

Hartree-Fock and MP2 Implementation Report

Arnav Brahmasandra, Jay Shen, Enoch Woldu

May 21, 2025

1 Overview

The Hartree-Fock method is a foundational approach in quantum chemistry for approximating the electronic structure of atoms and molecules. MP2 provides a post-Hartree-Fock correction to account for electron correlation effects. This report describes the implementation and results of these methods.

1.1 Code Structure

- `src/`
 - `molecule.py` – Molecule class representation
 - `integrals.py` – Computes 1- and 2-electron integrals using PySCF
 - `scf.py` – Restricted Hartree-Fock SCF procedure
 - `mp2.py` – Møller-Plesset perturbation theory energy corrections
 - `energies.py` – Computing total and nuclear repulsion energies
 - `orbital_plot.py` – 3D visualization of molecular orbitals using PyVista
 - `utils.py` – Miscellaneous utilities, including PySCF helper functions
 - `plot_utils.py` – Additional plotting functions.
- `examples/` – Usage demos for common molecules.
- `tests/` – Unit tests and PySCF-based validation.
- `main.py` – A command-line interface to run full SCF/MP2 workflows and visualize selected orbitals.

1.2 Algorithms

Hartree-Fock Self-Consistent Field (SCF)

The restricted Hartree-Fock (RHF) method approximates the many-electron wavefunction as a single Slater determinant of molecular orbitals. The resulting Hartree-Fock equation can

then be solved iteratively by making a mean-field assumption and running a self-consistent field (SCF) procedure. Here, we specifically solve a representation of the Hartree-Fock equation known as the Roothaan equations.

$$\mathbf{FC} = \mathbf{SC}\boldsymbol{\varepsilon}$$

We start from an initial guess for the density matrix \mathbf{P} , construct the Fock matrix \mathbf{F} , and then diagonalize it to obtain molecular orbital coefficients \mathbf{C} and energies $\boldsymbol{\varepsilon}$. \mathbf{C} is used to update \mathbf{P} and the electronic energy can be computed from \mathbf{P} and \mathbf{F} . This procedure is repeated until energy convergence. Annotated pseudo-codes for our SCF procedure, as well as the diagonalization of the Roothaan equations, are provided in Algorithms 1 and 2.

Algorithm 1 Hartree-Fock Self-Consistent Field (SCF) Method

Input: Atomic orbital basis set $\{\phi_i\}$; Convergence criteria ϵ
Output: Electronic energy E_{el} , MO energies $\boldsymbol{\varepsilon}$, MO coefficients \mathbf{C} , Density matrix \mathbf{P}

- 1: $G_{ijkl} \leftarrow (\phi_i \phi_j | \phi_k \phi_l)$ ▷ AO exchange integral matrix from PySCF
- 2: $S_{ij} \leftarrow \langle \phi_i | \phi_j \rangle$ ▷ AO overlap matrix from PySCF
- 3: $T_{ij} \leftarrow \langle \phi_i | -\frac{1}{2} \nabla^2 | \phi_j \rangle$ ▷ AO kinetic energy matrix from PySCF
- 4: $V_{ij} \leftarrow \langle \phi_i | -\sum_k^{\text{nuclei}} \frac{Z_k}{r_k} | \phi_j \rangle$ ▷ AO nuclear potential energy matrix from PySCF
- 5: $H_{ij} \leftarrow T_{ij} + V_{ij}$ ▷ Core Hamiltonian matrix
- 6: $P_{ij} \leftarrow 0$ ▷ Density matrix
- 7: **while** $\Delta E_{el} > \epsilon$ **do**
- 8: $F_{ij} \leftarrow H_{ij} + \sum_{kl} P_{kl} [G_{ijkl} - \frac{1}{2} G_{ikjl}]$ ▷ Fock matrix
- 9: $\mathbf{C}, \boldsymbol{\varepsilon} \leftarrow \text{SolveRoothaan}(\mathbf{F}, \mathbf{S})$ ▷ Compute MO coefficients and energies
- 10: $\mathbf{P} \leftarrow \mathbf{C} \mathbf{C}^T$ ▷ Update density matrix
- 11: $E_{el} \leftarrow \sum_{ij} P_{ij} (H_{ij} + F_{ij})$ ▷ Compute electronic energy
- 12: **end while**
- 13: **return** $E_{el}, \boldsymbol{\varepsilon}, \mathbf{C}, \mathbf{P}$

Algorithm 2 Solving the Roothaan equation $\mathbf{FC} = \mathbf{SC}\boldsymbol{\varepsilon}$ by diagonalizing

Input: Fock matrix \mathbf{F} ; Overlap matrix \mathbf{S}
Output: MO coefficient matrix \mathbf{C}

- 1: $\mathbf{F}' \leftarrow \mathbf{S}^{-\frac{1}{2}} \mathbf{F} \mathbf{S}^{-\frac{1}{2}}$ ▷ Move Fock matrix to orthonormal basis
- 2: $\boldsymbol{\varepsilon} \leftarrow \text{Eigenvalues}(\mathbf{F}')$ ▷ Compute MO energies using NumPy
- 3: $\mathbf{C}' \leftarrow \text{Eigenvectors}(\mathbf{F}')$ ▷ Compute MO coefficients using NumPy
- 4: $\mathbf{C} \leftarrow \mathbf{S}^{-\frac{1}{2}} \mathbf{C}'$ ▷ Move MO coefficient matrix out of orthonormal basis
- 5: **return** $\boldsymbol{\varepsilon}, \mathbf{C}$

MP2 Energy Correction

The Møller-Plesset perturbation theory of second order (MP2) systematically includes electron correlation effects neglected by RHF. Given the MOs, the perturbative correction is

computed by summing over all possible double excitations from occupied to virtual orbitals. This typically lowers the total energy, yielding more accurate results for systems where electron correlation plays a significant role. An annotated pseudo-code of our implementation is provided in Algorithm 3.

Algorithm 3 Computation of MP2 Energy Correction

Input: AO basis set $\{\phi_i\}$; MO coefficient matrix \mathbf{C} ; MO energies ϵ
Output: MP2 energy correction E_{MP2}

- 1: $G_{\mu\nu\lambda\sigma} \leftarrow (\phi_\mu\phi_\nu|\phi_\lambda\phi_\sigma)$ ▷ Compute AO two-electron integrals using PySCF
- 2: $\Gamma_{ijkl} \leftarrow \sum_{\mu\nu\lambda\sigma} C_{\mu i} C_{\nu j} C_{\lambda k} C_{\sigma l} \cdot G_{\mu\nu\lambda\sigma}$ ▷ Compute MO two-electron integrals
- 3: $E_{MP2} \leftarrow 0$ ▷ Initialize energy correction
- 4: **for all** occupied MOs ψ_i, ψ_j **do**
- 5: **for all** unoccupied MOs ψ_k, ψ_l **do**
- 6: $E_{MP2} \leftarrow E_{MP2} + \frac{\Gamma_{ijkl} (2 \cdot \Gamma_{ijkl} - \Gamma_{ikjl})}{\epsilon_i + \epsilon_j - \epsilon_k - \epsilon_l}$ ▷ Update energy correction
- 7: **end for**
- 8: **end for**
- 9: **return** E_{MP2}

2 Results

We applied the Hartree-Fock and MP2 implementation to several small molecules using the STO-3G basis set. The table below reports the computed SCF electronic energy, MP2 correlation correction, and the total MP2 energy (including nuclear repulsion) for each system.

Table 1: Computed Energies for Test Molecules (STO-3G)

Molecule	SCF (Ha)	MP2 Corr (Ha)	MP2 (Ha)	MP2 Reference (Ha)
H ₂	-1.1168	-0.01313	-1.1299	-1.1299
H ₂ O	-74.9459	-0.03090	-74.9768	-74.9768
NH ₃	-55.4379	-0.06264	-55.5005	-55.5005
CH ₄	-39.7267	-0.05652	-39.7832	-39.7832
HF	-98.5522	-0.02672	-98.5789	-98.5789

These values match the reference results we get from running PySCF’s own RHF and MP2 methods, validating the correctness of both the integral evaluation and the energy computation pipelines.

Molecular Orbital Visualizations

Representative molecular orbitals were visualized for each molecule using isosurfaces generated with PyVista. The figures below show the HOMO for each molecule overlaid on its atomic geometry.

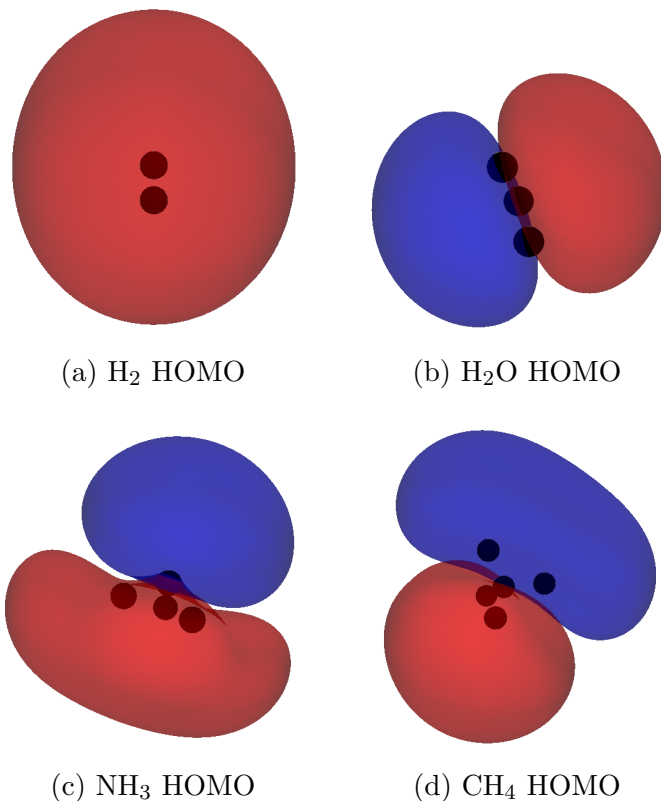


Figure 1: 3D visualizations of the HOMOs for each test molecule using isosurface rendering. Blue and red regions represent positive and negative orbital lobes, respectively.

3 Conclusion

This project presents a compact and functional implementation of Hartree-Fock and MP2 methods from first principles, capable of computing electronic energies and visualizing molecular orbitals for small molecules using the STO-3G basis set. The results show good agreement with reference calculations from PySCF, validating the correctness of the self-consistent field iteration, integral evaluation, and MP2 correlation energy computation.

Despite its correctness and clarity, the current implementation has several limitations. It supports only closed-shell, spin-restricted molecules, relies on a minimal basis set, and uses a memory-intensive four-index transformation for MP2 that limits scalability to larger systems. We also observe poor convergence for certain larger molecules of more than thirty atoms. Future improvements could include open-shell and unrestricted Hartree-Fock support, larger and more flexible basis sets, and density fitting techniques to reduce the cost of MP2. Additionally, implementing more advanced correlation methods such as CCSD(T) or DFT would enhance the accuracy and applicability of the code.

References

- Psi4NumPy MP2 Tutorial: https://github.com/psi4/psi4numpy/blob/master/Tutorials/05_Moller-Plesset/5a_conventional-mp2.ipynb
- Laura Gagliardi, "Hartree-Fock", Lecture 7
- Laura Gagliardi, "Perturbation Theory", Lecture 10
- Cramer, C. J. (2004). *Essentials of Computational Chemistry: Theories and Models*. John Wiley & Sons.
- VeloxChem RH-SCF Tutorial: <https://enccs.github.io/veloxchem-workshop/notebooks/rh-scf/>
- Sun, Q., Berkelbach, T. C., Blunt, N. S., Booth, G. H., Guo, S., Li, Z., ... & Chan, G. K.-L. (2018). *PySCF: the Python-based simulations of chemistry framework*. Wiley Interdisciplinary Reviews: Computational Molecular Science, 8(1), e1340. <https://pyscf.org>