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

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

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

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

$$\rho(r) = \sum_{\mu\nu} P_{\mu\nu} \phi_\mu(r) \phi_\nu^*(r)$$

then the density matrix is

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

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

$$F_{\mu\nu} = \int dr_1 \, \phi_\mu^*(1) h(1) \phi_\mu(1) + \sum_a^{N/2} \int dr_1 \, \phi_\mu^*(1)[2J_a(1) - K_a(1)]\phi_\nu(1)$$

$$F_{\mu\nu} = H_{\mu\nu}^{\text{core}} + \sum_a^{N/2} 2(\mu\nu|aa) - (\mu a|a\nu)$$

• Here, the core-Hamiltonian matrix is

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

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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

$$F_{\mu\nu} = H_{\mu\nu}^{\text{core}} + \sum_a^{N/2} \sum_{\lambda\sigma} C_{\lambda a} C_{\sigma a}^* [2(\mu\nu|\sigma\lambda) - (\mu\lambda|\sigma\nu)]$$

$$F_{\mu\nu} = H_{\mu\nu}^{\text{core}} \sum_{\lambda\alpha} P_{\lambda\sigma}[(\mu\nu|\sigma\lambda) - \frac{1}{2}(\mu\lambda|\sigma\nu)]$$

$$F_{\mu\nu} = H_{\mu\nu}^{\text{core}} + G_{\mu\nu}$$

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

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

- The two-electron integrals are

$$(\mu\nu|\lambda\sigma) = \int \mathrm{d}r_1 \, \mathrm{d}r_2 \, \phi_\mu^*(1)\phi_\nu(1) r_{12}^{-1} \phi_\lambda^*(2)\phi_\sigma(2)$$

1.4 Canonical orthogonalization

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

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

is

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

Canonical orthogonalization uses a transformation matrix

$$X = U s^{-1/2} \tag{3}$$

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

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

substituting C into the Roothaan equations gives

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

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if we define a new matrix F' by

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

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

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

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_{zmzn}, $H^{\text{core}}_{\mu\nu}$, 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 wether the procedure has converged

1.6   Integral evaluation with 1s primitive Gaussians

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

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

where α is the gaussian orbital exponent

The two-electron integals 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 $p = \alpha + \beta$

$$-\alpha|r - R_A|^2 - \beta|r - R_B|^2 = -(\alpha + \beta)|r|^2 + (2\alpha R_A + 2\beta R_\beta) \cdot r - (\alpha|R_A|^2 + \beta|R_B|^2)$$

$$= -p|r|^2 + 2pr \cdot \frac{\alpha R_A + \beta R_B}{\alpha + \beta} - p \left| \frac{\alpha R_A + \beta R_B}{\alpha + \beta} \right|^2$$

$$+ p \left| \frac{\alpha R_A + \beta R_B}{\alpha + \beta} \right|^2 - (\alpha|R_A|^2 + \beta|R_B|^2)$$

Haciendo $R_P = (\alpha R_A + \beta R_B)/(\alpha + \beta)$

$$-\alpha|r - R_A|^2 - \beta|r - R_B|^2 = (-p|r|^2 + 2pr \cdot R_P - p|R_P|^2) - \frac{\alpha\beta}{\alpha + \beta}(|R_A|^2 + |R_B|^2 - 2R_A \cdot R_B)$$

$$= -p|r - R_P|^2 - \frac{\alpha\beta}{\alpha + \beta}|R_A - R_B|^2$$

on the other hand

$$\left(\frac{4\alpha\beta}{\pi^2} \right)^2 = \left(\frac{2\alpha\beta}{(\alpha + \beta)\pi} \frac{2(\alpha + \beta)}{\pi} \right)^{3/4}$$

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

therefore

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

whith

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

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

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 pth 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 $N = 1, 2, 3, ...$ 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

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

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 coefficientes, 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

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

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

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