The Roothaan-Hall equations

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

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

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

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

$$\mathbf{H} = \mathbf{T} + \mathbf{V}\,. \tag{3}$$

3. Diagonalize $\mathbf{S}$

$$\mathbf{s} = \mathbf{U}^\dagger\mathbf{S}\mathbf{U} \tag{4}$$

   to obtain $\mathbf{X}$ as

$$\mathbf{X} = \mathbf{S}^{-1/2} \tag{5}$$

$$= \mathbf{U}\mathbf{s}^{-1/2}\mathbf{U}^\dagger\,. \tag{6}$$

4. Obtain a guess for the density matrix $\mathbf{P}$. This can be done by diagonalizing $\mathbf{H}^{\text{core}}$:

$$\mathbf{h}^{\text{core}} = \mathbf{C}_0^\dagger\mathbf{H}^{\text{core}}\mathbf{C}_0\,, \tag{7}$$

   and calculating the initial density matrix $\mathbf{P}_0$ as

$$P_{\mu\nu}^0 = 2\sum_a^{N/2} C_{\mu a}^0 C_{\nu a}^{0,*}\,. \tag{8}$$

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

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

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

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

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

$$\mathbf{F}' = \mathbf{X}^{\dagger}\mathbf{F}\mathbf{X}\,. \tag{11}$$

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

$$\boldsymbol{\epsilon} = \mathbf{C}'^{\dagger}\mathbf{F}'\mathbf{C}' \tag{12}$$

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

$$\mathbf{C} = \mathbf{X}\mathbf{C}' \tag{13}$$

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

$$P_{\mu\nu} = 2\sum_{a}^{N/2} C_{\mu a}C^{*}_{\nu a}\,. \tag{14}$$

11. Check for convergence on the density matrix $\mathbf{P}$, and if no convergence is yet achieved, return to step 5. We can check for converge by requiring that the Frobenius norm is smaller than a certain threshold ε:

$$||\mathbf{P}_i - \mathbf{P}_{i-1}||_{\text{F}} \leq \varepsilon. \tag{15}$$

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

$$E = \frac{1}{2}\sum_{\mu\nu} P_{\nu\mu}(H^{\text{core}}_{\mu\nu} + F_{\mu\nu})\,. \tag{16}$$

References

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