LIGAÇÕES QUÍMICAS: CERTEZAS E DÚVIDAS

1

Sérgio Emanuel Galembeck

- *"The more accurate the computations become, the more the concepts tend to vanish into air"* (Mulliken, 1965).

- *"Give me insights and numbers."* (Coulson, 1960).

- *"It is nice to know that the computer understands the problem. But I would like to understand it too"* (Wigner).

Ligação química:

► *"The chemical bond is the glue from which an entire chemical universe is constructed." (Shaik, 2007).*

► *"I believe the chemical bond is not so simple as some people seem to think." (Mulliken, 1960).*

Electronic Structure Theory
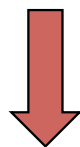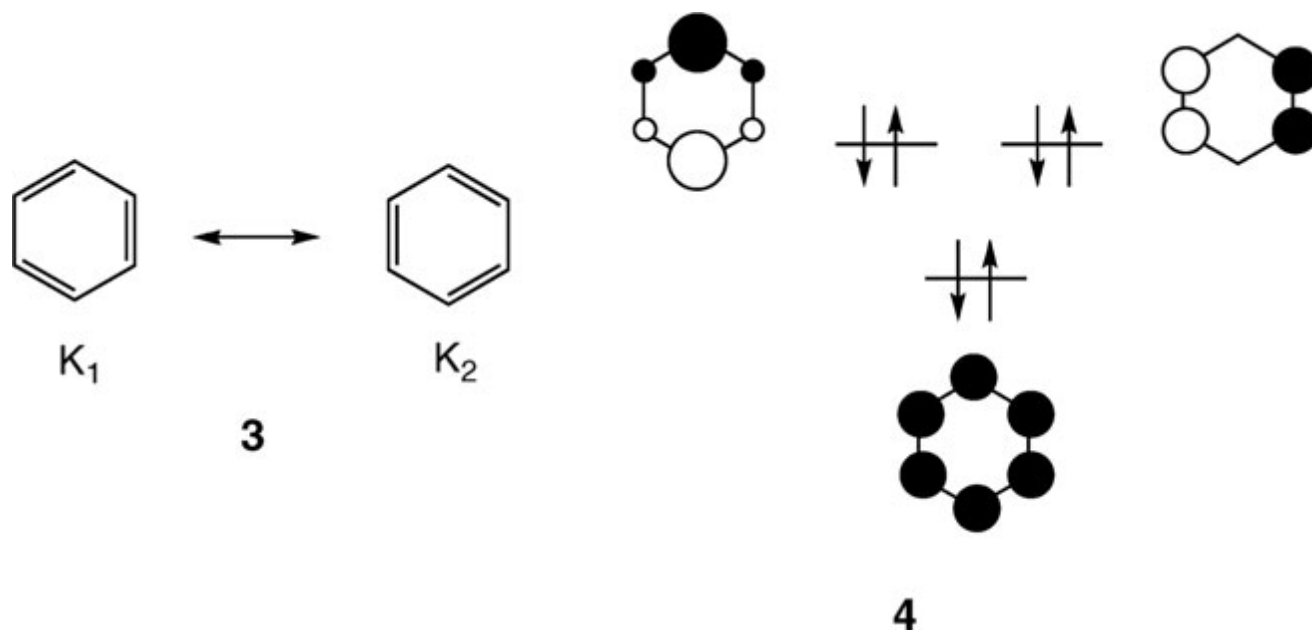
Molecular Orbital Theory

Molecular orbitals based

- ✓ Orthogonal
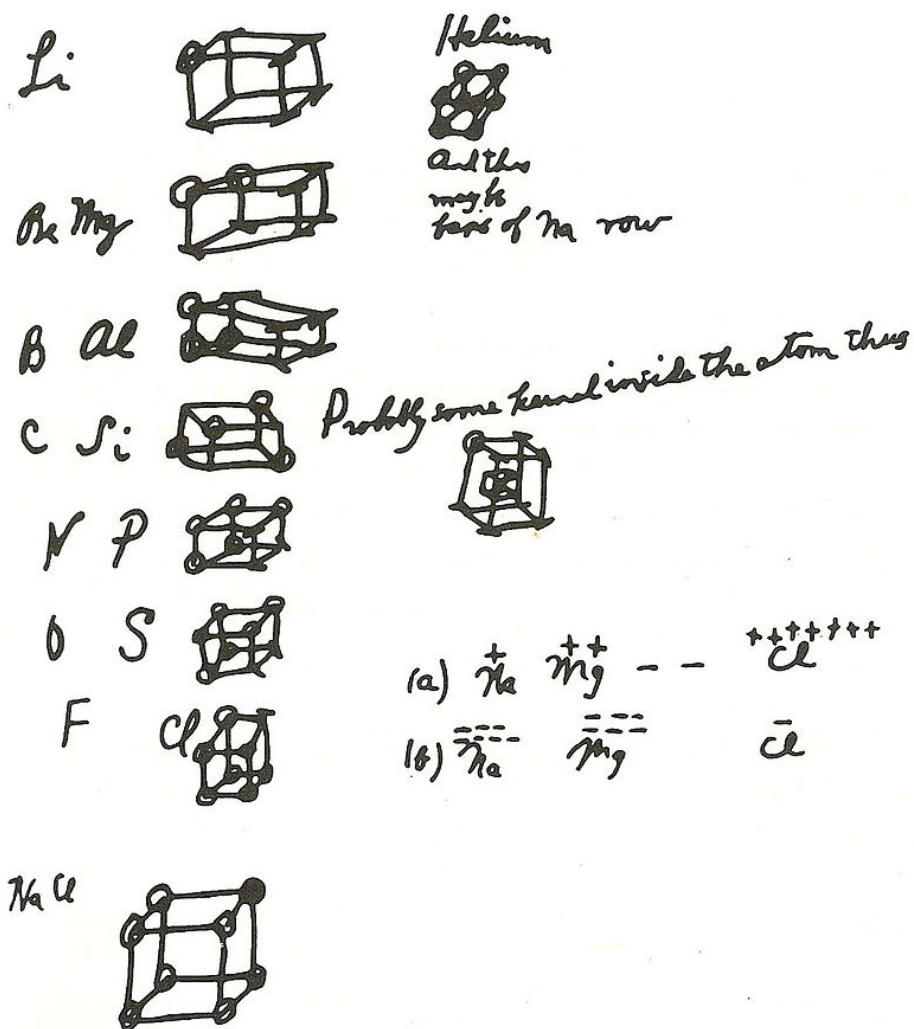- ✓ Delocalized

Valence Bond Theory
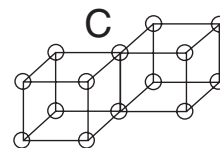
Atomic orbitals based
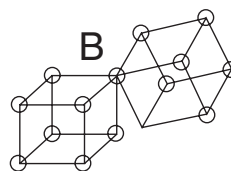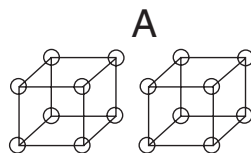
- ✓ Nonorthogonal
- ✓ Localized

K_1 K_2

3

4

8
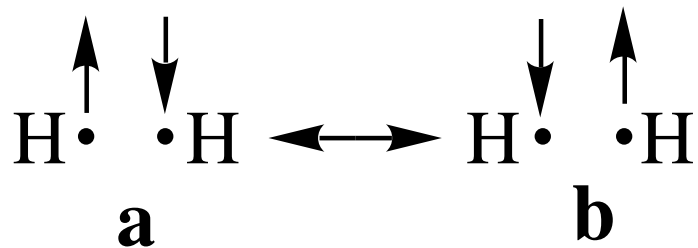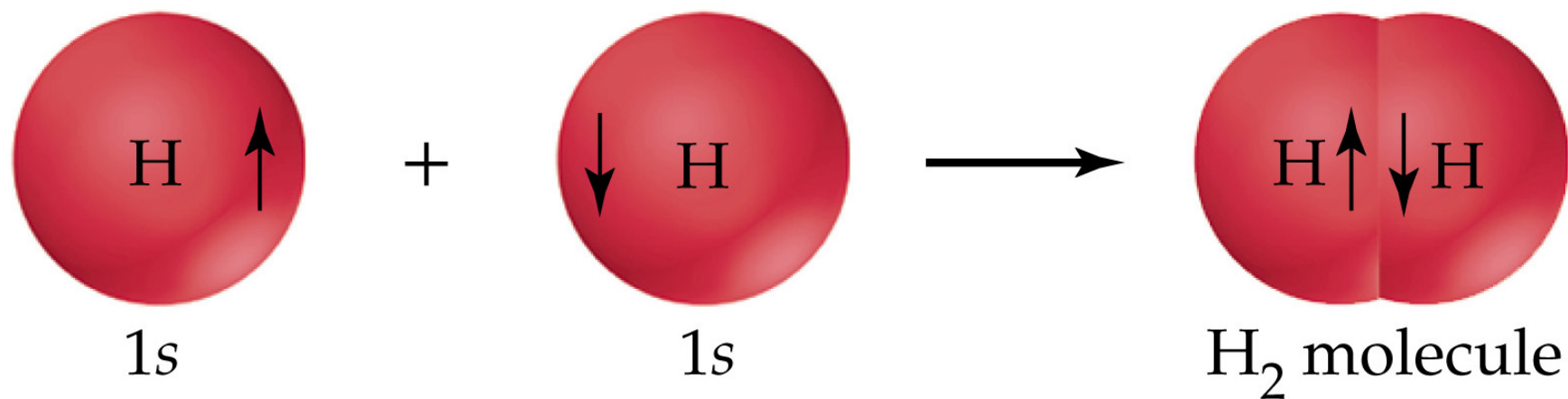
Gilbert N. Lewis

(1916)

A   B   C

Erwin Schrödinger

$$H\psi = E\psi$$

Heitler e London - (1928)

Teoria de Ligação de Valência (VB)

Heitler e London (1930)

Linus Pauling - (1930)

THE NATURE OF THE CHEMICAL BOND. APPLICATION OF RESULTS OBTAINED FROM THE QUANTUM MECHANICS AND FROM A THEORY OF PARAMAGNETIC SUSCEPTIBILITY TO THE STRUCTURE OF MOLECULES

BY LINUS PAULING

During the last four years the problem of the nature of the chemical bond has been attacked by theoretical physicists, especially Heitler and London, by the application of the quantum mechanics. This work has led to an approximate theoretical calculation of the energy of formation and of other properties of very simple molecules, such as H_2, and has also provided a formal justification of the rules set up in 1916 by G. N. Lewis for his electron-pair bond. In the following paper it will be shown that many more results of chemical significance can be obtained from the quantum mechanical equations, permitting the formulation of an extensive and powerful set of rules for the electron-pair bond supplementing those of Lewis. These rules provide information regarding the relative strengths of bonds formed by different atoms, the angles between bonds, free rotation or lack of free rotation about bond axes, the relation between the quantum numbers of bonding electrons and the number and spatial arrangement of the bonds, etc. A complete theory of the magnetic moments of molecules and complex ions is also developed, and it is shown that for many compounds involving elements of the transition groups this theory together with the rules for electron-pair bonds leads to a unique assignment of electron structures as well as a definite determination of the type of bonds involved.[1]

I. The Electron-Pair Bond

The Interaction of Simple Atoms.—The discussion of the wave equation for the hydrogen molecule by Heitler and London,[2] Sugiura,[3] and Wang[4] showed that two normal hydrogen atoms can interact in either of two ways, one of which gives rise to repulsion with no molecule formation, the other

[1] A preliminary announcement of some of these results was made three years ago [Linus Pauling, *Proc. Nat. Acad. Sci.*, **14**, 359 (1928)]. Two of the results (90° bond angles for p eigenfunctions, and the existence, but not the stability, of tetrahedral eigenfunctions) have been independently discovered by Professor J. C. Slater and announced at meetings of the National Academy of Sciences (Washington, April, 1930) and the American Physical Society (Cleveland, December, 1930).

[2] W. Heitler and F. London, *Z. Physik*, **44**, 455 (1927).

[3] Y. Sugiura, *ibid.*, **45**, 484 (1927).

[4] S. C. Wang, *Phys. Rev.*, **31**, 579 (1928).

H • —— • H   =   (H• •H)   —   (H• •H)

H • —— • H

H :   H
(−) (+)

H   : H
(+) (−)

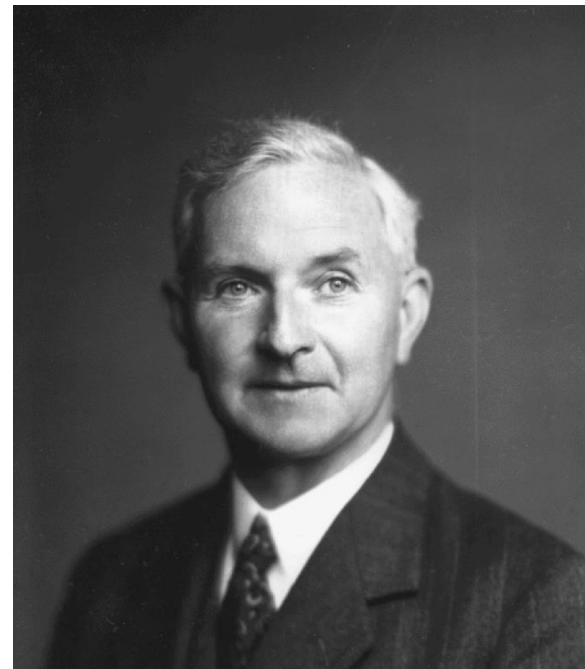80%   10%   10%

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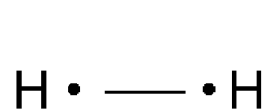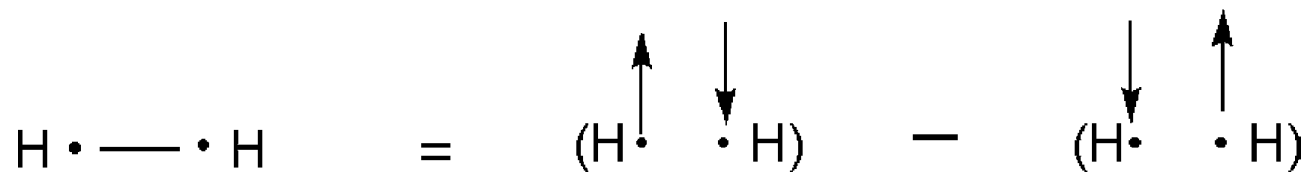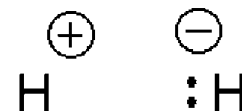
Método de Orbitais Moleculares (MO)
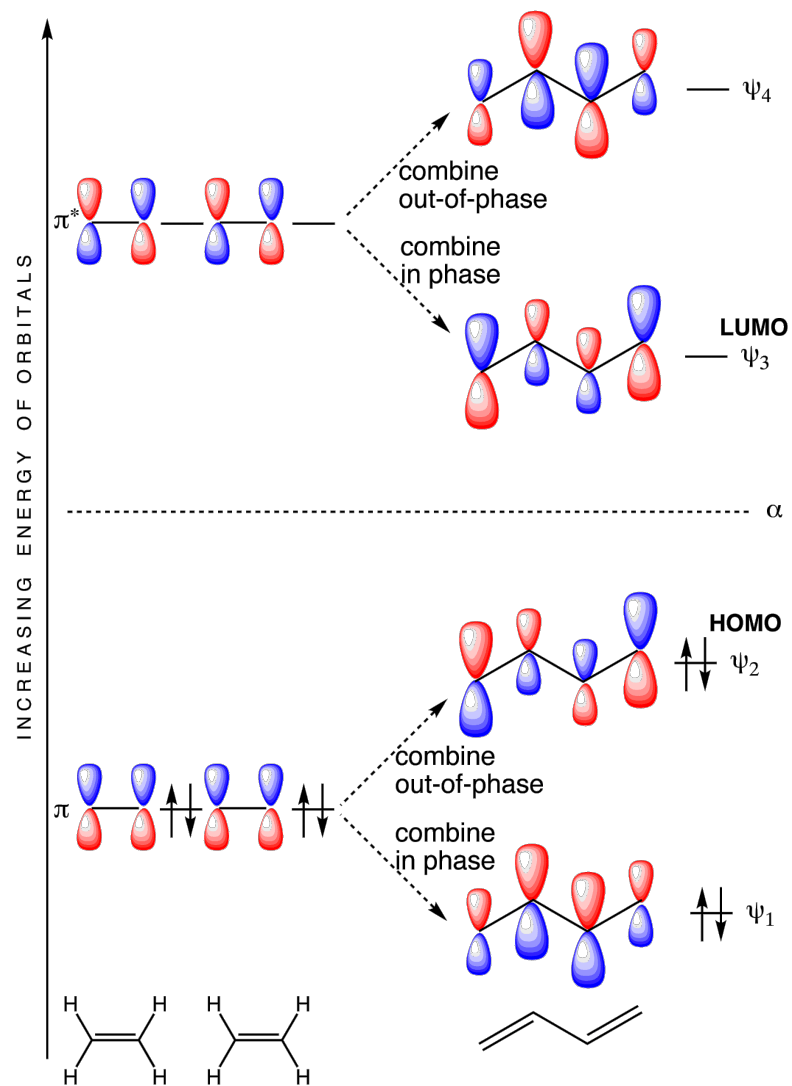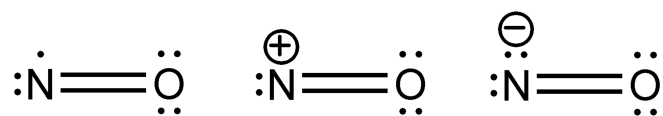
(Mulliken, Hund, Slater, Lennard-Jones (ap. 1930))

N   NO   O

$2\sigma^*$

$2p$ $1\pi^*$

2σ $2p$

1π

$1\sigma^*$

$2s$ $2s$

1σ

$2\sigma^*$

$1\pi^*$

2σ

1π

$1\sigma^*$

1σ

Energy
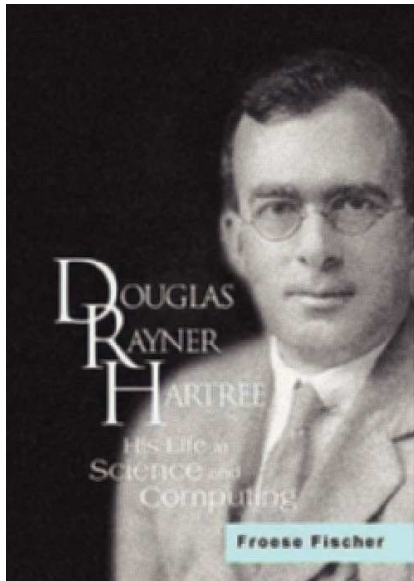
Hartree, Fock - (1928), Roothan - (1951)
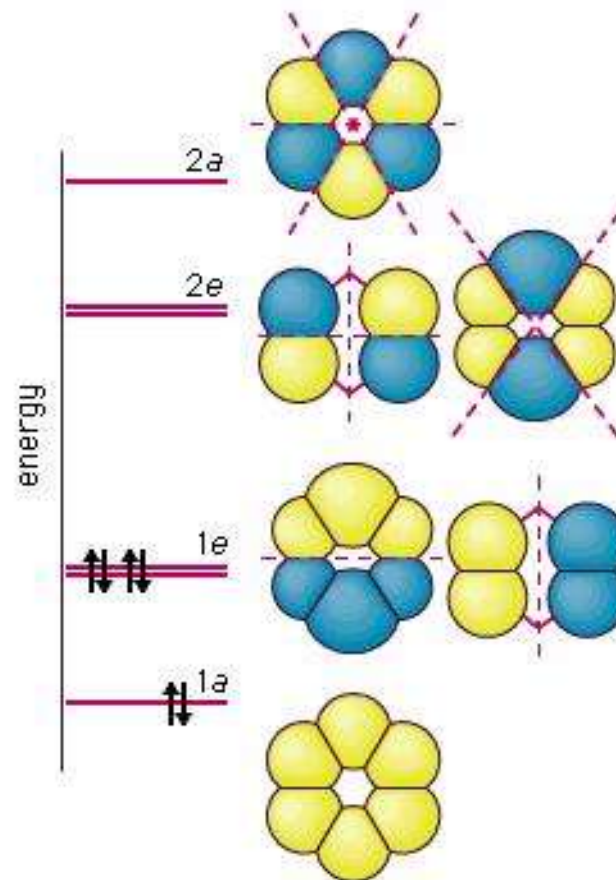
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Método de Hückel - (1930)

21

Ψ_4 ——

Ψ_3 ——

Ψ_2 $\upharpoonleft\!\downharpoonright$ HOMO

Ψ_1 $\upharpoonleft\!\downharpoonright$

π-system molecualr orbitals

H_3C—CH_3

$\left[H_3C \quad CH_3 \right]$

constructive orbital overlap

H_3C CH_3

symmetry allowed product
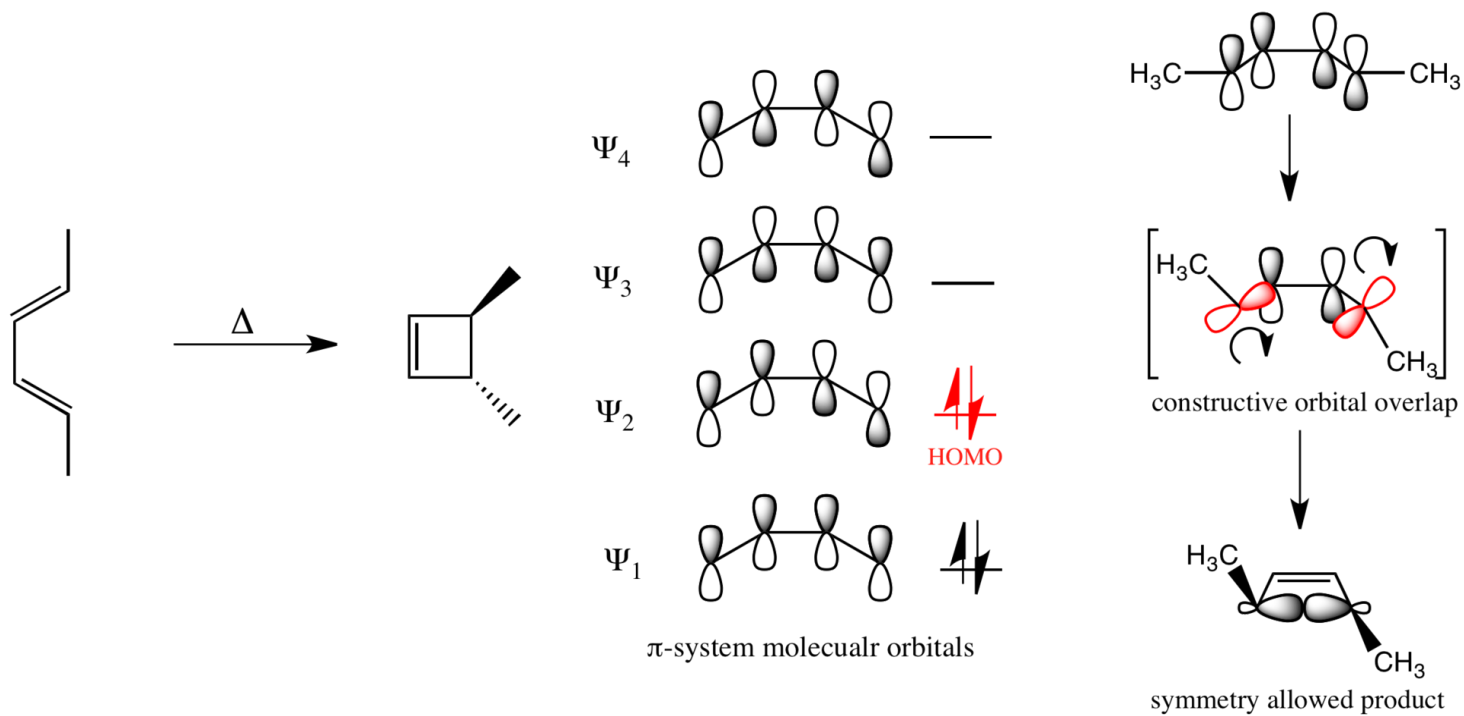
Regras de Woodward-Hoffmann - (1965)

22
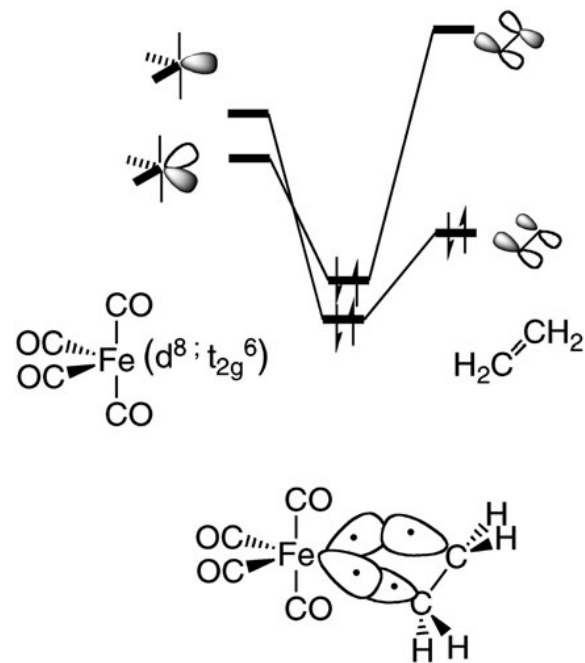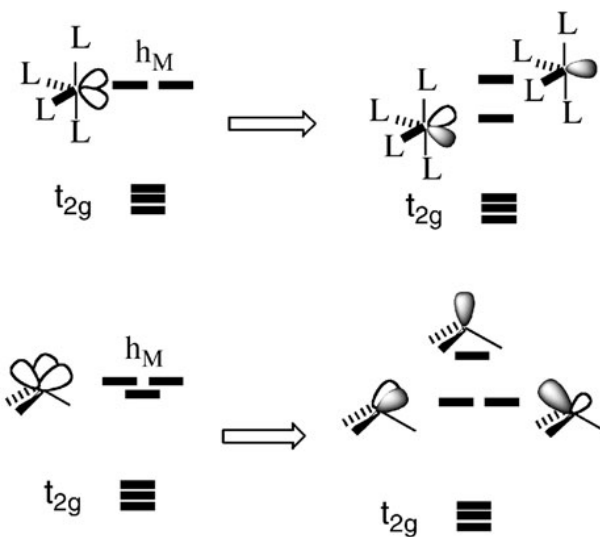
Analogia isolobal - Hoffmann - (1975)
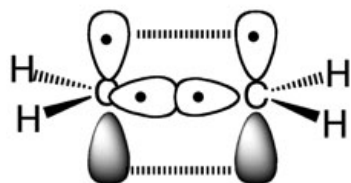
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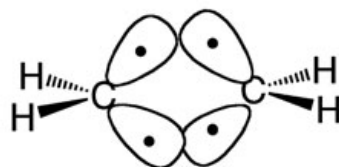
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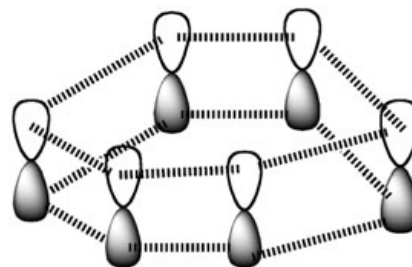
7

Coulson - (1952)

2 – A estrutura de átomos multieletrônicos

2.1 – A aproximação orbital

$$\psi(\vec{r}_1, \vec{r}_2, \vec{r}_3, \ldots) = \psi(\vec{r}_1)\, \psi(\vec{r}_2)\, \psi(\vec{r}_3) \ldots$$

implica que a repulsão intereletrônica é desprezada.

2.1.(a) – O átomo de hélio
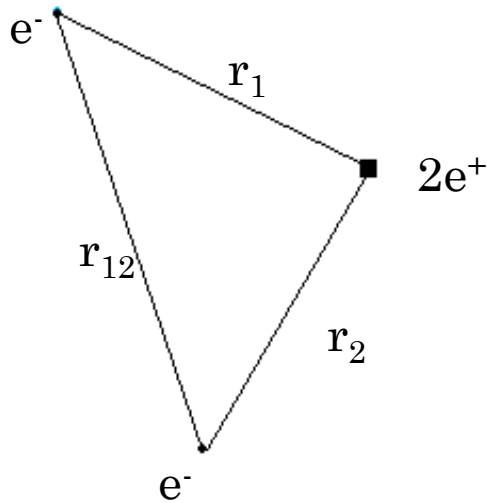
$$\hat{H} = \hat{E}_K(1) + \hat{V}(1) + \hat{E}_K(2) + \hat{V}(2) + \hat{V}(12)$$

$$\widehat{H} = -\frac{\hbar^2}{2m_e}\nabla_1^2\,\psi - \frac{2\,e^2}{4\pi\,\varepsilon_0 r_1} - \frac{\hbar^2}{2m_e}\nabla_2^2\,\psi - \frac{2\,e^2}{4\pi\,\varepsilon_0 r_2} + \frac{e^2}{4\pi\,\varepsilon_0 r_{12}}$$

$$\hat{H} = \hat{E}_K(1) + \hat{V}(1) + \hat{E}_K(2) + \hat{V}(2) = \hat{H}(He^+,1) + \hat{H}(He^+,2)$$

$$\psi(He) = \psi_{1s}(1)\, \psi_{1s}(2) = 1s(1)\, 1s(2)$$

$$E(He) = E(He^+,1) + E(He^+,2)$$

configuração eletrônica: A distribution of the electrons of an atom or a molecular entity over a set of one-electron wavefunctions called orbitals, according to the Pauli principle.

(http://goldbook.iupac.org)

He: $1s^2$

Princípio de Pauli:

Quando a posição de dois férmions idênticos é trocada, a função de onda total, ou **spin-orbital**, deve trocar de sinal, para ser aceitável.

$$\chi(2,1) = -\chi(1,2)$$

$$\chi(1,2) = \psi(1,2)\,\sigma(1,2)$$

$\psi(1,2)$: **orbital espacial**

$\sigma(1,2)$: **função de spin**

Determinante de Slater:

He:

$$\chi_-(1,2) = (\frac{1}{2^{1/2}}) \begin{vmatrix} \psi(1)\alpha(1) & \psi(2)\alpha(2) \\ \psi(1)\beta(1) & \psi(2)\beta(2) \end{vmatrix}$$

de forma geral:

$$\chi(1,2,...,N) = \frac{1}{(N!)^{1/2}} \begin{vmatrix} \psi_a(1)\alpha(1) & \psi_a(2)\alpha(2) & \psi_a(3)\alpha(3) & ... & \psi_a(N)\alpha(N) \\ \psi_a(1)\beta(1) & \psi_a(2)\beta(2) & \psi_a(3)\beta(3) & ... & \psi_a(N)\beta(N) \\ \psi_b(1)\alpha(1) & \psi_b(2)\alpha(2) & \psi_b(3)\alpha(3) & ... & \psi_b(N)\alpha(N) \\ ... & ... & ... & ... & ... \\ \psi_z(1)\beta(1) & \psi_z(2)\beta(2) & \psi_z(3)\beta(3) & ... & \psi_z(N)\beta(N) \end{vmatrix}$$

2.1.(c) – Teorema variacional

$$\frac{\int \phi^* \, \widehat{H} \, \phi \, dr}{\int \phi^* \, \phi \, d\tau} \geq E_{exata}$$

ϕ : função de onda aproximada, bem comportada.

Aplicando-se para ψ, função de onda exata:

$$\frac{\int \psi^* \, \widehat{H} \, \psi \, dr}{\int \psi^* \, \psi \, d\tau} = E_{exata} \int \psi^* \, \psi \, d\tau = E_{exata}$$

2.2 –Orbitais de campo autoconsistente

$$V = -\sum_i \frac{Ze^2}{4\pi\varepsilon_0 r_i} + \frac{1}{2}\sum_{i,j}{}' \frac{e^2}{4\pi\varepsilon_0 r_{ij}}$$

procedimento de **campo autoconsistente de Hartree-Fock** (HF-SCF)

Ne: $1s^2 2s^2 2p^6$

para um elétron do orbital *2p*:

$$\hat{H}(1)\psi_{2p}(1) + V(\text{other electrons})\psi_{2p}(1)$$
$$- V(\text{exchange correction})\psi_{2p}(1) = E_{2p}\psi_{2p}(1)$$
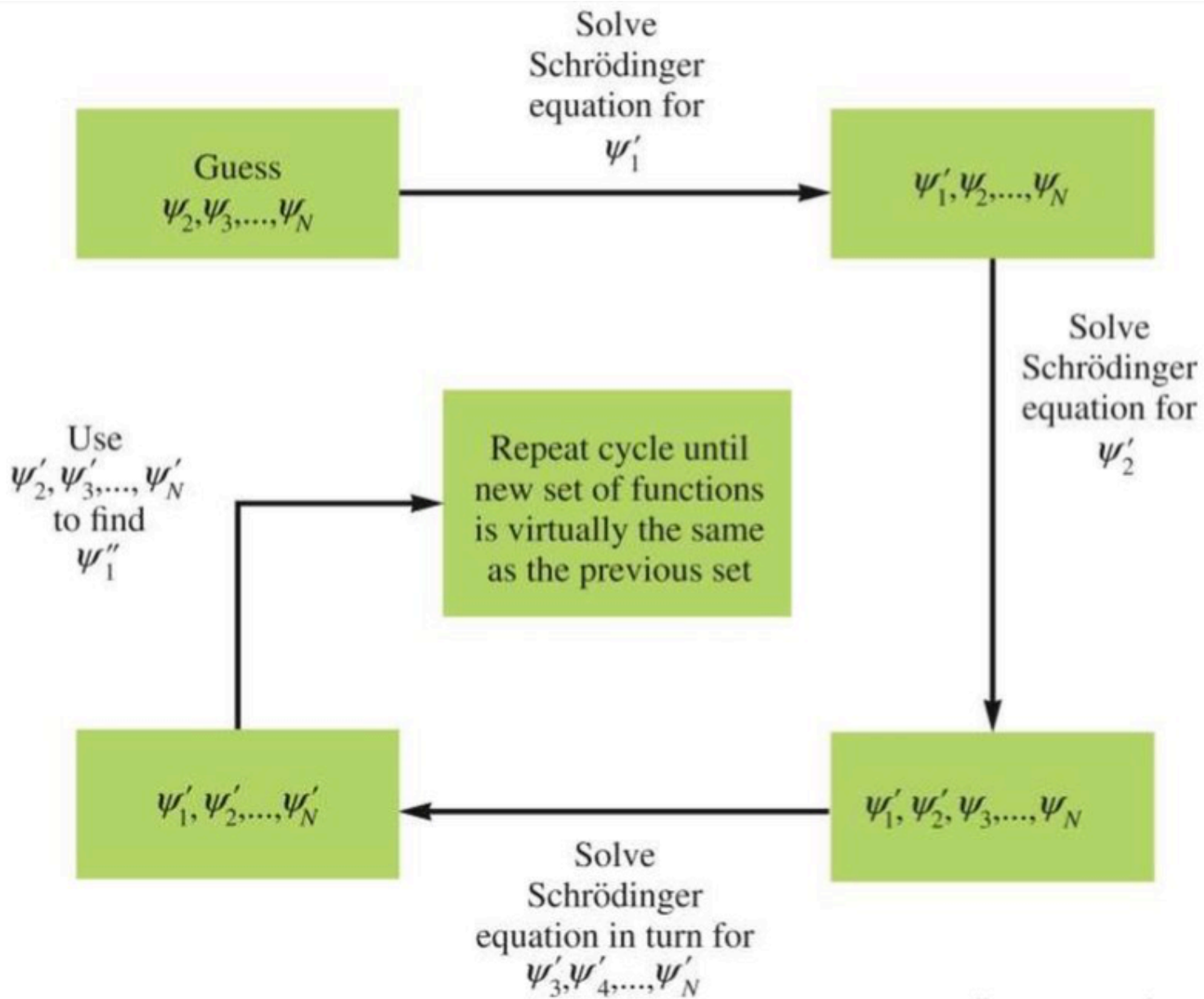
1 – A aproximação de Born-Oppenheimer
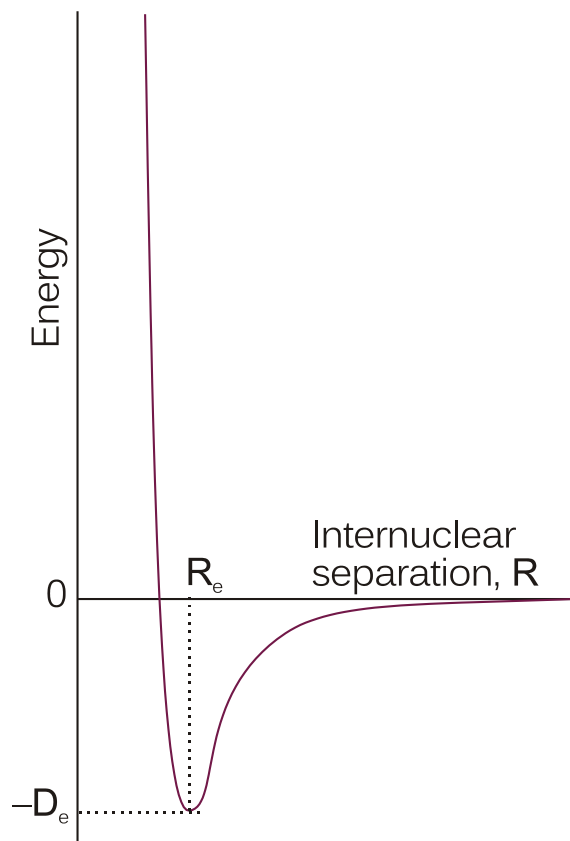
curva de energia potencial molecular

R_e: comprimento de ligação no equilíbrio

D_e: energia de dissociação no equilíbrio

D_0: energia de dissociação do estado fundamental vibracional.

$$D_0 = D_e - \frac{1}{2}\hbar\omega$$

Energy

Internuclear separation, R

R_e

0

$-D_e$

34

potential energy

74 pm

r

attractive forces

repulsive forces

−436 kJ/mol

most stable state
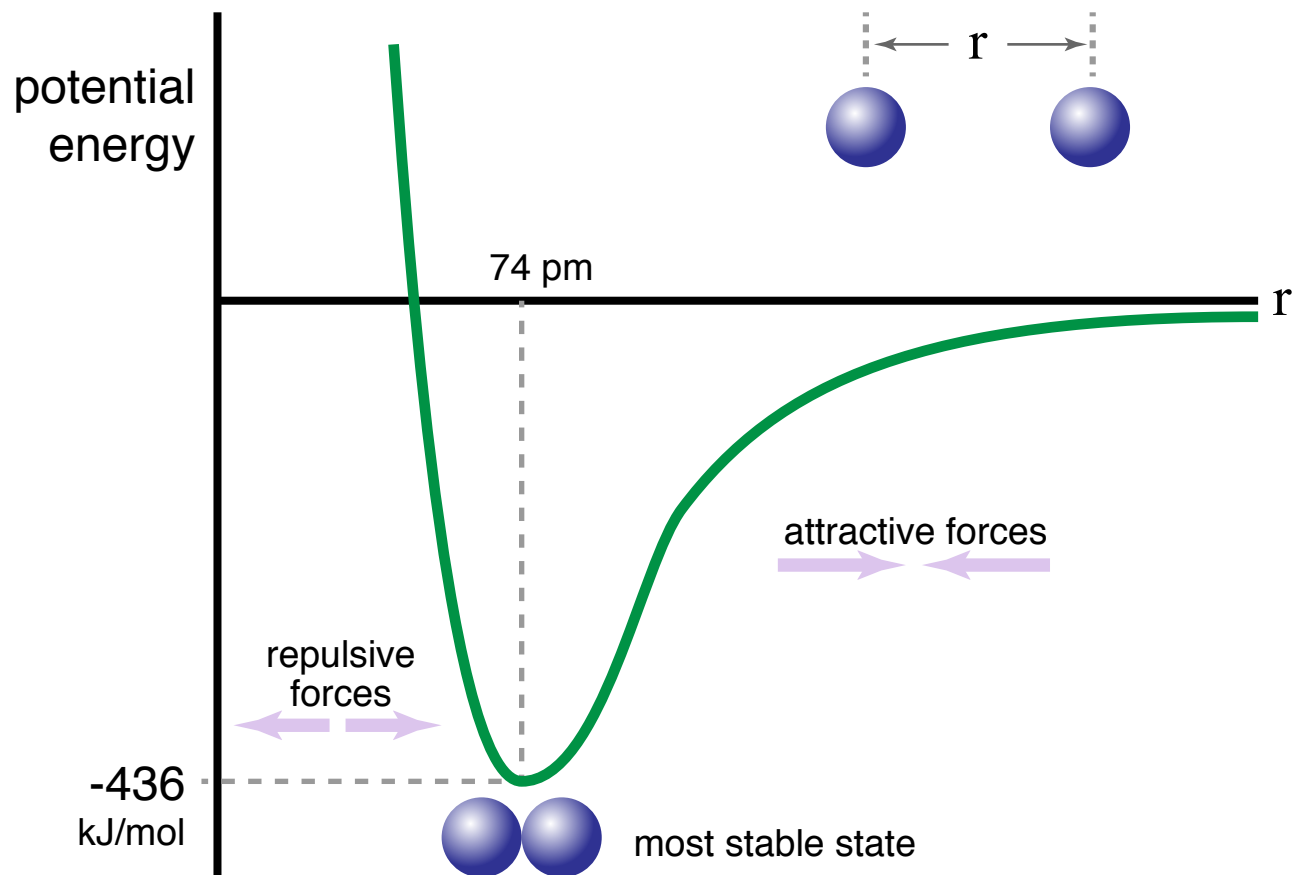
3.3.(c) – O princípio linear variacional

$$\frac{\int \phi^* \; \hat{H} \; \phi \, d\tau}{\int \phi^* \; \phi \, d\tau} \geq E_{exata}$$

ϕ : função de onda aproximada, bem comportada.

mas,

$$\phi = c_A A + c_B B$$

c_A e c_B: parâmetros variacionais.

A, B: **funções de base**.

Os coeficientes c_A e c_B são obtidos a partir das **equações seculares**:

$$\begin{cases} (\alpha_A - E)c_A + (\beta - E\,S)c_B = 0 \\ (\beta - E\,S)c_A + (\alpha_B - E)c_B = 0 \end{cases}$$

$$\alpha_A = H_{AA} = \int A\,\hat{H}\,A\,d\tau \qquad\qquad \alpha_B = H_{BB} = \int B\,\hat{H}\,B\,d\tau$$

$$\beta = H_{AB} = \int A\,\hat{H}\,B\,d\tau = \int B\,\hat{H}\,A\,d\tau$$

α_A e α_B: **integrais atômicas**

β_{AB}: **integral de ressonância**

As energias dos OMs são obtidos a partir do **determinante secular:**

$$\begin{vmatrix} \alpha_A - E & \beta - E\,S \\ \beta - E\,S & \alpha_B - E \end{vmatrix} = 0$$

Primeiro se obtém as energias e depois os coeficientes. Os orbitais moleculares devem ser normalizados:

$$\int \psi^2 \, d\tau = c_A^2 + c_B^2 + 2\,c_A c_B S = 1$$

3.3.(d) – Dois casos simples

1. Molécula diatômica homonuclear

$$\begin{vmatrix} \alpha - E & \beta - E\,S \\ \beta - E\,S & \alpha - E \end{vmatrix} = 0$$

$$E_{+} = \frac{\alpha + \beta}{1 + S} \qquad\qquad c_{A} = c_{B} = \frac{1}{[2(1+S)]^{\frac{1}{2}}}$$

$$E_{-} = \frac{\alpha - \beta}{1 - S} \qquad\qquad c_{A} = \frac{1}{[2(1-S)]^{\frac{1}{2}}} \qquad c_{B} = -c_{A}$$

4 – Orbitais moleculares de moléculas poliatômicas
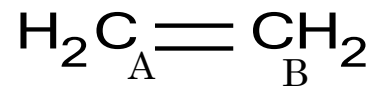
$$\psi_i = \sum_j c_{ij} \chi_j$$

ψ_i: orbital molecular

χ_j: orbital atômico

4.1 – O método de Hückel

- Orbitais π são tratados separadamente dos orbitais σ.

- Orbitais σ formam uma estrutura rígida que determina a forma da molécula.

- As integrais atômicas, α, para os orbitais π de quaisquer carbonos são iguais.

4.1.(a) – Eteno e os orbitais de fronteira

$$H_2C_A \!\!=\!\! CH_{2B}$$

$$\psi_\pi = c_A (A \pm B)$$

$$A = \psi_{2p,A} \qquad\qquad B = \psi_{2p,B}$$

$$\alpha_A = \alpha_B = \alpha$$

$$\begin{vmatrix} \alpha - E & \beta - E\,S \\ \beta - E\,S & \alpha - E \end{vmatrix} = 0$$

Aproximações de Hückel:

1. Todas as integrais de recobrimento são igualadas a zero.

2. Todas as integrais de ressonância entre átomos não vizinhos desconsideradas.

3. Todas as integrais de ressonância restantes são igualadas a β.

Estrutura do determinante secular:

1. Todas elementos diagonais: α - E.

2. Elementos fora da diagonal entre átomos vizinhos: β.

3. Todos os outros elementos: 0.

$$\begin{vmatrix} \alpha - E & \beta \\ \beta & \alpha - E \end{vmatrix} = 0$$

$$E_{\pm} = \alpha \pm \beta$$
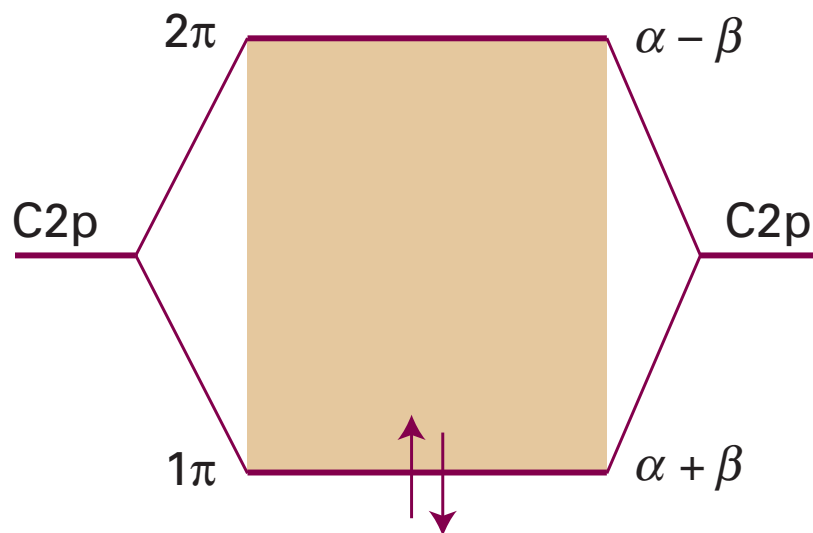
1π: **highest ocuppied molecular orbital (HOMO)**

2π: **lowest unoccupied molecular orbital (LUMO)**

orbitais de fronteira

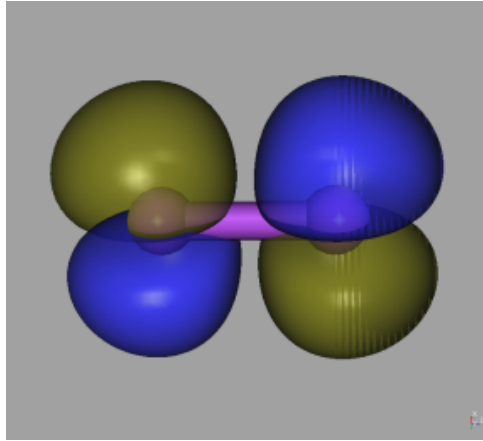orbitais moleculares:

$$\psi_\pi = c_A(A \pm B)$$

$$\int \psi^2 \, d\tau = c_A^2 + c_B^2 + 2\,c_A c_B S = 1$$
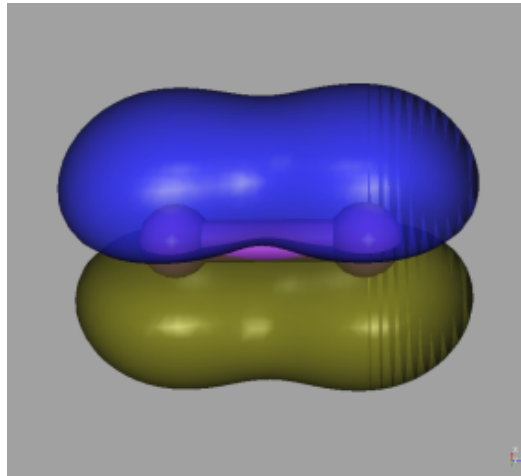
simplificando-se:

$$c_A^2 + c_B^2 = 1$$

$$\psi_\pm = \frac{1}{\sqrt{2}}(A \pm B)$$

$1\pi_g$

$1\pi_u$

4.1.(b) – A formulação matricial do método de Hückel

Equações seculares para um sistema com dois átomos e um orbital em cada átomo:

$$\begin{cases} (H_{AA} - E_i S_{AA})c_{i,A} + (H_{AB} - E_i S_{AB})c_{i,B} = 0 \\ (H_{BA} - E_i S_{BA})c_{i,A} + (H_{BB} - E_i S_{BB})c_{i,B} = 0 \end{cases}$$

E_i correspondem às autofunções:

$$\psi_i = c_{i,A}A + c_{i,B}B$$

Há dois orbitais atômicos, dois autovalores e dois autovetores, portanto:

$$\begin{cases} (H_{AA} - E_1 S_{AA})c_{1,A} + (H_{AB} - E_1 S_{AB})c_{1,B} = 0 \\ (H_{BA} - E_1 S_{BA})c_{1,A} + (H_{BB} - E_1 S_{BB})c_{1,B} = 0 \end{cases}$$

$$\begin{cases} (H_{AA} - E_2 S_{AA})c_{2,A} + (H_{AB} - E_2 S_{AB})c_{2,B} = 0 \\ (H_{BA} - E_2 S_{BA})c_{2,A} + (H_{BB} - E_2 S_{BB})c_{2,B} = 0 \end{cases}$$

pode-se simplificar a solução dessas equações com o uso de matrizes e vetores:

$$\mathbf{H} = \begin{pmatrix} H_{AA} & H_{AB} \\ H_{BA} & H_{BB} \end{pmatrix} \qquad \mathbf{S} = \begin{pmatrix} S_{AA} & S_{AB} \\ S_{BA} & S_{BB} \end{pmatrix} \qquad \mathbf{c}_i = \begin{pmatrix} c_{i,A} \\ c_{i,B} \end{pmatrix}$$

$\mathbf{H}$: matriz do hamiltoniano, $\mathbf{S}$: matriz de recobrimento.

Cada sistema de equações seculares pode ser escrito como:

$$(\mathbf{H} - E_i \mathbf{S})\mathbf{c}_i = 0 \qquad\qquad \mathbf{H}\,\mathbf{c}_i = \mathbf{S}\,\mathbf{c}_i E_i$$

Pode-se definir uma matriz dos coeficientes, **C**, e outra dos autovalores, **E**:

$$\mathbf{C} = (c_1 \quad c_2) = \begin{pmatrix} c_{1,A} & c_{2,A} \\ c_{1,B} & c_{2,B} \end{pmatrix} \qquad\qquad \mathbf{E} = \begin{pmatrix} E_1 & 0 \\ 0 & E_2 \end{pmatrix}$$

Pode-se escrever uma equação matricial:

$$\mathbf{H\,C = S\,C\,E}$$

Na aproximação de Hückel:

$$H_{AA} = H_{BB} = \alpha \qquad\qquad H_{AB} = H_{BA} = \beta \qquad\qquad \mathbf{S = 1}$$

$$H\,C = C\,E$$

$$C^{-1}H\,C = E$$

$$C^{-1}\,C = 1$$

ou seja, se **diagonaliza** a matriz **H**.

as colunas de **C** são os coeficientes dos orbitais atômicos, ou das **funções de base**.