

The Roothaan-Hall equations

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1 The implementation procedure for RHF

In Szabo [1], we can find a recipe to implement the Roothaan-Hall equations. However, we can omit the calculation of the matrix

$$\mathbf{X} = \mathbf{S}^{-1/2} \quad (1)$$

and subsequent transformations and back-transformations by recognizing that the Roothaan equation

$$\mathbf{FC} = \mathbf{SC}\epsilon \quad (2)$$

can be classified as a generalized eigenvalue problem. In the Roothaan equation, \mathbf{F} is the Fock matrix (cfr. equation (12)), \mathbf{C} is the $K \times K$ -coefficient matrix in which the first MO is described by the first column in terms of the basis functions, and \mathbf{S} is the overlap integral matrix.

In RHF, we can calculate the elements of the density matrix \mathbf{P} as

$$P_{\mu\nu} = 2 \sum_a^{N/2} C_{\mu a} C_{\nu a}^* \quad (3)$$

However, by introducing the $K \times K$ occupancy matrix

$$\mathbf{O} = \begin{pmatrix} 2 & & & & \\ & \ddots & & & \\ & & 2 & & \\ & & & 0 & \\ & & & & \ddots \\ & & & & & 0 \end{pmatrix}, \quad (4)$$

we can calculate the density matrix as

$$\mathbf{P} = \mathbf{COC}^\dagger \quad (5)$$

We can then implement the Roothaan-Hall SCF cycle as follows:

1. Specify a molecule (a set of nucleic coordinates, their charge and the number of electrons) and a basis set.
2. Calculate the overlap integral matrix \mathbf{S} , the kinetic integral matrix \mathbf{T} , the nuclear attraction integral matrix \mathbf{V} , and the two-electron integrals $(\mu\nu|\lambda\sigma)$, which are defined in

chemist's notation

$$(\mu\nu|\lambda\sigma) = \int \int d\mathbf{r}_1 d\mathbf{r}_2 \frac{\phi_\mu^*(\mathbf{r}_1)\phi_\nu(\mathbf{r}_1)\phi_\lambda^*(\mathbf{r}_2)\phi_\sigma(\mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|} \quad (6)$$

$$= \langle \mu\lambda | \nu\sigma \rangle, \quad (7)$$

and calculate the core Hamiltonian matrix \mathbf{H}^{core} :

$$\mathbf{H} = \mathbf{T} + \mathbf{V}. \quad (8)$$

3. Obtain a guess for the density matrix \mathbf{P} . This can be done by solving the generalized eigenvalue equation

$$\mathbf{H}^{\text{core}}\mathbf{C} = \mathbf{S}\mathbf{C}\mathbf{h}^{\text{core}} \quad (9)$$

for the coefficient matrix \mathbf{C} and calculating the density matrix \mathbf{P} from it.

4. Calculate the matrix \mathbf{G} as

$$G_{\mu\nu} = \sum_{\lambda\sigma} P_{\lambda\sigma} \left[(\mu\nu|\lambda\sigma) - \frac{1}{2}(\mu\lambda|\sigma\nu) \right] \quad (10)$$

$$= \sum_{\lambda\sigma} P_{\lambda\sigma} \left[\langle \mu\lambda | \nu\sigma \rangle - \frac{1}{2} \langle \mu\sigma | \lambda\nu \rangle \right]. \quad (11)$$

5. Calculate the Fock matrix \mathbf{F} as

$$\mathbf{F} = \mathbf{H}^{\text{core}} + \mathbf{G}. \quad (12)$$

6. Solve the Roothaan equation (cfr. equation (2)) for the coefficient matrix \mathbf{C} , and calculate an improved density matrix \mathbf{P} .
7. Check for convergence on the density matrix \mathbf{P} , and if no convergence is yet achieved, return to step 4. We can check for converge by requiring that the Frobenius norm is smaller than a certain threshold ε :

$$\|\mathbf{P}_i - \mathbf{P}_{i-1}\|_F \leq \varepsilon. \quad (13)$$

8. If convergence is achieved, output the results. The energy can be calculated by

$$E = \frac{1}{2} \sum_{\mu\nu} P_{\nu\mu} (H_{\mu\nu}^{\text{core}} + F_{\mu\nu}). \quad (14)$$

References

- [1] A. Szabo and N. S. Ostlund. *Modern Quantum Chemistry - Introduction to Advanced Electronic Structure Theory*. Dover, 1989.