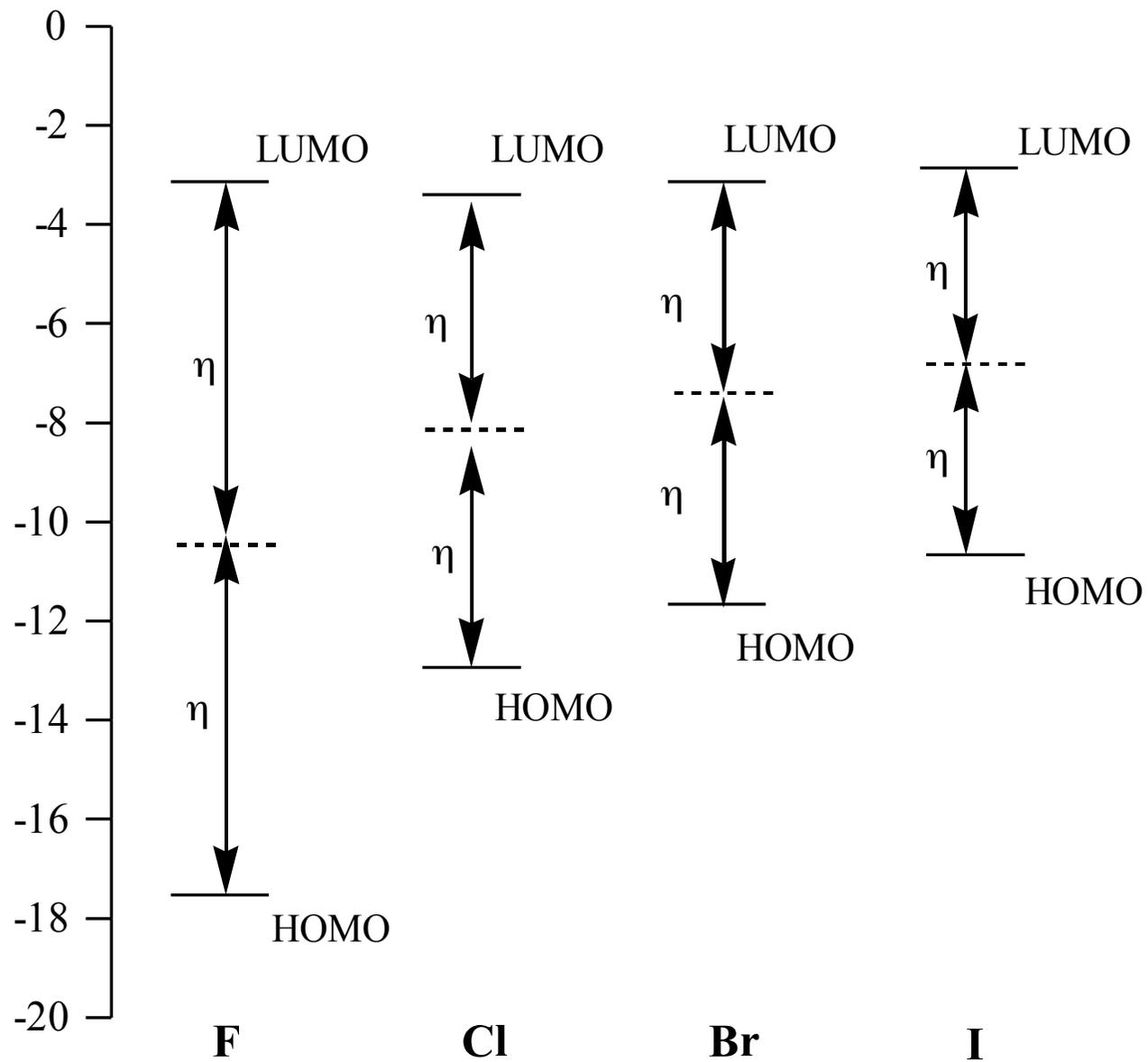
n^0 de elétrons na última
camada do elemento

Cr = 6; Pd = 8; Ni = 10

n^0 de elétrons na última
camada na presença
do ligante

Cr = 18; Pd = 14; Ni = 18

Energia (eV)



Bases (nucleófilos) Duros

H₂O, -OH, F⁻

MeCO₂⁻, PO₄⁻³, SO₄^{-?},

Cl⁻, CO₃⁻, ClO₄⁻, NO₃⁻

ROH, RO⁻, R₂O

Bases Moles

NH₃, RNH₂, N₂O₄

R₂S⁻, RSH, -SH

I⁻, SCN⁻, S₂O₃⁻²

R₃P, R₃As, (RO)₃P

CN⁻, RCN, CO

C₂H₄, C₆H₆

H⁻, R⁻

Bases de fronteira

PhNH₂, C₅H₅N, N₃⁻, Br⁻

NO₂⁻, SO₃

Ácidos de fronteira

Fe₂⁺, Co₂⁺, Ni₂⁺, Cu₂⁺, Zn₂⁺,

Pb₂⁺, Sn₂⁺, BMe₃, SO₂, NO⁺,

R₃C⁺, C₆H₅⁺

Ácidos (eletrófilos) Duros

H⁺, Li⁺, Na⁺, K⁺

Be₂⁺, Mg₂⁺, Ca₂⁺

Al₃⁺, Ga₃⁺

Cr₃⁺, Co₃⁺, Fe₃⁺

CH₃Sn₃⁺

Si₄⁺, Ti₄⁺

Ce₃⁺, Ti₄⁺

(CH₃)₂Sn₂⁺

BeMe₂, BF₃, B(RO)₃

AlMe₃, AlCl₃, AlH₃

RPO₂⁺, ROPO₂⁺

RSO₂⁺, ROSO₂⁺, SO₃

I₇⁺, I₅⁺, Cl₇⁺, Cr₆⁺

RCO⁺, CO₂, NC⁺

HX (moléculas com capacidade de fazer ligações hidrogênio)

Ácidos Moles

Cu⁺, Ag⁺, Au, Tl, Hg

Pd₂⁺, Cd₂⁺, Pt₂⁺, Hg₂⁺, MeHg⁺, CO(CN)₅⁻²

Tl₃⁺, Tl(CH₃)₃, BH₃

RS⁺, RSe⁺, RTe⁺

I⁺, Br⁺, HO⁺, RO⁺

I₂, Br₂, ICN

Trinitrobenzeno

Cloranil, quinonas

(NC)₂=C(CN)₂, etc

O, Cl, Br, I, N, RO., RO₂.

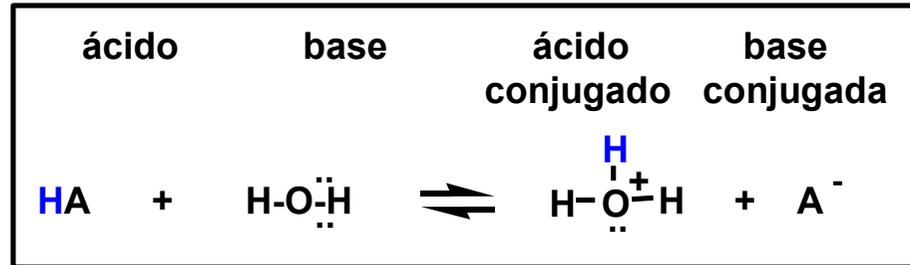
Mo (metais)

CH₂, carbenos

$$E_{\text{interação}} = - \sum_{ab} (q_a + q_b) \beta_{ab} S_{ab} \quad + \quad \sum_{k < l} \frac{q_k q_l}{\epsilon r_{kl}} \quad + \quad \sum_r^{\text{ocup}} \sum_s^{\text{não-ocup}} - \sum_r^{\text{ocup}} \sum_s^{\text{não-ocup}} \frac{2(\sum_{ab} c_{ra} c_{sb})^2}{E_r - E_s}$$

Ocupado – Ocupado *Eletrostático* *Sobreposição Orbital*

A constante de acidez em meio aquoso



HA mais ácido do que H₃O⁺, reação deslocada no sentido da dissociação

HA = H₃O⁺, 50% de dissociação

HA menos ácido do que H₃O⁺, a dissociação não ocorre ou ocorre em pequena extensão

$$K_{\text{eq}} = \frac{|\text{A}^-| |\text{H}_3\text{O}^+|}{|\text{HA}| |\text{H}_2\text{O}|} ; \quad \text{como } K_a = K_{\text{eq}} [\text{H}_2\text{O}] , \quad K_a = \frac{|\text{A}^-| |\text{H}_3\text{O}^+|}{|\text{HA}|}$$

A correlação entre a energia livre de Gibbs e a constante de acidez

$$\Delta G^\circ = -2,303RT \log K_a$$

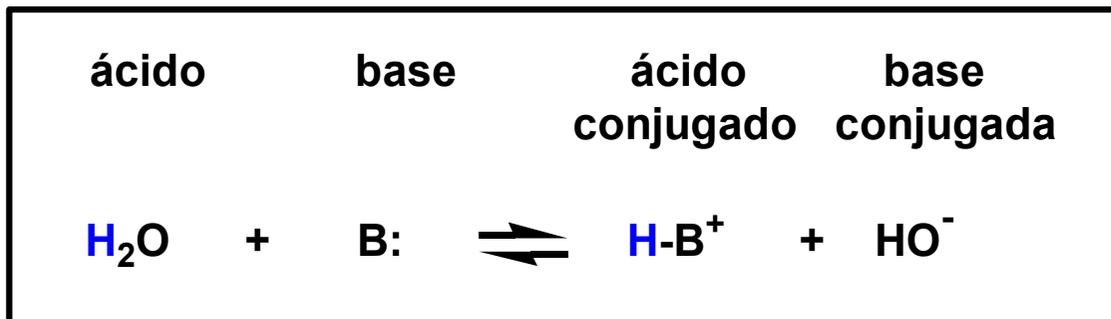
$$R = 1,987 \text{ cal.mol}^{-1}.\text{K}^{-1}$$

$$T = 298\text{K}$$

$$\text{p}K_a = -\log K_a$$

$$\Delta G^\circ \sim 1,4 \text{ p}K_a$$

A constante de basicidade em meio aquoso



Se B é base mais forte que HO^- , reação dirigida no sentido da dissociação

B = HO^- , 50% de dissociação

Se B é base mais fraca que HO^- , a dissociação não ocorre ou ocorre em pequena extensão

$$K_b = \frac{[\text{H-B}^+].[\text{HO}^-]}{[\text{B:}]}$$



$$K_a = \frac{[\text{H}_3\text{O}^+][\text{A}^-]}{[\text{HA}]}$$

A equação de Henderson-Hasselbalch

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{A}^-]}{[\text{HA}]} \implies -\log K_a = -\log \left(\frac{[\text{H}_3\text{O}^+][\text{A}^-]}{[\text{HA}]} \right) \implies$$

$$\text{pKa} = -\log [\text{H}_3\text{O}^+] - \log \frac{[\text{A}^-]}{[\text{HA}]} \xrightarrow[\text{-log } [\text{H}_3\text{O}^+] = \text{pH}]{-\log K_a = \text{pKa}} \text{pKa} = \text{pH} - \log \frac{[\text{A}^-]}{[\text{HA}]}$$

$$\text{pKa} = \text{pH} + \log \frac{[\text{HA}]}{[\text{A}^-]}$$

$$pK_a = pH + \frac{[HA]}{[A^-]} \quad \text{quando } [HA] = [A^-] \quad ; \quad pK_a = pH$$

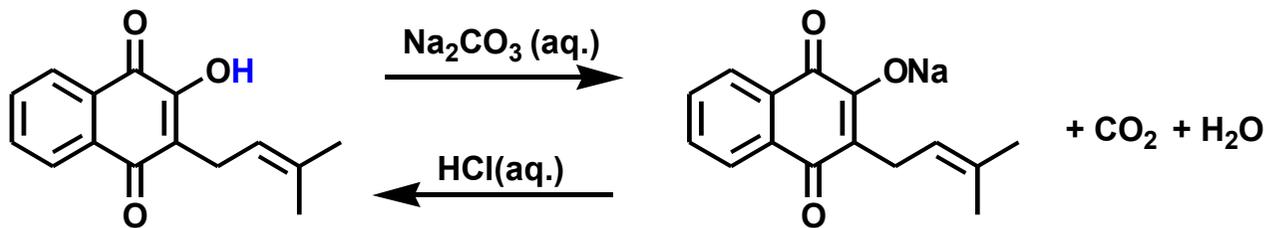
$$\log 1 = 0$$

Se o pKa de HA é igual a 5 a extensão da ionização em tampão de pH = 7 é:

$$5 = 7 + \log \frac{[HA]}{[A^-]}, \quad -2 = \log \frac{[HA]}{[A^-]}, \quad 2 = \log \frac{[A^-]}{[HA]}, \quad 100 = \frac{[A^-]}{[HA]}$$

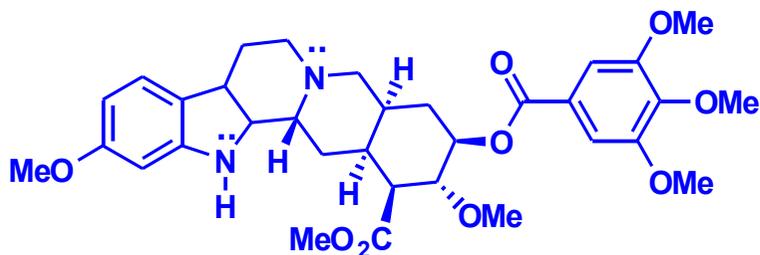
Se o pKa de HA é igual a 5 a extensão da ionização em tampão de pH = 3 é:

$$5 = 3 + \log \frac{[HA]}{[A^-]}, \quad 2 = \log \frac{[HA]}{[A^-]}, \quad 100 = \frac{[HA]}{[A^-]}$$

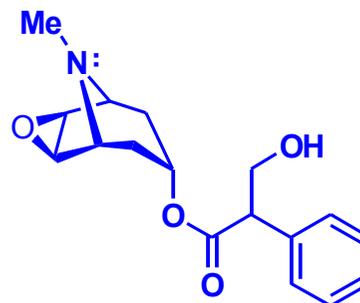


lapachol
 amarelo claro
 insolúvel em água

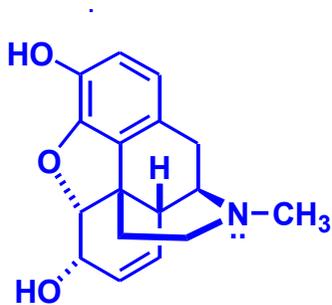
lapacholato de sódio
 vermelho
 sóluvel em água



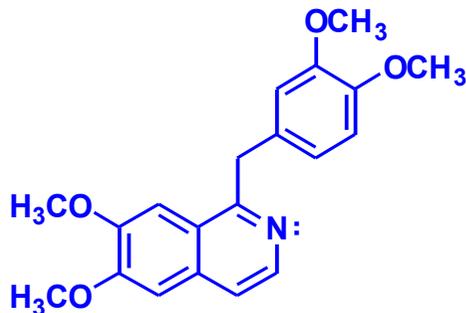
Reserpina (*Rauwolfia serpentina*. Benth)
 isolada em 1952, ainda usada no controle da hipertensão



Hyoscina (*Atropa belladonna*)
 Usada no tratamento da asma
 e como hipnótico e sedativo



Morfina (papola)
 Analgésico

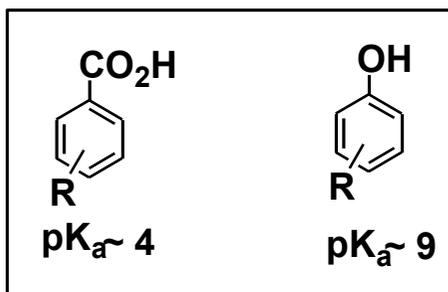
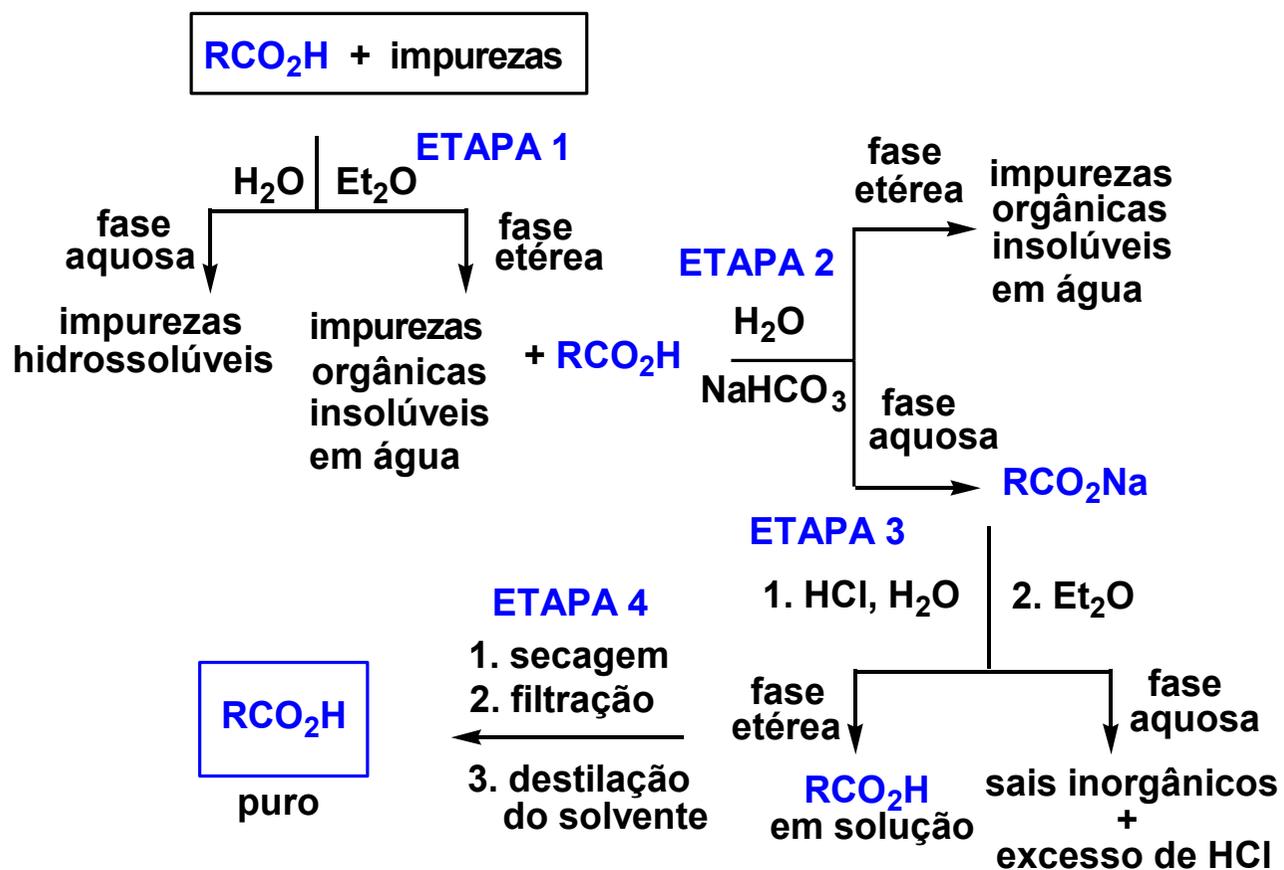


Papaverina (papola)
 Vasodilatador cerebral



(S)-Nicotina (fumo)
 Bioligante de receptores
 nicotínicos

A Extração Ácido-Base na Purificação de Ácidos Carboxílicos



A correlação entre a energia livre de Gibbs e a constante de acidez

$$\Delta G^\circ = -2,303RT \log K_a$$

$$R = 1,987 \text{ cal.mol}^{-1}.\text{K}^{-1}$$

$$T = 298\text{K}$$

$$\text{p}K_a = -\log K_a$$

$$\Delta G^\circ \sim 1,4 \text{ p}K_a$$

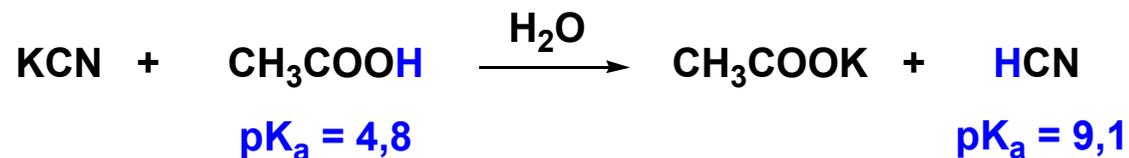
$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

Entropia, entalpia e energia livre em solução

Os valores de ΔG° são calculados com os reagentes e produtos em condições padrão (1 atm, 298K, para os gases e 1M para soluções). Reações com valores de ΔG° mais negativos que -3,11 Kcal/mol (13 KJ mol⁻¹) estão completamente deslocadas na direção dos produtos, enquanto que para reações com valores de ΔG° mais positivo que +3,11 estão completamente deslocadas na direção dos reagentes.

Uma variação negativa de entalpia ($-\Delta H^\circ$) contribui para um valor negativo (favorável) de energia livre. Por outro lado, uma mudança negativa de entropia ($-\Delta S^\circ$), saindo de um sistema menos ordenado para um mais ordenado, tende o valor de ΔG° para positivo (desfavorável). Por outro lado, uma mudança entrópica positiva, saindo de um sistema mais ordenado para um mais desordenado ($+\Delta S^\circ$), contribui para um valor de ΔG° negativo (favorável).

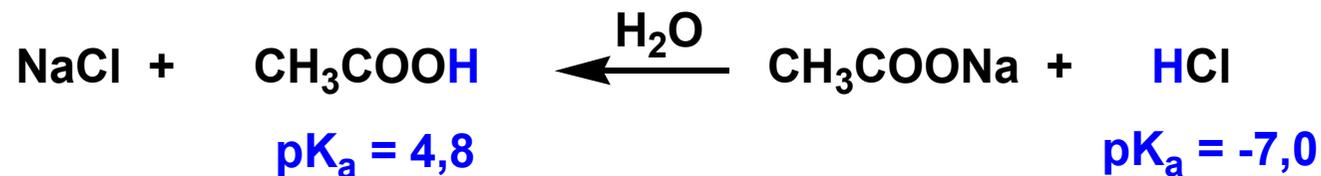
A posição do equilíbrio na reação do cianeto de potássio e ácido acético



$$\Delta\text{pK}_a = \text{pK}_{a1} - \text{pK}_{a2}; \quad 4,8 - 9,1 = -4,3$$

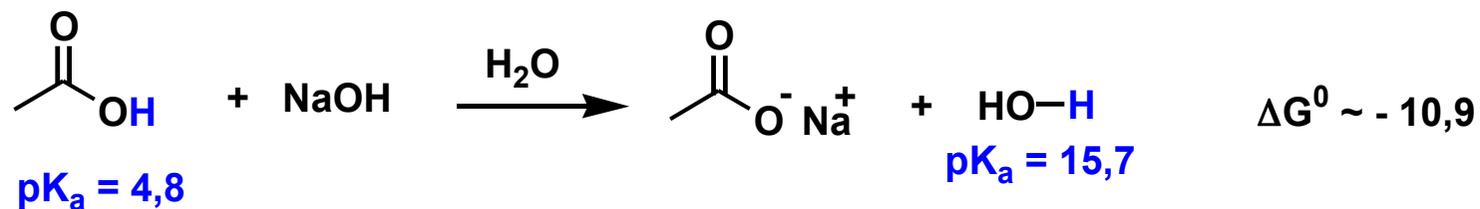
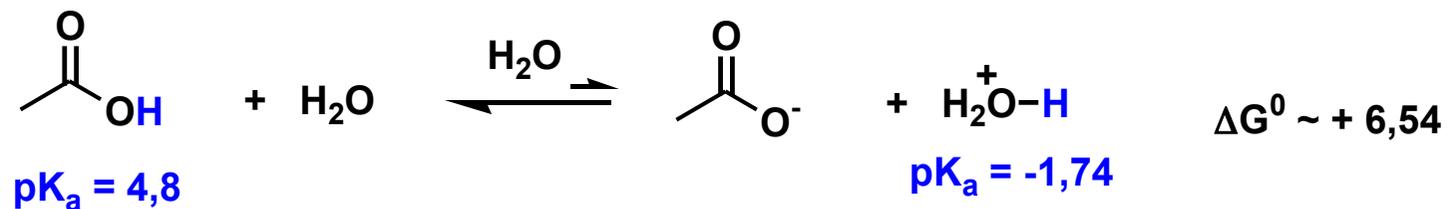
$$\Delta\text{G}^0 = 1,4 \text{ pK}_a = -6,02$$

A posição do equilíbrio na reação do cloreto de sódio com o ácido acético

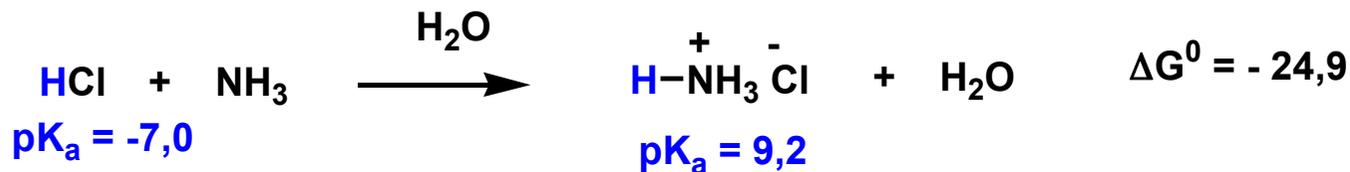
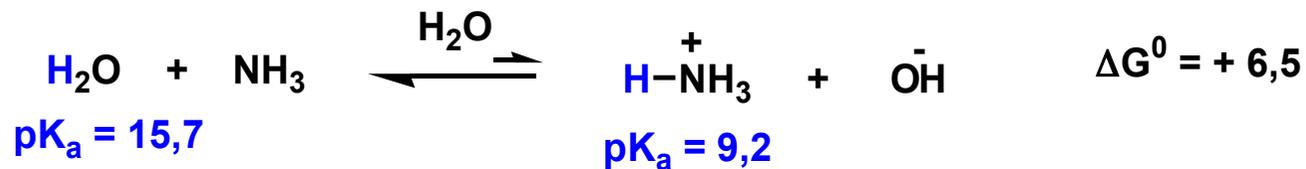


$$\Delta\text{pK}_a = \text{pK}_{a1} - \text{pK}_{a2}; \quad 4,8 - (-7) = +11,8 \quad \Delta\text{G}^0 = +15,5$$

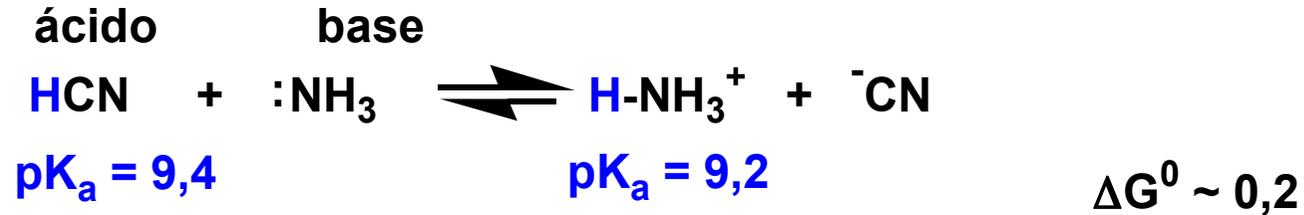
Dissociação do ácido acético em água e água/hidróxido de sódio



Protonação da amônia em água e água/ácido clorídrico



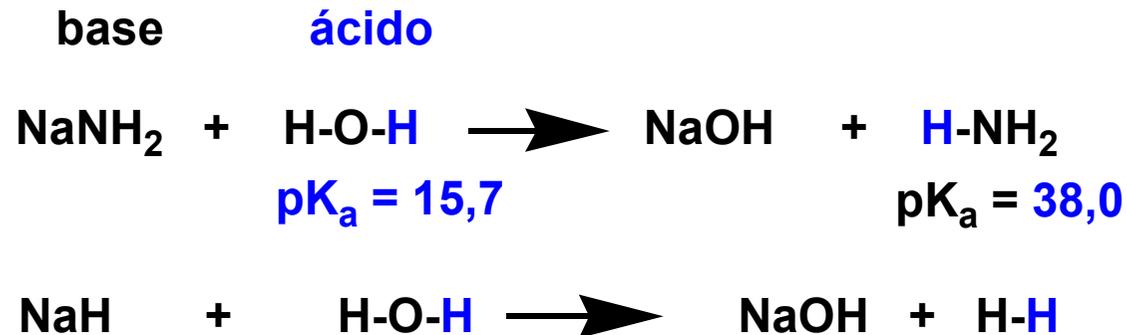
Constante de equilíbrio da reação entre ácido cianídrico e amônia



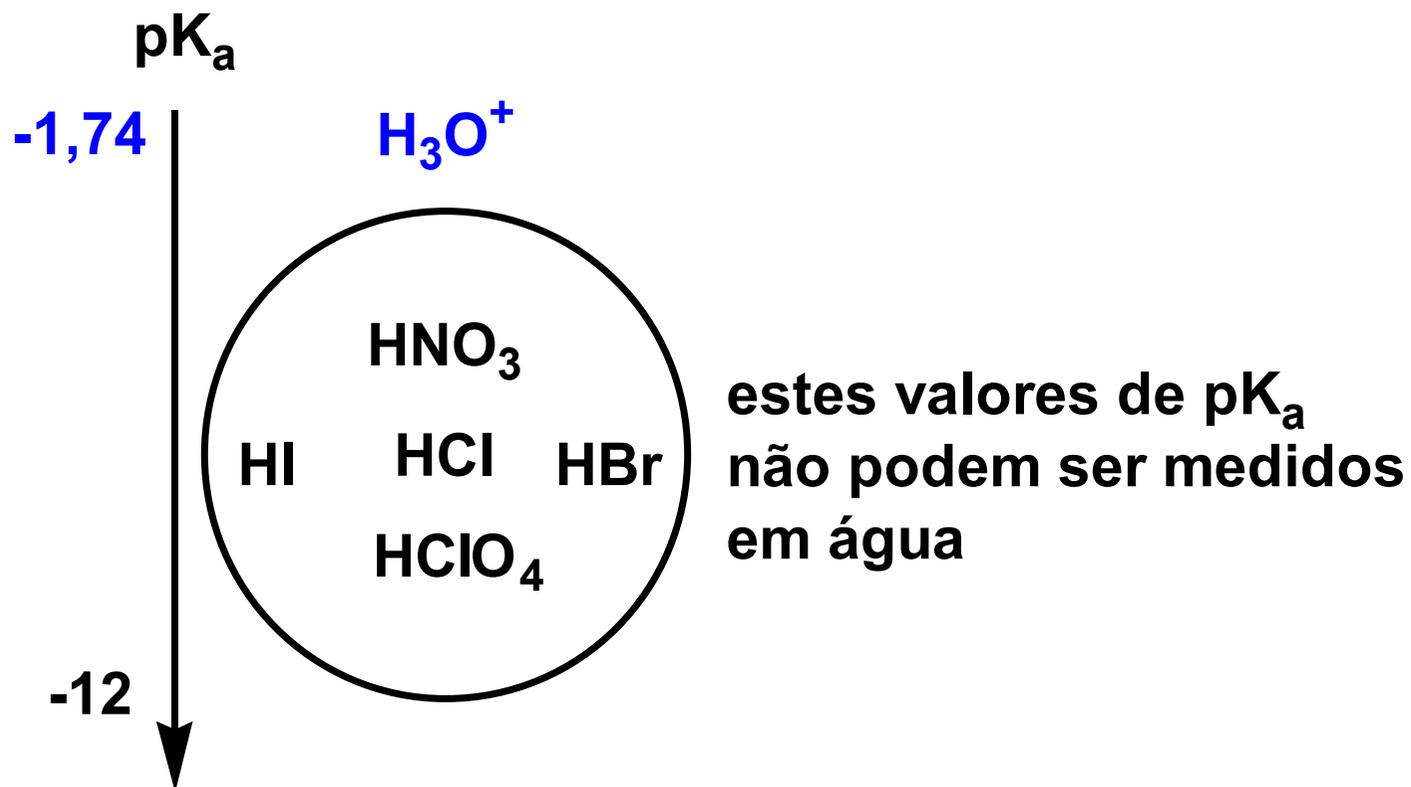
Concentrações no equilíbrio (equiv.)

0.47	0.47	0.53	0.53
------	------	------	------

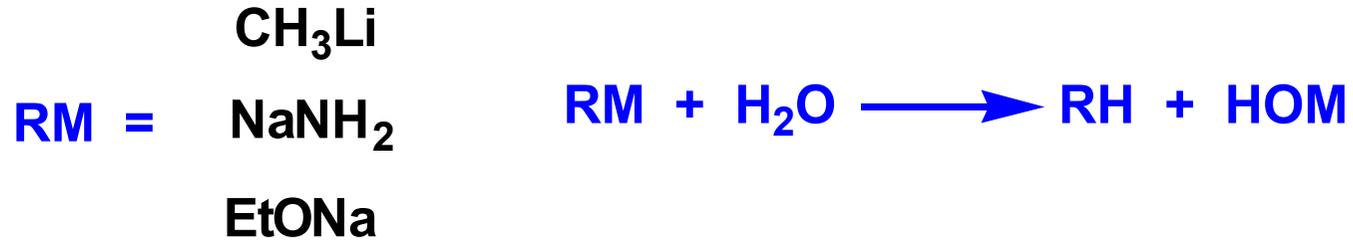
Dissociação da água na presença de amideto de sódio e hidreto de sódio



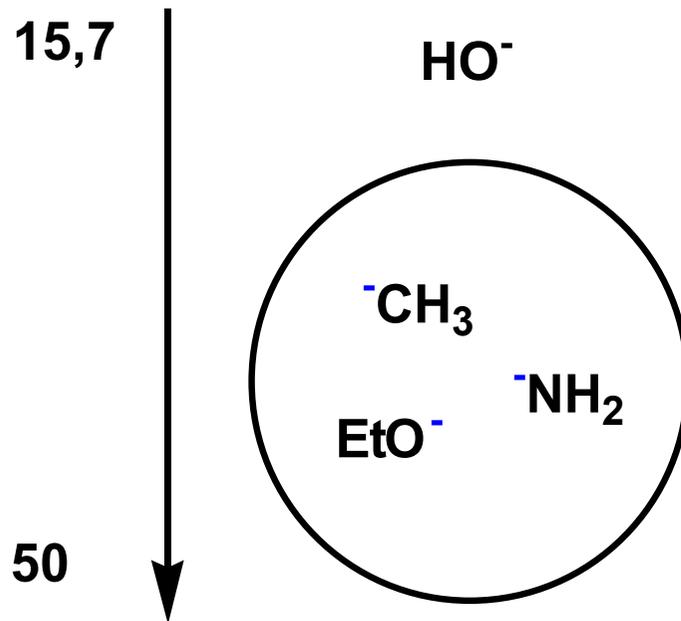
Efeito nivelador da água na dissociação de ácidos fortes



Efeito nivelador da água na força básica

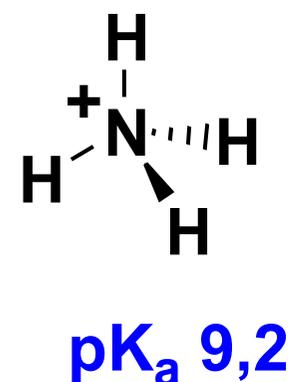
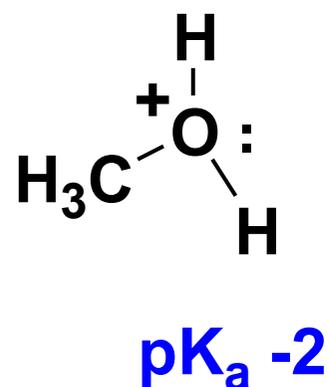
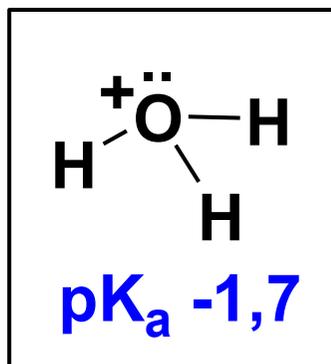
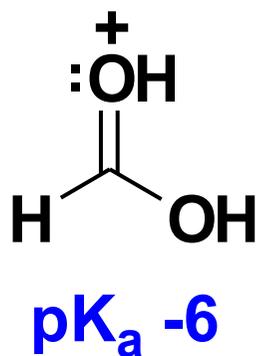


pK_a do ácido conjugado



estes valores de pK_a
não podem ser medidos
em água

Solventes não aquosos e a medida de pKa de ácidos mais fortes do que o cátion hidrônio



HCl

$\text{pK}_a -7,0$

H₂SO₄

$\text{pK}_a <-9,0$

HNO₃

$\text{pK}_a -1,4$

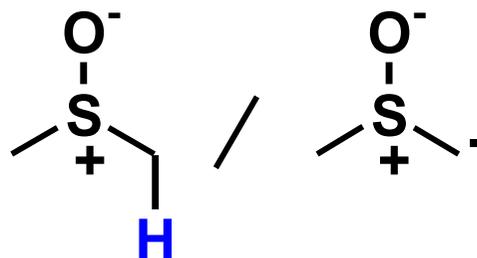
CH₃COOH

$\text{pK}_a 4,8$

Meios usados para a determinação do pKa de ácidos mais fracos do que a água



faixa entre 1-14



faixa entre 13-38



faixa entre 14-20



faixa entre 18-32

Dissociação de HA em fase gasosa: O efeito da entalpia e da entropia na energia livre

Fase gasosa íons isolados, **sem solvatação**



$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

$$S^\circ_{(p)} > S^\circ_{(r)} \quad \Delta S^\circ \text{ positivo (+15 a +25 Kcal/mol), favorável}$$

$$H^\circ_{(p)} > H^\circ_{(r)} \quad \Delta H^\circ \text{ positivo (+100 a +400 Kcal/mol), desfavorável}$$

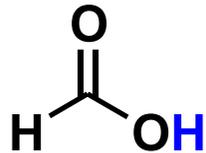
contribuição

$$\Delta H^\circ \gg \Delta S^\circ$$

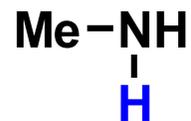
dissociação controlada
pela variação de entalpia

ΔG° muito grande (~ +100 a + 400 Kcal/mol), processos altamente desfavoráveis

Parâmetros termodinâmicos para a dissociação do ácido fórmico, metanol e metilamina em fase gasosa (ΔS^0 , ΔH^0 e ΔTS^0 em Kcal/mol e ΔS^0 em cal/molK)

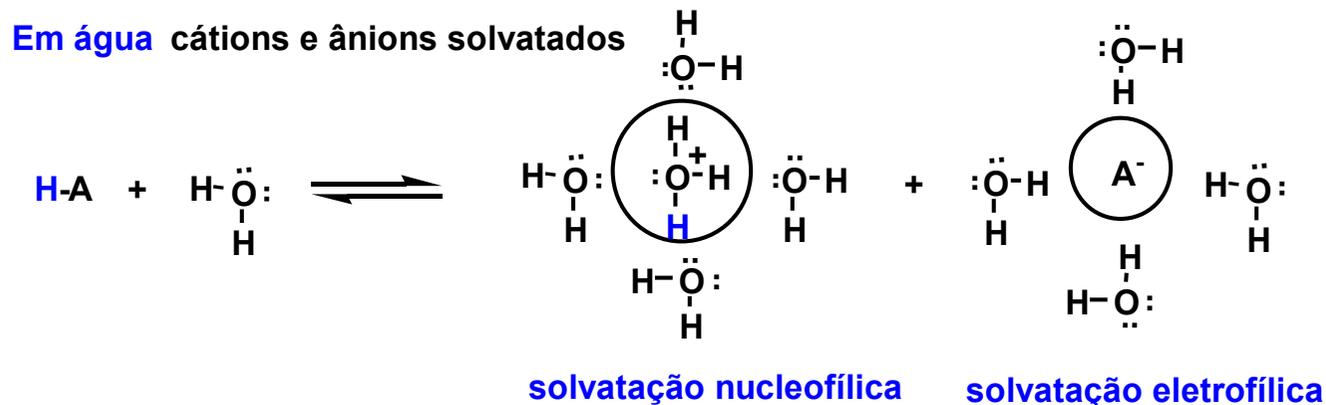


ΔG^0	ΔH^0	ΔS^0	$T\Delta S^0$	ΔG^0	ΔH^0	ΔS^0	$T\Delta S^0$
338,3	345,3	23,5	7,0	375,1	382,0	23,1	6,9



ΔG^0	ΔH^0	ΔS^0	$T\Delta S^0$
394,5	402,0	25,2	7,5

Dissociação de HA em água: O efeito da entalpia e da entropia na energia livre para ácidos orgânicos mais comuns



$$\Delta G^{\circ} = \Delta H^{\circ} - T\Delta S^{\circ}$$

$$S^{\circ}_{(p)} < S^{\circ}_{(r)} \quad T\Delta S^{\circ} \text{ é negativo}$$

(-4 a -8 Kcal/mol)

$$H^{\circ}_{(p)} > H^{\circ}_{(r)} \quad \Delta H^{\circ} \text{ positivo (0,1 a 0,9 Kcal/mol)}$$

ou

$$H^{\circ}_{(p)} < H^{\circ}_{(r)} \quad \Delta H^{\circ} \text{ negativo (-0,04 a -0,6 Kcal/mol)}$$

se a contribuição

$$\Delta H^{\circ} > T\Delta S^{\circ}$$

{ dissociação controlada
pela variação de entalpia

se a contribuição

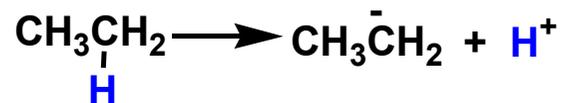
$$\Delta H^{\circ} < T\Delta S^{\circ}$$

{ dissociação controlada
pela variação de entropia

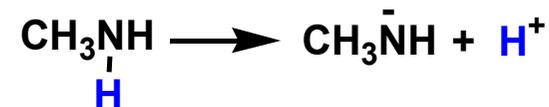
$$\Delta G^{\circ} \text{ pouco positivo ou negativo}$$

Dissociação em fase gasosa (Kcal/mol) para ligações C-H, O-H, N-H e

F-H



ΔG^0	ΔH^0	ΔS^0	$T\Delta S^0$
411,7	420,1	28,2	8,4



ΔG^0	ΔH^0	ΔS^0	$T\Delta S^0$
394,5	402,0	25,2	7,5



ΔG^0	ΔH^0	ΔS^0	$T\Delta S^0$
375,1	382,0	23,1	6,9



ΔG^0	ΔH^0	ΔS^0	$T\Delta S^0$
365,5	371,3	19,5	5,8

Forças de ligação

C-H ~96-105 Kcal/mol

HO-H 119 Kcal/mol

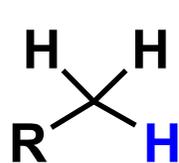
H₂N-H 107 Kcal/mol

F-H 135,8 Kcal/mol

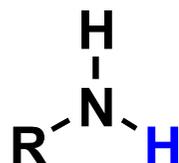
Comparação dos valores de pK_a para alcanos, aminas, álcoois e HF



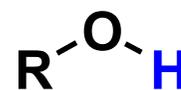
Acidez



$pK_a \sim 50$



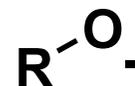
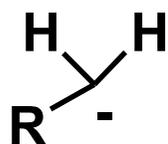
$pK_a \sim 37$



$pK_a \sim 16$

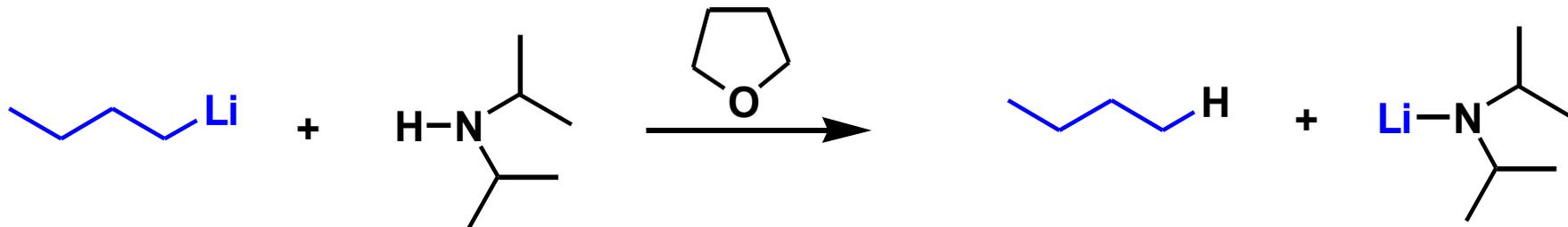
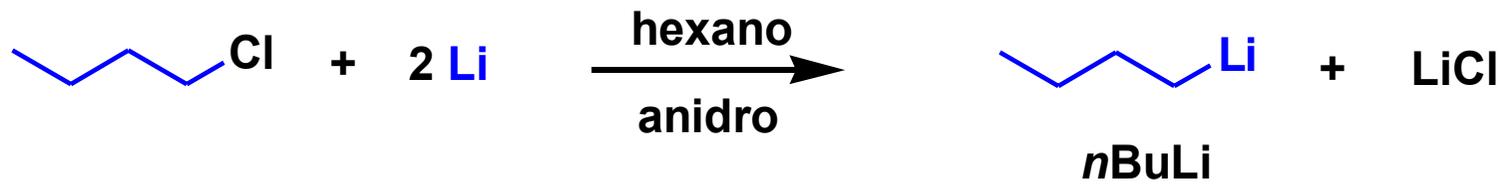


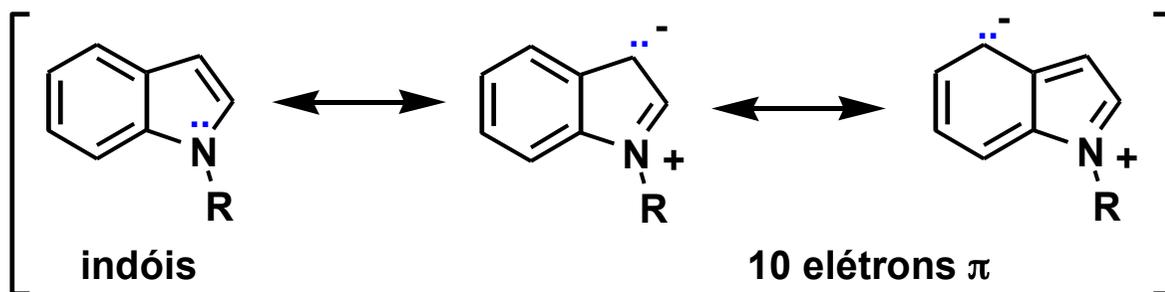
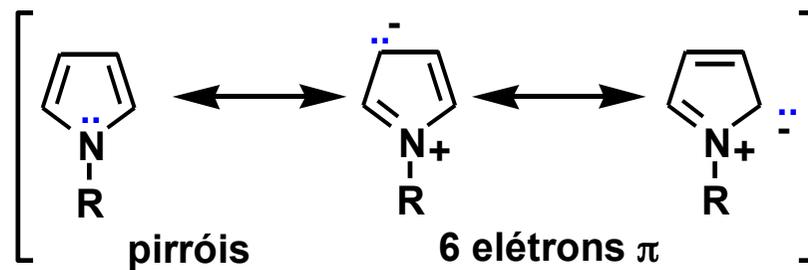
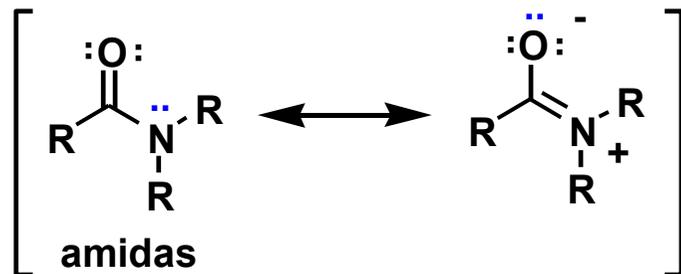
$pK_a 3,17$



Basicidade

Formação de amidetos e alcóxidos

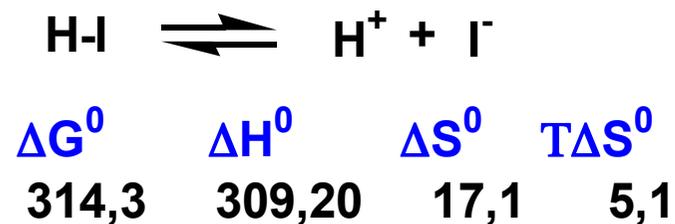
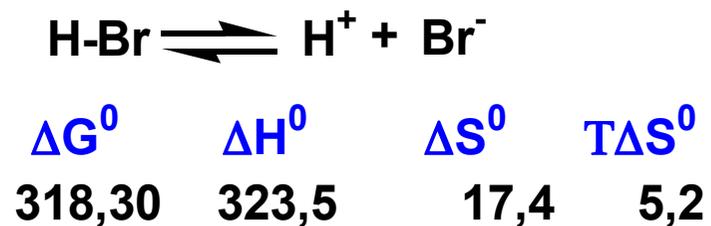
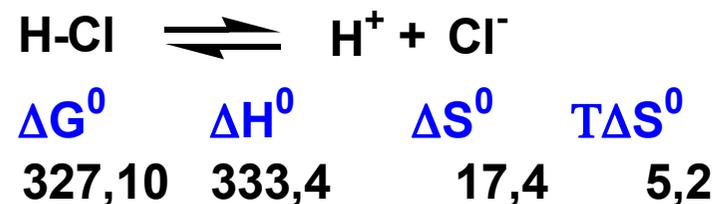
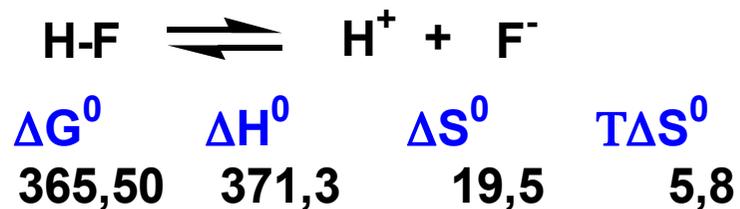




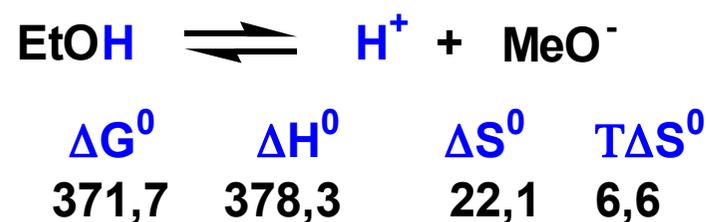
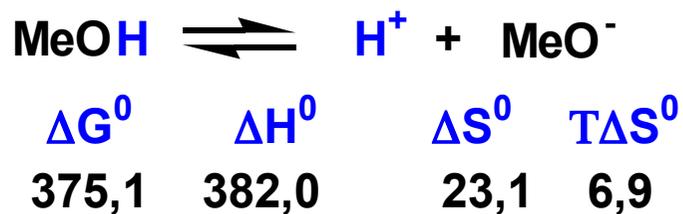
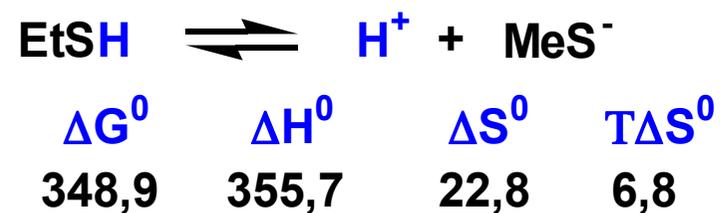
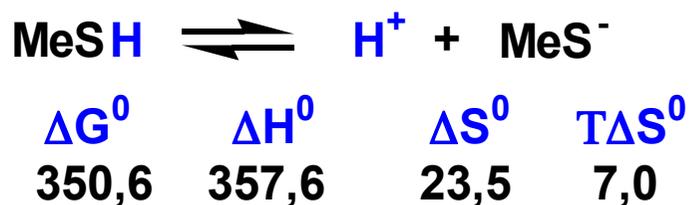
Lei de Huckel

Substâncias aromáticas
são planares e possuem
número de elétrons = $4n+2$,
onde n = número inteiro,

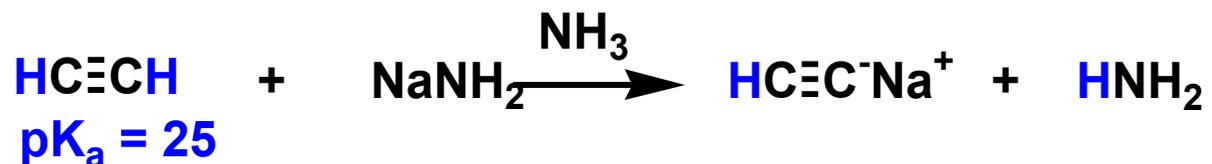
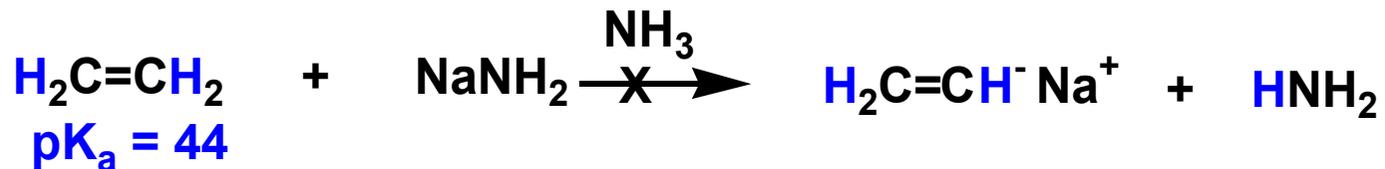
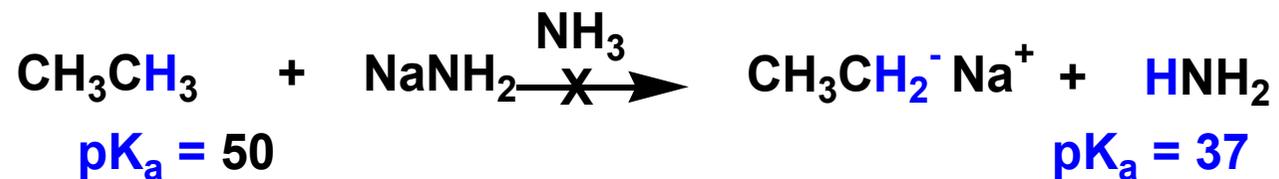
Dissociação de ácidos halogenídricos em fase gasosa (ΔG^0 , ΔH^0
e $T\Delta S^0$ em Kcal/mol e ΔS^0 em cal/molK)

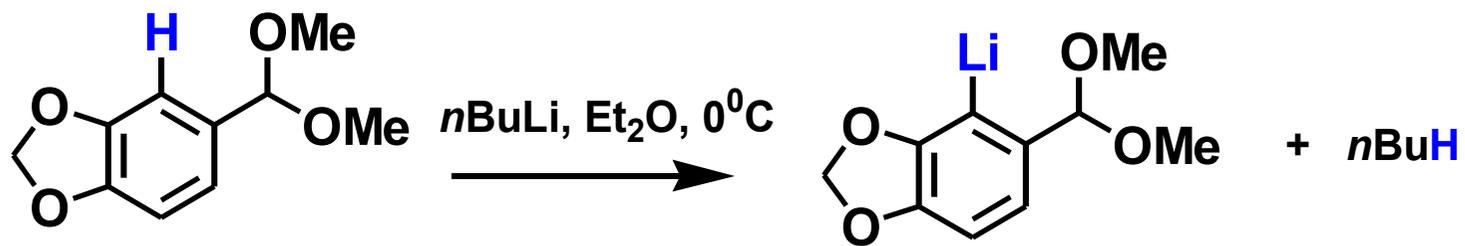
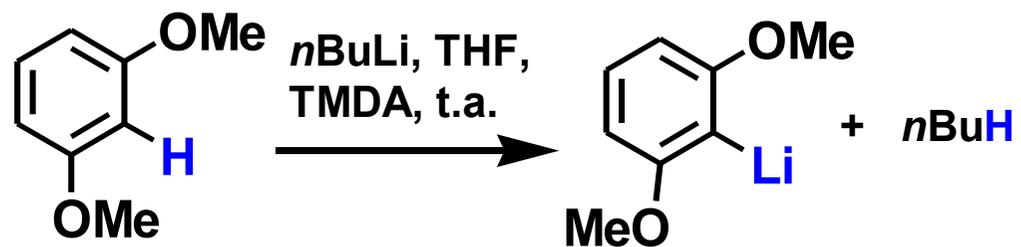


Dissociação de álcoois e tióis em fase gasosa (Kcal/mol)

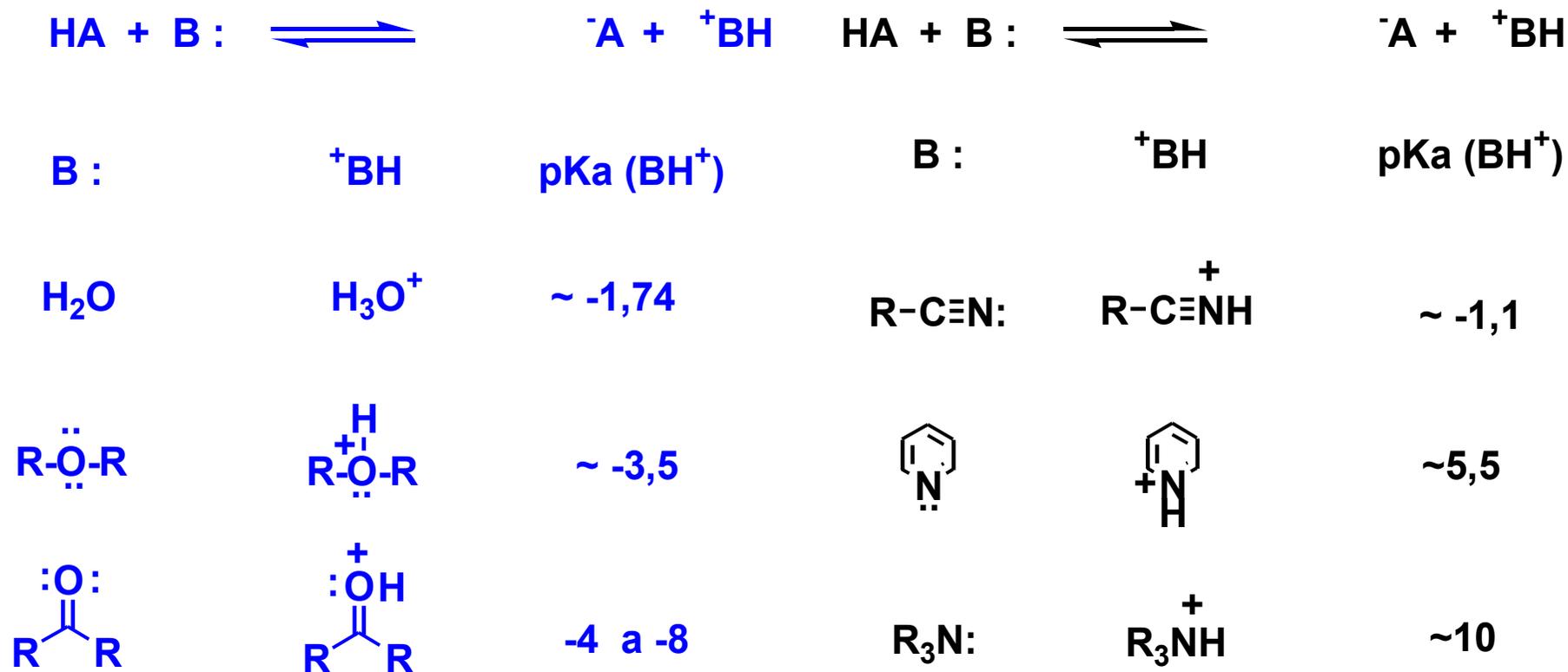


Hibridização e acidez de ligações C-H

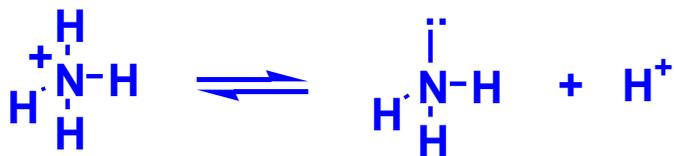




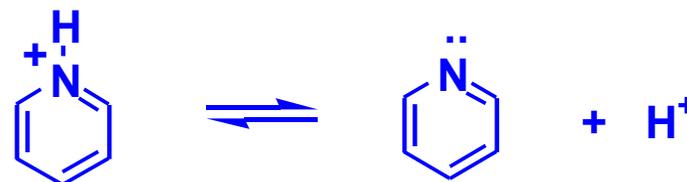
O efeito da hibridização na basicidade de derivados oxigenados e nitrogenados



(ΔG^0 , ΔH^0 e $T\Delta S^0$ em Kcal/mol e ΔS^0 em cal/molK)



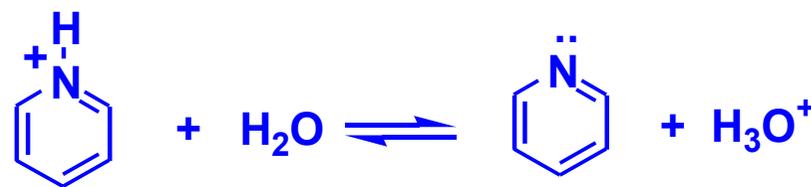
ΔG^0	ΔH^0	ΔS^0	$T\Delta S^0$
195,7	204,0	27,8	8,3



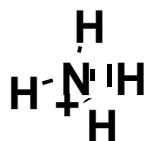
ΔG^0	ΔH^0	ΔS^0	$T\Delta S^0$
214,7	222,0	24,5	7,3



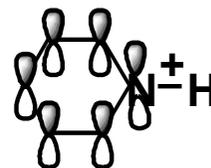
ΔG^0	ΔH^0	ΔS^0	$T\Delta S^0$	pK_a
12,6	12,4	+0,7	-0,2	9,245



ΔG^0	ΔH^0	ΔS^0	$T\Delta S^0$	pK_a
7,1	4,4	-9,1	-2,75	5,21

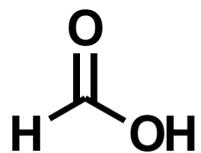


cátion mais solvatado,
4 átomos de H

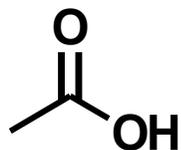


cátion menos solvatado,
1 átomo de H

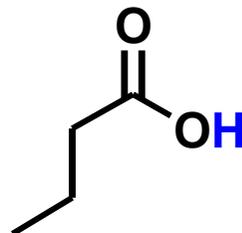
Valores de pK_a para ácidos carboxílicos halogenados



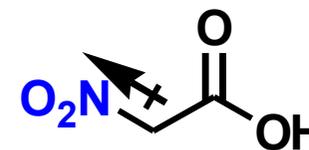
3,752



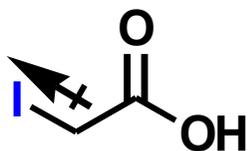
4,74



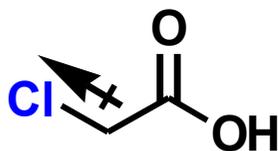
4,82



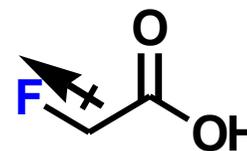
1,7



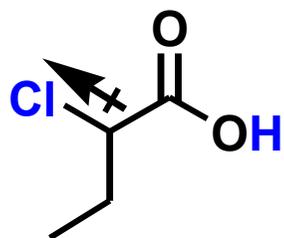
2,9



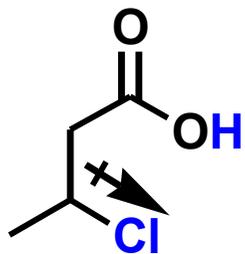
2,85



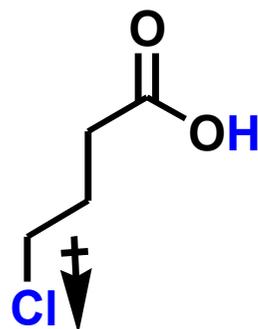
2,7



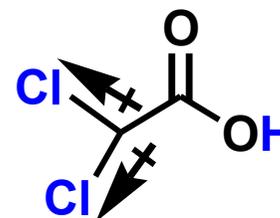
2,85



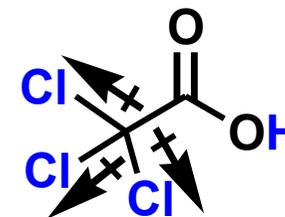
4,04



4,52



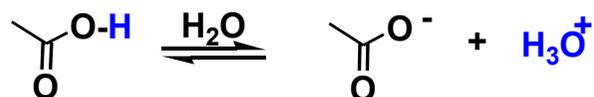
-1,3



-0,65

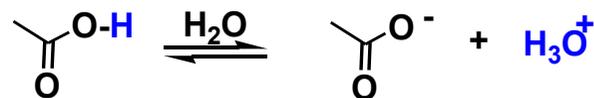
Dissociações de ácidos carboxílicos em fase gasosa e água (ΔG^0 , ΔH^0 e $T\Delta S^0$ em Kcal/mo e ΔS^0 em cal/molk)

dissociação em fase gasosa



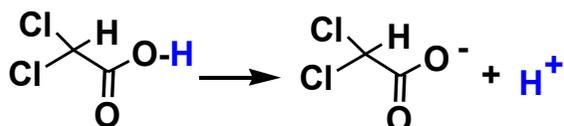
ΔG^0	ΔH^0	ΔS^0	ΔTS^0
341,1	348,1	25,6	7,0

dissociação em água



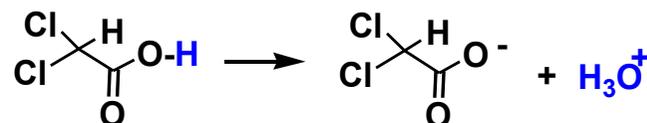
ΔG^0	ΔH^0	ΔS^0	ΔTS^0	pK_a
6,5	-0,11	-22,0	-6,55	4,756

dissociação em fase gasosa



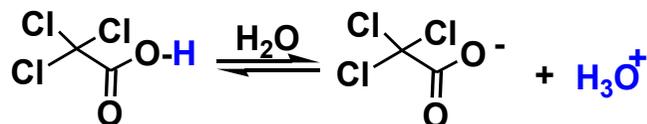
ΔG^0	ΔH^0	ΔS^0	ΔTS^0
321,9	328,4	221,8	6,5

dissociação em água



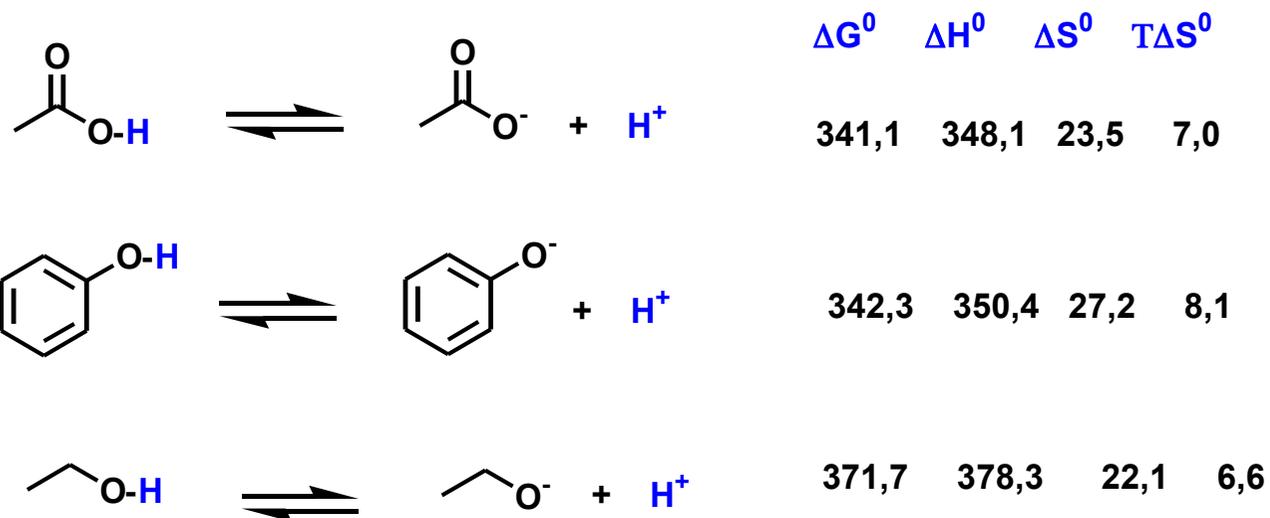
ΔG^0	ΔH^0	ΔS^0	ΔTS^0	pK_a
1,8	-6,1	-6,0	-1,78	1,3

dissociação em água

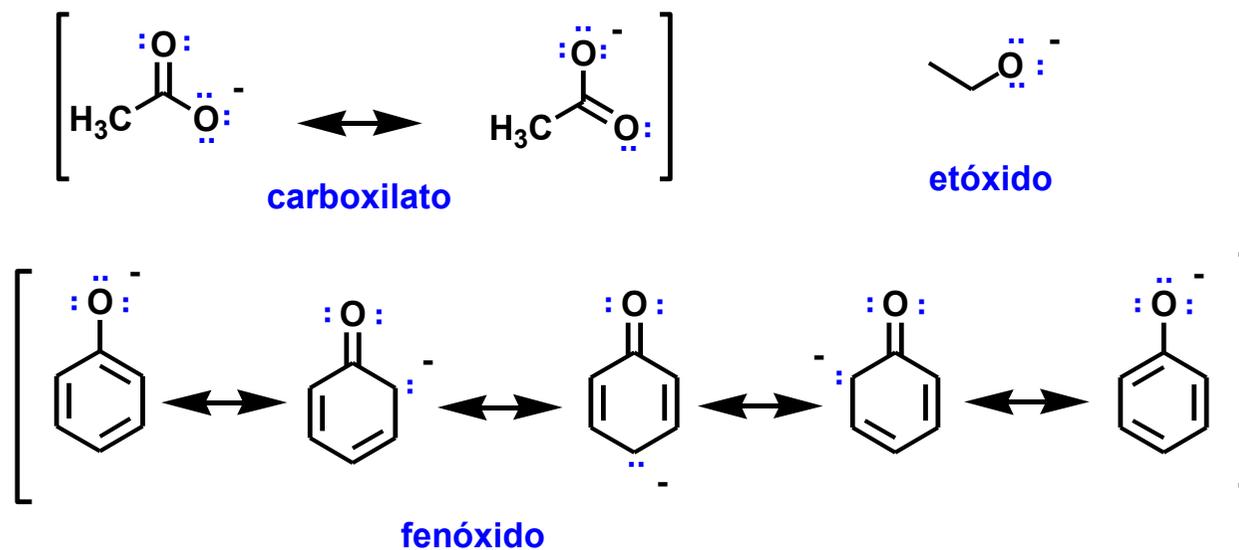


ΔG^0	ΔH^0	ΔS^0	ΔTS^0	pK_a
0,87	1,0	2,0	0,6	0,64

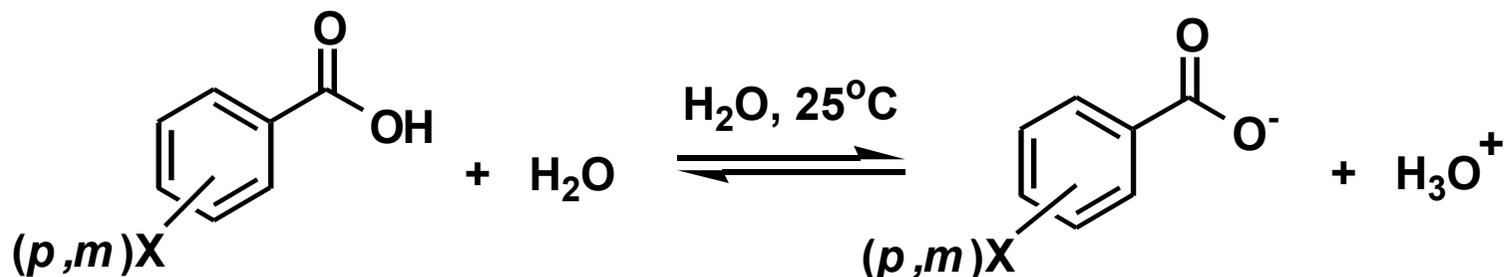
Dissociações em fase gasosa do ácido acético, fenol e etanol



Estruturas canônicas no acetato e no fenolato



A equação de Hammett para ácidos benzóicos substituídos



equação de Hammett

$$\log \frac{K_X}{K_H} = \rho \sigma_X$$

K_H = constante de acidez para a ionização do ácido benzóico

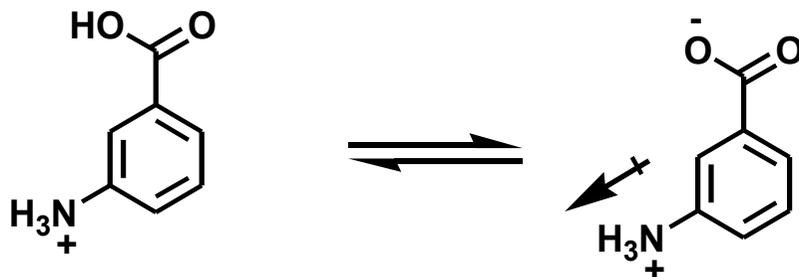
K_X = constante de acidez para a ionização do ácido benzóico substituído

σ_X = constante de Hammett para o substituinte X

ρ = sensibilidade da reação ao substituinte, definido neste caso como 1

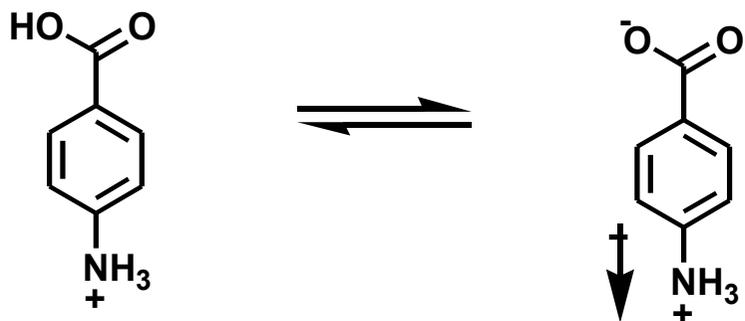
Se $\rho = 1,0$: $\sigma_X = \log (K_a)_X - \log (K_a)_H$ ou $\sigma_X = pK_{a(X)} - pK_{a(H)}$

Dissociação dos ácidos *m* e *p*-amônio benzóicos



$$\text{pK}_a = 4,20 + 0,88 = 5,08$$

$$\sigma_{(m)} = 0,88$$



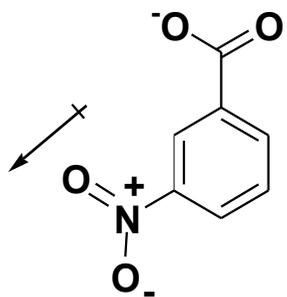
$$\text{pK}_a = 4,20 + 0,82 = 5,02$$

$$\sigma_{(p)} = 0,82$$

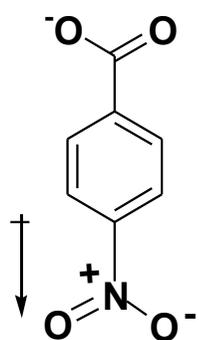
$^+\text{N}(\text{H})_3$ só opera por efeito de campo

efeitos de campo são aproximadamente iguais nas posições *m* e *p*

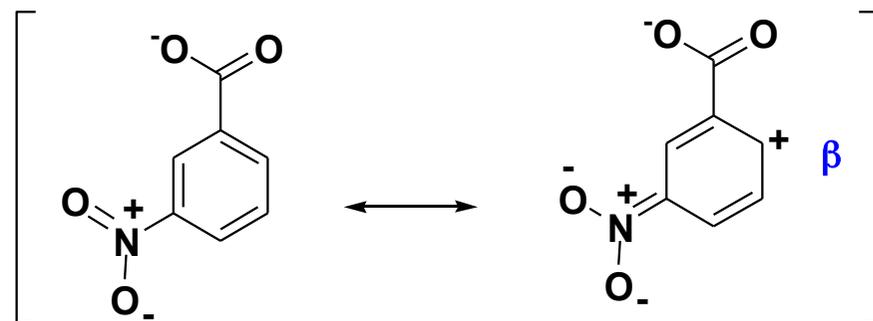
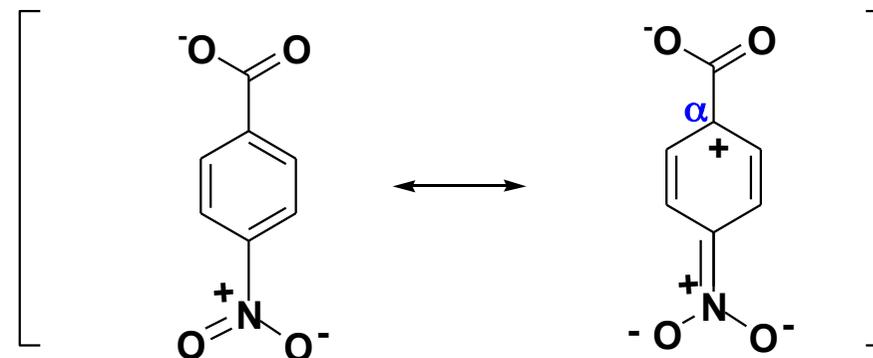
Efeitos de campo e ressonância



$pK_a = 3,49$
 $\sigma_{(m)} = 0,71$

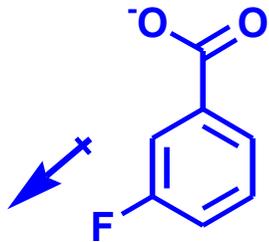


$pK_a = 3,42$
 $\sigma_{(p)} = 0,78$

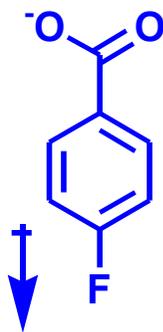


NO₂, CN, COR e CO₂R efeitos de campo e de ressonância

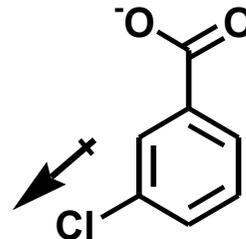
Valores de pK_a e de σ para as dissociações de ácidos benzóicos substituídos por halogênios (ácido benzóico, $pK_a = 4,20$)



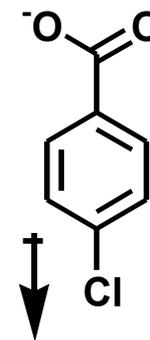
$pK_a = 4,54$
 $\sigma = 0,34$



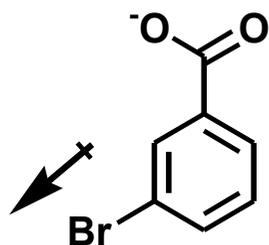
$pK_a = 4,26$
 $\sigma = 0,06$



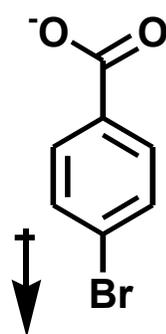
$pK_a = 4,57$
 $\sigma = 0,37$



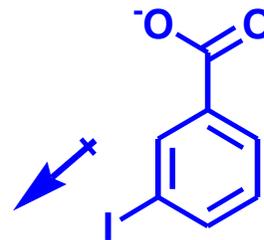
$pK_a = 4,43$
 $\sigma = 0,23$



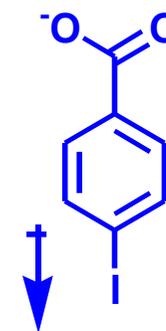
$pK_a = 4,59$
 $\sigma = 0,39$



$pK_a = 4,43$
 $\sigma = 0,23$

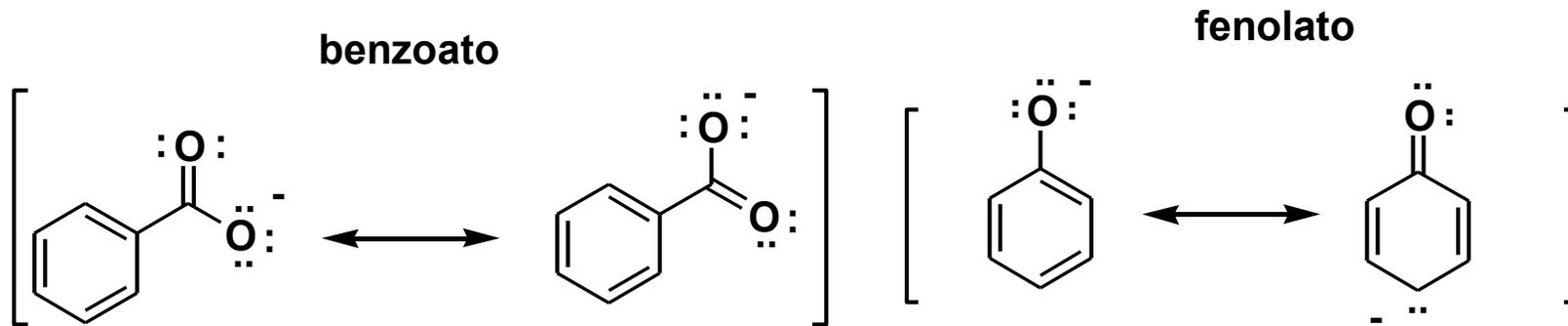


$pK_a = 4,55$
 $\sigma = 0,35$



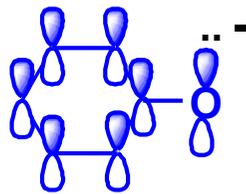
$pK_a = 4,40$
 $\sigma = 0,20$

A estabilização de benzoatos e fenóxidos

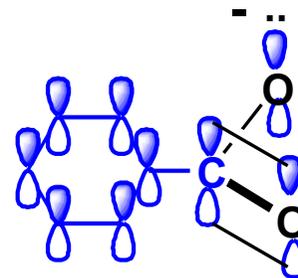


estruturas canônicas sem
separação de cargas

fenolato
par de elétrons
conjugado com
o anel aromático



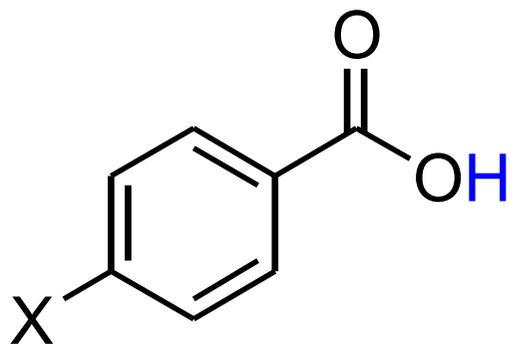
orbital p que contém a carga negativa
está situado consecutivamente ao anel
aromático e paralelo com o sistema π



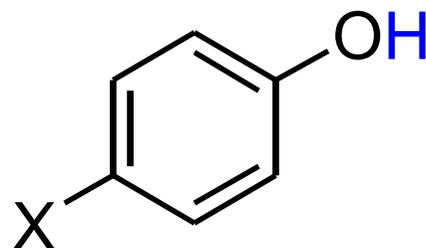
benzoato
par de elétrons
conjugado com
a carbonila

orbital p que contém a carga negativa
está situado consecutivamente à carbonila
porem longe do anel aromático

Comparação dos valores de ρ para a dissociação de ácidos benzóicos e fenóis.



$$\rho = 1$$



$$\rho = +2,11$$

$$X = \text{H}, \quad \text{pK}_a = 4,21$$

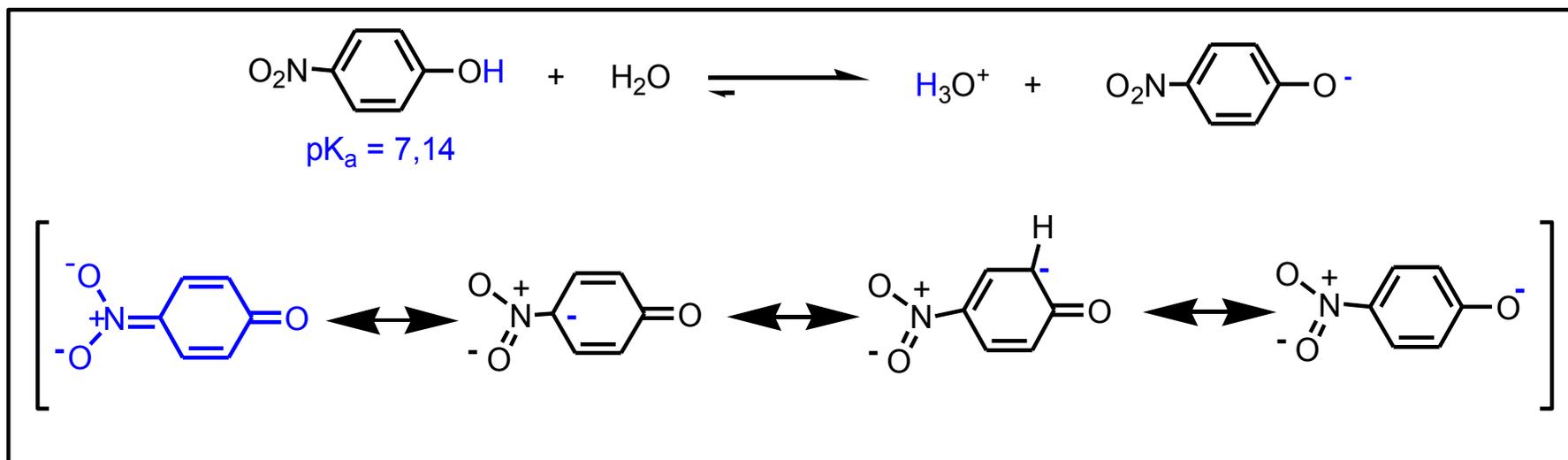
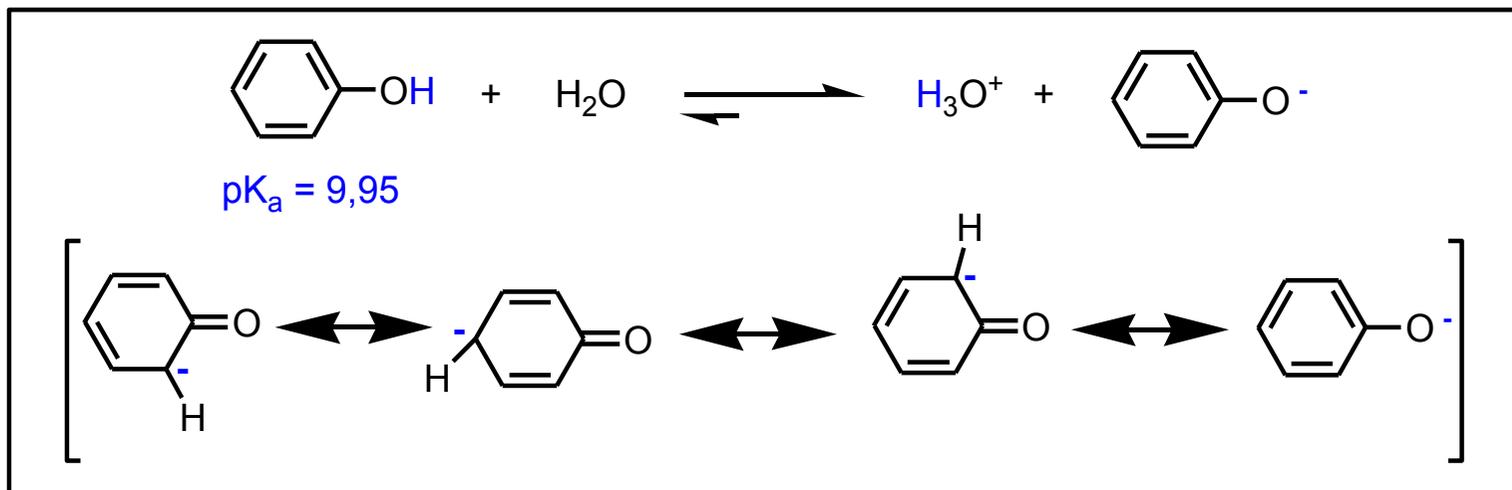
$$X = \text{NO}_2, \quad \text{pK}_a = 3,42$$

$$X = \text{H}, \quad \text{pK}_a = 9,95$$

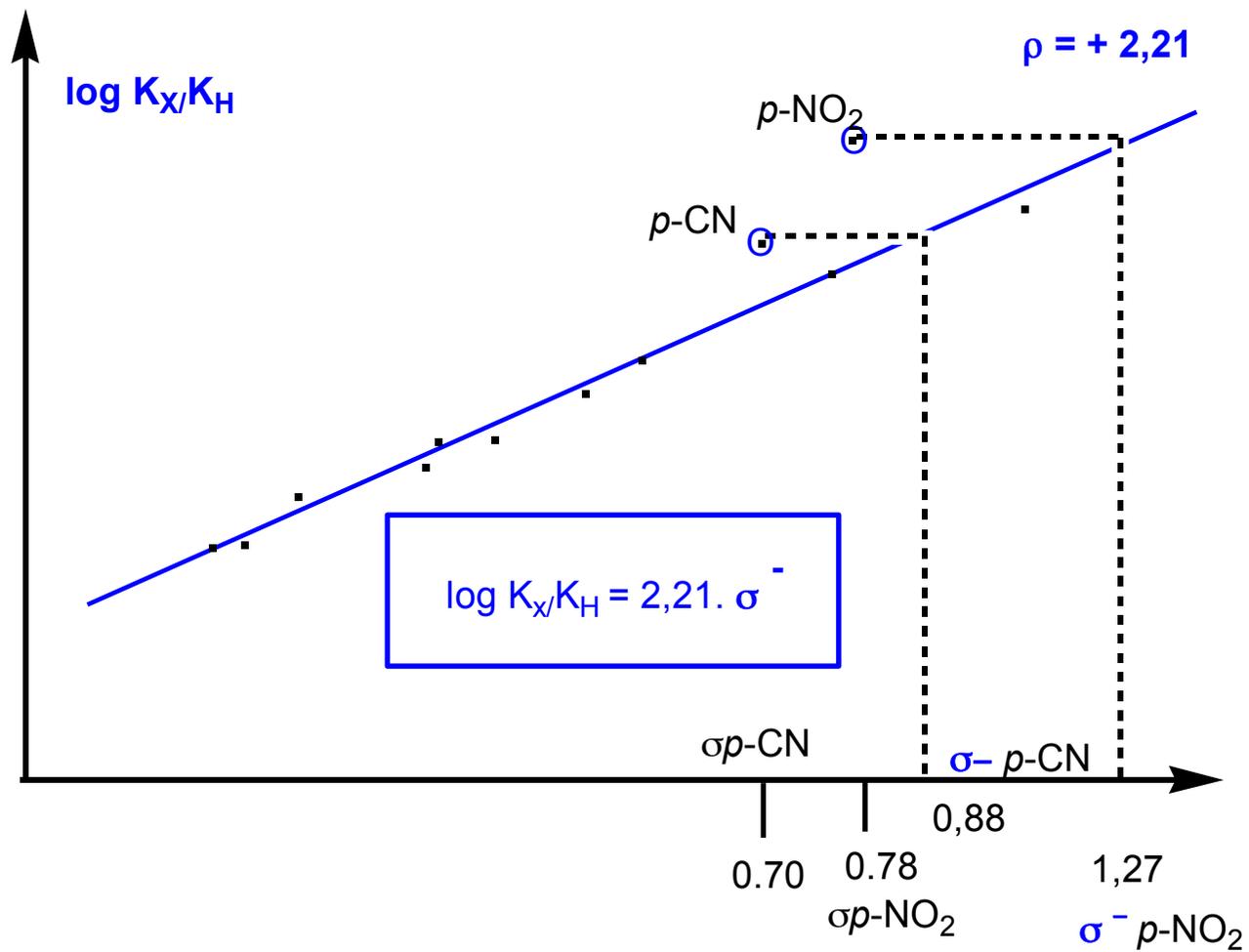
$$X = \text{NO}_2, \quad \text{pK}_a = 7,14$$

valores calculados em H_2O ,
a 25°C

Esquema 4.10 Dissociação de fenóis substituídos



Cálculo de σ^- a partir da dissociação de fenóis.

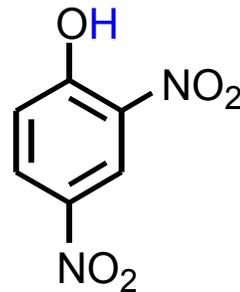


X(para)	σ	σ^-
NO ₂	0,78	1,27
CN	0,70	0,88
CH ₃ CO	0,48	0,84
CO ₂ C ₂ H ₅	0,45	0,74
CHO	0,44	1,04

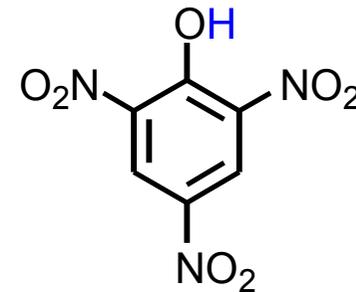
O efeito aditivo de grupos nitro na dissociação de fenóis



$pK_a = 7,14$

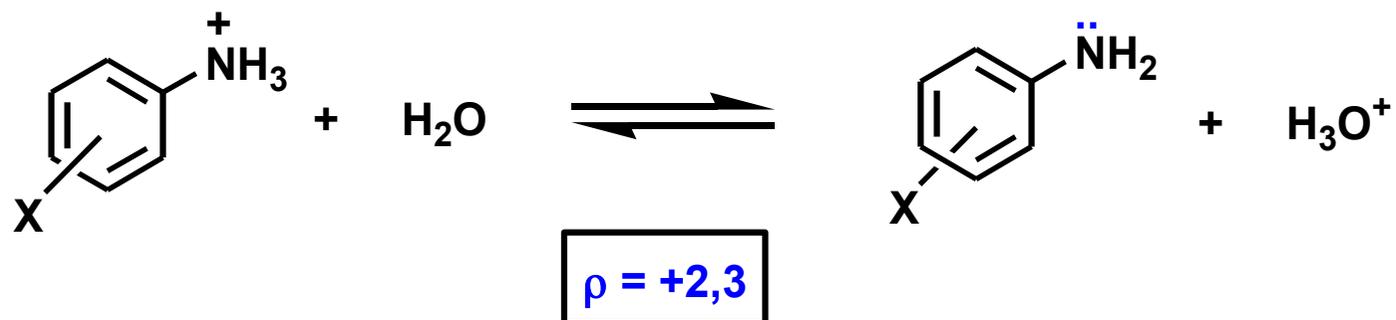


$pK_a = 4,01$

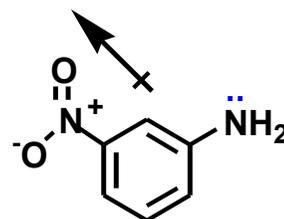
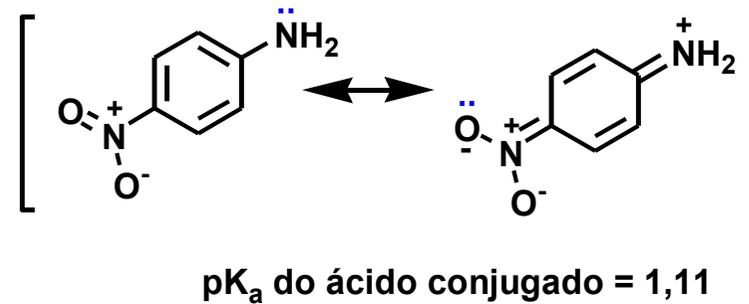
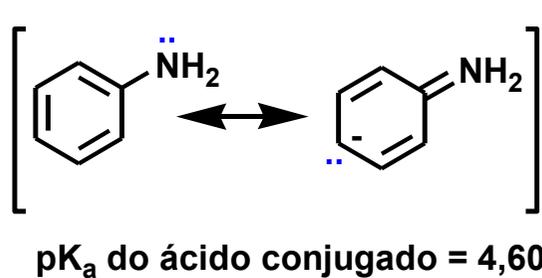


$pK_a = 1,02$

Dissociação de anilínios

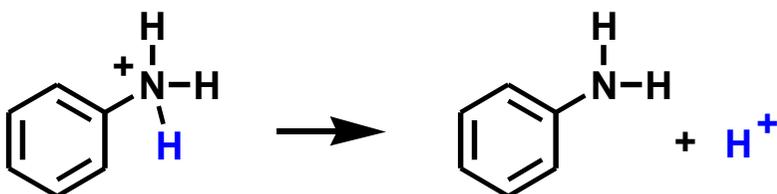


Efeito do substituinte na basicidade de anilinas



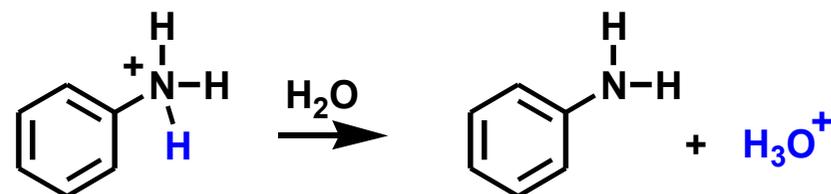
Comparação da basicidade da anilina e da amônia em fase gasosa e em água (ΔG^0 , ΔH^0 , ΔTS^0 em Kcal/mol, ΔS^0 em cal/molK)

dissociação em fase gasosa



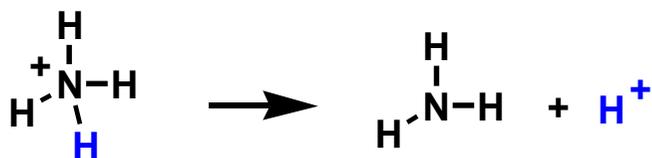
ΔG^0	ΔH^0	ΔS^0	ΔTS^0
203,3	210,9	25,4	7,6

dissociação em água



ΔG^0	ΔH^0	ΔS^0	ΔTS^0	pK_a
6,27	7,38	3,7	1,10	4,6

dissociação em fase gasosa



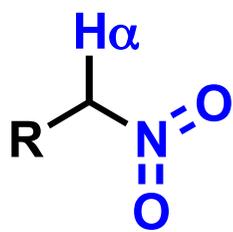
ΔG^0	ΔH^0	ΔS^0	ΔTS^0
195,7	204,0	27,8	8,3

dissociação em água

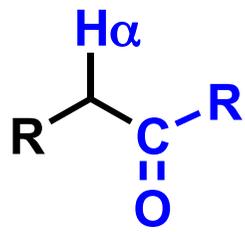


ΔG^0	ΔH^0	ΔS^0	ΔTS^0	pK_a
12,6	12,4	0,7	-0,2	9,245

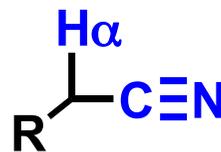
Efeito do substituinte na acidez (pK_a em água) de ligações C-H



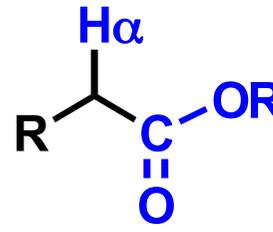
$pK_a \sim 10$



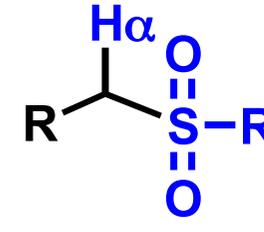
$pK_a \sim 20$



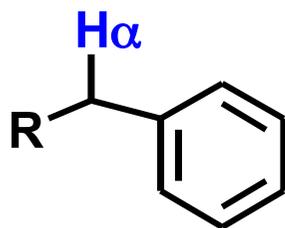
$pK_a \sim 25$



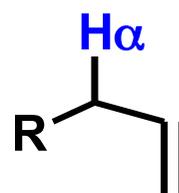
$pK_a \sim 25$



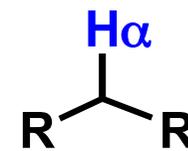
$pK_a \sim 33$



$pK_a \sim 41$

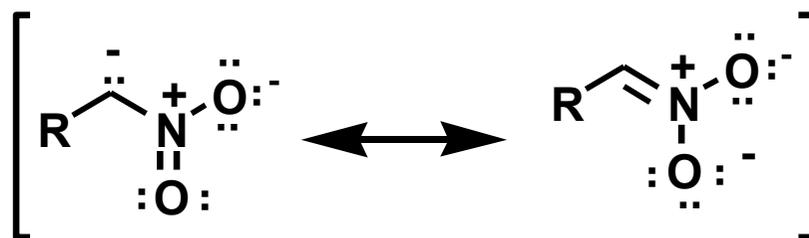
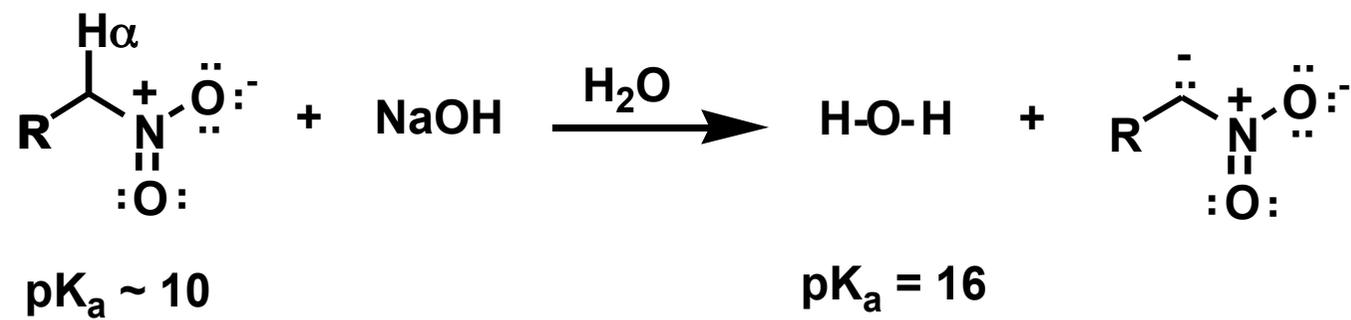


$pK_a \sim 43$

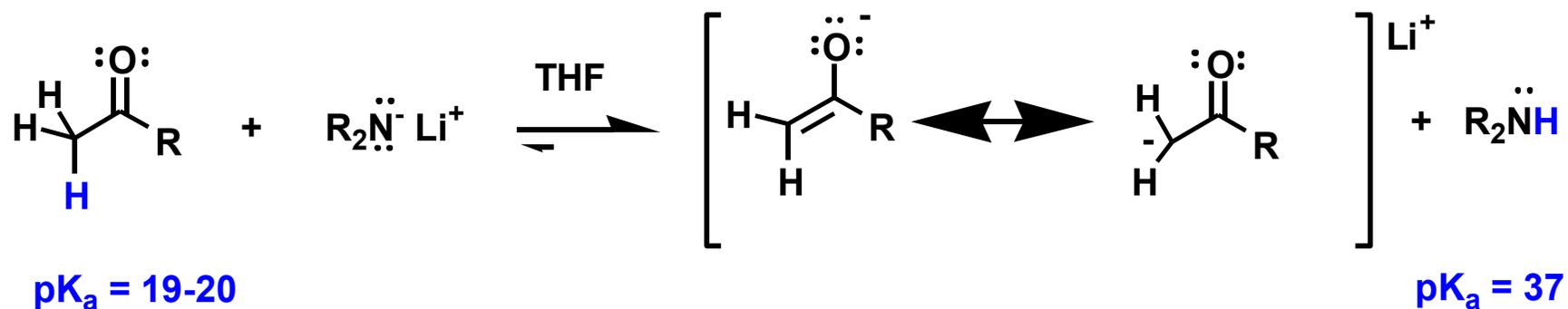
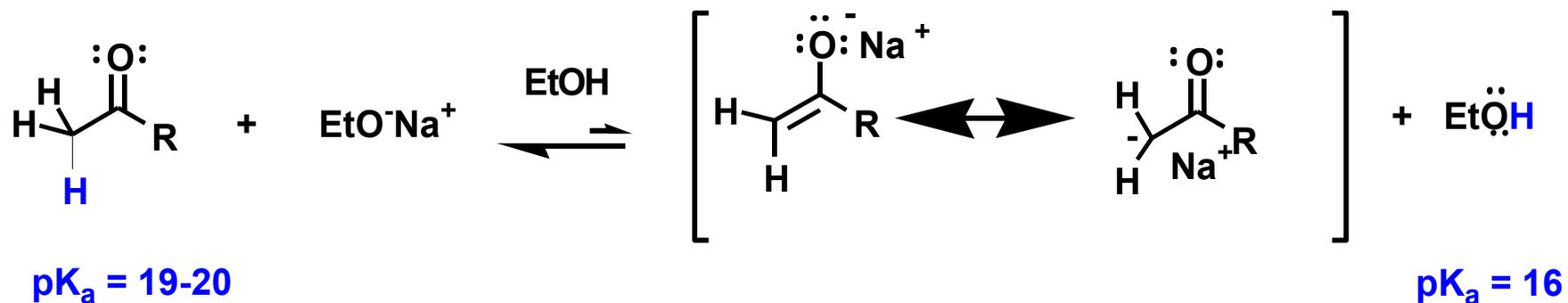


$pK_a \sim 49$

Dissociação de nitroalcanos

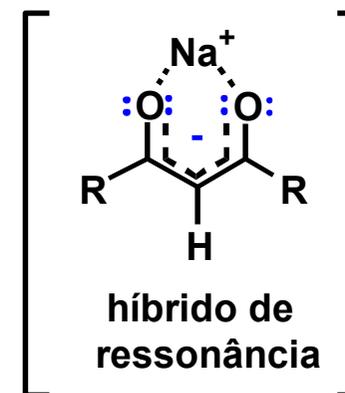
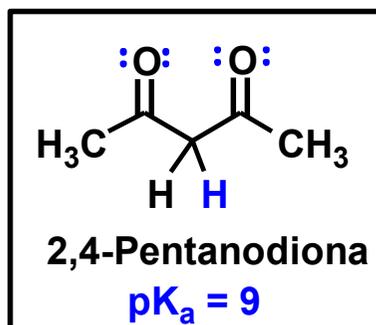
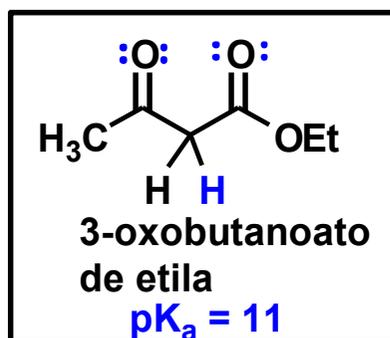
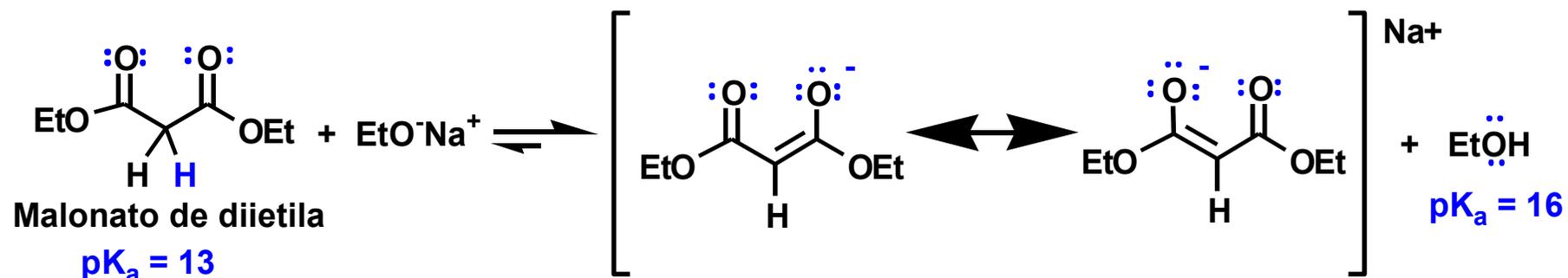


Dissociação de derivados carbonilados: A força da base e a posição do equilíbrio



$\text{R} = \text{H}, \text{alquil}, \text{OR}, \text{NR}_2$

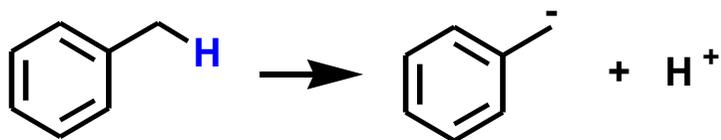
Dissociações do malonato de etila, etilacetato de etila e β -dicetona



Dissociações de hidrocarbonetos: A estabilização de ânions benzílicos e alílicos
 (ΔG° , ΔH° e $T\Delta S^\circ$ em Kcal/mol e ΔS° em cal/mol)



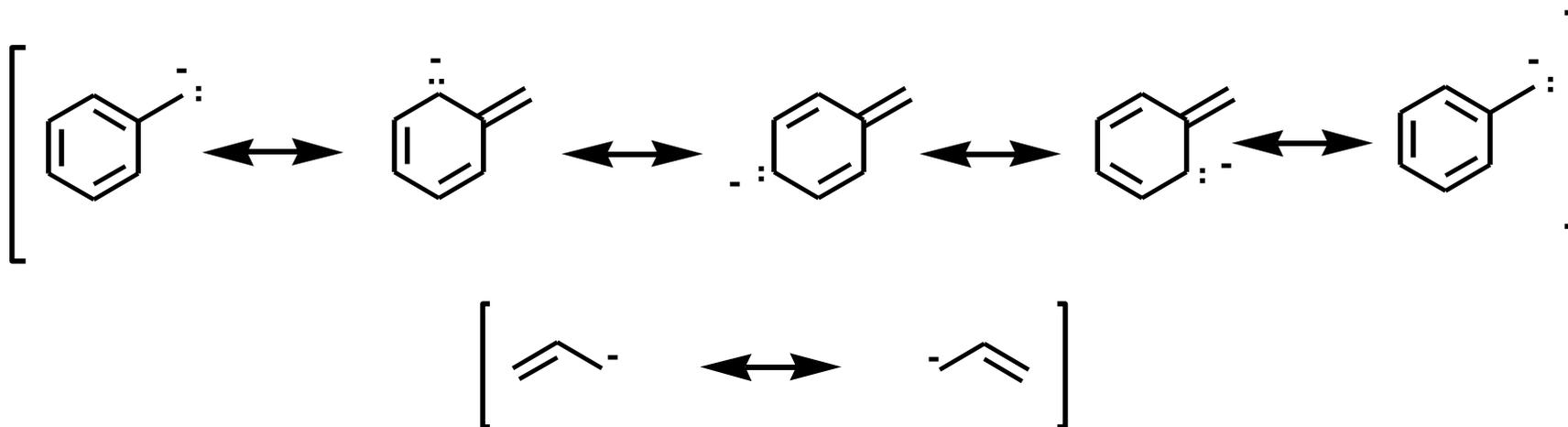
ΔG°	ΔH°	ΔS°	$T\Delta S^\circ$
408,68	416,70	27,2	8,1



ΔG°	ΔH°	ΔS°	$T\Delta S^\circ$
372,1	379,2	23,8	7,1



ΔG°	ΔH°	ΔS°	$T\Delta S^\circ$
382,5	389,1	22,1	6,6



<i>n</i>		pKa	
constante de nucleofilicidade		ácido conjugado da base	
CH ₃ OH	0	CH ₃ OH ₂ ⁺	-1,7
F ⁻	2,7	HF	3,43
PhO ⁻	5,8	PhOH	9,8
Br ⁻	5,8	HBr	9,89
CH ₃ O ⁻	6,3	CH ₃ OH	15,7

<i>n</i>		pKa	
constante de nucleofilicidade		ácido conjugado da base	
OH ⁻	6,5	H ₂ O	15,7
CN ⁻	6,7	HCN	6,7
I ⁻	7,4	HI	10,7
PhS ⁻	9,9	PhSH	6,5