

Hartree-Fock theory

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1 SCF Implementation

1.1 Roothaan equations

- Once the spin is integrated out, the HF equations in spatial orbital form are

$$f(r_1)\psi_i(r_1) = \epsilon_i\psi_i(r_1)$$

- Introducing a basis

$$\psi_i = \sum_{\mu=1}^K C_{\mu i} \phi_{\mu}$$

leads to the integrated HF equations in matrix form, the **Roothaan** equations

$$FC = SC\epsilon$$

- The fock matrix F has elements

$$F_{\mu\nu} = \int dr_1 \phi_{\mu}^*(1)f(1)\phi_{\nu}(1)$$

- The overlap matrix S has elements

$$S_{\mu\nu} = \int dr_1 \phi_{\mu}^*(1)\phi_{\nu}(1)$$

- The expansion coefficients $C_{\mu i}$ form a $K \times K$ matrix C

$$C = \begin{pmatrix} C_{11} & C_{12} & \cdots & C_{1K} \\ C_{21} & C_{22} & \cdots & C_{2K} \\ \vdots & \vdots & & \vdots \\ C_{K1} & C_{K2} & \cdots & C_{KK} \end{pmatrix}$$

Las columnas de esta matriz describen a los orbitales moleculares, i.e. $\psi_i = \sum_{\mu} C_{\mu i} \phi_{\mu}$

- The orbital energies ϵ_i in matrix form are

$$\epsilon = \begin{pmatrix} \epsilon_1 & & & 0 \\ & \epsilon_2 & & \\ 0 & & \ddots & \\ & & & \epsilon_k \end{pmatrix}$$

1.2 Density matrix

In restricted HF (for closed-shell) molecules, the charge density is

$$\rho(r) = 2 \sum_a^{N/2} |\psi_a(r)|^2$$

Introducing the basis expansion gives

$$\begin{aligned} \rho(r) &= \sum_{\mu\nu} \left[2 \sum_a^{N/2} C_{\mu a} C_{\nu a}^* \right] \phi_{\mu}(r) \phi_{\nu}^*(r) \\ \rho(r) &= \sum_{\mu\nu} P_{\mu\nu} \phi_{\mu}(r) \phi_{\nu}^*(r) \end{aligned}$$

then the density matrix is

$$P_{\mu\nu} = 2 \sum_a^{N/2} C_{\mu a} C_{\nu a}^* \quad (1)$$

1.3 Fock matrix

The matrix representation of the Fock operator $f(1) = h(1) + \sum_a^{N/2} 2J_a(1) - K_a(1)$ in the basis $\{\phi_{\mu}\}$ is

$$\begin{aligned} F_{\mu\nu} &= \int dr_1 \phi_{\mu}^*(1) h(1) \phi_{\nu}(1) + \sum_a^{N/2} \int dr_1 \phi_{\mu}^*(1) [2J_a(1) - K_a(1)] \phi_{\nu}(1) \\ F_{\mu\nu} &= H_{\mu\nu}^{\text{core}} + \sum_a^{N/2} 2(\mu\nu|aa) - (\mu a|a\nu) \end{aligned}$$

- Here, the core-Hamiltonian matrix is

$$H_{\mu\nu}^{\text{core}} = \int dr_1 \phi_{\mu}^*(1) h(1) \phi_{\nu}(1)$$

to evaluate this matrix, we need the kinetic energy integrals and the nuclear attraction integrals

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

This matrix need only be evaluated once in the SCF procedure

- In the Fock matrix, when we insert the linear expansion of the molecular orbitals into the two-electron terms

$$\begin{aligned} F_{\mu\nu} &= H_{\mu\nu}^{\text{core}} + \sum_a^{N/2} \sum_{\lambda\sigma} C_{\lambda a} C_{\sigma a}^* [2(\mu\nu|\sigma\lambda) - (\mu\lambda|\sigma\nu)] \\ F_{\mu\nu} &= H_{\mu\nu}^{\text{core}} \sum_{\lambda\alpha} P_{\lambda\sigma} [(\mu\nu|\sigma\lambda) - \frac{1}{2}(\mu\lambda|\sigma\nu)] \\ F_{\mu\nu} &= H_{\mu\nu}^{\text{core}} + G_{\mu\nu} \end{aligned}$$

where $G_{\mu\nu}$ is the two-electron part of the Fock matrix

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

- The two-electron integrals are

$$(\mu\nu|\lambda\sigma) = \int dr_1 dr_2 \phi_\mu^*(1) \phi_\nu(1) r_{12}^{-1} \phi_\lambda^*(2) \phi_\sigma(2)$$

1.4 Canonical orthogonalization

The condition that a transformation matrix X must obey in order to form an orthonormal set

$$\int dr \phi_\mu'^*(r) \phi_\nu'(r) = \delta_{\mu\nu}$$

is

$$X^\dagger S X = \mathbb{I}$$

Canonical orthogonalization uses a transformation matrix

$$X = U s^{-1/2} \quad (3)$$

where U is a unitary matrix that diagonalizes S

$$U^\dagger S U = s$$

and s is a diagonal matrix of the eigenvalues of S

Consider a new coefficient matrix C' related to the old coefficient matrix C by

$$C' = X^{-1} C, \quad C = X C' \quad (4)$$

substituting C into the Roothaan equations gives

$$F X C' = S X C' \epsilon$$

if we define a new matrix F' by

$$F' = X^\dagger F X \quad (5)$$

and use the orthonormality condition on S , $X^\dagger S X = \mathbb{I}$, then by multiplying on the left by X^\dagger

$$F' C' = C' \epsilon \quad (6)$$

this transformed Roothaan equations can be solved for C' by diagonalizing F' , which can be used to get C .

Therefore, given F , we can use (6), (5), and (4) to solve the Roothaan equations $FC = SC\epsilon$ for C and ϵ

1.5 SCF procedure

The Hartree-Fock limit is when the basis set is essentially complete and Hartree-Fock procedure is used in this case, but it can also be used in this case interchangeable as SCF procedure

1. Specify a molecule, which is a set of nuclear coordinate $\{R_A\}$, atomic numbers $\{Z_A\}$, and number of electrons N , then a basis set $\{\phi_\mu\}$
2. Calculate all required molecular integrals, $S_{\mu\nu}$, $H_{\mu\nu}^{\text{core}}$, and $(\mu\nu|\lambda\sigma)$
3. Diagonalize the overlap matrix S and obtain a transformation matrix X from (3)
4. Obtain a guess at the density matrix P
5. Calculate the matrix G of equation (2) from the density matrix P and the two-electron integrals $(\mu\nu|\lambda\sigma)$
6. Add G to the core-Hamiltonian to obtain the Fock matrix $F = H^{\text{core}} + G$
7. Calculate the transformed Fock matrix $F' = X^\dagger F X$
8. Diagonalize F' to obtain C' and ϵ
9. Calculate $C = XC'$
10. Form a new density matrix P from C using (1)
11. Determine whether the procedure has converged

1.6 Integral evaluation with 1s primitive Gaussians

1.7 Obara-Saika

1.7.1 Two-electron integrals

Recurrence expressions for the electron repulsion integrals over s and p Cartesian Gaussian functions

- $(ss, ss)^{(0)} = (\zeta + \eta)^{-1/2} K(\zeta_a, \zeta_b, A, B) K(\zeta_c, \zeta_d, C, D) F_0(T)$
- $(p_i s, ss)^{(0)} = (P_i - A_i)(ss, ss)^{(0)} + (W_i - P_i)(ss, ss)^{(1)}$
- $(p_i s, p_k s)^{(0)} = (Q_k - C_k)(p_i s, ss)^{(0)} + (W_k - Q_k)(p_i s, ss)^{(1)} + \frac{\delta_{ik}}{2(\zeta + \eta)}(ss, ss)^1$
- $(p_i p_j, ss)^{(0)} = (P_j - B_j)(p_i s, ss)^{(0)} + (W_j - P_j)(p_i s, ss)^{(1)} + \frac{\delta_{ij}}{2\zeta} \{ (ss, ss)^{(0)} - \frac{\rho}{\zeta} (ss, ss)^{(1)} \}$

- $(p_i p_j, p_k s)^{(0)} = (Q_k - C_k)(p_i p_j, s s)^{(0)} + (W_k - Q_k)(p_i p_j, s s)^{(1)} + \frac{1}{2(\zeta + \eta)} \{ \delta_{ij}(s p_j, s s)^{(1)} + \delta_{jk}(p_i s, s s)^{(1)} \}$
- $(p_i p_j, p_k p_l)^{(0)} = (Q_l - D_l)(p_i p_j, p_k s)^{(0)} + (W_l - Q_l)(p_i p_j, p_k s)^{(1)} + \frac{1}{2(\zeta + \eta)} \{ \delta_{il}(s p_j, p_k s)^{(1)} + \delta_{jl}(p_i s, p_k s)^{(1)} \} + \frac{\delta_{kl}}{2\eta} \{ (p_i p_j, s s)^{(0)} - \frac{\rho}{\eta} (p_i p_j, s s)^{(1)} \}$

The variables involved are

- $\zeta = \zeta_a + \zeta_b$
- $P = \frac{\zeta_a A + \zeta_b B}{\zeta}$
- $G = \frac{\zeta P + \zeta_c C}{\zeta + \zeta_c}$
- $\eta = \zeta_c + \zeta_d$
- $\rho = \frac{\zeta \eta}{\zeta + \eta}$
- $Q = \frac{1}{\eta} (\zeta_c C + \zeta_d D)$
- $W = \frac{\zeta P + \eta Q}{\zeta + \eta}$
- $F_m(T)$ is the mth order Boys function
- $T = \rho(P - Q)^2$
- $K(\zeta, \zeta', R, R') = 2^{1/2} \frac{\pi^{5/4}}{\zeta + \zeta'} \exp(-\frac{\zeta \zeta'}{\zeta + \zeta'} (R - R')^2)$

Then the auxiliary repulsion integral $(ab, cd)^{(m)}$ is defined by

$$(ab, cd)^{(m)} = \frac{2}{\pi^{1/2}} \int_0^\infty du \left(\frac{u^2}{\rho + u^2} \right)^m (ab|u|cd)$$

where the integral in u is introduced by the integral representation of the r_{12}^{-1} operator in (ab, cd) and in particular, the true ERI is $(ab, cd)^{(0)}$

1.7.2 One-electron integrals

Recurrence expressions for the nuclear attraction integrals

- $(s|A_0|s)^{(0)} = 2(\frac{\zeta}{\pi})^{1/2} (s||s) F_0(U)$
- $(p_i|A_0|s)^{(0)} = (P_i - A_i)(s|A_0|s)^{(0)} - (P_i - C_i)(s|A_0|s)^{(1)}$
- $(p_i|A_0|p_j)^{(0)} = (P_j - B_j)(p_i|A_0|s)^{(0)} - (P_j - C_j)(p_i|A_0|s)^{(1)}$
- $(d_{ij}|A_0|s)^{(0)} = (P_j - A_j)(p_i|A_0|s)^{(0)} - (P_j - C_j)(p_i|A_0|s)^{(1)} + \frac{\delta_{ij}}{2\zeta} \{ (s|A_0|s)^{(0)} - (s|A_0|s)^{(1)} \}$
- $(d_{ij}|A_0|p_k)^{(0)} = (P_k - B_k)(d_{ij}|A_0|s)^{(0)} - (P_k - C_k)(d_{ij}|A_0|s)^{(1)} + \frac{\delta_{ik}}{2\zeta} \{ (p_j|A_0|s)^{(0)} - (p_j|A_0|s)^{(1)} \} + \frac{\delta_{jk}}{2\zeta} \{ (p_i|A_0|s)^{(0)} - (p_i|A_0|s)^{(1)} \}$
- $(d_{ij}|A_0|d_{kl})^{(0)} = (P_l - B_l)(d_{ij}|A_0|p_k)^{(0)} - (P_l - C_l)(d_{ij}|A_0|p_k)^{(1)} + \frac{\delta_{il}}{2\zeta} \{ (p_j|A_0|p_k)^{(0)} - (p_j|A_0|p_k)^{(1)} \} + \frac{\delta_{jl}}{2\zeta} \{ (p_i|A_0|p_k)^{(0)} - (p_i|A_0|p_k)^{(1)} \} + \frac{\delta_{kl}}{2\zeta} \{ (d_{ij}|A_0|s)^{(0)} - (d_{ij}|A_0|s)^{(1)} \}$

The new symbols are

- $(s||s)$ is the overlap integral between two s type Cartesian Gaussian functions $(s||s) = (\pi/\zeta)^{3/2} \exp(-\xi(A - B)^2)$
- The Boys function is evaluated on $U = \zeta(P - C)^2$

2 STO-3G basis set

- Slater-type functions are nice for atom orbitals
- For molecules it is preferred to use a gaussian-type function to make the integrals easier to evaluate, this provides less precision than Slater-types, but for molecules it doesn't matter
- The normalized 1s Gaussian-type function, centered at R_A , has the form

$$\phi_{1s}^{GF}(\alpha, r - R_A) = (2\alpha/\pi)^{3/4} e^{-\alpha|r-R_A|^2}$$

where α is the gaussian orbital exponent

The two-electron integrals are of the form

$$(\mu_A \nu_B | \lambda_C \sigma_D) = \int dr_1 dr_2 \phi_{\nu}^{A*}(r_1) \phi_{\nu}^B(r_1) r_{12}^{-1} \phi_{\lambda}^{C*}(r_2) \phi_{\sigma}^D(r_2)$$

The product of two 1s Gaussian functions, each on different centers, is, apart from a constant, a 1s Gaussian function on a third center

$$\phi_{1s}^{GF}(\alpha, r - R_A) \phi_{1s}^{GF}(\beta, r - R_B) = \left(\frac{4\alpha\beta}{\pi^2} \right)^{3/4} \exp(-\alpha|r - R_A|^2 - \beta|r - R_B|^2)$$

we can expand the exponent, with $p = \alpha + \beta$

$$\begin{aligned} -\alpha|r - R_A|^2 - \beta|r - R_B|^2 &= -(\alpha + \beta)|r|^2 + (2\alpha R_A + 2\beta R_B) \cdot r - (\alpha|R_A|^2 + \beta|R_B|^2) \\ &= -p|r|^2 + 2pr \cdot \frac{\alpha R_A + \beta R_B}{\alpha + \beta} - p \left| \frac{\alpha R_A + \beta R_B}{\alpha + \beta} \right|^2 \\ &\quad + p \left| \frac{\alpha R_A + \beta R_B}{\alpha + \beta} \right|^2 - (\alpha|R_A|^2 + \beta|R_B|^2) \\ &\text{Haciendo } R_P = (\alpha R_A + \beta R_B)/(\alpha + \beta) \\ -\alpha|r - R_A|^2 - \beta|r - R_B|^2 &= (-p|r|^2 + 2pr \cdot R_P - p|R_P|^2) - \frac{\alpha\beta}{\alpha + \beta}(|R_A|^2 + |R_B|^2 - 2R_A \cdot R_B) \\ &= -p|r - R_P|^2 - \frac{\alpha\beta}{\alpha + \beta}|R_A - R_B|^2 \end{aligned}$$

on the other hand

$$\begin{aligned} \left(\frac{4\alpha\beta}{\pi^2} \right)^2 &= \left(\frac{2\alpha\beta}{(\alpha + \beta)\pi} \frac{2(\alpha + \beta)}{\pi} \right)^{3/4} \\ &= \left(\frac{2\alpha\beta}{(\alpha + \beta)\pi} \right)^{3/4} \left(\frac{2p}{\pi} \right)^{3/4} \end{aligned}$$

therefore

$$\phi_{1s}^{GF}(\alpha, r - R_A) \phi_{1s}^{GF}(\beta, r - R_B) = \left(\frac{2\alpha\beta}{(\alpha + \beta)\pi} \right)^{3/4} \left(\frac{2p}{\pi} \right)^{3/4} \exp(-p|r - R_P|^2) \exp\left(\frac{\alpha\beta}{\alpha + \beta} |R_A - R_B|^2 \right)$$

with

$$K_{AB} = \left(\frac{2\alpha\beta}{(\alpha + \beta)\pi} \right)^{3/4} \exp\left(-\frac{\alpha\beta}{\alpha + \beta} |R_A - R_B|^2 \right)$$

$$\phi_{1s}^{GF}(p, r - R_P) = \left(\frac{2p}{\pi} \right)^{3/4} \exp(-p|r - R_P|^2)$$

we get

$$\phi_{1s}^{GF}(\alpha, r - R_A) \phi_{1s}^{GF}(\beta, r - R_B) = K_{AB} \phi_{1s}^{GF}(p, r - R_P)$$

As a result, the four-center integral reduces, for 1s Gaussians, to the two-center integral

$$(\mu_A \nu_B | \lambda_C \sigma_D) = K_{AB} K_{CD} \int dr_1 dr_2 \phi_{1s}^{GF}(p, r_1 - R_P) r_{12}^{-1} \phi_{1s}^{GF}(q, r_2 - R_Q)$$

which can be readily evaluated

Since Gaussian functions are not optimum basis functions we use as a basis fixed linear combinations of the primitive Gaussian functions ϕ_p^{GF} . These linear combinations, called contractions, lead to contracted gaussian functions (CGF)

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

where L is the length of the contraction and $d_{p\mu}$ is a contraction coefficient. The p th normalized primitive Gaussian ϕ_p^{GF} in the basis function ϕ_μ^{CGF} has a functional dependence on the Gaussian orbital exponent (contraction exponent) $\alpha_{p\mu}$. The idea is to choose in advance the contraction length, contraction coefficients, and contraction exponents that fit the CGF to a desirable set of basis functions ϕ_μ^{CGF} .

This procedure is commonly applied to fitting a Slater-type orbital (STO) to a linear combination of $N = 1, 2, 3, \dots$ primitive Gaussian functions, the STO-NG procedure. In particular we'll use the STO-3G basis set.

First we consider fitting a Slater function having Slater exponent $\zeta = 1$. Considering contractions up to length three so that the three fits we seek to find are

$$\begin{aligned} \phi_{1s}^{CGF}(\zeta = 1.0, STO - 1G) &= \phi_{1s}^{GF}(\alpha_{11}) \\ \phi_{1s}^{CGF}(\zeta = 1.0, STO - 1G) &= d_{12} \phi_{1s}^{GF}(\alpha_{12}) + d_{22} \phi_{1s}^{GF}(\alpha_{22}) \\ \phi_{1s}^{CGF}(\zeta = 1.0, STO - 1G) &= d_{13} \phi_{1s}^{GF}(\alpha_{13}) + d_{23} \phi_{1s}^{GF}(\alpha_{23}) + d_{33} \phi_{1s}^{GF}(\alpha_{33}) \end{aligned}$$

where the $\phi_1^{CGF}(\zeta = 1.0, STO - NG)$ are the basis functions that approximate as best as possible a Slater-type function with $\zeta = 1.0$. So we need to find the coefficients $d_{p\mu}$ and exponents $\alpha_{p\mu}$ that provide the best fit. The fitting criterion is one that fits the contracted Gaussian function to the Slater function in a least-squares sense, i.e., by minimizing the integral

$$I = \int dr [\phi_{1s}^{SF}(\zeta = 1.0, r) - \phi_{1s}^{CGF}(\zeta = 1.0, STO - NG, r)]^2$$

equivalently, since the two functions are normalized, one can maximize the overlap between the two functions, i.e., one maximizes

$$S = \int dr \phi_{1s}^{SF}(\zeta = 1.0, r) \phi_{1s}^{CGF}(\zeta = 1.0, STO - NG, r)$$

For the STO-1G case, there are no contraction coefficients, and we only need to find the primitive Gaussian exponent α which maximizes the overlap

$$S = (\pi)^{-1/2} (2\alpha/\pi)^{3/4} \int dr e^{-r} e^{-\alpha r^2}$$

DO YOUR OWN ALGORITHM TO GET YOUR OWN TABLE

α	S
0.1	0.8641
0.2	0.9673
0.3	0.9772
0.4	0.9606
0.5	0.9355

The optimum fit occurs for $\alpha = 0.270950$.

WHEN I DO MY OPTIMIZATION for the STO-2G and STO-3g cases, I should get

$$\phi_{1s}^{CGF}(\zeta = 1.0, STO - 1G) = \phi_{1s}^{GF}(0.270950)$$

$$\phi_{1s}^{CGF}(\zeta = 1.0, STO - 2G) = 0.678914\phi_{1s}^{GF}(0.151623) + 0.430129\phi_{1s}^{GF}(0.851819)$$

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