

# 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

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

$$= \langle \mu\lambda | \nu\sigma \rangle , \quad (2)$$

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

$$\mathbf{H} = \mathbf{T} + \mathbf{V} . \quad (3)$$

3. Diagonalize  $\mathbf{S}$

$$\mathbf{s} = \mathbf{U}^\dagger \mathbf{S} \mathbf{U} \quad (4)$$

to obtain  $\mathbf{X}$  as

$$\mathbf{X} = \mathbf{S}^{-1/2} \quad (5)$$

$$= \mathbf{U} \mathbf{S}^{-1/2} \mathbf{U}^\dagger . \quad (6)$$

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

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

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

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

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

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

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

$$\mathbf{F} = \mathbf{H}^{\text{core}} + \mathbf{G} . \quad (10)$$

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

$$\mathbf{F}' = \mathbf{X}^\dagger \mathbf{F} \mathbf{X} . \quad (11)$$

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

$$\epsilon = \mathbf{C}'^\dagger \mathbf{F}' \mathbf{C}' \quad (12)$$

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

$$\mathbf{C} = \mathbf{X} \mathbf{C}' \quad (13)$$

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

$$P_{\mu\nu} = 2 \sum_a^{N/2} C_{\mu a} C_{\nu a}^* . \quad (14)$$

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  $\epsilon$ :

$$||\mathbf{P}_i - \mathbf{P}_{i-1}||_{\text{F}} \leq \epsilon . \quad (15)$$

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.