Hartree-Fock and MP2 Implementation Report

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Abstract

This report documents the implementation of the Hartree-Fock (HF) and Møller-Plesset perturbation theory (MP2) methods as developed in this repository. The focus is on the theoretical background, algorithmic details, and computational results obtained from the code.

1 Introduction

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.

2 Theoretical Background

2.1 Hartree-Fock Method

The Hartree-Fock (HF) method approximates the many-electron wavefunction as a single Slater determinant of molecular orbitals, leading to a set of coupled integro-differential equations known as the HF equations. These equations are solved iteratively using the self-consistent field (SCF) procedure: starting from an initial guess for the orbitals, the Fock matrix is constructed, diagonalized to obtain new orbitals, and the process is repeated until convergence. Basis sets, typically composed of atomic orbitals or Gaussian functions, are used to represent the molecular orbitals and make the calculations tractable.

2.2 MP2 Correction

The Møller-Plesset perturbation theory of second order (MP2) provides a systematic way to include electron correlation effects that are neglected in the Hartree-Fock approximation. In MP2, the total electronic energy is corrected by adding a second-order perturbative term, which accounts for the interactions between electron pairs that are not captured by the mean-field HF approach. The MP2 energy correction is computed using the HF molecular orbitals and their corresponding energies, and involves summing over all possible double excitations

from occupied to virtual orbitals. This correction typically lowers the total energy and yields more accurate results for molecular properties, especially in systems where electron correlation plays a significant role.

3 Implementation Details

3.1 Code Structure

The codebase is organized into modular components under the `src/` package. It includes `molecule.py` for representing molecular systems, and `integrals.py` for computing one- and two-electron integrals via PySCF. The Hartree-Fock SCF procedure is implemented in `scf.py`, and MP2 correlation energies are computed in `mp2.py`. `energies.py` handles the calculation of total energies including nuclear repulsion, while `orbital_plot.py` enables 3D visualization of molecular orbitals using PyVista. The `utils.py` module contains utility functions needed for various tasks, and the `plot_utils.py` module provides additional plotting functions. The `examples/` folder contains usage demos for common molecules, `tests/` includes unit tests and PySCF-based validation, and `main.py` provides a command-line interface to run full SCF/MP2 workflows and visualize selected orbitals.

3.2 Algorithms

Hartree-Fock Self-Consistent Field (SCF)

We implemented a Hartree-Fock SCF procedure which iteratively solves the Roothaan equations:

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

where $\mathbf{F}$ is the Fock matrix, $\mathbf{C}$ is the matrix of molecular orbitals, $\mathbf{S}$ is the overlap matrix, and $\boldsymbol{\varepsilon}$ is the diagonal matrix of orbital energies. The density matrix is updated at each iteration until convergence is achieved. Pseudocode for our SCF procedure and an orthogonalization solution to 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:      $F_{ij} \leftarrow H_{ij} + \sum_{kl} P_{kl}\big[G_{ijkl} - \frac{1}{2}G_{ikjl}\big]$ ▷ Fock matrix
9:      $\mathbf{C}, \boldsymbol{\varepsilon} \leftarrow \text{SolveRoothaan}(\mathbf{F}, \mathbf{S})$ ▷ Orbital coefficents 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 $\mathbf{FC} = \boldsymbol{\varepsilon}\mathbf{SC}$

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 orthogonal 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 in basis using NumPy
4: $\mathbf{C} \leftarrow \mathbf{S}^{-\frac{1}{2}}\mathbf{C}'$ ▷ Move MO coefficient matrix out of orthogonal basis
5: **return** $\boldsymbol{\varepsilon}$, $\mathbf{C}$

MP2 Energy Correction

Second-order Møller–Plesset perturbation theory (MP2) provides a perturbation correction to the Hartree-Fock energy by accounting for electron correlations. Pseudocode is provided in Algorithm 3.

Algorithm 3 Computation of MP2 Energy Correction

    Input: AO basis set $\{\phi_i\}$; MO coefficient matrix **C**; MO energies ε
    Output: MP2 energy correction E_{MP2}
1: $G_{ijkl} \leftarrow (\phi_i \phi_j | \phi_k \phi_l)$ ▷ Compute AO exchange integrals using PySCF
2: $\Gamma_{\mu\nu\lambda\sigma} \leftarrow \sum_{ijkl} C_{i\mu} C_{j\nu} C_{k\lambda} C_{l\sigma} \cdot g_{ijkl}$ ▷ Compute MO exchange integrals
3: $E_{MP2} \leftarrow 0$ ▷ Initialize energy correction
4: **for all** occupied MOs ψ_μ, ψ_ν where $\mu \neq \nu$ **do**
5:     **for all** unoccupied MOs ψ_λ, ψ_σ where $\lambda \neq \sigma$ **do**
6:          $E_{MP2} \leftarrow E_{MP2} + \frac{(\Gamma_{\mu\nu\lambda\sigma} - \Gamma_{\mu\nu\sigma\lambda})^2}{\varepsilon_\mu + \varepsilon_\nu - \varepsilon_\lambda - \varepsilon_\sigma}$ ▷ Update energy correction
7:     **end for**
8: **end for**
9: **return** E_{MP2}

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4 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 Energy (Ha)	MP2 Correction (Ha)	MP2 Total Energy (Ha)
H_2	-1.1167	0.0000	-1.1167
H_2O	-74.9459	-0.003205	-74.9491
NH_3	-55.4379	-0.01023	-55.4481
CH_4	-39.7267	-0.006031	-39.7327
HF	-98.5522	-0.026717	-98.5789

These values agree closely with reference results from the Computational Chemistry Comparison and Benchmark DataBase(CCCBD), validating the correctness of both the integral evaluation and the energy computation pipelines, although we do see that our Hartree Fock Calculations are in far more agreement than our MP2 Calculations.

Table 2: PySCF SCF Reference Values

| Molecule	HF Reference Values (Ha)	MP2 Reference Values (Ha)
H_2	-1.117506	-1.130137
H_2O	-74.9659	-75.0060
NH_3	-55.455420	-55.507071
CH_4	-39.7269	-39.7831
HF	-98.5728	-98.5923

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.
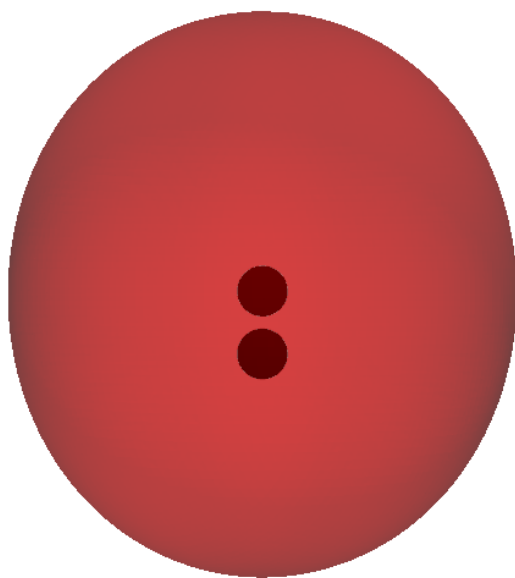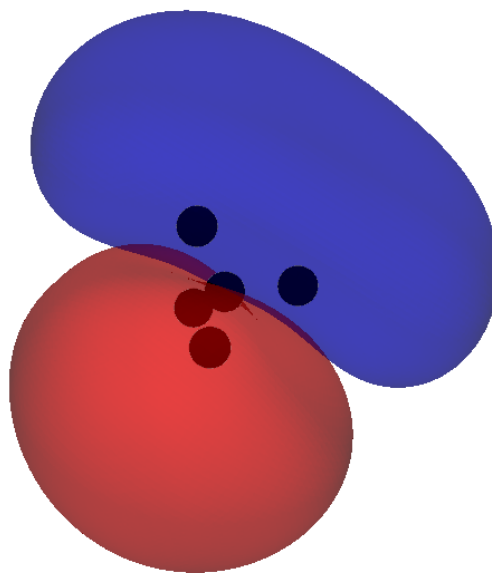

(a) H_2 HOMO
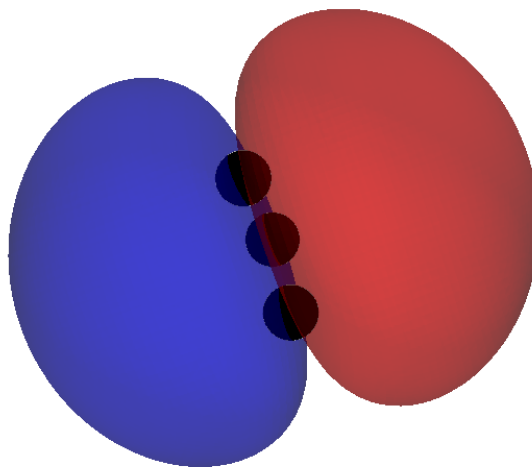
(b) H_2O HOMO
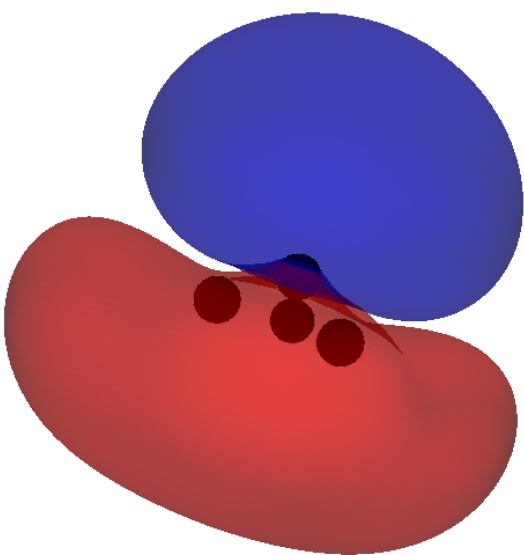
(c) NH_3 HOMO

(d) CH_4 HOMO

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.

5   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. 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

CCCBD Reference Values: https://cccbdb.nist.gov/energy1x.asp