

# O Método de Hartree-Fock

## CF740 – Tópicos Especiais de Física Atômica e Molecular

Cálculos de Estrutura Eletrônica Utilizando Funcionais de Densidade

Departamento de Física

Universidade Federal do Paraná



## Método Variacional

- $E_0 = \langle \Psi_0 | \mathcal{H} | \Psi_0 \rangle$ , onde  $|\Psi_0\rangle = |\chi_1 \chi_2 \dots \chi_a \chi_b \dots \chi_N\rangle$
- $\mathcal{H}$  é o hamiltoniano eletrônico (na aproximação de Born-Oppenheimer), dado por:

$$\mathcal{H} = - \sum_{i=1}^N \frac{1}{2} \nabla_i^2 - \sum_{i=1}^N \sum_{A=1}^M \frac{Z_A}{|\mathbf{r}_i - \mathbf{R}_A|} + \sum_{i=1}^N \sum_{j>i}^N \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|}$$

- A energia total é então escrita na forma de um funcional dos spin-orbitais:

$$E_0[\{\chi_a\}] = \sum_{a=1}^N [a|h|a] + \frac{1}{2} \sum_{a=1}^N \sum_{b=1}^N [aa|bb] - [ab|ba]$$

onde

$$\int d\mathbf{x}_1 \chi_a^*(\mathbf{x}_1) \chi_b(\mathbf{x}_1) = [a|b] = \langle a|b \rangle = \delta_{ab}$$

- Vamos minimizar  $E_0[\chi_a^*, \chi_a] = E_0[\{\chi_a\}]$  em relação aos spin orbitais  $\{\chi_a\}$ , mantendo o vínculo acima, ou seja  $[a|b] = \delta_{ab}$ . Para isso vamos construir o funcional

$$\mathcal{L}[\{\chi_a\}] = E_0[\{\chi_a\}] - \sum_{a=1}^N \sum_{b=1}^N \varepsilon_{ba} ([a|b] - \delta_{ab})$$

onde  $\varepsilon_{ba}$  são os multiplicadores de Lagrange.

# Método Variacional

- $\mathcal{L}[\{\chi_a\}]$  é real e portanto  $\varepsilon_{ba} = \varepsilon_{ab}^*$  ( $[a|b] = [b|a]^*$ ).
- Vamos fazer

$$\chi_a \rightarrow \chi_a + \delta\chi_a$$

e impor que  $\mathcal{L}[\{\chi_a\}]$  seja estacionário, ou seja

$$\delta\mathcal{L}[\{\chi_a\}] = \delta E_0[\{\chi_a\}] - \sum_{a=1}^N \sum_{b=1}^N \varepsilon_{ba} \delta[a|b] = 0$$

- Como resultado obtemos

$$\begin{aligned} \delta\mathcal{L}[\{\chi_a\}] = & \sum_{a=1}^N [\delta\chi_a | h | \chi_a] + \sum_{a=1}^N \sum_{b=1}^N [\delta\chi_a \chi_a | \chi_b \chi_b] - [\delta\chi_a \chi_b | \chi_b \chi_a] - \\ & - \sum_{a=1}^N \sum_{b=1}^N \varepsilon_{ba} [\delta\chi_a | \chi_b] + \text{complexo conjugado} = 0 \end{aligned}$$

# Método Variacional

- Os operadores de Coulomb  $\mathcal{J}_b(1)$  e de troca (exchange)  $\mathcal{K}_b(1)$  são definidos como

$$\mathcal{J}_b(1)\chi_a(1) = \left[ \int d\mathbf{x}_2 \chi_b^*(2) \frac{1}{r_{12}} \chi_b(2) \right] \chi_a(1)$$

$$\mathcal{K}_b(1)\chi_a(1) = \left[ \int d\mathbf{x}_2 \chi_b^*(2) \frac{1}{r_{12}} \chi_a(2) \right] \chi_b(1)$$

tal que

$$\langle \chi_a(1) | \mathcal{J}_b(1) | \chi_a(1) \rangle = [aa|bb]; \quad \langle \chi_a(1) | \mathcal{K}_b(1) | \chi_a(1) \rangle = [ab|ba]$$

- Assim  $\delta\mathcal{L}[\{\chi_a\}] = 0$  resulta em

$$\delta\mathcal{L}[\{\chi_a\}] = \sum_{a=1}^N \int d\mathbf{x}_1 \delta\chi_a^*(1) \left\{ h(1)\chi_a(1) + \sum_{b=1}^N [\mathcal{J}_b(1) - \mathcal{K}_b(1)] \chi_a(1) - \sum_{b=1}^N \varepsilon_{ba} \chi_b(1) \right\} + \text{+complexo conjugado} = 0$$

## Método Variacional

- Como as variações  $\delta\chi_a^*(1)$  (e  $\delta\chi_a(1)$ ) são arbitrárias o termo entre chaves se anula (o mesmo acontece com o c.c.), resultando em

$$\left\{ h(1) + \sum_{b=1}^N [\mathcal{J}_b(1) - \mathcal{K}_b(1)] \right\} \chi_a(1) = \sum_{b=1}^N \varepsilon_{ba} \chi_b(1); \quad a = 1, 2, \dots, N$$

- Definimos o operador de Fock  $f(1)$  como

$$f(1) = h(1) + \sum_{b=1}^N [\mathcal{J}_b(1) - \mathcal{K}_b(1)]$$

tal que

$$f|\chi_a\rangle = \sum_{b=1}^N \varepsilon_{ba} |\chi_b\rangle$$

A expressão acima representa uma equação de autovalores, mas que não está na forma padrão.

# Equações de Hartree-Fock

- Vamos “rodar” os spin-orbitais através de uma transformação unitária  $U (U^\dagger = U^{-1})$

$$\chi'_a = \sum_b \chi_b U_{ba}$$

Neste caso

$$|\Psi'_0\rangle = \det(U)|\Psi_0\rangle = \exp(i\theta)|\Psi_0\rangle, f'(1) = f(1)$$

o que resulta em

$$f|\chi'_a\rangle = \varepsilon'_a|\chi'_a\rangle$$

- Vamos considerar as equações de Hartree-Fock na forma canônica como

$$f|\chi_a\rangle = \varepsilon_a|\chi_a\rangle, f^\dagger = f$$

ou

$$\left\{ h(1) + \sum_{b=1}^N [\mathcal{J}_b(1) - \mathcal{K}_b(1)] \right\} \chi_a(1) = \varepsilon_a \chi_a(1); a = 1, 2, \dots, N$$

que é um conjunto de equações íntegro-diferenciais acopladas.

# Autovalores

- Uma vez definido o operador de Fock  $f$  temos

$$f|\chi_j\rangle = \varepsilon_j|\chi_j\rangle, j = 1, 2, \dots, \infty$$

Qual o significado dos autovalores  $\varepsilon_j$ ?

Considere

$$\langle\chi_i|f|\chi_j\rangle = \varepsilon_j\langle\chi_i|\chi_j\rangle = \varepsilon_i\delta_{ij}$$

ou

$$\begin{aligned}\langle\chi_i|f|\chi_i\rangle &= \langle\chi_i|h + \sum_{b=1}^N [\mathcal{J}_b - \mathcal{K}_b]|\chi_i\rangle = \langle\chi_i|h|\chi_i\rangle + \sum_{b=1}^N [\langle\chi_i|\mathcal{J}_b|\chi_i\rangle - \langle\chi_i|\mathcal{K}_b|\chi_i\rangle] = \\ &= \langle i|h|i\rangle + \sum_{b=1}^N [\langle ib|ib\rangle - \langle ib|bi\rangle] = \langle i|h|i\rangle + \sum_{b=1}^N \langle ib||ib\rangle = \varepsilon_i\end{aligned}$$

Em particular

$$\varepsilon_a = \langle a|h|a\rangle + \sum_{b \neq a}^N [\langle ab|ab\rangle - \langle ab|ba\rangle], \langle aa||aa\rangle = 0$$

$$\varepsilon_r = \langle r|h|r\rangle + \sum_{b=1}^N [\langle rb|rb\rangle - \langle rb|br\rangle]$$

- Somando

$$\sum_{a=1}^N \varepsilon_a = \sum_{a=1}^N \langle a|h|a\rangle + \sum_{a=1}^N \sum_{b=1}^N [\langle ab|ab\rangle - \langle ab|ba\rangle]$$

que não é igual a  $E_0$

$$E_0 = \sum_{a=1}^N \langle a|h|a\rangle + \frac{1}{2} \sum_{a=1}^N \sum_{b=1}^N [\langle ab|ab\rangle - \langle ab|ba\rangle]$$



# Teorema de Koopmans

- A interpretação dos autovalores do operador de Fock  $\epsilon_i$  é dada pelo Teorema de Koopmans:

$$IP = E_a^{N-1} - E_0^N = -\epsilon_a ; EA = E_0^N - E_r^{N+1} = -\epsilon_r$$

onde  $E_a^{N-1}$  e  $E_r^{N+1}$  são as energias totais da molécula com (N-1)-elétrons e (N+1)-elétrons respectivamente, obtidas com os mesmos orbitais utilizados no cálculo de  $E_0$ .

$$|^{N-1}\Psi_a\rangle = |\chi_1 \chi_2 \cdots \chi_{a-1} \chi_{a+1}, \cdots \chi_N\rangle$$

$$|^{N+1}\Psi_r\rangle = |\chi_1 \chi_2 \cdots \chi_N \chi_r\rangle$$

# Teorema de Brillouin

- Teorema de Brillouin

Excitações simples  $|\Psi_a^r\rangle$  não interagem diretamente com o estado de referência Hartree-Fock  $|\Psi_0\rangle$ , isto é  $\langle\Psi_0|\mathcal{H}|\Psi_a^r\rangle = 0$ .

$$\langle\Psi_0|\mathcal{H}|\Psi_a^r\rangle = \langle a|h|r\rangle + \sum_{b=1}^N \langle ab||rb\rangle = \langle a|f|r\rangle = 0$$

## Sistemas com Camada Fechada

- Para sistemas com camada fechada, podemos somar as equações de Hartree-Fock sobre os spins, obtendo

$$f(\mathbf{r}_1)\psi_j(\mathbf{r}_1) = h(\mathbf{r}_1)\psi_j(\mathbf{r}_1) + \left[ 2 \sum_{c=1}^{N/2} \int d^3r_2 \psi_c^*(\mathbf{r}_2) \frac{1}{r_{12}} \psi_c(\mathbf{r}_2) \right] \psi_j(\mathbf{r}_1) - \left[ \sum_{c=1}^{N/2} \int d^3r_2 \psi_c^*(\mathbf{r}_2) \frac{1}{r_{12}} \psi_j(\mathbf{r}_2) \right] \psi_c(\mathbf{r}_1) = \varepsilon_j \psi_j(\mathbf{r}_1)$$

- O operador de Fock neste caso fica

$$f(\mathbf{r}_1) = h(\mathbf{r}_1) + \sum_{a=1}^{N/2} [2J_a(\mathbf{r}_1) - K_a(\mathbf{r}_1)]$$

onde

$$J_a(\mathbf{r}_1) = \int d^3r_2 \psi_a^*(\mathbf{r}_2) \frac{1}{r_{12}} \psi_a(\mathbf{r}_2)$$

e

$$K_a(\mathbf{r}_1)\psi_i(\mathbf{r}_1) = \left[ \int d^3r_2 \psi_a^*(\mathbf{r}_2) \frac{1}{r_{12}} \psi_i(\mathbf{r}_2) \right] \psi_a(\mathbf{r}_1)$$

- Ou, de forma simples

$$f(1)\psi_j(1) = \varepsilon_j\psi_j(1)$$

- $E_0$  fica

$$E_0 = 2 \sum_{a=1}^{N/2} h_{aa} + \sum_{a=1}^{N/2} \sum_{b=1}^{N/2} [2J_{ab} - K_{ab}]$$

- $\varepsilon_i$  fica

$$\varepsilon_i = h_{ii} + \sum_{b=1}^{N/2} [2J_{ib} - K_{ib}]$$

# Equações de Hartree-Fock-Roothaan

- A solução das equações de Hartree-Fock é obtida expandindo-se os orbitais moleculares  $\psi_i$  em termos de um conjunto (não completo) composto por  $K$  orbitais atômicos  $\{\phi_\mu\}$ :

$$\psi_i(\vec{r}) = \sum_{\mu=1}^K C_{\mu i} \phi_\mu(\vec{r}); \quad S_{\mu\nu} = \int d\vec{r}_1 \phi_\mu(1) \phi_\nu(1)$$

- Representação de  $\phi_\mu \rightarrow$  funções Gaussianas Cartesianas:

$$\lambda_{lmn}^{(\alpha\vec{A})} = N_{lmn} (x - A_x)^l (y - A_y)^m (z - A_z)^n e^{-\alpha|\vec{r} - \vec{A}|^2}$$

$$s : l + m + n = 0; \quad p : l + m + n = 1; \quad d : l + m + n = 2$$

- Equação de Hartree-Fock-Roothaan, onde as incógnitas passam a ser os coeficientes reais  $C_{\mu i}$ .

$$\mathbf{FC} = \mathbf{SC}\epsilon \rightarrow \sum_{\nu=1}^K F_{\mu\nu} C_{\nu i} = \epsilon_i \sum_{\nu=1}^K S_{\mu\nu} C_{\nu i}, \quad i = 1, 2, \dots, K$$

# Equações de Hartree-Fock-Roothaan

- Matriz de Fock  $F_{\mu\nu}$

$$F_{\mu\nu} = \int d\vec{r}_1 \phi_\mu(1) f(1) \phi_\nu(1) = H_{\mu\nu}^{core} + G_{\mu\nu}$$

- Termo do “core”

$$H_{\mu\nu}^{core} = T_{\mu\nu} + V_{\mu\nu}^{core}$$

- Energia cinética

$$T_{\mu\nu} = \int d\vec{r}_1 \phi_\mu(1) \left[ -\frac{1}{2} \nabla_1^2 \right] \phi_\nu(1)$$

- Potencial nuclear

$$V_{\mu\nu}^{core} = \int d\vec{r}_1 \phi_\mu(1) \left[ \sum_{\alpha=1}^M -\frac{Z_\alpha}{|\vec{r}_1 - \vec{r}_\alpha|} \right] \phi_\nu(1)$$

- Matriz  $G_{\mu\nu}$

$$G_{\mu\nu} = \sum_{\lambda\sigma} P_{\lambda\sigma} [(\mu\nu|\sigma\lambda) - \frac{1}{2}(\mu\lambda|\sigma\nu)]$$

- Integrais de dois elétrons

$$(\mu\nu|\sigma\lambda) = \int \int d\vec{r}_1 d\vec{r}_2 \phi_\mu(1) \phi_\nu(1) \frac{1}{|\vec{r}_1 - \vec{r}_2|} \phi_\sigma(2) \phi_\lambda(2)$$

# Equações de Hartree-Fock-Roothaan

- Matriz densidade

$$P_{\lambda\sigma} = 2 \sum_{i=1}^{\frac{N}{2}} C_{\lambda i} C_{\sigma i}$$

- Energia eletrônica

$$E_0 = \frac{1}{2} \sum_{\mu} \sum_{\nu} P_{\mu\nu} (H_{\mu\nu}^{core} + F_{\mu\nu})$$

- Energia total

$$E_{tot} = E_0 + \sum_A \sum_{B>A} \frac{Z_A Z_B}{R_{AB}}$$

## Etapas do processo SCF (cálculo *ab initio*)

- 1 Especificar a molécula, fornecendo  $\{\vec{R}_A\}$ ,  $\{Z_A\}$ ,  $N$ , e definir a base  $\{\phi_\mu\}$  a ser utilizada.
- 2 Calcular todas as integrais primitivas:  $S_{\mu\nu}$ ,  $H_{\mu\nu}^{core}$ ,  $(\mu\nu|\lambda\sigma)$ .
- 3 Diagonalizar  $S$  para obter a matriz de transformação  $X$ .
- 4 Fornecer um “chute” inicial para  $P$  ( $P_{\mu\nu} = 2 \sum_{a=1}^{N/2} C_{\mu a} C_{\nu a}^*$ ).
- 5 Calcular  $G$ , usando  $P$  e  $(\mu\nu|\lambda\sigma)$  ( $G_{\mu\nu} = \sum_{\lambda=1}^K \sum_{\sigma=1}^K P_{\lambda\sigma} [(\mu\nu|\sigma\lambda) - 1/2(\mu\lambda|\sigma\nu)]$ ).
- 6 Formar  $F$  a partir de  $G$  e  $H^{core}$  ( $F = H^{core} + G$ ).
- 7 Calcular  $F' = X^\dagger F X$ .
- 8 Diagonalizar  $F'$  para obter  $C'$  e  $\epsilon$ .
- 9 Calcular  $C = X C'$ .
- 10 Formar nova  $P$  usando  $C$  ( $P_{\mu\nu} = 2 \sum_{a=1}^{N/2} C_{\mu a} C_{\nu a}^*$ ).
- 11 Calcular  $E_0$  e  $E_{tot}$  ( $E_0 = \frac{1}{2} \sum_{\mu=1}^K \sum_{\nu=1}^K P_{\nu\mu} (H_{\mu\nu}^{core} + F_{\mu\nu})$ ).
- 12 Determinar se o processo convergiu.



# Self-consistent field (SCF)

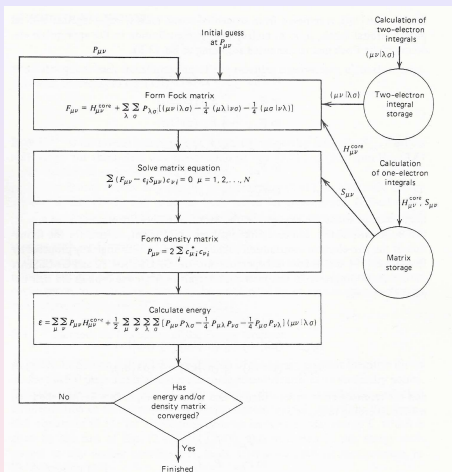


FIGURE 3.4. Sequence of program steps required for the solution of the Roothaan-Hall equations for a closed-shell system. The loop involving the steps labeled "Form Fock matrix," "Solve matrix equation," "Form density matrix," and "Calculate energy" is initiated by specification of a guess at the density matrix, and terminated upon satisfaction of convergence for either the density matrix or the energy. The one- and two-electron integrals ( $S_{\mu\nu}$ ,  $H_{\mu\nu}^{core}$ , and  $(\mu\nu|\lambda\sigma)$ ) have been calculated and placed in mass storage prior to the start of execution of the SCF procedure. They are accessed during each cycle of the SCF procedure.

# Funções Gaussianas Cartesianas

- “ The choice of a basis is more of an art than a science” (Szabo-Ostlund).
- MO-LCAO

$$\psi_i(\vec{r}) = \sum_{\mu=1}^K C_{\mu i} \phi_{\mu}(\vec{r}); S_{\mu\nu} = \int d\vec{r}_1 \phi_{\mu}^*(1) \phi_{\nu}(1)$$

- Representação de  $\phi_{\mu} \rightarrow$  funções Gaussianas Cartesianas:

$$\lambda_{lmn}^{(\alpha\vec{A})} = N_{lmn} (x - A_x)^l (y - A_y)^m (z - A_z)^n e^{-\alpha|\vec{r}-\vec{A}|^2}$$

$$s : l + m + n = 0; p : l + m + n = 1; d : l + m + n = 2$$

- Bases contraídas:

$$\phi_{\mu}^{(CGF)}(\vec{r} - \vec{R}_A) = \sum_{p=1}^L d_{p\mu} g_p(\alpha_{p\mu}^{GF}, \vec{r} - \vec{R}_A); g_p(\alpha_{p\mu}^{GF}, \vec{r} - \vec{R}_A) \rightarrow \text{primitivas}$$

$$\phi_{\mu}^{(CGF)}(\vec{r} - \vec{R}_A) = \sum_{p=1}^L d_{p\mu} g_p(\alpha_{p\mu}, \vec{r} - \vec{R}_A)$$

$$g_{1s}(\alpha, \vec{r}) = \left(\frac{8\alpha^3}{\pi^3}\right)^{1/4} \exp(-\alpha r^2)$$

$$g_{1p_x}(\alpha, \vec{r}) = \left(\frac{128\alpha^5}{\pi^3}\right)^{1/4} x \exp(-\alpha r^2)$$

$$g_{1d_{xy}}(\alpha, \vec{r}) = \left(\frac{2048\alpha^7}{\pi^3}\right)^{1/4} xy \exp(-\alpha r^2)$$

- Conjuntos de base (internas ao pacote GAMESS): STO-3G, 3-21G, 4-31G, 6-31G, 6-31G\*, 6-31G\*\*, 6-311G, 6-311G\*, 6-311G\*\*, DZV, TZV ...

# Contrações

- Exemplo: contração (4s)/[2s] para o hidrogênio de Huzinaga.  
primitivas (4s):

$$\begin{aligned}\psi_{1s} = & 0.50907g_{1s}(0.123317, \vec{r}) \\ & + 0.47449g_{1s}(0.453757, \vec{r}) \\ & + 0.13424g_{1s}(2.0133, \vec{r}) \\ & + 0.01906g_{1s}(13.3615, \vec{r})\end{aligned}$$

contraído a (4s)/[2s]:

$$\begin{aligned}\phi_1(\vec{r}) &= g_{1s}(0.123317, \vec{r}) \\ \phi_2(\vec{r}) &= 0.817238g_{1s}(0.453757, \vec{r}) \\ &+ 0.231208g_{1s}(2.0133, \vec{r}) \\ &+ 0.032828g_{1s}(13.3615, \vec{r}) \\ \psi_{1s} \longrightarrow \psi_{1s} &= \phi_1 + \phi_2\end{aligned}$$

- Átomos pesados: (9s5p)/[3s2p]
- Átomos pesados + hidrogênio: (9s5p/4s)/[3s2p/2s]

- Hidrogênio:

$$\phi'_{1s} = \sum_{i=1}^3 d'_{i,1s} g_{1s}(\alpha'_{i,1s}, \vec{r})$$

$$\phi''_{1s} = g_{1s}(\alpha''_{1s}, \vec{r})$$

- Para Li até F:

$$\phi_{1s} = \sum_{i=1}^4 d_{i,1s} g_{1s}(\alpha_{i,1s}, \vec{r})$$

$$\phi'_{2s} = \sum_{i=1}^3 d'_{i,2s} g_{2s}(\alpha'_{i,2s}, \vec{r})$$

$$\phi''_{2s} = g_{2s}(\alpha''_{2s}, \vec{r})$$

$$\phi'_{2p} = \sum_{i=1}^3 d'_{i,2p} g_{2p}(\alpha'_{i,2p}, \vec{r})$$

$$\phi''_{2p} = g_{2p}(\alpha''_{2p}, \vec{r})$$

## 6-31G\* e 6-31G\*\*

- \*: função do tipo  $d$  no átomo pesado
- \*\*: função do tipo  $d$  no átomo pesado e função do tipo  $p$  no hidrogênio.
- Hierarquia das bases: STO-3G, 4-31G, 6-31G, 6-31G\* e 6-31G\*\*
- Outras bases: DZV, TZV, 6-311G . . .
- Notação: 6-311+G(1d), 6-311++G(1d)
  - + : funções difusas do tipo  $s$  e do tipo  $p$  no átomo pesado.
  - ++ : funções difusas do tipo  $s$  e do tipo  $p$  no átomo pesado e função difusa do tipo  $s$  no hidrogênio.

$$(\mu_A \nu_B | \lambda_C \sigma_D) = \int d\vec{r}_1 \int d\vec{r}_2 \phi_\mu^{A*}(1) \phi_\nu^B(1) \frac{1}{|\vec{r}_1 - \vec{r}_2|} \phi_\lambda^{C*}(2) \phi_\sigma^D(2)$$

$$\phi_{1s}^{GF}(\alpha, \vec{r} - \vec{R}_A) = \left(\frac{2\alpha}{\pi}\right)^{3/4} \exp\left[-\alpha|\vec{r} - \vec{R}_A|^2\right]$$

$$\phi_{1s}^{GF}(\alpha, \vec{r} - \vec{R}_A) \phi_{1s}^{GF}(\beta, \vec{r} - \vec{R}_B) = K_{AB} \phi_{1s}^{GF}(p, \vec{r} - \vec{R}_P)$$

$$K_{AB} = \left(\frac{2\alpha\beta}{(\alpha + \beta)\pi}\right)^{3/4} \exp\left[-\frac{\alpha\beta}{(\alpha + \beta)}|\vec{R}_A - \vec{R}_B|^2\right]$$

$$p = \alpha + \beta, \vec{R}_P = \frac{\alpha\vec{R}_A + \beta\vec{R}_B}{\alpha + \beta}$$

$$(\mu_A \nu_B | \lambda_C \sigma_D) = K_{AB} K_{CD} \int d\vec{r}_1 \int d\vec{r}_2 \phi_{1s}^{GF}(p, \vec{r}_1 - \vec{R}_P) \frac{1}{|\vec{r}_1 - \vec{r}_2|} \phi_{1s}^{GF}(q, \vec{r}_2 - \vec{R}_Q)$$

$$\phi_{\mu}^{(CGF)}(\vec{r} - \vec{R}_A) = \sum_{p=1}^L d_{p\mu} \phi_p(\alpha_{p\mu}^{GF}, \vec{r} - \vec{R}_A)$$

$$\begin{aligned} \phi_{1s}^{CGF}(\zeta = 1.0, STO - 3G) = & 0.444635\phi_{1s}(\alpha = 0.109818) \\ & + 0.535328\phi_{1s}(\alpha = 0.405771) \\ & + 0.154329\phi_{1s}(\alpha = 2.22766) \end{aligned}$$

Fator de escala dos expoentes:  $\zeta_H = 1.24, \zeta_{He} = 2.0925$

$$\exp[-(\zeta r)] \leftrightarrow \exp[-(\sqrt{\alpha}r)^2]$$

$$\frac{\zeta'}{\zeta} = \left(\frac{\alpha'}{\alpha}\right)^{1/2} \rightarrow \alpha = \alpha(\zeta = 1.0) \times \zeta^2$$



$$\begin{aligned} H : \phi_{1s}^{CGF}(\zeta = 1.24, STO - 3G) = & \quad 0.444635\phi_{1s}(\alpha = 0.168856) \\ & + \quad 0.535328\phi_{1s}(\alpha = 0.623913) \\ & + \quad 0.154329\phi_{1s}(\alpha = 3.42525) \end{aligned}$$

$$\begin{aligned} He : \phi_{1s}^{CGF}(\zeta = 2.0925, STO - 3G) = & \quad 0.444635\phi_{1s}(\alpha = 0.229794) \\ & + \quad 0.535328\phi_{1s}(\alpha = 0.849076) \\ & + \quad 0.154329\phi_{1s}(\alpha = 4.661379) \end{aligned}$$

No GAMESS  $\zeta_{He} = 1.69$ :

$$\begin{aligned} \phi_{1s}^{CGF}(\zeta = 1.69, STO - 3G) = & \quad 0.444635\phi_{1s}(\alpha = 0.0313651) \\ & + \quad 0.535328\phi_{1s}(\alpha = 1.158922) \\ & + \quad 0.154329\phi_{1s}(\alpha = 6.362420) \end{aligned}$$

## Base mínima: $H_2$

Vimos em aula, que no modelo de base mínima para a molécula de  $H_2$  temos:

$$\psi_1 = \frac{1}{\sqrt{2(1+S_{12})}}(\phi_1 + \phi_2); \psi_2 = \frac{1}{\sqrt{2(1-S_{12})}}(\phi_1 - \phi_2)$$

$$\mathbf{C} = \begin{pmatrix} \frac{1}{\sqrt{2(1+S_{12})}} & \frac{1}{\sqrt{2(1-S_{12})}} \\ \frac{1}{\sqrt{2(1+S_{12})}} & -\frac{1}{\sqrt{2(1-S_{12})}} \end{pmatrix}$$

$$\mathbf{P} = \frac{1}{1+S_{12}} \begin{pmatrix} 1 & 1 \\ 1 & 1 \end{pmatrix}$$

$$S_{\mu\nu} = \int d\vec{r} \phi_{\mu}^{CGF*}(\vec{r} - \vec{R}_A) \phi_{\nu}^{CGF}(\vec{r} - \vec{R}_B) = \sum_{p=1}^L \sum_{q=1}^L d_{p\mu}^* d_{q\nu} S_{pq}$$

$$\mathbf{S} = \begin{pmatrix} 1 & 0.6593 \\ 0.6593 & 1 \end{pmatrix}$$

$$\begin{vmatrix} 1-s & S_{12} \\ S_{12} & 1-s \end{vmatrix} = 0 \rightarrow s = 1 \pm S_{12}$$

$$s_1 = 1.6593, s_2 = 0.3407$$

$$\mathbf{s}^{-1/2} = \begin{pmatrix} 0.7763 & 0 \\ 0 & 1.7133 \end{pmatrix}$$

$$\mathbf{U} = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 & 1 \\ 1 & -1 \end{pmatrix}$$

## Base mínima: $H_2$

Vamos utilizar a ortogonalização canônica  $\mathbf{X} = \mathbf{U}\mathbf{S}^{-1/2}$

$$\mathbf{X} = \begin{pmatrix} 0.5489 & 1.2115 \\ 0.5489 & -1.2115 \end{pmatrix}$$

$$\mathbf{C} = \begin{pmatrix} 0.5489 & 1.2115 \\ 0.5489 & -1.2115 \end{pmatrix}$$

$$\mathbf{P} = \begin{pmatrix} 0.6027 & 0.6027 \\ 0.6027 & 0.6027 \end{pmatrix}$$

SCF CALCULATION FOR H2 MOLECULE

THE MAXIMUM NUMBER OF ITERATIONS IS EQUAL TO 10

THE CONVERGENCE CRITERION IS 0.10E-09

STO-3G FOR ATOMIC NUMBERS 1.00 AND 1.00

R	ZETA1	ZETA2	S12	T11
1.400000	1.240000	1.240000	0.659319	0.760033
T12	T22	V11A	V12A	V22A
0.236455	0.760033	-1.226615	-0.597418	-0.653828
V11B	V12B	V22B	V1111	V2111
-0.653828	-0.597418	-1.226615	0.774608	0.444109
V2121	V2211	V2221	V2222	
0.297029	0.569678	0.444109	0.774608	

```
THE S      ARRAY
           1              2
1          0.1000000000E+01  0.6593189894E+00
2          0.6593189894E+00  0.1000000000E+01

THE X      ARRAY
           1              2
1          0.5489339108E+00  0.1211465466E+01
2          0.5489339108E+00 -0.1211465466E+01

THE H      ARRAY
           1              2
1          -0.1120410675E+01 -0.9583811907E+00
2          -0.9583811907E+00 -0.1120410675E+01
```

H<sub>2</sub>

```
( 1 1 1 1 ) 0.774608
( 1 1 1 2 ) 0.444109
( 1 1 2 1 ) 0.444109
( 1 1 2 2 ) 0.569678
( 1 2 1 1 ) 0.444109
( 1 2 1 2 ) 0.297029
( 1 2 2 1 ) 0.297029
( 1 2 2 2 ) 0.444109
( 2 1 1 1 ) 0.444109
( 2 1 1 2 ) 0.297029
( 2 1 2 1 ) 0.297029
( 2 1 2 2 ) 0.444109
( 2 2 1 1 ) 0.569678
( 2 2 1 2 ) 0.444109
( 2 2 2 1 ) 0.444109
( 2 2 2 2 ) 0.774608
```

```
THE P      ARRAY
          1          2
1          0.0000000000E+00  0.0000000000E+00
2          0.0000000000E+00  0.0000000000E+00
```





START OF ITERATION NUMBER = 1

THE G ARRAY

	1	2
1	0.0000000000E+00	0.0000000000E+00
2	0.0000000000E+00	0.0000000000E+00

THE F ARRAY

	1	2
1	-0.1120410675E+01	-0.9583811907E+00
2	-0.9583811907E+00	-0.1120410675E+01

ELECTRONIC ENERGY = 0.0000000000E+00

```
THE F'   ARRAY
          1           2
1      -0.1252798214E+01  0.2602085214E-17
2      -0.8044780120E-16 -0.4756046848E+00
```

```
THE C'   ARRAY
          1           2
1      0.1000000000E+01 -0.3348053113E-17
2     -0.3348053113E-17 -0.1000000000E+01
```

```
THE E    ARRAY
          1           2
1     -0.1252798214E+01  0.0000000000E+00
2      0.0000000000E+00 -0.4756046848E+00
```



```
THE C      ARRAY
           1              2
1          0.5489339108E+00 -0.1211465466E+01
2          0.5489339108E+00  0.1211465466E+01

THE P      ARRAY
           1              2
1          0.6026568769E+00  0.6026568769E+00
2          0.6026568769E+00  0.6026568769E+00

DELTA(CONV OF DENSITY MATRIX) = 0.602656876933E+00
```



START OF ITERATION NUMBER = 2

THE G ARRAY

	1	2
1	0.7548735870E+00	0.3644955252E+00
2	0.3644955252E+00	0.7548735870E+00

THE F ARRAY

	1	2
1	-0.3655370883E+00	-0.5938856654E+00
2	-0.5938856654E+00	-0.3655370883E+00

ELECTRONIC ENERGY = -0.183100093420E+01

```
THE F'   ARRAY
          1           2
1      -0.5782027204E+00  0.1371515748E-16
2      0.1100465205E-16  0.6702709280E+00
```

```
THE C'   ARRAY
          1           2
1      0.1000000000E+01 -0.1098554022E-16
2     -0.1098554022E-16 -0.1000000000E+01
```

```
THE E    ARRAY
          1           2
1     -0.5782027204E+00  0.0000000000E+00
2      0.0000000000E+00  0.6702709280E+00
```

```
THE C      ARRAY
           1              2
1          0.5489339108E+00 -0.1211465466E+01
2          0.5489339108E+00  0.1211465466E+01

THE P      ARRAY
           1              2
1          0.6026568769E+00  0.6026568769E+00
2          0.6026568769E+00  0.6026568769E+00

DELTA(CONV OF DENSITY MATRIX) = 0.000000000000E+00
```



CALCULATION CONVERGED

ELECTRONIC ENERGY = -0.183100093420E+01

TOTAL ENERGY = -0.111671521992E+01

THE PS ARRAY

	1	2
1	0.1000000000E+01	0.1000000000E+01
2	0.1000000000E+01	0.1000000000E+01

TRACO DE PS = 2.0000

# GAMESS

```
!...Exemplo de input para H2...  
$CONTRL SCFTYP=RHF COORD=CART UNITS=BOHR $END  
$SYSTEM MEMORY=10000000 TIMLIM=60000 $END  
$SCF DIRSCF=.TRUE. $END  
$BASIS GBASIS=STO NGAUSS=3 $END  
$DATA  
...H2-RHF/STO-3G...  
Dnh 2  
  
H 1.0 0.0 0.0 0.7  
H 1.0 0.0 0.0 -0.7  
$END
```



# Resultados

				1	2
				-0.5782	0.6703
				AG	B1U
1	H	1	S	0.548934	1.211464
2	H	2	S	0.548934	-1.211464

ONE ELECTRON ENERGY = -2.5055941252  
TWO ELECTRON ENERGY = 0.6745940858  
NUCLEAR REPULSION ENERGY = 0.7142857143  
TOTAL ENERGY = -1.1167143251