The Roothaan-Hall equations

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Thursday 19$^{\text{th}}$ October, 2017   16:30

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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

$$\mathbf{X} = \mathbf{S}^{-1/2} \tag{1}$$

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

$$\mathbf{FC} = \mathbf{SC}\varepsilon \tag{2}$$

can be classified as a generalized eigenvalue problem. In the Roothaan equation, $\mathbf{F}$ is the Fock matrix (cfr. equation (10)), $\mathbf{C}$ 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

$$P_{\mu\nu} = 2 \sum_a^{N/2} C_{\mu a} C_{\nu a}^* . \tag{3}$$

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

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

we can calculate the density matrix as

$$\mathbf{P} = \mathbf{COC}^\dagger . \tag{5}$$

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

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

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

$$\mathbf{H} = \mathbf{T} + \mathbf{V} \,. \tag{7}$$

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

$$\mathbf{H}^{\text{core}}\mathbf{C} = \mathbf{S}\mathbf{C}\mathbf{h}^{\text{core}} \tag{8}$$

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

4. Calculate the matrix $\mathbf{G}$ as

$$G_{\mu\nu} = \sum_{\lambda\sigma} P_{\lambda\sigma}\left[(\mu\nu|\sigma\lambda) - \frac{1}{2}(\mu\lambda|\sigma\nu)\right] \,. \tag{9}$$

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

$$\mathbf{F} = \mathbf{H}^{\text{core}} + \mathbf{G} \,. \tag{10}$$

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:

$$||\mathbf{P}_i - \mathbf{P}_{i-1}||_{\text{F}} \leq \varepsilon. \tag{11}$$

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

$$E = \frac{1}{2}\sum_{\mu\nu} P_{\nu\mu}(H_{\mu\nu}^{\text{core}} + F_{\mu\nu}) \,. \tag{12}$$

References

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