Programming Projects on Basic Quantum Chemistry Methods

Hong-Zhou Ye*[1]

[1]*Department of Chemistry and Biochemistry and Institute for Physical Science and Technology*
University of Maryland, College Park, MD, 20742

Aug 2024

This document collects a few programming projects that help you build basic skills for quantum chemistry programming by turning the methods you learned in Szabo & Ostlund into computer programs. There are excellent notes/tutorials available on similar topics:

- Notes by Prof. David Sherrill: link
- Programming Projects by Prof. Eugene DePrince: link
- Programming Projects by Prof. Daniel Crawford: link
- Programming Tutorials by ajz34: link

When having a hard time with your own code, try to read relevant materials from these notes/tutorials.

1 Hartree-Fock (HF)

1.1 Simple fixed point algorithm

Using the AO basis integrals provided in the directory `reference` for a water molecule in the STO-3G basis, write a function that does the spin-restricted HF (RHF) calculations as follows:

```
e_tot, mo_energy, mo_coeff = do_rhf(h, V, S, nocc, enuc)
```

where

- h and V are the one-electron and two-electron integrals in the AO basis, where V is in the chemists' notations, i.e., $(11|22)$. S is the AO basis overlap matrix. These integrals are stored in `npy` format and can be loaded using `numpy.load`.
- `nocc` is the number of occupied orbitals (i.e., half the number of electrons).
- `enuc` is the nuclear repulsion energy, which is 9.189222125371913 Ha for the reference water molecule.

The reference HF total energy from PySCF is -74.9631463874825 Ha.

1.2 DIIS

You may notice that your SCF code, which is based on a simple fixed-point algorithm, takes a few tens of cycles to converge. The convergence can be significantly sped up using the DIIS algorith, which stands for *direct inversion of iterative subspace*. Read any of the tutorials on DIIS (e.g., DePrince `diis` folder; Crawford `Project #8`) and implement DIIS for your SCF code.

*hzyechem@gmail.com

2 Second-order MÃÿller-Plesset perturbation theory (MP2)

MP2 is the simplest electron correlation theory. Implementing a function for calculating the MP2 correlation energy using the RHF solutions generated by your SCF code. Test your implementation using the water/STO-3G system. The reference MP2 energy from PySCF is -0.0356082692564318 Ha.

You may find Crawford `Project #4` helpful.