

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)

The Hartree-Fock SCF procedure iteratively solves the Roothaan equations to find self-consistent molecular orbitals:

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

where \mathbf{F} is the Fock matrix, \mathbf{C} is the matrix of molecular orbitals, \mathbf{S} is the overlap matrix, and $\boldsymbol{\epsilon}$ is the diagonal matrix of orbital energies. The density matrix is updated at each iteration until convergence is achieved.

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

Input: Basis set $\{\phi\}$, nuclear coordinates $\{\vec{R}\}$

Output: Molecular orbitals, total energy E_{HF}

- 1: Compute overlap matrix $S_{ij} = \langle \phi_i | \phi_j \rangle$
 - 2: Compute core Hamiltonian $H_{ij} = \langle \phi_i | \hat{T} + \hat{V}_{\text{nuc}} | \phi_j \rangle$
 - 3: Compute two-electron integrals $G_{ijkl} = (\phi_i \phi_j | \phi_k \phi_l)$
 - 4: Initialize density matrix P_{ij} (e.g., from atomic guess)
 - 5: **repeat**
 - 6: Build Fock matrix: $F_{ij} = H_{ij} + \sum_{kl} P_{kl} [G_{ijkl} - \frac{1}{2}G_{ikjl}]$
 - 7: Solve Roothaan equations: $FC = SC\varepsilon$ to obtain new orbitals C and energies ε
 - 8: Update density matrix: $P_{ij} = 2 \sum_a^{\text{occ}} C_{ia} C_{ja}$
 - 9: Compute electronic energy: $E_{\text{elec}} = \sum_{ij} P_{ij} (H_{ij} + F_{ij}) / 2$
 - 10: **until** convergence of P_{ij} or E_{elec}
 - 11: Compute total energy: $E_{\text{HF}} = E_{\text{elec}} + E_{\text{nuc}}$
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MP2 Energy Correction

Second-order Møller–Plesset perturbation theory (MP2) provides a correction to the Hartree-Fock energy by accounting for electron correlation through pairwise excitations from occupied to virtual orbitals. In this implementation, the two-electron integrals are first transformed from the atomic orbital (AO) basis to the molecular orbital (MO) basis using the SCF orbital coefficients. The MP2 correlation energy is then computed by looping over all occupied and virtual orbital pairs and summing antisymmetrized contributions of the form:

$$E_{\text{MP2}} = \sum_{ij}^{\text{occ}} \sum_{ab}^{\text{virt}} \frac{[(ij|ab) - (ij|ba)]^2}{\varepsilon_i + \varepsilon_j - \varepsilon_a - \varepsilon_b}$$

This approach avoids recomputing transformations inside the loop and uses the antisymmetrized two-electron integrals in the MO basis for improved efficiency and clarity.

Algorithm 2 MP2 Energy Computation

1: Transform 4-index ERIs to MO basis:

$$\text{eri_mo}[i, j, a, b] \leftarrow \sum_{\mu\nu\lambda\sigma} C_{\mu i} C_{\nu j} C_{\lambda a} C_{\sigma b} (\mu\nu|\lambda\sigma)$$

2: Initialize $E_{\text{MP2}} \leftarrow 0$

3: **for all** occupied orbitals i, j **do**

4: **for all** virtual orbitals a, b **do**

5: $(ij|ab) \leftarrow \text{eri_mo}[i, j, a, b]$

6: $(ij|ba) \leftarrow \text{eri_mo}[i, j, b, a]$

7: numerator $\leftarrow [(ij|ab) - (ij|ba)]^2$

8: denominator $\leftarrow \varepsilon_i + \varepsilon_j - \varepsilon_a - \varepsilon_b$

9: $E_{\text{MP2}} \leftarrow E_{\text{MP2}} + \frac{\text{numerator}}{\text{denominator}}$

10: **end for**

11: **end for**

4 Results

Using our code, we calculated the energies of different molecular systems, where we calculated the energy and compared these results with the established literature values

- Energy of H₂O: -84.2310577768
- Energy of H₂:

Present sample results, such as total energies for test molecules, and compare HF and MP2 results.

5 Conclusion

Summarize findings and discuss possible improvements or future work.

References

List references to textbooks, articles, or documentation used.