

Hartree–Fock Theory Implementation in Python

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Contents

1	Introduction	2
2	SCF Procedure	2
3	Computations	3
3.1	The Overlap Matrix S	3
3.1.1	Constructing S	3
3.1.2	Orthogonalizing S	4
3.2	The Fock Matrix F	4
3.2.1	Transforming $F, C \rightarrow F', C'$	4
3.2.2	Forming F	5
3.3	Finalizing SCF Procedure	5
4	Results	5
5	Conclusion	6

1 Introduction

Hartree–Fock (HF) method is a method of approximation for the determination of the wave function and the energy of a chemical system. The Hartree–Fock method assumes that the exact N-body wave function of the system can be approximated by a single Slater determinant or by a single permanent N spin-orbitals. By invoking the variational method, one can derive a set of N-coupled equations for the N spin orbitals. A solution of these equations yields the Hartree–Fock wave function and energy of the system. In this report, I will construct the Self-Consistent-Field (*SCF*) procedure to carry out Hartree–Fock calculations.

2 SCF Procedure

The main objective of this report is to implement the *SCF* procedure. In order to achieve that, we will go through these steps:

1. Specify molecule, basis functions.
2. Form the overlap matrix \mathbf{S} from the basis functions.
3. Provide an initial guess for the orbitals \mathbf{C} .
4. Form the density matrix $\mathbf{D}_{\mathbf{pq}} = \sum_{\mathbf{i}}^{\text{occ}} \mathbf{c}_{\mathbf{pi}}^* \mathbf{c}_{\mathbf{qi}}$.
5. Form the Fock matrix $\mathbf{F} = \mathbf{H} + 2\mathbf{J} - \mathbf{K}$
6. Solve the Hartree-Fock-Roothan equation: $\mathbf{FC} = \mathbf{SCE}$ to get a new orbital matrix \mathbf{C} .
7. Calculate the Fock matrix \mathbf{F} using the new orbital matrix \mathbf{C} .
8. Repeat from step 4 until the orbital matrix \mathbf{C} and the orbital energies converges.

Now that we know how to design the *SCF* procedure, we are left to compute all the necessary mathematical objects which will be discussed in the next section.

3 Computations

In order to design the *SCF*, we will need to compute all of the matrices required to satisfy the Hartree–Fock–Roothan (*HFR*) equation:

$$\sum_{\nu} F_{\mu\nu} C_{\nu i} = \sum_{\nu} S_{\mu\nu} C_{\nu i} E_i$$

$$FC = SCE$$

Therefore, we shall compute all of the following:

1. The Fock matrix **F**.
2. The matrix of wavefunction amplitudes for each MO **C**.
3. The overlap matrix **S**.
4. The density matrix **D**.

3.1 The Overlap Matrix *S*

3.1.1 Constructing *S*

The overlap matrix **S** contains the information about how the basis functions ϕ overlaps. Each element in the matrix is the Bra-ket of those basis functions. We shall form it using a matrix **B** that contains the basis vectors as its columns:

$$S_{ij} = \langle \phi_i | \phi_j \rangle$$

$$B = \begin{pmatrix} | & | & | \\ |\phi_1\rangle & |\phi_2\rangle & |\phi_3\rangle \\ | & | & | \end{pmatrix} \quad B^\dagger = \begin{pmatrix} - & \langle \phi_1 | & - \\ - & \langle \phi_2 | & - \\ - & \langle \phi_3 | & - \end{pmatrix}$$

$$B^\dagger B = \begin{pmatrix} - & \langle \phi_1 | & - \\ - & \langle \phi_2 | & - \\ - & \langle \phi_3 | & - \end{pmatrix} \begin{pmatrix} | & | & | \\ |\phi_1\rangle & |\phi_2\rangle & |\phi_3\rangle \\ | & | & | \end{pmatrix} \equiv S = \begin{pmatrix} \langle \phi_1 | \phi_1 \rangle & \langle \phi_1 | \phi_2 \rangle & \langle \phi_1 | \phi_3 \rangle \\ \langle \phi_2 | \phi_1 \rangle & \langle \phi_2 | \phi_2 \rangle & \langle \phi_2 | \phi_3 \rangle \\ | & | & | \end{pmatrix}$$

If we have an orthonormal set of basis functions ϕ_i , then the overlap matrix *S* will be the same as the identity matrix. Since the diagonal elements represents the normalization $\langle \phi_i | \phi_i \rangle = 1$ and the off-diagonal element will represent the orthogonality $\langle \phi_i | \phi_j \rangle = 0, i \neq j$. However, our basis functions are not necessarily orthonormal, so we will need to **orthogonalize** *S* into an orthonormal representation.

3.1.2 Orthogonalizing S

In order to orthogonalize S , we will use some Linear Algebra to construct an orthogonalizing matrix A . S is symmetric, and we can choose it to be real. Since S is symmetric and real, A is also symmetric and real. Therefore $A^\dagger = A$. This matrix is important and we will use it in the next articles.

$$\begin{aligned} A^\dagger S A &= 1 \\ A^\dagger S A &= A S A = A^2 S = 1 \\ \Rightarrow A &= S^{-1/2} \end{aligned}$$

Now that we found A , we will use it to transform $S \rightarrow S'$, S' is S represented in the orthonormal basis set. We will do that by transforming B and B^\dagger using A :

$$\begin{aligned} B' &= B A \\ S' &= B'^\dagger B' \\ S' &= (B A)^\dagger (B A) = A^\dagger B^\dagger B A \\ S' &= A^\dagger S A = A S A \end{aligned}$$

3.2 The Fock Matrix F

3.2.1 Transforming $F, C \rightarrow F', C'$

Now we have S represented in the orthonormal basis set. We will carry out the same transformation for the rest of HFR equation:

$$\begin{aligned} F C &= S C E \\ F(\mathbf{1}) C &= S(\mathbf{1}) C E \\ F A A^{-1} C &= S A A^{-1} C E \\ \text{Multiply by } A \text{ from the left} \\ A F A A^{-1} C &= A S A A^{-1} C E \end{aligned}$$

We can recognize $S' = A S A$, we can define $F' = A F A$ and $C' = A^{-1} C$

$$F' C' = S' C' E,$$

Since $S' = 1$ in the orthonormal basis set.

$$F' C' = C' E.$$

3.2.2 Forming F

For closed-shell systems, F has the form $F = H + 2J - K$. Where H is the one-electron Hamiltonian $H = T + V$, J is the Coulomb integral matrix, and K is the exchange integral matrix. We will take H as our initial guess for F , then we need to solve HFR equation to get C . After obtaining C , we will use it to construct new F .

Now we will use C to obtain a new matrix D which is called **Density Matrix**, then we will compute a new tensor I which is called **Repulsive Tensor**. Using D and I we will have everything to form F .

$$D_{pq} = \sum_i^{occ} c_{pi}^* c_{qi}$$

Where $c_{pi}^* c_{qi}$ are the probability of some basis function p contributing to the MO i

$$I_{pqrs} = \int d\tau \phi_p^*(1) \phi_q(1) \frac{1}{r_{ij}} \phi_r^*(2) \phi_s(2)$$

Using D and I we can now get J and K

$$J_{pq} = \sum_{rs} D_{rs} I_{pqrs} \quad K_{ps} = \sum_{rq} D_{rq} I_{pqrs}$$

3.3 Finalizing SCF Procedure

Now we have everything we need, we will obtain the energy using this expression: $E = E_{nuc} + \sum_{pq} (H_{pq} + F_{pq}) D_{pq}$, where E_{nuc} is the nuclear repulsion energy.

By reaching here, we have completed one iteration of the SCF procedure. We can see that $F_{Guessed} \rightarrow C \rightarrow D, J, K \rightarrow F_{New} \rightarrow C \rightarrow D...$, F (which depends on C) will yield a new C . This forms a Self-Consistent-Field SCF which we need to solve iteratively until our orbital coefficients and our orbital energies converge.

4 Results

After implementing the SCF procedure in Python, and using *Psi4* library to compute all integrals. I tested it for four different molecules: HF , H_2O , NH_3 , CH_4 , and H_2S . I tested the code for two different basis sets: *STO-3G* and *6-31g(d)*. The accuracy was exact to the 10⁸th digit. However, there was some noticable time different in execution. Figure 1 shows the time comparison between my implementation and Psi4's.

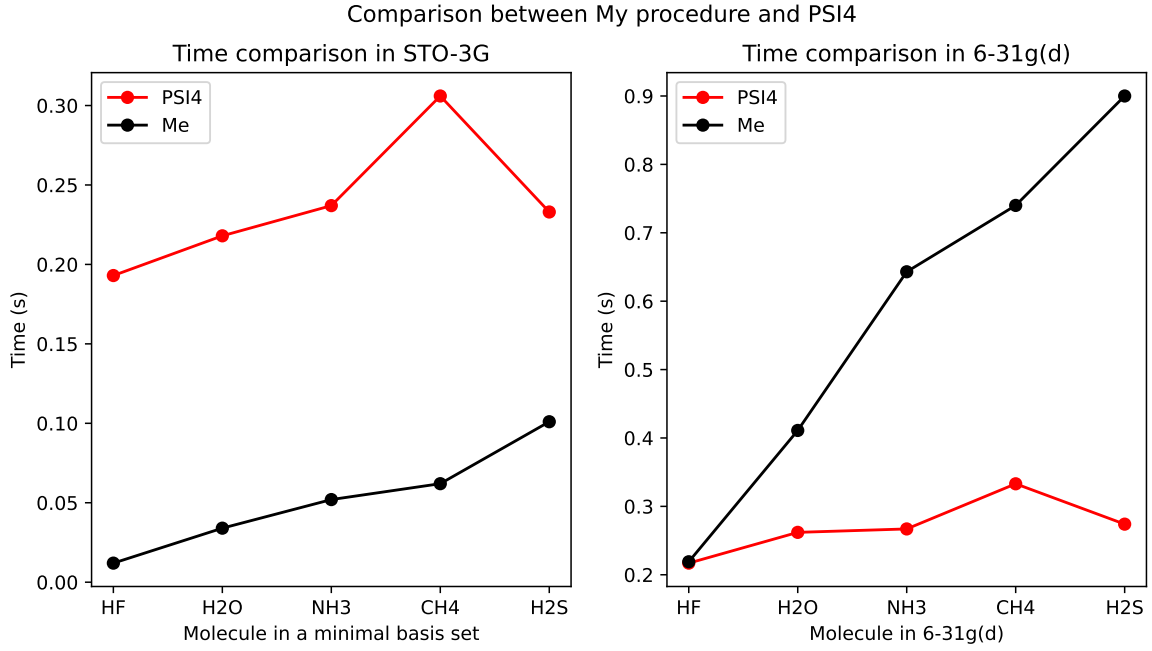


Figure 1: Comparison between my procedure and Psi4's

5 Conclusion

In conclusion, we have constructed the Self-Consistent-Field (*SCF*) procedure to carry out Hartree–Fock calculations. We started by proposing a set of basis functions and constructed its overlap matrix, then we used the overlap matrix to orthogonalize our entire Hartree–Fock–Roothan equation. Then we initialized a guess for our fock matrix to rebuild it again using the *HFR* equation. This procedure is variational, and we need to solve it iteratively until we meet a specific convergence condition.

My python implementation of the procedure was shown to be slightly faster in the minimal basis set *STO-3G*. I believe this is because Psi4 calculations need fractions of a second to start up before doing the calculations, which is about $0.2s$. As we can see in the *6-31g(d)* basis set, Psi4 started from $0.2s$ and was increased slightly for heavier and more complicated molecules. Whereas my calculations time increased dramatically.

References

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- [2] McDonald, A. *Psi4Education Hartree-Fock Lab*, 2020. https://github.com/Psi4Education/psi4education/tree/master/labs/Hartree_Fock