HF Final Project

Austin M. Wallace

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Hartree-Fock Overview

The objective of Hartree-Fock (HF) is to solve the Schrodinger Equation through the usage of optimizing coefficients for a linear combination of atomic orbitals (LCAO) to create molecular orbitals that minimize the electronic energy. Because this procedure depends on the electronic energy, the nuclear energy is not added until the very end of the self-consistent field procedure is complete. Within this procedure, orbitals can be optimized by minimizing the electronic energy due to the varitaional theorem.

Effectively, this process relies on nuclear coordinates, charge, multiplicity, and a basis set – the present work uses atom-centered Gaussian functions to describe atomic orbitals. From here, the overalp of atomic orbitals is computed to forumlate S along with compiting kinetic (T) and potential (V) energy intregals at the beginning. Next, the Core Hamiltonian is formed $H_{\mu\nu} = T_{\mu\nu} + V_{\mu\nu}$. Before constructing the core Fock matrix (Equation 1) for a naive initial density matrix guess (Equation 3), one must orthogonalize $S^{-1/2}$ through diagonalizing S and transforming to $S^{-1/2}$.

$$F_0' = (S^{-1/2})^\dagger H S^{-1/2} \tag{1}$$

Through diagonlizing the core Fock matrix with the orthogonalized basis, one can construct C_0.

$$C_0 = S^{-1/2} C_0' \tag{2}$$

Using these sorted eigenvectors, we compute our density guess.

$$D_{\mu\nu} = \sum_i^{N/2} C_{\mu i} C_{\nu i} \tag{3}$$

With these inital values, the SCF procedure may begin, where we iteratively compute a new Fock matrix (Equation 4), compute electronic energy (Equation 5), transform Fock matrix to the orthonormal basis (Equation 6), diagonlaize F, (Equation 7) update C (Equation 8), and update the density (Equation 9) until converging the energy.

$$F_{\mu\nu} = H_{\mu\nu} + \sum_{\rho\sigma}^{AO} D_{\rho\sigma} 2[\mu\nu|\rho\sigma] - [\mu\rho|\nu\sigma] \tag{4}$$

$$E = \sum_{\mu\nu}^{AO} D_{\mu\nu}(H_{\mu\nu} + F_{\mu\nu}) \tag{5}$$

$$F' = (S^{-1/2})^\dagger F S^{-1/2} \tag{6}$$

$$C'^\dagger F' C' = \epsilon \tag{7}$$

$$C = S^{-1/2} C' \tag{8}$$

$$D_{\mu\nu} = \sum_i^{N/2} C_{\mu i} C_{\nu i} \tag{9}$$

At the end of each iteration, convergence is checked by computing the energy and comparing with the previous iteration and comparing with a user defined threshold to break the iterative process. Once below the threshold, the electronic energy is added to the nuclear energy to get the HF energy.

Specific Implementation Details

I have implemented the abstract described HF procedure above in C++ through the usage of Eigen3 for performing linear algebra operations with Lapack under the hood. C++ was selected due to having strong support with OpenMP and MPI for parallelization and to improve fundamental knowledege for aspring to become a Psi4 developer.

The project allowed me to learn how to create my own cmake files for building the library across OSX and Ubuntu with ease using the pitchfork convention. Using CMakeLists.txt took some initial learning but provides a seamless path for finding libraries and repeatedly building the project during development. Additionally, it makes it easier for others to know what is needed for getting the project to run on their own machine.

The initial test case for getting the library working follows the "Coding Strategy #1" from canvas; however, the T, V, S, and ERI sections were broken into separate files for a simplier parsing function to generate Eigen::MatrixXd objects. For the larger system testing, the input data is generated with Psi4 through the Python3 API. The Eigen library provided an easy option for solving for eigenvalues and eigenvectors through passing your matrix to the SelfAdjointEigenSolver object initialization. The eigenvectors and eigenvalues already returned sorted and have methods to reverse the sorting if needed.

Code

The project is available on GitHub, where I plan to continue to implement parallelization towards a distributed HF code.

The most important files are `hf.cpp`, `input.cpp`, and `helper.cpp` which are displayed below. Also, the data generator for other systems is seen in the `main.py` file.

hf.cpp

```cpp
#include "helper.hpp"
#include "input.hpp"
#include "omp.h"
#include "stdio.h"
#include <Eigen/Dense>
#include <ctime>
#include <fstream>
#include <iostream>
#include <string>
#include <vector>

using namespace std;

void HF_og() {
  // Specify Data Path
  /* std::string dataPath = "data/t1"; */
  std::string dataPath = "data/t0";
  double t1 = 1e-8, t2 = 1e-8;

  // Make pointers to store input data
  int num_atoms;
  double E = 0, e_nuc = 0;
```

```
23  std::vector<int> *elements = nullptr;
24  std::vector<double> *eri = nullptr;
25
26  Eigen::MatrixXd *coords = nullptr;
27  Eigen::MatrixXd *T = nullptr;
28  Eigen::MatrixXd *V = nullptr;
29  Eigen::MatrixXd *e1 = nullptr;
30  Eigen::MatrixXd *S = nullptr;
31
32  // Read Data
33  input::gatherData(dataPath, num_atoms, &elements, &eri, &coords, &T, &V, &e1,
34                    &S, &e_nuc);
35  cout << "e_nuc: " << e_nuc << endl;
36
37  // Starting HF Code
38  // Allocate Memory for Matrices
39  Eigen::MatrixXd *H = nullptr;
40  Eigen::MatrixXd *S_12 = nullptr;
41  Eigen::MatrixXd *F = nullptr;
42  Eigen::MatrixXd *C = nullptr;
43  Eigen::MatrixXd *C_0_prime = nullptr;
44  Eigen::MatrixXd *D = nullptr;
45
46  // Allocate memory for energy and electron count
47  int num_electrons;
48
49  // Set Number of Electrons for a Neutral Molecule
50  helper::getNumberOfElectrons(num_atoms, elements, &num_electrons);
51
52  H = new Eigen::MatrixXd(T->rows(), T->cols());
53  *H = *T + *V;
54  cout << endl << "H Matrix: " << endl << endl << *H << endl;
55
56  // Orthogonalization of S
57  cout << endl << "S Matrix: " << endl << endl << *S << endl;
58  S_12 = new Eigen::MatrixXd(S->rows(), S->cols());
59  helper::orthoS(S, S_12);
60  cout << endl << "S_12 Matrix: " << endl << endl << *S_12 << endl;
61
62  // Build initial Fock Matrix
63  F = new Eigen::MatrixXd(H->rows(), H->cols());
64  *F = (*S_12).transpose() * *H * (*S_12);
65  cout << endl << "F Matrix: " << endl << endl << *F << endl;
66
67  C_0_prime = new Eigen::MatrixXd(H->rows(), H->cols());
68  helper::getC_0_prime(F, C_0_prime);
69  cout << endl << "C_0_prime Matrix: " << endl << endl << *C_0_prime << endl;
70
71  C = new Eigen::MatrixXd(H->rows(), H->cols());
72  *C = (*S_12) * (*C_0_prime);
73  cout << endl << "C Matrix: " << endl << endl << *C << endl;
74
75  D = new Eigen::MatrixXd(H->rows(), H->cols());
76  helper::updateDensityMatrix(C, D, num_electrons);
77  cout << endl << "D Matrix: " << endl << endl << *D << endl;
78
79  helper::SCF(eri, S_12, H, F, C, D, C_0_prime, num_electrons, &E, e_nuc, t1,
80              t2);
81  E += e_nuc;
```

```
  cout.precision(15);
  cout << endl << "Final HF Energy: " << E << endl;

  // Free Allocations
  free(elements);
  free(coords);
  free(T);
  free(V);
  free(e1);
  free(S);
  free(eri);
  printf("\nFreed Memory\n");
}

void HF(int num_atoms, double E = 0, double e_nuc = 0,
        std::vector<int> *elements = nullptr,
        std::vector<double> *eri = nullptr, Eigen::MatrixXd *coords = nullptr,
        Eigen::MatrixXd *T = nullptr, Eigen::MatrixXd *V = nullptr,
        Eigen::MatrixXd *S = nullptr

) {
  // Specify Data Path
  double t1 = 1e-8, t2 = 1e-8;

  // Starting HF Code
  // Allocate Memory for Matrices
  Eigen::MatrixXd *H = nullptr;
  Eigen::MatrixXd *S_12 = nullptr;
  Eigen::MatrixXd *F = nullptr;
  Eigen::MatrixXd *C = nullptr;
  Eigen::MatrixXd *C_0_prime = nullptr;
  Eigen::MatrixXd *D = nullptr;

  // Allocate memory for energy and electron count
  int num_electrons;
  // Set Number of Electrons for a Neutral Molecule
  helper::getNumberOfElectrons(num_atoms, elements, &num_electrons);

  H = new Eigen::MatrixXd(T->rows(), T->cols());
  *H = *T + *V;
  /* cout << endl << "H Matrix: " << endl << endl << *H << endl; */

  // Orthogonalization of S
  /* cout << endl << "S Matrix: " << endl << endl << *S << endl; */
  S_12 = new Eigen::MatrixXd(S->rows(), S->cols());
  helper::orthoS(S, S_12);
  /* cout << endl << "S_12 Matrix: " << endl << endl << *S_12 << endl; */

  // Build initial Fock Matrix
  F = new Eigen::MatrixXd(H->rows(), H->cols());
  *F = (*S_12).transpose() * *H * (*S_12);
  /* cout << endl << "F Matrix: " << endl << endl << *F << endl; */

  C_0_prime = new Eigen::MatrixXd(H->rows(), H->cols());
  helper::getC_0_prime(F, C_0_prime);
  /* cout << endl << "C_0_prime Matrix: " << endl << endl << *C_0_prime << endl;
   */

  C = new Eigen::MatrixXd(H->rows(), H->cols());
```

```
141   *C = (*S_12) * (*C_0_prime);
142   /* cout << endl << "C Matrix: " << endl << endl << *C << endl; */
143
144   D = new Eigen::MatrixXd(H->rows(), H->cols());
145   helper::updateDensityMatrix(C, D, num_electrons);
146   /* cout << endl << "D Matrix: " << endl << endl << *D << endl; */
147
148   helper::SCF(eri, S_12, H, F, C, D, C_0_prime, num_electrons, &E, e_nuc, t1,
149               t2);
150   E += e_nuc;
151   cout.precision(15);
152   cout << endl << "Final HF Energy: " << E << endl;
153
154   // Free Allocations
155   free(elements);
156   free(coords);
157   free(T);
158   free(V);
159   free(S);
160   free(eri);
161   printf("\nFreed Memory\n");
162 }
163
164 void timings(std::string dataPath, int num_threads) {
165   int num_atoms;
166   double E = 0, e_nuc = 0;
167   time_t start, end;
168   double itime, ftime, exec_time;
169
170   std::vector<int> *elements = nullptr;
171   std::vector<double> *eri = nullptr;
172
173   Eigen::MatrixXd *coords = nullptr;
174   Eigen::MatrixXd *T = nullptr;
175   Eigen::MatrixXd *V = nullptr;
176   Eigen::MatrixXd *S = nullptr;
177   input::gatherData(dataPath, num_atoms, &elements, &eri, &coords, &T, &V, &S,
178                     &e_nuc);
179   omp_set_num_threads(num_threads);
180   Eigen::setNbThreads(num_threads);
181   double totTime;
182   omp_set_num_threads(num_threads);
183   Eigen::setNbThreads(num_threads);
184   start = clock();
185   itime = omp_get_wtime();
186   HF(num_atoms, E, e_nuc, elements, eri, coords, T, V, S);
187   ftime = omp_get_wtime();
188   end = clock();
189   totTime = (double)(end - start);
190   exec_time = ftime - itime;
191
192   cout << "Time (CPU) : " << (double)(totTime / CLOCKS_PER_SEC) << endl;
193   cout << "Time (USR) : " << exec_time << endl << endl ;
194 }
195
196 void timings_parrallel(std::string dataPath, int num_threads) {
197   int num_atoms;
198   double E = 0, e_nuc = 0;
199   time_t start, end;
```

```
  double serial_t;
  double itime, ftime, exec_time;

  // Required code for which execution time needs to be computed
  std::vector<int> *elements = nullptr;
  std::vector<double> *eri = nullptr;
  Eigen::MatrixXd *coords = nullptr;
  Eigen::MatrixXd *T = nullptr;
  Eigen::MatrixXd *V = nullptr;
  Eigen::MatrixXd *S = nullptr;
  input::gatherData(dataPath, num_atoms, &elements, &eri, &coords, &T, &V, &S,
                    &e_nuc);
  omp_set_num_threads(1);
  Eigen::setNbThreads(1);
  start = clock();
  HF(num_atoms, E, e_nuc, elements, eri, coords, T, V, S);
  end = clock();
  serial_t = (double)(end - start) / CLOCKS_PER_SEC;
  cout << "Serial Time: " << serial_t << endl;

  input::gatherData(dataPath, num_atoms, &elements, &eri, &coords, &T, &V, &S,
                    &e_nuc);
  double omp_t;
  /* int num_threads = 10; */
  omp_set_num_threads(num_threads);
  Eigen::setNbThreads(num_threads);
  start = clock();
  itime = omp_get_wtime();
  HF(num_atoms, E, e_nuc, elements, eri, coords, T, V, S);
  ftime = omp_get_wtime();
  end = clock();
  omp_t = (double)(end - start);
  exec_time = ftime - itime;
  double ompSpeedUp = serial_t / exec_time;
  double eff = serial_t / (exec_time * num_threads);

  cout << "Serial Time (CPU) : " << serial_t << endl;
  cout << "OMP    Time (CPU) : " << (double)(omp_t / CLOCKS_PER_SEC) << endl;
  cout << "OMP    Time (USR) : " << exec_time << endl;
  cout << "Omp Speedup       : " << ompSpeedUp << endl;
  cout << "Parallel Efficieny: " << eff << endl;
}

int main(int argc, char *argv[]) {
  printf("\nRunning: %s\n\n", argv[0]);
  if (argc == 1) {
    printf("You must pass a data path and number of threads like "
           "below:\n\t./hf data/t1 4\n");
    return 1;
  }
  std::string dataPath = "";
  int numThreads = 1;
  if (argc >= 2) {
    dataPath = argv[1];
    numThreads = atoi(argv[2]);
  }
  cout << "Data Path: " << dataPath << endl;
  cout << "Num Threads: " << numThreads << endl;
  cout.precision(15);
```

```
  /* timings_parrallel(dataPath, numThreads); */
  timings(dataPath, numThreads);
  return 0;
}
```

input.cpp

```
#include "input.hpp"
#include "helper.hpp"
#include <Eigen/Dense>
#include <algorithm>
#include <fstream>
#include <iostream>
#include <sstream>
#include <string>
#include <vector>

using namespace std;

void input::readVector(std::string fn, std::vector<std::vector<double>> **arr) {
  std::ifstream file(fn);
  if (!file) {
    std::cout << "Could not open file: " << fn << std::endl;
    return;
  }
  std::string line;
  int count = 0;

  while (getline(file, line)) {
    count++;
  }
  file.clear();
  file.seekg(0);

  *arr = new std::vector<std::vector<double>>(count);
  for (int i = 0; i < count; ++i) {
    (*arr)->at(i) = std::vector<double>(count);
  }

  int i = 0, j;
  while (getline(file, line)) {
    j = 0;
    std::stringstream ss(line);
    std::vector<double> values;
    double value;
    while (ss >> value) {
      (*arr)->at(i).at(j) = value;
      /* std::cout << value << " "; */
      j++;
    }
    /* std::cout << std::endl; */
    i++;
  }
  file.close();
  return;
}

void input::readVector(std::string fn, Eigen::MatrixXd **arr) {
```

```
52    std::ifstream file(fn);
53    if (!file) {
54      std::cout << "Could not open file: " << fn << std::endl;
55      return;
56    }
57    std::string line;
58    int count = 0;
59
60    while (getline(file, line)) {
61      count++;
62    }
63    file.clear();
64    file.seekg(0);
65
66    *arr = new Eigen::MatrixXd(count, count);
67
68    int i = 0, j;
69    while (getline(file, line)) {
70      j = 0;
71      std::stringstream ss(line);
72      std::vector<double> values;
73      double value;
74      while (ss >> value) {
75        /* std::cout << value << " " << i << " " << j << std::endl; */
76        (**arr)(i, j) = value;
77        j++;
78      }
79      /* std::cout << std::endl; */
80      i++;
81    }
82    file.close();
83    return;
84  }
85  void input::readVector(std::string fn, std::vector<double> **arr) {
86    std::ifstream file(fn);
87    if (!file) {
88      std::cout << "Could not open file: " << fn << std::endl;
89      return;
90    }
91    std::string line;
92    int count = 0;
93
94    while (getline(file, line)) {
95      count++;
96    }
97    file.clear();
98    file.seekg(0);
99
100   *arr = new std::vector<double>(count);
101
102   int i = 0;
103   while (getline(file, line)) {
104     std::stringstream ss(line);
105     ss >> (*arr)->at(i);
106     i++;
107   }
108   file.close();
109   return;
110 }
```

```
111
112 void input::readERI(std::string fn, std::vector<double> **arr, int n_basis) {
113   std::ifstream file(fn);
114   if (!file) {
115     std::cout << "Could not open file: " << fn << std::endl;
116     return;
117   }
118   std::string line;
119   int count = 0;
120
121   while (getline(file, line)) {
122     count++;
123   }
124   file.clear();
125   file.seekg(0);
126   /* int arrSize = */
127       /* helper::indexIJKL(n_basis - 1, n_basis - 1, n_basis - 1, n_basis - 1) + 1; */
128
129   /* cout << "arrSize: " << arrSize << endl; */
130   /* cout << "count: " << count << endl; */
131
132   *arr = new std::vector<double>(count);
133
134   int i, j, k, l;
135   double value;
136   int ijkl;
137   while (getline(file, line)) {
138     std::stringstream ss(line);
139     ss >> i >> j >> k >> l >> value;
140     ijkl = helper::indexIJKL(i, j, k, l);
141     /* std::cout << ijkl << " " << i << " " << j << " " << k << " " << l << " "
142      */
143     /*           << value << std::endl; */
144     (*arr)->at(ijkl) = value;
145   }
146   file.close();
147   return;
148 }
149
150 void input::gatherData(std::string dataPath, int &num_atoms,
151                        std::vector<int> **elements, std::vector<double> **eri,
152                        std::vector<std::vector<double>> **coords,
153                        std::vector<std::vector<double>> **T,
154                        std::vector<std::vector<double>> **V,
155                        std::vector<std::vector<double>> **e1,
156                        std::vector<std::vector<double>> **overlap
157
158 ) {
159   std::string geom = dataPath + "/geom.xyz";
160   std::string eriFN = dataPath + "/eri.dat";
161   std::string TFN = dataPath + "/T.dat";
162   std::string VFN = dataPath + "/V.dat";
163   std::string e1FN = dataPath + "/e1.dat";
164   std::string overlapFN = dataPath + "/overlap.dat";
165   // Gathering Geometry
166   input::readGeometry(geom, num_atoms, elements, coords);
167   std::cout << "Number of atoms: " << num_atoms << std::endl;
168   input::printElements(*elements);
169   input::printVector(*coords);
```

```
170
171   // Gathering T, V, e1, overlap
172   input::readVector(TFN, T);
173   /* input::printVector(*T); */
174   input::readVector(VFN, V);
175   /* input::printVector(*V); */
176   input::readVector(e1FN, e1);
177   /* input::printVector(*e1); */
178   input::readVector(overlapFN, overlap);
179   input::readVector(eriFN, eri);
180   /* printVector(*eri); */
181 }
182 void input::gatherData(std::string dataPath, int &num_atoms,
183                        std::vector<int> **elements, std::vector<double> **eri,
184                        Eigen::MatrixXd **coords, Eigen::MatrixXd **T,
185                        Eigen::MatrixXd **V,
186                        Eigen::MatrixXd **overlap, double *enuc) {
187   std::string geom = dataPath + "/geom.xyz";
188   std::string eriFN = dataPath + "/eri.csv";
189   std::string TFN = dataPath + "/T.csv";
190   std::string VFN = dataPath + "/V.csv";
191   std::string overlapFN = dataPath + "/S.csv";
192   std::string enucFN = dataPath + "/enuc.dat";
193   // Gathering Geometry
194   input::readGeometry(geom, num_atoms, elements, coords);
195
196   // Gathering T, V, e1, overlap
197   input::readVector(TFN, T);
198   input::readVector(VFN, V);
199   input::readVector(overlapFN, overlap);
200
201   // Gathering eri
202   int n_basis = (*T)->rows();
203   cout << "n_basis: " << n_basis << endl;
204   input::readERI(eriFN, eri, n_basis);
205   input::readNumber(enucFN, *enuc);
206 }
207
208 void input::numAtoms(std::string filename, int &num_atoms) {
209   std::ifstream file(filename);
210   if (!file) {
211     std::cout << "Could not open file " << filename << std::endl;
212     return;
213   }
214   file >> num_atoms;
215 }
216
217 void input::gatherData(std::string dataPath, int &num_atoms,
218                        std::vector<int> **elements, std::vector<double> **eri,
219                        Eigen::MatrixXd **coords, Eigen::MatrixXd **T,
220                        Eigen::MatrixXd **V, Eigen::MatrixXd **e1,
221                        Eigen::MatrixXd **overlap, double *enuc) {
222   std::string geom = dataPath + "/geom.xyz";
223   std::string eriFN = dataPath + "/eri.dat";
224   std::string TFN = dataPath + "/T.dat";
225   std::string VFN = dataPath + "/V.dat";
226   std::string e1FN = dataPath + "/e1.dat";
227   std::string overlapFN = dataPath + "/overlap.dat";
228   std::string enucFN = dataPath + "/enuc.dat";
```

```
229   // Gathering Geometry
230   input::readGeometry(geom, num_atoms, elements, coords);
231
232   // Gathering T, V, e1, overlap
233   input::readVector(TFN, T);
234   input::readVector(VFN, V);
235   input::readVector(e1FN, e1);
236   input::readVector(overlapFN, overlap);
237
238   // Gathering eri
239   int n_basis = (*T)->rows();
240   cout << "n_basis: " << n_basis << endl;
241   input::readERI(eriFN, eri, n_basis);
242   input::readNumber(enucFN, *enuc);
243 }
244
245 void input::readGeometry(std::string filename, int &num_atoms,
246                          std::vector<int> **elements,
247                          Eigen::MatrixXd **coords) {
248   std::ifstream file(filename);
249   if (!file) {
250     std::cout << "Could not open file " << filename << std::endl;
251     return;
252   }
253
254   file >> num_atoms;
255   *elements = new std::vector<int>(num_atoms);
256   *coords = new Eigen::MatrixXd(num_atoms, 3);
257
258   std::string line;
259   std::getline(file, line); // read in the comment line
260
261   for (int i = 0; i < num_atoms; ++i) {
262     int el = -1;
263     double x, y, z;
264     file >> el >> x >> y >> z;
265     (*elements)->at(i) = el;
266     (**coords)(i, 0) = x;
267     (**coords)(i, 1) = y;
268     (**coords)(i, 2) = z;
269   }
270   file.close();
271   return;
272 }
273
274 void input::readGeometry(std::string filename, int &num_atoms,
275                          std::vector<int> **elements,
276                          std::vector<std::vector<double>> **coords) {
277   std::ifstream file(filename);
278   if (!file) {
279     std::cout << "Could not open file " << filename << std::endl;
280     return;
281   }
282
283   file >> num_atoms;
284   *elements = new std::vector<int>(num_atoms);
285   *coords = new std::vector<std::vector<double>>(num_atoms);
286   for (int i = 0; i < num_atoms; ++i) {
287     (*coords)->at(i) = std::vector<double>(3);
```

```
  }

  std::string line;
  std::getline(file, line); // read in the comment line

  for (int i = 0; i < num_atoms; ++i) {
    int el = -1;
    double x, y, z;
    file >> el >> x >> y >> z;
    (*elements)->at(i) = el;
    (*coords)->at(i).at(0) = x;
    (*coords)->at(i).at(1) = y;
    (*coords)->at(i).at(2) = z;
  }
  file.close();
  return;
}

void input::printVector(std::vector<std::vector<double>> *matrix) {
  std::cout << std::endl;
  for (int i = 0; u_int64_t(i) < matrix->size(); ++i) {
    for (int j = 0; u_int64_t(j) < matrix->at(i).size(); ++j) {
      std::cout.precision(12);
      std::cout << matrix->at(i).at(j) << " ";
    }
    std::cout << std::endl;
  }
  std::cout << std::endl;
}

void input::printVector(std::vector<double> *matrix) {
  std::cout << std::endl;
  for (int i = 0; u_int64_t(i) < matrix->size(); ++i) {
    std::cout.precision(12);
    std::cout << matrix->at(i) << " ";
  }
  std::cout << std::endl;
}

void input::printElements(std::vector<int> *matrix) {
  for (int i = 0; u_int64_t(i) < matrix->size(); ++i) {
    std::cout << matrix->at(i) << " ";
    std::cout << std::endl;
  }
}

void input::readNumber(std::string filename, double &number) {
  std::ifstream file(filename);
  if (!file) {
    std::cout << "Could not open file " << filename << std::endl;
    return;
  }
  file >> number;
  file.close();
}
```

helper.cpp

```cpp
#include "helper.hpp"
#include "stdio.h"
#include <Eigen/Dense>
#include <iostream>
#include <vector>

using namespace Eigen;
using namespace std;

void helper::orthoS(Eigen::MatrixXd *S, Eigen::MatrixXd *S12) {
  // Diagonalize S
  Eigen::SelfAdjointEigenSolver<Eigen::MatrixXd> es(*S);
  /* #pragma omp parallel public(es, LAMBDA) */
  Eigen::MatrixXd LAMBDA = es.eigenvalues().asDiagonal();
  Eigen::MatrixXd U = es.eigenvectors();
  // Invert D

  // TOOD: Parallelize
#pragma omp parallel for
  for (int i = 0; i < LAMBDA.rows(); i++) {
    LAMBDA(i, i) = 1 / sqrt(LAMBDA(i, i));
  }
  // Calculate X
  *S12 = U * LAMBDA * U.transpose();
}

void helper::initialFockMatrix(Eigen::MatrixXd *X, Eigen::MatrixXd *H,
                               Eigen::MatrixXd *F) {
  // Calculate F
  *F = (*X).transpose() * *H * (*X);
}

void helper::getC_0_prime(Eigen::MatrixXd *F, Eigen::MatrixXd *C) {
  // Diagonalize F
  SelfAdjointEigenSolver<MatrixXd> eigensolver(*F);
  if (eigensolver.info() != Success)
    abort(); // check for errors
  *C = eigensolver.eigenvectors();
}

void helper::computeEnergy(Eigen::MatrixXd *D, Eigen::MatrixXd *H,
                           Eigen::MatrixXd *F, double *E) {
  // Calculate E
  *E = 0;
  *E = (*D).cwiseProduct((*H) + (*F)).sum();
}

void helper::getNumberOfElectrons(int num_atoms, std::vector<int> *elements,
                                  int *num_electrons) {
  // Calculate number of electrons
  *num_electrons = 0;
  for (int i = 0; i < num_atoms; i++) {
    *num_electrons += elements->at(i);
  }
}

int helper::indexIJKL(int i, int j, int k, int l) {
  if (j > i) {
    std::swap(i, j);
```

```
  }
  if (l > k) {
    std::swap(k, l);
  }
  int ij = i * (i + 1) / 2 + j;
  int kl = k * (k + 1) / 2 + l;
  if (ij < kl) {
    std::swap(ij, kl);
  }
  int ijkl = ij * (ij + 1) / 2 + kl;
  return ijkl;
}

void helper::updateDensityMatrix(Eigen::MatrixXd *C, Eigen::MatrixXd *D,
                                 int num_electrons) {
  // Calculate D
  // TODO: Parallelize
#pragma omp parallel for
  for (int i = 0; i < C->rows(); i++) {
    for (int j = 0; j < C->rows(); j++) {
      (*D)(i, j) = 0;
      for (int k = 0; k < num_electrons / 2; k++) {
        (*D)(i, j) += (*C)(i, k) * (*C)(j, k);
      }
    }
  }
}

void helper::updateFockMatrix(Eigen::MatrixXd *H, Eigen::MatrixXd *D,
                              Eigen::MatrixXd *F, std::vector<double> *eri) {
  // Update Fock Matrix
  *F = *H;
#pragma omp parallel for
  for (int mu = 0; mu < H->rows(); mu++) {
    for (int nu = 0; nu < H->cols(); nu++) {
      for (int rho = 0; rho < H->rows(); rho++) {
        for (int sig = 0; sig < H->cols(); sig++) {
          (*F)(mu, nu) += (*D)(rho, sig) *
                          (2 * eri->at(helper::indexIJKL(mu, nu, rho, sig)) -
                           eri->at(helper::indexIJKL(mu, rho, nu, sig)));
        }
      }
    }
  }
}

void helper::SCF(std::vector<double> *eri, Eigen::MatrixXd *S_12,
                 Eigen::MatrixXd *H, Eigen::MatrixXd *F, Eigen::MatrixXd *C,
                 Eigen::MatrixXd *D, Eigen::MatrixXd *C_0_prime,
                 int num_electrons, double *E, double e_nuc, double t1,
                 double t2) {
  // Calculate SCF

  bool converged = false;
  double E2 = 0;
  int iter = 0, max_iter = 100;
  while (!converged) {
    // Update Fock Matrix
    helper::updateFockMatrix(H, D, F, eri);
```

```
    /* cout << endl <<"F Matrix: " << endl << endl <<*F << endl; */
    /* cout << endl <<"E: " << endl << endl <<*E << endl; */
    helper::computeEnergy(D, H, F, E);
    *F = (*S_12).transpose() * *F * (*S_12);

    helper::getC_0_prime(F, C_0_prime);
    /* cout << endl <<"C_0_prime Matrix: " << endl <<endl << *C_0_prime << endl;
     */

    *C = (*S_12) * (*C_0_prime);
    /* cout << endl <<"C Matrix: " << endl <<endl << *C << endl; */
    helper::updateDensityMatrix(C, D, num_electrons);
    /* cout << endl <<"D Matrix: " << endl << endl <<*D << endl; */

    cout << "iter: " << iter << " Energy: " << *E << " Delta E: " << (*E - E2)
         << endl;
    if (abs(*E - E2) < t1) {
      converged = true;
    } else if (iter > max_iter) {
      cout << "Max iterations reached" << endl;
      converged = true;
    } else {
      E2 = *E;
      iter++;
    }
  }
}
```

main.py

```
import psi4
import numpy as np
import pandas as pd
from qm_tools_aw import tools
import qcelemental as qcel


def psi4_compute(mol, outdata="t2"):
    with open(f"{outdata}/geom.xyz", 'w') as f:
        n = mol.count('\n')
        f.write(f"{n}\n\n")
        f.write(mol)

    mol = psi4.geometry(mol)
    psi4.set_memory('4 GB')
    psi4.set_num_threads(10)
    psi4.core.set_output_file(f'{outdata}/output.dat', False)
    psi4.set_options({"basis": "aug-cc-pvdz"})
    wfn = psi4.core.Wavefunction.build(mol,
                                       psi4.core.get_global_option("basis"))
    mints = psi4.core.MintsHelper(wfn.basisset())
    S = np.asarray(mints.ao_overlap())
    np.savetxt(f"{outdata}/S.csv", S, delimiter=" ")
    T = np.asarray(mints.ao_potential())
    np.savetxt(f"{outdata}/T.csv", T, delimiter=" ")
    V = np.asarray(mints.ao_kinetic())
    np.savetxt(f"{outdata}/V.csv", V, delimiter=" ")

```

```
    I = np.asarray(mints.ao_eri())
    nbf = len(I)
    print(f"{nbf = }")

    with open(f"{outdata}/eri.csv", 'w') as f:
        for i in range(nbf):
            for j in range(i + 1):
                for k in range(i + 1):
                    for l in range(k + 1):
                        line = f"{i} {j} {k} {l} {I[i,j,k,l]}\n"
                        f.write(line)

    e = psi4.energy("HF/aug-cc-pvdz")
    print(f"{e =}")
    return

def find_geoms(size=10) -> None:
    """
    find_geoms
    """
    mol = psi4.geometry("""
0 1
8    0.000000000000    0.000000000000    -0.071151380605
1    0.000000000000    0.757939245855    0.564612021746
1    0.000000000000    -0.757939245855    0.564612021746
    """)
    df = pd.read_pickle("schr.pkl")
    print(df)
    for n, r in df.iterrows():
        if len(r['monAs']) == size:
            mmA = r['Geometry'][r['monAs'], :]
            # tools.print_cartesians_pos_carts(mmA[:,0], mmA[:,1:])
            return tools.print_cartesians_pos_carts(mmA[:,0], mmA[:,1:])

def benzene():
    return """
6        1.5000000000    -1.8000000000    -1.3915000000
6        2.7050743494    -1.8000000000    -0.6957500000
6        2.7050743494    -1.8000000000    0.6957500000
6        1.5000000000    -1.8000000000    1.3915000000
6        0.2949256506    -1.8000000000    0.6957500000
6        0.2949256506    -1.8000000000    -0.6957500000
1        1.5000000000    -1.8000000000    -2.4715000000
1        3.6403817855    -1.8000000000    -1.2357500000
1        3.6403817855    -1.8000000000    1.2357500000
1        1.5000000000    -1.8000000000    2.4715000000
1        -0.6403817855    -1.8000000000    1.2357500000
1        -0.6403817855    -1.8000000000    -1.2357500000
"""

def main():
    d = find_geoms(6) # Ethene
    # return
    # d = benzene()
    psi4_compute(d, outdata="t3")
    return


if __name__ == "__main__":
```

```
    main()
```

Output

The initial output is from using the "Coding Strategy #1" water geometry with the STO-3G basis set using the HF_og function. Additionally, I performed timing tests for speedup and efficiency for both Water HF/STO-3G and Ethene HF/aug-cc-pVDZ as can be seen below.

HF_og()

```
-- The CXX compiler identification is GNU 12.2.0
-- Checking whether CXX compiler has -isysroot
-- Checking whether CXX compiler has -isysroot - yes
-- Checking whether CXX compiler supports OSX deployment target flag
-- Checking whether CXX compiler supports OSX deployment target flag - yes
-- Detecting CXX compiler ABI info
-- Detecting CXX compiler ABI info - done
-- Check for working CXX compiler: /usr/local/bin/g++-12 - skipped
-- Detecting CXX compile features
-- Detecting CXX compile features - done
-- Found OpenMP_CXX: -fopenmp (found version "4.5")
-- Found OpenMP: TRUE (found version "4.5")
-- Looking for sgemm_
-- Looking for sgemm_ - not found
-- Performing Test CMAKE_HAVE_LIBC_PTHREAD
-- Performing Test CMAKE_HAVE_LIBC_PTHREAD - Success
-- Found Threads: TRUE
-- Looking for dgemm_
-- Looking for dgemm_ - found
-- Found BLAS: /Applications/Xcode.app/Contents/Developer/Platforms/MacOSX.platform/
    ↪ Developer/SDKs/MacOSX13.3.sdk/System/Library/Frameworks/Accelerate.framework
-- Looking for cheev_
-- Looking for cheev_ - found
-- Found LAPACK: /Applications/Xcode.app/Contents/Developer/Platforms/MacOSX.platform/
    ↪ Developer/SDKs/MacOSX13.3.sdk/System/Library/Frameworks/Accelerate.framework;-lm
    ↪ ;-ldl
-- Found MPI_CXX: /Users/austinwallace/miniconda3/envs/qcn/lib/libmpicxx.dylib (found
    ↪ version "3.1")
-- Found MPI: TRUE (found version "3.1")
-- Found OpenMP_CXX: -fopenmp (found version "4.5")
-- Configuring done
-- Generating done
-- Build files have been written to: /Users/austinwallace/gits/HF/cpp/build
[ 25%] Building CXX object src/CMakeFiles/hf.dir/hf.cpp.o
[ 50%] Building CXX object src/CMakeFiles/hf.dir/input.cpp.o
[ 75%] Building CXX object src/CMakeFiles/hf.dir/helper.cpp.o
[100%] Linking CXX executable hf
ld: warning: directory not found for option '-L/usr/include/eigen3'
[100%] Built target hf
n_basis: 7
arrSize: 406
count: 406
e_nuc: 8.90771

H Matrix:

  -32.6851    -7.60432           0           0 -0.0186797     -1.6196     -1.6196
```

```
  -7.60432   -9.30206          0          0   -0.22216   -3.54321   -3.54321
         0          0   -7.43084          0          0          0          0
         0          0          0   -7.56702          0   -1.89086    1.89086
-0.0186797   -0.22216          0          0   -7.52666   -1.65879   -1.65879
   -1.6196   -3.54321          0   -1.89086   -1.65879   -4.95649   -1.56026
   -1.6196   -3.54321          0    1.89086   -1.65879   -1.56026   -4.95649

S Matrix:

        1  0.236704         0         0        -0 0.0500137 0.0500137
 0.236704         1         0         0        -0  0.453995  0.453995
        0         0         1         0         0         0         0
        0         0         0         1         0  0.292739 -0.292739
        0        -0         0         0         1  0.245551  0.245551
0.0500137  0.453995         0  0.292739  0.245551         1  0.251002
0.0500137  0.453995         0 -0.292739  0.245551  0.251002         1

S_12 Matrix:

     1.02406    -0.141659 -3.22048e-18            0   -0.0100026    0.0212116
        ↪ 0.0212116
   -0.141659      1.22192 -2.96899e-17  2.47692e-18     0.105912    -0.275658
      ↪ -0.275658
-3.22048e-18 -2.96899e-17            1  4.23252e-17  1.97909e-17  1.30612e-16   8.2861
   ↪ e-17
           0  2.47692e-18  4.23252e-17      1.09816 -1.62843e-16    -0.213038
              ↪ 0.213038
  -0.0100026     0.105912  1.97909e-17 -1.62843e-16      1.05609    -0.146486
     ↪ -0.146486
   0.0212116    -0.275658  1.30612e-16    -0.213038    -0.146486      1.19048
      ↪ -0.0903463
   0.0212116    -0.275658   8.2861e-17     0.213038    -0.146486   -0.0903463
      ↪ 1.19048

F Matrix:

    -32.3609     -2.78101  5.24172e-17  1.11022e-16    0.0165515    -0.273188
       ↪ -0.273188
    -2.78101     -8.32926  -5.1327e-17  4.44089e-16    -0.281188    -0.481149
       ↪ -0.481149
 5.24172e-17  -5.1327e-17     -7.43084 -6.96731e-16 -5.38842e-16 -1.57009e-15 -9.77471
    ↪ e-16
  1.8735e-16  1.66533e-16 -6.96731e-16     -7.66432  2.35922e-15    -0.134212
     ↪ 0.134212
   0.0165515    -0.281188 -5.38842e-16  2.44249e-15     -7.57829    -0.146808
      ↪ -0.146808
   -0.273188    -0.481149 -1.57009e-15    -0.134212    -0.146808     -4.24477
      ↪ -0.0501421
   -0.273188    -0.481149 -9.77471e-16     0.134212    -0.146808   -0.0501421
      ↪ -4.24477

C_0_prime Matrix:

   -0.993361    -0.104697 -6.45607e-16    0.0476199 -7.98146e-15   4.0881e-16
      ↪ 0.00222819
   -0.113883     0.887058    5.797e-15    -0.417863  6.99798e-14 -2.99761e-14
      ↪ -0.159843
 3.15273e-19  1.64226e-15  4.80473e-15  1.71258e-13            1 -1.14056e-16 -7.14186
    ↪ e-16
```

```
  9.7715e-18 -2.46936e-15     0.998516  8.28671e-15 -4.55392e-15    0.0544598 -9.44874
    ↪ e-15
-0.000754957     0.418666 -6.32026e-15     0.906926 -1.55863e-13 -8.64117e-15
    ↪ -0.0469432
  -0.0114923     0.115943    0.0385089   -0.0174439  3.15953e-15    -0.706057
    ↪ 0.697224
  -0.0114923     0.115943   -0.0385089   -0.0174439  3.58246e-15     0.706057
    ↪ 0.697224

C Matrix:

    -1.00161    -0.232145 -1.42291e-15    0.0981483  -1.6388e-14  1.02331e-14
      ↪ 0.054973
  0.00781923      1.07916  6.54511e-15    -0.411669  6.82443e-14 -1.08663e-13
    ↪ -0.584993
  4.4273e-18   1.6493e-15  4.84883e-15  1.71285e-13            1 -1.45466e-16 -5.61539
    ↪ e-16
-4.33681e-18 -2.62637e-15      1.08012  8.75992e-15 -4.86851e-15     0.360639 -6.61415
    ↪ e-14
 0.000444284     0.503178 -6.19296e-15     0.918173 -1.58082e-13 -5.01404e-14
    ↪ -0.270795
 -0.00221056    -0.180521    -0.163398   -0.0358456   7.9105e-15    -0.915938
    ↪ 0.818024
 -0.00221056    -0.180521     0.163398   -0.0358456  6.46414e-15     0.915938
    ↪ 0.818024

D Matrix:

    1.06675    -0.298759  3.60303e-17 -6.31019e-17   -0.0271382    0.0406029
      ↪ 0.0406029
   -0.298759      1.33412 -4.88497e-16  6.29026e-16     0.165031    -0.180072
     ↪ -0.180072
 3.60303e-17 -4.88497e-16            1  3.68824e-16  1.73216e-17  6.80666e-16  8.18881
    ↪ e-16
-6.31019e-17  6.29026e-16  3.68824e-16      1.16667  3.24209e-17     -0.17649
    ↪ 0.17649
  -0.0271382     0.165031  1.73216e-17  3.24209e-17      1.09623    -0.123747
     ↪ -0.123747
   0.0406029    -0.180072  6.80666e-16    -0.17649    -0.123747    0.0605765
     ↪ 0.00717853
   0.0406029    -0.180072  8.18881e-16     0.17649    -0.123747   0.00717853
     ↪ 0.0605765
iter: 0 Energy: -82.1486 Delta E: -82.1486
iter: 1 Energy: -83.8388 Delta E: -1.69013
iter: 2 Energy: -83.8722 Delta E: -0.0333948
iter: 3 Energy: -83.8734 Delta E: -0.00128959
iter: 4 Energy: -83.8736 Delta E: -0.000137273
iter: 5 Energy: -83.8736 Delta E: -2.36545e-05
iter: 6 Energy: -83.8736 Delta E: -4.48631e-06
iter: 7 Energy: -83.8736 Delta E: -8.72434e-07
iter: 8 Energy: -83.8736 Delta E: -1.70848e-07
iter: 9 Energy: -83.8736 Delta E: -3.35253e-08
iter: 10 Energy: -83.8736 Delta E: -6.58248e-09

Final HF Energy: -74.9659010585405

Freed Memory
Serial Time: 0.011638
```

Water HF/STO-3G

```
\nTiming for data/t1\n
./hf data/t1 1

Running: ./hf

Data Path: data/t1
Num Threads: 1
n_basis: 7
iter: 0 Energy: -82.1486 Delta E: -82.1486
iter: 1 Energy: -83.8388 Delta E: -1.69013
iter: 2 Energy: -83.8722 Delta E: -0.0333948
iter: 3 Energy: -83.8734 Delta E: -0.00128959
iter: 4 Energy: -83.8736 Delta E: -0.000137273
iter: 5 Energy: -83.8736 Delta E: -2.36545e-05
iter: 6 Energy: -83.8736 Delta E: -4.48631e-06
iter: 7 Energy: -83.8736 Delta E: -8.72434e-07
iter: 8 Energy: -83.8736 Delta E: -1.70848e-07
iter: 9 Energy: -83.8736 Delta E: -3.35253e-08
iter: 10 Energy: -83.8736 Delta E: -6.58248e-09

Final HF Energy: -74.9659010585405

Freed Memory
Time (CPU) : 0.008954
Time (USR) : 0.00894462922587991

./hf data/t1 2

Running: ./hf

Data Path: data/t1
Num Threads: 2
n_basis: 7
iter: 0 Energy: -82.1486 Delta E: -82.1486
iter: 1 Energy: -83.8388 Delta E: -1.69013
iter: 2 Energy: -83.8722 Delta E: -0.0333948
iter: 3 Energy: -83.8734 Delta E: -0.00128959
iter: 4 Energy: -83.8736 Delta E: -0.000137273
iter: 5 Energy: -83.8736 Delta E: -2.36545e-05
iter: 6 Energy: -83.8736 Delta E: -4.48631e-06
iter: 7 Energy: -83.8736 Delta E: -8.72434e-07
iter: 8 Energy: -83.8736 Delta E: -1.70848e-07
iter: 9 Energy: -83.8736 Delta E: -3.35253e-08
iter: 10 Energy: -83.8736 Delta E: -6.58248e-09

Final HF Energy: -74.9659010585405

Freed Memory
Time (CPU) : 0.012446
Time (USR) : 0.00687378598377109

./hf data/t1 4

Running: ./hf

Data Path: data/t1
Num Threads: 4
```

```
n_basis: 7
iter: 0 Energy: -82.1486 Delta E: -82.1486
iter: 1 Energy: -83.8388 Delta E: -1.69013
iter: 2 Energy: -83.8722 Delta E: -0.0333948
iter: 3 Energy: -83.8734 Delta E: -0.00128959
iter: 4 Energy: -83.8736 Delta E: -0.000137273
iter: 5 Energy: -83.8736 Delta E: -2.36545e-05
iter: 6 Energy: -83.8736 Delta E: -4.48631e-06
iter: 7 Energy: -83.8736 Delta E: -8.72434e-07
iter: 8 Energy: -83.8736 Delta E: -1.70848e-07
iter: 9 Energy: -83.8736 Delta E: -3.35253e-08
iter: 10 Energy: -83.8736 Delta E: -6.58248e-09

Final HF Energy: -74.9659010585405

Freed Memory
Time (CPU) : 0.022395
Time (USR) : 0.00679890578612685

./hf data/t1 6

Running: ./hf

Data Path: data/t1
Num Threads: 6
n_basis: 7
iter: 0 Energy: -82.1486 Delta E: -82.1486
iter: 1 Energy: -83.8388 Delta E: -1.69013
iter: 2 Energy: -83.8722 Delta E: -0.0333948
iter: 3 Energy: -83.8734 Delta E: -0.00128959
iter: 4 Energy: -83.8736 Delta E: -0.000137273
iter: 5 Energy: -83.8736 Delta E: -2.36545e-05
iter: 6 Energy: -83.8736 Delta E: -4.48631e-06
iter: 7 Energy: -83.8736 Delta E: -8.72434e-07
iter: 8 Energy: -83.8736 Delta E: -1.70848e-07
iter: 9 Energy: -83.8736 Delta E: -3.35253e-08
iter: 10 Energy: -83.8736 Delta E: -6.58248e-09

Final HF Energy: -74.9659010585405

Freed Memory
Time (CPU) : 0.020431
Time (USR) : 0.00625808583572507

./hf data/t1 8

Running: ./hf

Data Path: data/t1
Num Threads: 8
n_basis: 7
iter: 0 Energy: -82.1486 Delta E: -82.1486
iter: 1 Energy: -83.8388 Delta E: -1.69013
iter: 2 Energy: -83.8722 Delta E: -0.0333948
iter: 3 Energy: -83.8734 Delta E: -0.00128959
iter: 4 Energy: -83.8736 Delta E: -0.000137273
iter: 5 Energy: -83.8736 Delta E: -2.36545e-05
iter: 6 Energy: -83.8736 Delta E: -4.48631e-06
iter: 7 Energy: -83.8736 Delta E: -8.72434e-07
```

```
iter: 8 Energy: -83.8736 Delta E: -1.70848e-07
iter: 9 Energy: -83.8736 Delta E: -3.35253e-08
iter: 10 Energy: -83.8736 Delta E: -6.58248e-09

Final HF Energy: -74.9659010585405

Freed Memory
Time (CPU) : 0.030145
Time (USR) : 0.00609015300869942

./hf data/t1 10

Running: ./hf

Data Path: data/t1
Num Threads: 10
n_basis: 7
iter: 0 Energy: -82.1486 Delta E: -82.1486
iter: 1 Energy: -83.8388 Delta E: -1.69013
iter: 2 Energy: -83.8722 Delta E: -0.0333948
iter: 3 Energy: -83.8734 Delta E: -0.00128959
iter: 4 Energy: -83.8736 Delta E: -0.000137273
iter: 5 Energy: -83.8736 Delta E: -2.36545e-05
iter: 6 Energy: -83.8736 Delta E: -4.48631e-06
iter: 7 Energy: -83.8736 Delta E: -8.72434e-07
iter: 8 Energy: -83.8736 Delta E: -1.70848e-07
iter: 9 Energy: -83.8736 Delta E: -3.35253e-08
iter: 10 Energy: -83.8736 Delta E: -6.58248e-09

Final HF Energy: -74.9659010585405

Freed Memory
Time (CPU) : 0.045239
Time (USR) : 0.0056780893355608
```

Ethene HF/aug-cc-pVDZ

```
Timing for data/t3
./hf data/t3 1

Running: ./hf

Data Path: data/t3
Num Threads: 1
n_basis: 82
iter: 0 Energy: -97.0923 Delta E: -97.0923
iter: 1 Energy: -98.28 Delta E: -1.18774
iter: 2 Energy: -107.398 Delta E: -9.11804
iter: 3 Energy: -105.85 Delta E: 1.5485
iter: 4 Energy: -109.396 Delta E: -3.54656
iter: 5 Energy: -107.579 Delta E: 1.81723
iter: 6 Energy: -110.004 Delta E: -2.42545
iter: 7 Energy: -110.756 Delta E: -0.75169
iter: 8 Energy: -111.276 Delta E: -0.52038
iter: 9 Energy: -111.42 Delta E: -0.143198
iter: 10 Energy: -111.448 Delta E: -0.0283181
iter: 11 Energy: -111.453 Delta E: -0.00491031
iter: 12 Energy: -111.454 Delta E: -0.000809715
```

```
iter: 13 Energy: -111.454 Delta E: -0.000131563
iter: 14 Energy: -111.454 Delta E: -2.12882e-05
iter: 15 Energy: -111.454 Delta E: -3.44269e-06
iter: 16 Energy: -111.454 Delta E: -5.57065e-07
iter: 17 Energy: -111.454 Delta E: -9.02316e-08
iter: 18 Energy: -111.454 Delta E: -1.46336e-08
iter: 19 Energy: -111.454 Delta E: -2.37615e-09

Final HF Energy: -78.0435868316762

Freed Memory
Time (CPU) : 196.674979
Time (USR) : 196.682998436969

./hf data/t3 2

Running: ./hf

Data Path: data/t3
Num Threads: 2
n_basis: 82
iter: 0 Energy: -97.0923 Delta E: -97.0923
iter: 1 Energy: -98.28 Delta E: -1.18774
iter: 2 Energy: -107.398 Delta E: -9.11804
iter: 3 Energy: -105.85 Delta E: 1.5485
iter: 4 Energy: -109.396 Delta E: -3.54656
iter: 5 Energy: -107.579 Delta E: 1.81723
iter: 6 Energy: -110.004 Delta E: -2.42545
iter: 7 Energy: -110.756 Delta E: -0.75169
iter: 8 Energy: -111.276 Delta E: -0.52038
iter: 9 Energy: -111.42 Delta E: -0.143198
iter: 10 Energy: -111.448 Delta E: -0.0283181
iter: 11 Energy: -111.453 Delta E: -0.00491031
iter: 12 Energy: -111.454 Delta E: -0.000809715
iter: 13 Energy: -111.454 Delta E: -0.000131563
iter: 14 Energy: -111.454 Delta E: -2.12882e-05
iter: 15 Energy: -111.454 Delta E: -3.44269e-06
iter: 16 Energy: -111.454 Delta E: -5.57065e-07
iter: 17 Energy: -111.454 Delta E: -9.02316e-08
iter: 18 Energy: -111.454 Delta E: -1.46336e-08
iter: 19 Energy: -111.454 Delta E: -2.37615e-09

Final HF Energy: -78.0435868316762

Freed Memory
Time (CPU) : 200.002911
Time (USR) : 106.574036244769

./hf data/t3 4

Running: ./hf

Data Path: data/t3
Num Threads: 4
n_basis: 82
iter: 0 Energy: -97.0923 Delta E: -97.0923
iter: 1 Energy: -98.28 Delta E: -1.18774
iter: 2 Energy: -107.398 Delta E: -9.11804
iter: 3 Energy: -105.85 Delta E: 1.5485
```

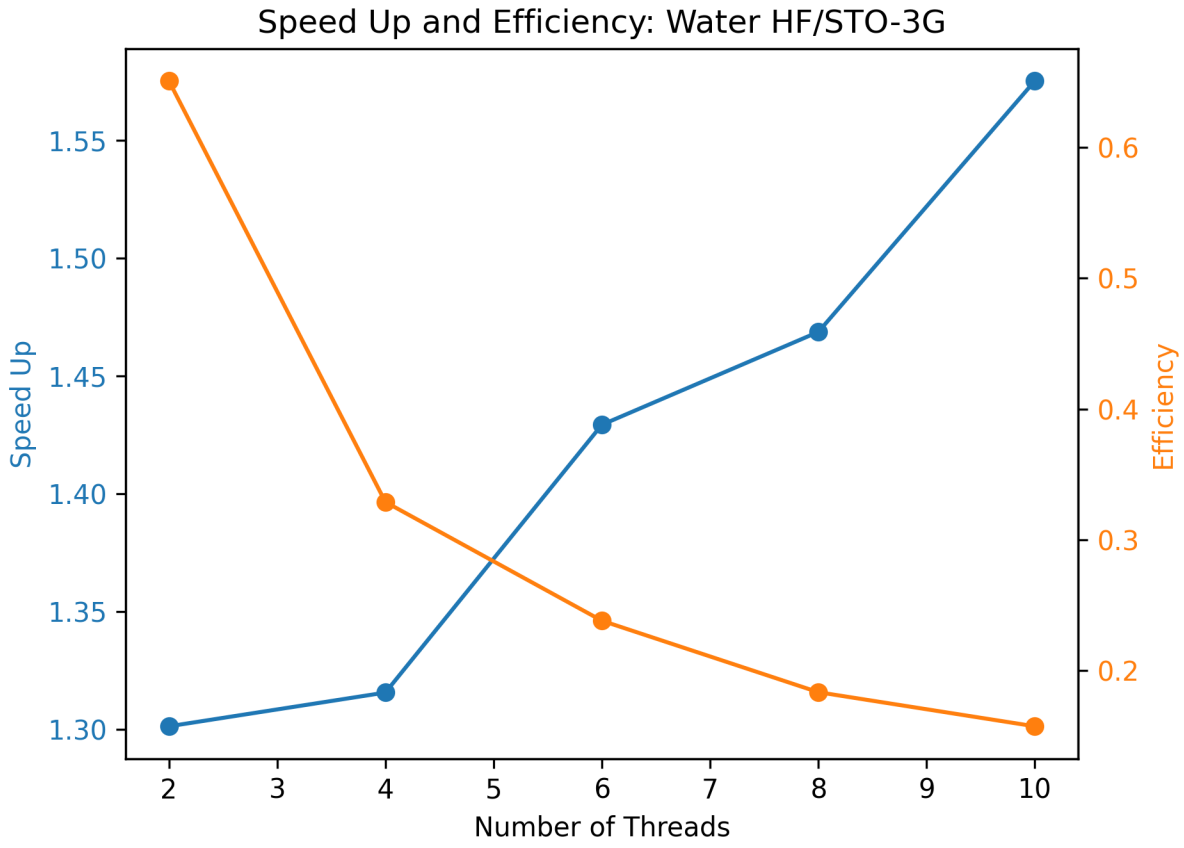
```
iter: 4 Energy: -109.396 Delta E: -3.54656
iter: 5 Energy: -107.579 Delta E: 1.81723
iter: 6 Energy: -110.004 Delta E: -2.42545
iter: 7 Energy: -110.756 Delta E: -0.75169
iter: 8 Energy: -111.276 Delta E: -0.52038
iter: 9 Energy: -111.42 Delta E: -0.143198
iter: 10 Energy: -111.448 Delta E: -0.0283181
iter: 11 Energy: -111.453 Delta E: -0.00491031
iter: 12 Energy: -111.454 Delta E: -0.000809715
iter: 13 Energy: -111.454 Delta E: -0.000131563
iter: 14 Energy: -111.454 Delta E: -2.12882e-05
iter: 15 Energy: -111.454 Delta E: -3.44269e-06
iter: 16 Energy: -111.454 Delta E: -5.57065e-07
iter: 17 Energy: -111.454 Delta E: -9.02316e-08
iter: 18 Energy: -111.454 Delta E: -1.46336e-08
iter: 19 Energy: -111.454 Delta E: -2.37615e-09

Final HF Energy: -78.0435868316762

Freed Memory
Time (CPU) : 207.655153
Time (USR) : 60.0388427260332

./hf data/t3 6

Running: ./hf

Data Path: data/t3
Num Threads: 6
n_basis: 82
iter: 0 Energy: -97.0923 Delta E: -97.0923
iter: 1 Energy: -98.28 Delta E: -1.18774
iter: 2 Energy: -107.398 Delta E: -9.11804
iter: 3 Energy: -105.85 Delta E: 1.5485
iter: 4 Energy: -109.396 Delta E: -3.54656
iter: 5 Energy: -107.579 Delta E: 1.81723
iter: 6 Energy: -110.004 Delta E: -2.42545
iter: 7 Energy: -110.756 Delta E: -0.75169
iter: 8 Energy: -111.276 Delta E: -0.52038
iter: 9 Energy: -111.42 Delta E: -0.143198
iter: 10 Energy: -111.448 Delta E: -0.0283181
iter: 11 Energy: -111.453 Delta E: -0.00491031
iter: 12 Energy: -111.454 Delta E: -0.000809715
iter: 13 Energy: -111.454 Delta E: -0.000131563
iter: 14 Energy: -111.454 Delta E: -2.12882e-05
iter: 15 Energy: -111.454 Delta E: -3.44269e-06
iter: 16 Energy: -111.454 Delta E: -5.57065e-07
iter: 17 Energy: -111.454 Delta E: -9.02316e-08
iter: 18 Energy: -111.454 Delta E: -1.46336e-08
iter: 19 Energy: -111.454 Delta E: -2.37615e-09

Final HF Energy: -78.0435868316762

Freed Memory
Time (CPU) : 213.795112
Time (USR) : 42.3328502173536

./hf data/t3 8

```

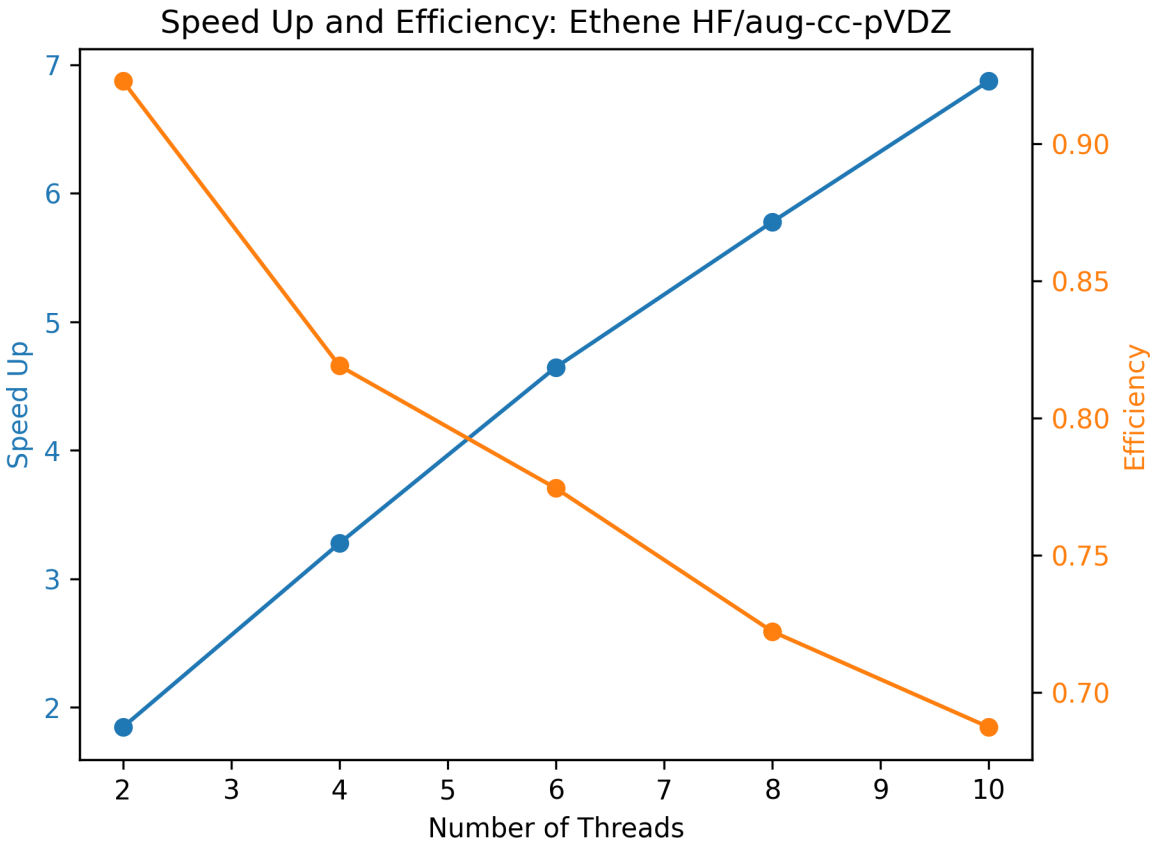
```
Running: ./hf

Data Path: data/t3
Num Threads: 8
n_basis: 82
iter: 0 Energy: -97.0923 Delta E: -97.0923
iter: 1 Energy: -98.28 Delta E: -1.18774
iter: 2 Energy: -107.398 Delta E: -9.11804
iter: 3 Energy: -105.85 Delta E: 1.5485
iter: 4 Energy: -109.396 Delta E: -3.54656
iter: 5 Energy: -107.579 Delta E: 1.81723
iter: 6 Energy: -110.004 Delta E: -2.42545
iter: 7 Energy: -110.756 Delta E: -0.75169
iter: 8 Energy: -111.276 Delta E: -0.52038
iter: 9 Energy: -111.42 Delta E: -0.143198
iter: 10 Energy: -111.448 Delta E: -0.0283181
iter: 11 Energy: -111.453 Delta E: -0.00491031
iter: 12 Energy: -111.454 Delta E: -0.000809715
iter: 13 Energy: -111.454 Delta E: -0.000131563
iter: 14 Energy: -111.454 Delta E: -2.12882e-05
iter: 15 Energy: -111.454 Delta E: -3.44269e-06
iter: 16 Energy: -111.454 Delta E: -5.57065e-07
iter: 17 Energy: -111.454 Delta E: -9.02316e-08
iter: 18 Energy: -111.454 Delta E: -1.46336e-08
iter: 19 Energy: -111.454 Delta E: -2.37615e-09

Final HF Energy: -78.0435868316762

Freed Memory
Time (CPU) : 218.198771
Time (USR) : 34.0461984351277

./hf data/t3 10

Running: ./hf

Data Path: data/t3
Num Threads: 10
n_basis: 82
iter: 0 Energy: -97.0923 Delta E: -97.0923
iter: 1 Energy: -98.28 Delta E: -1.18774
iter: 2 Energy: -107.398 Delta E: -9.11804
iter: 3 Energy: -105.85 Delta E: 1.5485
iter: 4 Energy: -109.396 Delta E: -3.54656
iter: 5 Energy: -107.579 Delta E: 1.81723
iter: 6 Energy: -110.004 Delta E: -2.42545
iter: 7 Energy: -110.756 Delta E: -0.75169
iter: 8 Energy: -111.276 Delta E: -0.52038
iter: 9 Energy: -111.42 Delta E: -0.143198
iter: 10 Energy: -111.448 Delta E: -0.0283181
iter: 11 Energy: -111.453 Delta E: -0.00491031
iter: 12 Energy: -111.454 Delta E: -0.000809715
iter: 13 Energy: -111.454 Delta E: -0.000131563
iter: 14 Energy: -111.454 Delta E: -2.12882e-05
iter: 15 Energy: -111.454 Delta E: -3.44269e-06
iter: 16 Energy: -111.454 Delta E: -5.57065e-07
iter: 17 Energy: -111.454 Delta E: -9.02316e-08
iter: 18 Energy: -111.454 Delta E: -1.46336e-08
iter: 19 Energy: -111.454 Delta E: -2.37615e-09
```

```
199
200 Final HF Energy: -78.0435868316762
201
202 Freed Memory
203 Time (CPU) : 221.635326
204 Time (USR) : 28.618671390228
```

Results

The final energy produced from the wather HF/STO-3G yielded -74.965901 Ha while Psi4 on the same geometry and basis set with default options yields -74.965990 Ha. Meanwhile the ethene HF/aug-cc-pVDZ yieled -78.043587 Ha versus the Psi4 result of -78.043510 Ha. The difference between these energies is likely due to me not implementing a cutoff threshold for the commutator of the density and Fock matrix for checking convergence, along with me not using density fitting like Psi4.





The speedups for the water are very marginal and inefficient; however, it is likely due to the size of the system not being large enough and only calling OMP threads for a few of the steps while bottlenecked by serial steps. On the case for ethene with the larger basis set, we experience close to a speedup of 7 at 10 OMP threads, which is still quite inefficient. With that said, the efficiency for only two threads is quite high with nearly a speedup of 2, meaning that adding a few extra threads for this program will give the most improvement for the cost.