The Roothaan-Hall equations

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Contents

1 A naive implementation procedure

In Szabo [1], we can find a recipe to implement the Roothaan-Hall equations:

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 $\mathbf{V}$, the core Hamiltonian matrix $\mathbf{H}^{\text{core}}$ and the two-electron integrals $(\mu\nu|\lambda\sigma)$, which are defined in chemists's notation

$$(\mu\nu|\sigma\lambda) = \int\int \mathrm{d}\mathbf{r}_1\,\mathrm{d}\mathbf{r}_2\,\frac{\phi_\mu^*(\mathbf{r}_1)\phi_\nu(\mathbf{r}_1)\phi_\lambda^*(\mathbf{r}_2)\phi_\sigma(\mathbf{r}_2)}{|\mathbf{r}_1-\mathbf{r}_2|} \tag{1}$$

$$= \langle\mu\lambda|\nu\sigma\rangle\ . \tag{2}$$

3. Diagonalize $\mathbf{S}$ to obtain $\mathbf{X}$ as

$$\mathbf{X} = \mathbf{S}^{-1/2}\,. \tag{3}$$

4. Obtain a guess for the density matrix $\mathbf{P}$.

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

$$G_{\mu\nu} = \sum_{\lambda\sigma} P_{\lambda\sigma}\left[(\mu\nu|\lambda\sigma) - \frac{1}{2}(\mu\lambda|\sigma\nu)\right]. \tag{4}$$

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

$$\mathbf{F} = \mathbf{H}^{\text{core}} + G\,. \tag{5}$$

7. Transform the Fock matrix to $\mathbf{F}'$ as

$$\mathbf{F}' = \mathbf{X}^\dagger\mathbf{F}\mathbf{X}\,. \tag{6}$$

8. Diagonalize $\mathbf{F}'$ to obtain $\mathbf{C}'$ and $\boldsymbol{\epsilon}$:

$$\boldsymbol{\epsilon} = \mathbf{C}'^\dagger\mathbf{F}'\mathbf{C}' \tag{7}$$

9. Calculate the improved coefficient matrix $\mathbf{C}$ as

$$\mathbf{C} = \mathbf{X}\mathbf{C}' \tag{8}$$

10. Form an improved density matrix $\mathbf{P}$ from the improved coefficient matrix $\mathbf{C}$:

$$P_{\mu\nu} = 2\sum_{a}^{N/2} C_{\mu a} C_{\nu a}^{*} \,. \tag{9}$$

11. Check for convergence on the density matrix $\mathbf{P}$, and if no convergence is yet achieved, return to step 4.

12. If convergence is achieved, output the results.

References

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