Hartree Fock Fortran Project

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1   Goal

The goal of this project is to write a working Hartree-Fock program in Fortran for the Scientific programming course. We will write the SCF cycle ourself using code provided by Luuk Visscher for the Dirac program. The Dirac program calculates the integral matrices (one- and two-electron) and also the nuclear repulsion energy (and also does SCF, which we use for comparison). A procedure is also provided for diagonalisation of matrices. The goal is to get close to the HF energies as calculated by Dirac.

2   Background

We are working in a space of n orthogonal spinorbitals, so overlap matrix is unit matrix and is not needed in our calculations. We start with a diagonal density matrix for our trial matrix.

We wish to calculate the HF energy for a given system. We exploit the variational theorem to optimize the wavefunction we were provided. To that end we employ the SCF method to minimise the energy. A schematic overview of the used method is provided in Figure 1.

2.1   SCF

We first read in the settings file and obtain also the core-Hamiltonian and two-electron matrices. Next we initialise the density matrix, usually as identity matrix. We then start the SCF cycles. The first step of an SCF cycle is to calculate the Fock matrix as follows,

$$F_{pq}^n = h_{pq}^{core} + \sum_{r,s}^{occ.} g_{prqs} D_{rs} \tag{1}$$

with the latter sum only running over the occupied spinorbitals. The upperscript n denotes that this is the Fock matrix of the n-th cycle. In UHF this is equal to summing over the first n spinorbitals, for a system of n electrons. In RHF we half the number of spinorbitals to sum over, since now each spinorbital holds
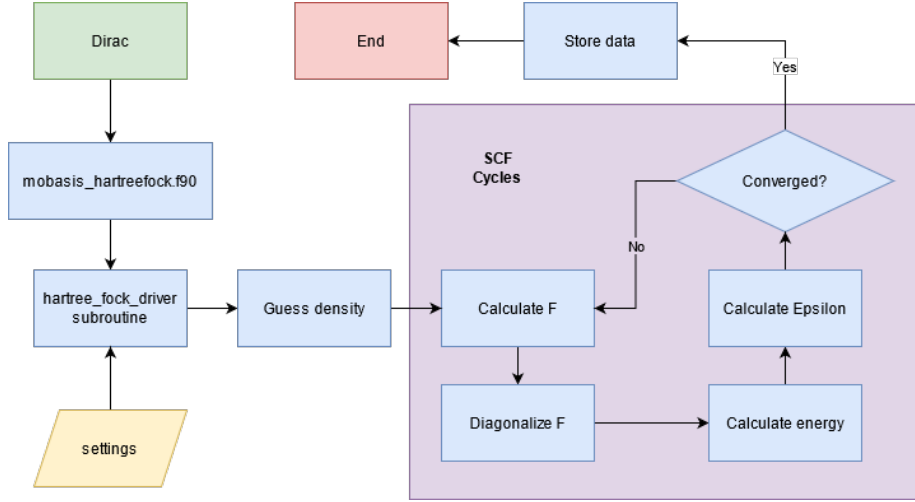
Figure 1: Implementation of the Hartree Fock method.

two electrons. In the program, the matrices h^{core} and g are complex. For some calculations it is easier to work with matrices where the complex part is extended into an extra axis in real arrays.

With the new Fock matrix we first check for convergence. We use the Fock-density commutator criterium:

$$\epsilon^n = \sqrt{\sum_{p,q}(([F^n, D^{n-1}])^2_{pq}} \tag{2}$$

If this value is smaller than a threshold value or if the maximum number of cycles is reached, we stop the SCF.

After calculating the Fock matrix we may diagonalize it. The diagonalization procedure is included in the Dirac program and is called by the hartree_fock_driver subroutine. Diagonalization yields eigenvalues and eigenvectors C. The latter are used to calculate the new density matrix as follows,

$$D^n_{pq} = \sum_{i}^{occ.} C^*_{pi} C_{qi}. \tag{3}$$

To improve the stability of the SCF procedure it is possible to update the density using mixing or DIIS (P. Pulay, Chem. Phys. Lett. 73, 393 (1980).), or any other method. The current program uses mixing as a simple linear interpolation:

$$D^n_{pq} \leftarrow \lambda D^n_{pq} + (1 - \lambda) D^{n-1}_{pq}. \tag{4}$$

We can calculate now the HF energy as follows:

2

$$E^{HF} = \sum_{p,q} h_{pq}^{core} D_{pq} + \frac{1}{2} \sum_{p,q,r,s}^{occ.} g_{prqs} D_{pq} D_{rs} + E_{nuc} \qquad (5)$$

The E_{nuc} is the nuclear repulsion energy provided by Dirac.

The cycle is now finished after printing any data we wish for further processing. We can now repeat all these steps for the next cycle.

3 Program Flow

3.1 Program Folder

The relevant directories and files are shown below in a tree-like structure.
SciProgHF
– src
—– exacorr
——– mobasis_hartreefock.f90
– runs
—– {molecule name}
——– {molecule name}.xyz
——– hf.inp
——– settings
——– hf_{molecule name}.out
—– h2_pes.py
—– hf_result_reader.py

The program is run from Dirac, and is called using the pam executable. After Dirac finishes, the subroutine hartree_fock_driver is called from mobasis_hartreefock.f90.

3.2 Calling Dirac

Dirac is called using the pam executable. If we are inside a folder in the runs directory (so any {molecule name} folder), we can call pam as

pam —inp=hf.inp —mol={molecule name}.xyz —copy=settings

Here we specify the input file and geometry file as well as options to copy the settings file into the Dirac scratch directory. It is important to copy over the settings file, as it is read into our program. It will only be read from the scratch directory.

3.3 settings

Our program needs a number of settings in order to function. These settings are stored in the settings file. An example settings file is provided below:

```
Use unrestricted HF
.false.
Number of electrons
2
Use linear mixing of density matrices
.true.
Mixing strength
0.2
Max iterations
150
```

Only every second line is read, so every first line functions as a comment line. The options themselves should be understandable. The settings files are read from the scratch directory.

The UHF setting only changes the sizes of the matrices. The number of spinors, as well as the number of occupied spinorbitals is doubled. However, UHF seems to generate very unstable results. It is not yet sure why that is.

3.4 hf_result_reader.py

This python script provides a function to read in the data from an output file from the HF runs. One may enter the path to the output file (hf_{molecule name}.out) in the python script and run it. The program then reads in the data and outputs two files, energy.png and anim.gif, which contain the energies and density matrices as function of SCF cycle. The frames for anim.gif are also stored in the frames directory.

3.5 h2_pes.py

The script is called in the terminal by simply using

```
python3 h2_pes.py
```

This python script calculates the potential energy surface of the bondlength in the H_2 molecule, it functioned also as the test system during development of our program. The script works by simply calling the Dirac program and providing it with a new molecular geometry each time. The energies for our program and also as calculated by Dirac are then read and plotted in runs/pes.png, an example is given in Figure 2. It is possible to change the range of bond lengths and also the number of steps. There is also an option to read the density matrices and make an animation of how they change during the SCF cycles. Additionally a plot is generated showing the energy change during the SCF cycles.

4 Improvements

The energies from the PES calculations are not close to the Dirac energies. It is not yet clear why that is, but it is very important to figure out why that
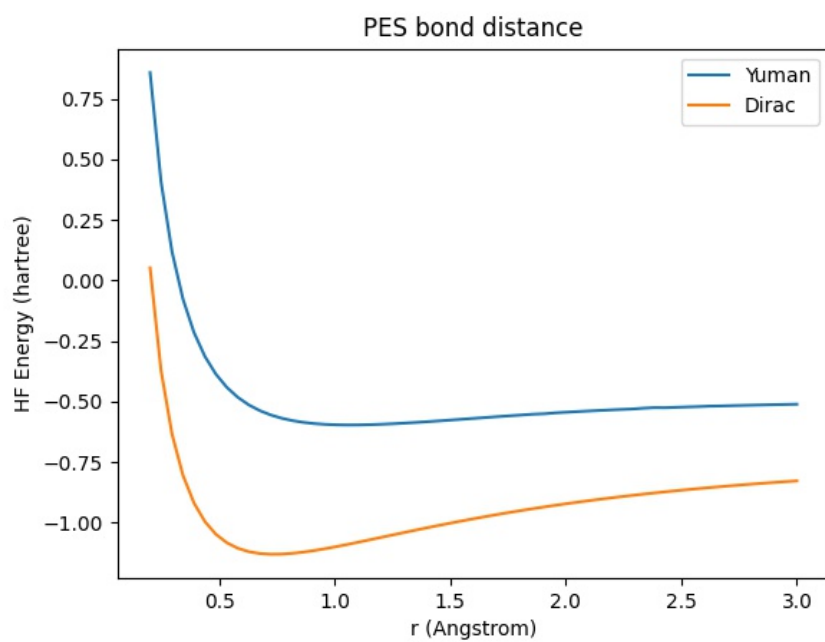
Figure 2: PES of H_2 bond distance. Shown are energies from our RHF program (blue) and Dirac (orange).

is. Further improvements could be made by implementing DIIS. Especially for large systems it would be good to use this convergence accelerator. The UHF setting is also not working correctly. It generates very unstable energies with a lot of oscillations.