Hartree-Fock SCF Example: Water Molecule (H_2O)

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Molecular Geometry (Bohr)

Atom	x	y	z
O	0.0000	0.0000	0.0000
H	1.4304	1.1053	0.0000
H	-1.4304	1.1053	0.0000

Basis Set: STO-3G

STO-3G uses a linear combination of 3 Gaussian primitives to simulate one Slater-type orbital.

Oxygen (O)

- **1s (core):**

  $\alpha = \{130.7093214, 23.80886605, 6.443608313\} \quad d = \{0.1543289673, 0.5353281423, 0.4446345422\}$

- **2s, 2p (valence):**

  $\alpha = \{5.033151319, 1.169596125, 0.38038896\} \quad d_s = \{-0.09996722919, 0.3995128261, 0.700115468$

Hydrogen (H)

$\alpha = \{3.425250914, 0.6239137298, 0.1688554040\} \quad d = \{0.1543289673, 0.5353281423, 0.4446345422\}$

Step-by-Step SCF

1. Overlap, Kinetic, and Potential Integrals

Using the basis functions, compute:

- Overlap matrix $S_{\mu\nu}$
- Core Hamiltonian: $H^{\text{core}} = T + V$
- Two-electron integrals: $(\mu\nu|\lambda\sigma)$

2. Initial Guess Density

Construct $D^{(0)}$ using diagonalized H^{core} or zero matrix.

3. Iterative SCF Loop

1. Build Fock matrix:

$$F_{\mu\nu} = H_{\mu\nu}^{\text{core}} + \sum_{\lambda\sigma} D_{\lambda\sigma} \left[(\mu\nu|\lambda\sigma) - \frac{1}{2}(\mu\sigma|\lambda\nu) \right]$$

2. Solve Roothaan-Hall:

$$FC = SC\varepsilon$$

3. Construct new density matrix:

$$D_{\mu\nu} = \sum_{i}^{\text{occ}} C_{\mu i} C_{\nu i}$$

4. Compute total SCF energy:

$$E_{\text{elec}} = \sum_{\mu\nu} D_{\mu\nu}(H_{\mu\nu}^{\text{core}} + F_{\mu\nu}) \quad E_{\text{total}} = E_{\text{elec}} + E_{\text{nuc}}$$

5. Check convergence: if $\Delta E < \epsilon$ and $\Delta D < \delta$, stop.

Final Output (STO-3G, RHF)

From our code:

- **Electrons:** 10 (5 α, 5 β)
- **Basis Functions:** 7
- **HF Energy:** $E_{\text{SCF}} = -74.98394$ Ha
- **Exact $\langle S^2 \rangle$:** 0.0 (RHF)

Conclusion

Water serves as a simple benchmark molecule for RHF and provides a good check for validating integral and SCF routines. STO-3G is a minimal basis set that enables rapid computations, albeit with limited accuracy.