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Hartree–Fock Theory Implementation in Python

Introduction to Quantum–Chemical Calculations

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SCF Procedure

Mathematical Objects

Hartree–Fock–Roothan Equation:

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

$$FC = SCE$$

Where:
F: Fock matrix, for closed shell systems F = H + 2J - K.
C: The orbital coefficient matrix.
S: Overlap matrix.
E: The orbital energy diagonal matrix.
H, J, K: Matrices representing one and two electron integrals.

SCF Procedure

1. Specify molecule, basis functions.
2. Form the overlab matrix $\mathbf{S}$ from the basis functions.
3. Provide an initial guess for the orbitals **C**.
4. Form the density matrix $\mathbf{D_{pq}} = \sum_{\mathbf{i}}^{\mathbf{occ}} \mathbf{c^*_{pi}} \mathbf{c_{qi}}$.
5. Form the Fock matrix $\mathbf{F} = \mathbf{H} + \mathbf{2J} - \mathbf{K}$
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.

Computing The Matrices:

The overlap matrix $\mathbf{S}$ 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 $\mathbf{B}$ that contains the basis vectors as its columns:

$$S_{ij} = \langle \phi_i | \phi_j \rangle = \begin{pmatrix} \langle \phi_1 | \phi_1 \rangle & \langle \phi_1 | \phi_2 \rangle & \langle \phi_1 | \phi_3 \rangle \\ \langle \phi_2 | \phi_1 \rangle & \langle \phi_2 | \phi_2 \rangle & \langle \phi_2 | \phi_3 \rangle \\ | & | & | \end{pmatrix}$$

$$B = \begin{pmatrix} | & | & | \\ |\phi_1\rangle & |\phi_2\rangle & |\phi_3\rangle \\ | & | & | \end{pmatrix}$$

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

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

S to S':

S Has to be orthonormal. This is not always the case, to ensure this orthonormality, we will construct an orthogonalization matrix A to orthogonalize S. Then, we will use A to transform S to be represented in the orthonormal basis S'

$$A = S^{-1/2}$$

$$B' = BA$$

$$S' = B'^{\dagger} B',$$

$$= (BA)^{\dagger}(BA),$$

$$= A^{\dagger} B^{\dagger} BA,$$

$$= A^{\dagger} SA.$$

$$S' = ASA$$

Transforming HFR Equation:

Now we will use $\mathbf{A}$ and some mathematical tricks to transform Hartree–Fock–Roothan $\mathbf{HFR}$ equation to the new orthonormal basis set:

$$FC = SCE$$
$$F(\mathbf{1})C = S(\mathbf{1})CE$$
$$FAA^{-1}C = SAA^{-1}CE$$

Mutliply by A from the left

$$AFAA^{-1}C = ASAA^{-1}CE$$

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

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

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

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

We will now start with an initial guess of F then we will get C by solving $\mathbf{HFR}$ Eq.

Density Matrix and I, J, K:

Recall $F = H + 2J - K$, in order to move forwars, we need J, K tp form F. We will define a density matrix D from the occupied orbitals in C, and a repulsive tensor I that will help us obtain these matrices.

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

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

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

Using D and I we can now get J and K

$$J_{pq} = \sum_{rs} D_{rs} I_{pqrs}$$

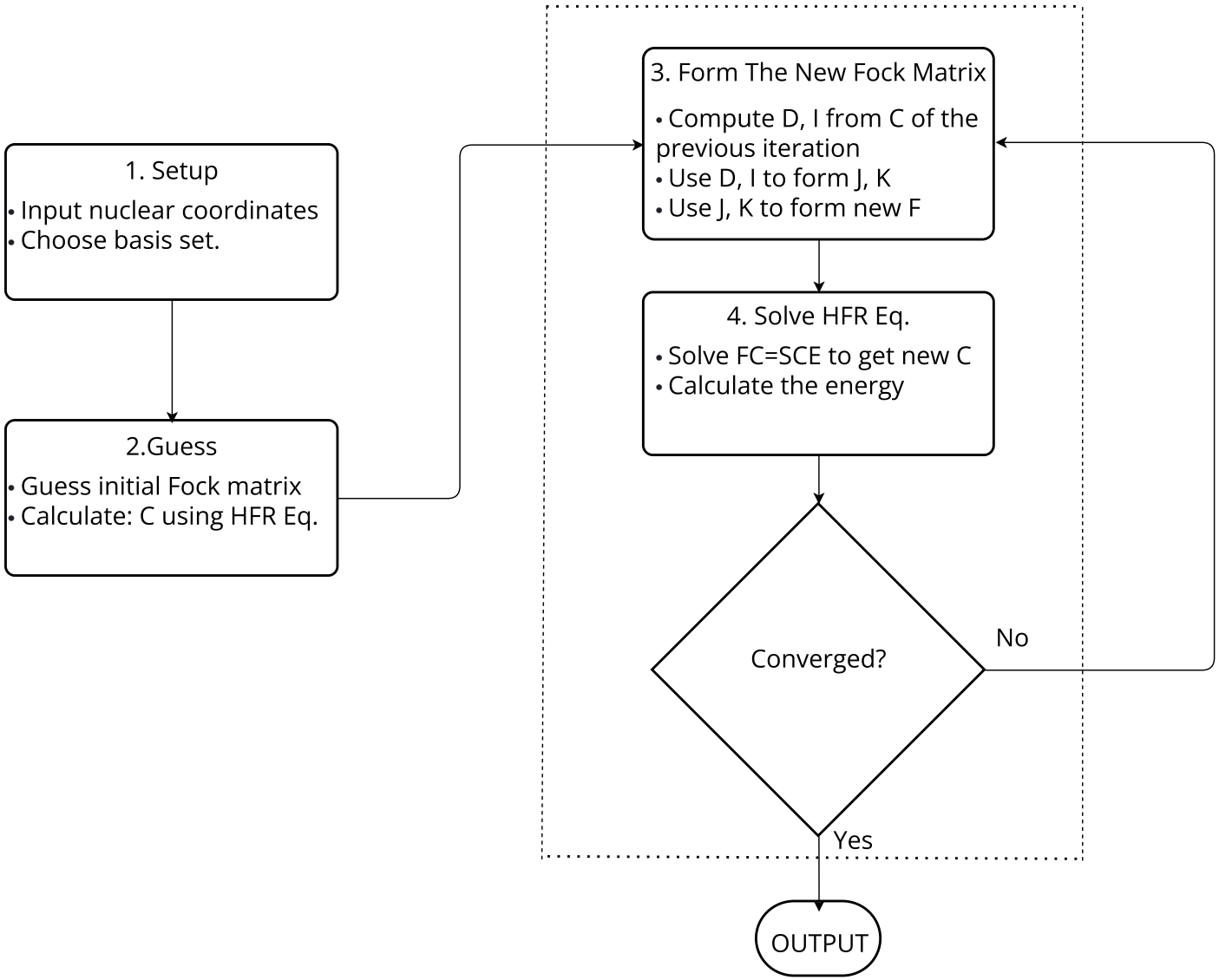
$$K_{ps} = \sum_{rq} D_{rq} I_{pqrs}$$

Calculating the energy and starting the iterative 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.

However, since $F_{Guessed} \rightarrow C \rightarrow D, J, K \rightarrow F_{New} \rightarrow C \rightarrow D...$, F (which depends on C) will yield a new C. This forms a Self-Consistent-Field SCF which we will solve iteratively until our orbital coefficients and our orbital energies converge.

Summary:


1. Setup
• Input nuclear coordinates
• Choose basis set.
2.Guess
• Guess initial Fock matrix
• Calculate: C using HFR Eq.
3. Form The New Fock Matrix
• Compute D, I from C of the previous iteration
• Use D, I to form J, K
• Use J, K to form new F
4. Solve HFR Eq.
• Solve FC=SCE to get new C
• Calculate the energy
Converged?
No
Yes
OUTPUT

Python Implementation

PSI4 objects

```
wfn = psi4.core.Wavefunction.build(mol, psi4.core.get_global_option('basis'))
ndocc = wfn.nalpha()    #Number of doubly occupied orbitals
nbf = wfn.basisset().nbf()
mints = psi4.core.MintsHelper(wfn.basisset())   #Molecular integrals object
S_matrix = mints.ao_overlap()
S = np.asarray(S_matrix)
```

Pre-iterative Calculations

```
A = splinalg.sqrtm(np.linalg.inv(S))     #A=S^-1/2
S_p = A.dot(S.dot(A))    #S'=ASA
T = np.asarray(mints.ao_kinetic())
V = np.asarray(mints.ao_potential())
H = T + V
F_p = A.dot(H.dot(A))    #Initial guess of F = Core hamiltonian
vals, vecs = np.linalg.eigh(F_p)     #Solve HFR to get C
C=A.dot(vecs)
C_occ = C[:, :ndocc]
I = np.asarray(mints.ao_eri())
D = np.einsum('pi,qi->pq',C_occ ,C_occ )     #Using einsum to compute D, J, K
J = np.einsum('rs,pqrs->pq',D,I )
K = np.einsum('rq,pqrs->ps',D,I )
F = H + 2*J - K
```

Pre-iterative Calculations

Recall the expressions for D, J, and K

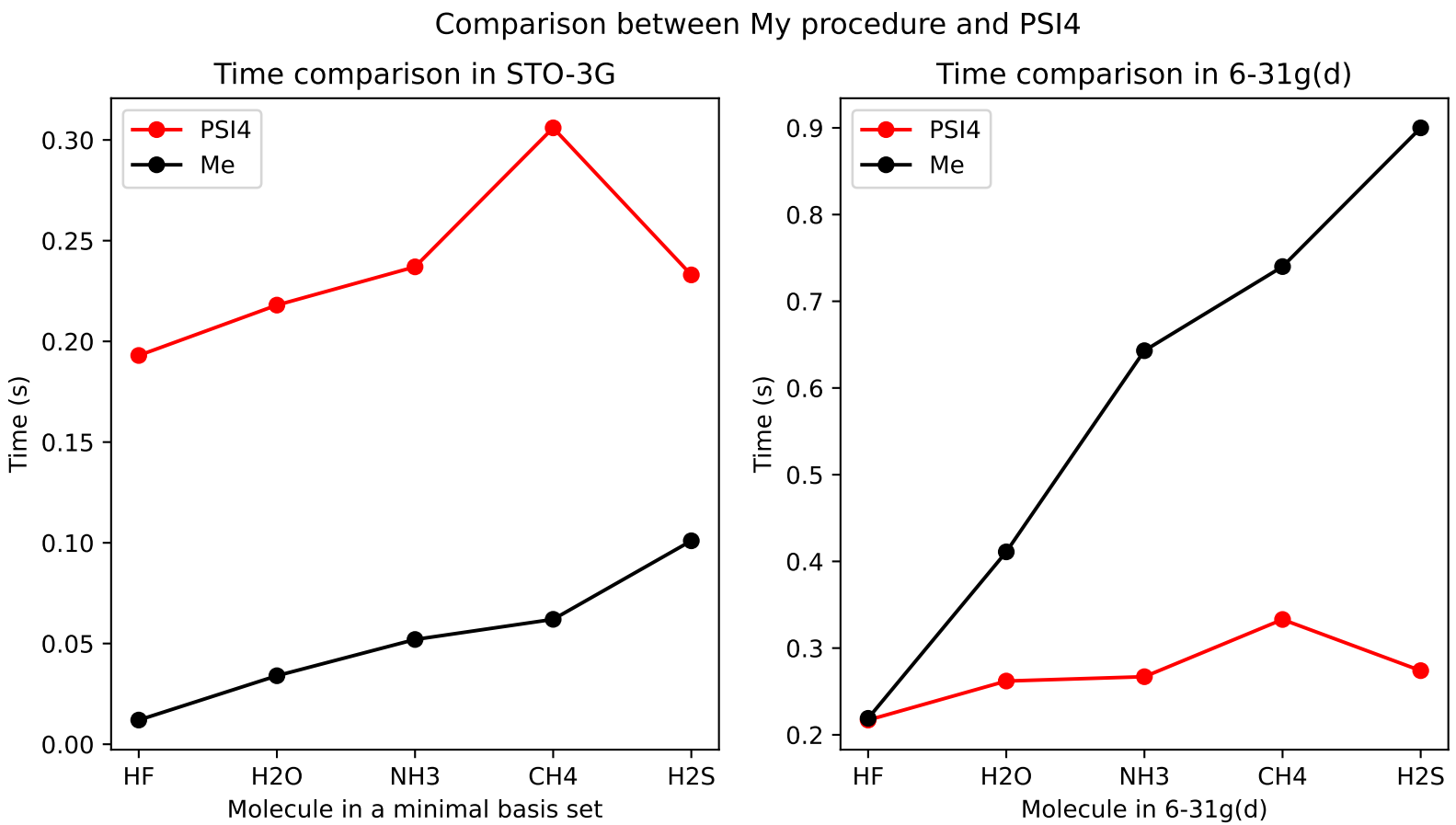
$$D_{pq} = \sum_{i}^{occ} c_{pi}^{*} c_{qi} \qquad J_{pq} = \sum_{rs} D_{rs} I_{pqrs} \qquad K_{ps} = \sum_{rq} D_{rq} I_{pqrs}$$

```
D = np.einsum('pi,qi->pq',C_occ ,C_occ )     #Using einsum to compute D, J, K
J = np.einsum('rs,pqrs->pq',D,I )
K = np.einsum('rq,pqrs->ps',D,I )
F = H + 2*J - K
```

SCF Procedure

```
# Begin Iterations
for scf_iter in range(1, MAXITER + 1):
    I = np.asarray(mints.ao_eri())
    J = np.einsum('rs,pqrs->pq',D,I )
    K = np.einsum('rq,pqrs->ps',D,I )
    F = H + 2*J - K
    SCF_E = E_nuc + np.einsum('pq->',(H+F)*(D))
    print(F'SCF Iteration {scf_iter}: Energy = {SCF_E:.8f} dE = {SCF_E - E_old:.8f}')
    if (abs(SCF_E - E_old) < E_conv):
        break
    E_old = SCF_E
    F_p=A.dot(F.dot(A))
    vals, vecs = np.linalg.eigh(F_p)
    C=A.dot(vecs)
    C_occ = C[:, :ndocc]
    D = np.einsum('pi,qi->pq',C_occ ,C_occ )
    if (scf_iter == MAXITER):
        psi4.core.clean()
        raise Exception("Maximum number of SCF iterations exceeded.")
```

Time Comparison



Thank you!

Questions?

References

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