Hartree-Fock

Choose Geometry

Choose basis

Read S,1e and 2e

Construct $X = S^{-\frac{1}{2}}$

Guess D

Construct F

Construct $F' = X^{\dagger} F X$

Diagonalize F' to get C'

Construct $C = XC'$

Calculate Energy

Construct D

Check for Convergence

no

Exit

yes

Build the Orthogonalization Matrix

git clone https://github.com/ChemistryCourses/hatreefock.git

cd hatreefock

$$X = S^{-\frac{1}{2}}$$

Diagonalize the overlap matrix:

$$\mathbf{S}\mathbf{L}_S = \mathbf{L}_S\Lambda_S,$$ **linalg.eigh**

where L_S is the matrix of eigenvectors (columns) and
Λ_S is the diagonal matrix of corresponding eigenvalues.

Build the symmetric orthogonalization matrix using:

$$\mathbf{S}^{-1/2} \equiv \mathbf{L}_S\Lambda^{-1/2}\tilde{\mathbf{L}}_S,$$

where the tilde denotes the matrix transpose.

$S^{-\frac{1}{2}}$ Matrix

Table 1

	1	2	3	4	5	6	7
1	1.0236346	-0.1368547	0.0000000	-0.0074873	0.0000000	0.0190279	0.0190279
2	-0.1368547	1.1578632	0.0000000	0.0721601	0.0000000	-0.2223326	-0.2223326
3	0.0000000	0.0000000	1.0733148	0.0000000	0.0000000	-0.1757583	0.1757583
4	-0.0074873	0.0721601	0.0000000	1.0383050	0.0000000	-0.1184626	-0.1184626
5	0.0000000	0.0000000	0.0000000	0.0000000	1.0000000	0.0000000	0.0000000
6	0.0190279	-0.2223326	-0.1757583	-0.1184626	0.0000000	1.1297234	-0.0625975
7	0.0190279	-0.2223326	0.1757583	-0.1184626	0.0000000	-0.0625975	1.1297234

Guess D

Build the density matrix using the occupied MOs:

$$D^0_{\mu\nu} = \sum_{m}^{\text{occ.}} (\mathbf{C}_0)^m_\mu \, (\mathbf{C}_0)^m_\nu$$

where m indexes the columns of the coefficient matrices, and the summation includes only the occupied spatial MOs.

Construct the Fock matrix

$$F_{\mu\nu} = H^{core}_{\mu\nu} + \sum_{\lambda=1}^{nbasis} \sum_{\sigma=1}^{nbasis} D_{\lambda\sigma} \left[2\left(\mu\nu\middle|\lambda\sigma\right) - \left(\mu\lambda\middle|\nu\sigma\right) \right]$$

Form F'

$$F'_0 = X^\dagger F_0 X$$

F_0' Matrix

Table 1

	1	2	3	4	5	6	7
1	-32.2545866	-2.7914909	0.0000000	0.0086110	0.0000000	-0.1812967	-0.1812967
2	-2.7914909	-8.2368891	0.0000000	-0.2282926	0.0000000	-0.3857987	-0.3857987
3	0.0000000	0.0000000	-7.5428890	0.0000000	0.0000000	-0.1132121	0.1132121
4	0.0086110	-0.2282926	0.0000000	-7.4570295	0.0000000	-0.1102196	-0.1102196
5	0.0000000	0.0000000	0.0000000	0.0000000	-7.3471449	0.0000000	0.0000000
6	-0.1812967	-0.3857987	-0.1132121	-0.1102196	0.0000000	-4.0329547	-0.0446466
7	-0.1812967	-0.3857987	0.1132121	-0.1102196	0.0000000	-0.0446466	-4.0329547

Diagonalize the Fock matrix

$$\mathbf{F}'_0\mathbf{C}'_0 = \mathbf{C}'_0\epsilon_0$$

Note that the ε_0 matrix contains the initial orbital energies.

Transform the eigenvectors into the original (non-orthogonal) AO basis:

$$C_0 = XC'_0$$

Table 1

	1	2	3	4	5	6	7
1	-1.0015436	0.2336245	0.0000000	0.0856842	0.0000000	-0.0482226	0.0000000
2	0.0071893	- 1.0579388	- 0.0000000	- 0.3601105	- 0.0000000	0.4631213	0.0000000
3	0.0000000	- 0.0000000	1.0610702	0.0000000	- 0.0000000	0.0000000	0.2965071
4	0.0002671	- 0.4272843	- 0.0000000	0.9399425	0.0000000	0.2129401	0.0000000
5	0.0000000	0.0000000	- 0.0000000	0.0000000	- 1.0000000	0.0000000	0.0000000
6	-0.0018213	0.1492533	- 0.1377210	- 0.0378579	0.0000000	-0.7807003	-0.8501403
7	-0.0018213	0.1492533	0.1377210	- 0.0378579	- 0.0000000	-0.7807003	0.8501403

Rebuild the density matrix using the new coeffcient

	1	2	3	4	5	6	7
1	1.0650117	-0.2852166	-0.0000000	-0.0195534	-0.0000000	0.0334496	0.0334496
2	-0.2852166	1.2489657	0.0000000	0.1135594	0.0000000	-0.1442809	-0.1442809
3	-0.0000000	0.0000000	1.1258701	-0.0000000	-0.0000000	-0.1461317	0.1461317
4	-0.0195534	0.1135594	-0.0000000	1.0660638	0.0000000	-0.0993583	-0.0993583
5	-0.0000000	0.0000000	-0.0000000	0.0000000	1.0000000	-0.0000000	-0.0000000
6	0.0334496	-0.1442809	-0.1461317	-0.0993583	-0.0000000	0.0426802	0.0047460
7	0.0334496	-0.1442809	0.1461317	-0.0993583	-0.0000000	0.0047460	0.0426802

The SCF electronic energy may be computed using the density matrix as:

$$E_{\text{elec}}^{0} = \sum_{\mu\nu}^{\text{AO}} D_{\mu\nu}^{0} \left(H_{\mu\nu}^{\text{core}} + F_{\mu\nu} \right)$$

Initial Electronic Energy:-125.842077437699 Hartree