

# Project 1 report: Hartree Fock with Integrals

Benjamin Peyton

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## 1 Overview

For this project, a code was developed according to the directions given in the Final Project 1 Description pdf. The code for the project spans across three files: `ints.py`, `hf.py`, and `opt.py`. The integral evaluation code is split into functions within `ints.py`, the Hartree Fock method is split into functions (and a total HF function is also implemented) within `hf.py` which calls on the integral functions from `ints.py` for the required integral matrices, and finally `opt.py` calls the HF procedure and uses it to perform a geometry optimization on  $H_2$  using Newton-Raphson steps with approximated derivatives. The complete code can be found on my github page at [github.com/bgpeyton/HF\\_Int](https://github.com/bgpeyton/HF_Int) along with a `README` which outlines the code and describes dependencies (`math`, `numpy`, and `scipy` packages).

## 2 Derivations and Procedure

### 2.1 Integral Evaluation

Before integral evaluation, a closed expression for the integral in Eq (1) was derived to be used later for Gaussian-type integrals (derivations separate).

$$R_k = \int_{-\infty}^{\infty} x^k e^{-\alpha x^2} dx \quad (1)$$

Next, using the Gaussian product theorem, a closed expression for the overlap integral between two primitive non-normalized Gaussians was derived. The function `gen_S()` was coded in `ints.py` to evaluate these overlap integrals, and another function `S_mat()` returns a matrix of such integrals given a molecule and basis set. A `normalize()` function was also implemented,

which returns the inverse square root of the self-overlap of a given basis function to be used as a normalization constant for  $S$  and all future matrices.

For kinetic energy integrals, again a closed form expression was derived. This expression was implemented in `gen_K()` within `ints.py` and then `K_mat()` generates a matrix of these integrals given a molecule and basis set.

An expression for nuclear attraction integrals was given, and this was implemented as `gen_V()` within `ints.py` and followed by `V_mat()`. Similarly, the expression for the electron repulsion integrals was given and implemented as `gen_eri()`, followed by `eri_mat()` which returns the later-discussed  $\mathbf{G}$ -matrix necessary for the Hartree Fock procedure.

## 2.2 Hartree Fock Procedure

Evaluation of the Hartree Fock equations (Eq (2)) is made relatively simple using the functions defined in `ints.py`. The core Hamiltonian matrix  $\mathbf{H}$  is directly solved from the  $\mathbf{T}$  and  $\mathbf{V}$  matrices solved using the corresponding generating functions from `ints.py`. An orthogonalization matrix  $\mathbf{S}^{-1/2}$  is generated and used to diagonalize the Hamiltonian, and the eigenvectors  $c$  are used to form the density matrix according to Eq (3).

$$\mathbf{H}\mathbf{c}_i^{(0)} = e_i\mathbf{S}\mathbf{c}_i^{(0)} \quad (2)$$

$$P_{ij} = \sum_{m=1}^{N/2} c_{mi}c_{mj} \quad (3)$$

The  $\mathbf{G}$  matrix is then computed using the before-mentioned `eri_mat()` and the Fock matrix  $\mathbf{F}$  is computed as the sum of  $\mathbf{G}$  and  $\mathbf{H}$ , to be used in the next HF step. An initial energy is computed (first using  $\mathbf{H}$ , then using  $\mathbf{F}$  in subsequent iterations) using Eq (4), and this process is repeated until convergence of the energy is reached. A single-HF-loop function `loop_hf()` was designed to take a molecule, basis,  $\mathbf{H}$ , and  $\mathbf{F}$  matrices. This function is then called in a loop within the `full_hf()` function, which computes the entire HF energy from start to finish with only a molecular coordinate array and basis set array as arguments (with optional convergence argument, the default being  $10^{-12}$ ).

$$E = \sum_{i=1}^M \sum_{j=1}^M (2H_{ih} + G_{ij})P_{ij} \quad (4)$$

## 2.3 Geometry Optimization

A geometry optimization was implemented in `opt.py`. The first ( $E'$ ) and second ( $E''$ ) derivatives of the energy are approximated using small  $0.001au$  steps in the geometry ( $R$ ), then used to take Newton-Raphson steps according to Eq (5). This is repeated until the absolute value of  $E''$  was less than  $10^{-6}au$ .

$$R^{new} = R - \frac{E'(R)}{E''(R)} \quad (5)$$

## 3 Results

The Hartree Fock geometry optimization procedure produced values comparable (though not exactly equivalent to) a `Psi4` output using similar methods and starting values. The input and output are included as `input.dat` and `output.dat`. The bond distance, energies, derivatives, and second derivatives of each step are printed by `opt.py` and are included in Table (1) for an  $H_2$  molecule starting with the atoms  $1au$  apart and using the basis set provided in the project pdf.

Table 1: Energies and derivatives

R (au)	E (au)	E' (au)	E'' (au)
1.0	-1.07263860249	-0.32892177304	1.53767876387
1.21390798961	-1.11524236275	-0.097629478193	0.735004021202
1.34673648493	-1.12257966082	-0.0185942960007	0.474442480858
1.38592837172	-1.12295919264	-0.00114918519656	0.416997325114
1.3886842292	-1.1229607803	-5.20953924443e-06	0.413221389106

`Psi4` predicts an equilibrium bond distance of  $0.734828003532\text{\AA}$ , or roughly  $1.388623575au$ , with an energy of  $-1.122965336026au$ . These are in good (though not perfect) agreement with the calculated values from `opt.py`, with discrepancies small enough to be attributed to slight differences in the basis set and procedure used in the calculation.

The NIST webbook lists the equilibrium bond distance of  $H_2$  as  $0.74144\text{\AA}$ , or roughly  $1.40112au$ . This discrepancy is not surprising- Hartree Fock ignores a lot of contributions,

including electron correlation, and this is hardly an ideal HF calculation considering the small uncontracted basis used. The literature shows a bond dissociation energy (BDE) of  $-1.12296au$ , while this calculation predicts  $BDE = 2(-0.5)au - (-1.12296au) = 0.12296au$ , using the analytical solution of  $0.5au$  per hydrogen atom. Again, this discrepancy is most likely due to shortcomings in the HF procedure.