

REPO LINK: <https://github.com/neal-p/CHEM279>

HW4

Compilation Instructions

1. Go to the top level repo directory `CHEM279/`
2. `mkdir -p build`
3. `cd build`
4. `cmake ..`
5. `make hw4 scan`

Run Instructions

Once you have compiled, there will be two executables: - `CHEM279/HW4/hw4` - `CHEM279/HW4/scan`

Main CNDO/2 Program: `hw4`

This executable takes in an xyz file in the specification of our class and a basis set file in Gaussian format. It calculates and prints the following info as shown in the provided example output including the gamma matrix, initial density matrices of all Os, and the initial CNDO/2 Fock matrices for alpha and beta electrons. The program then performs the self consistent field algorithm to minimize the energy and solve for the optimal electron densities. An example output of HF is shown below:

```
./hw4 sample_input/HF.txt basis/basis_set.txt
```

```
p=4, q=4
```

```
gamma:
```

```
21.0778  14.402
 14.402  25.2019
```

```
overlap:
```

```
      1  0.45346 -0.351578      0      0
 0.45346      1      0      0      0
-0.351578      0      1      0      0
      0      0      0      1      0
      0      0      0      0      1
```

```
Hcore:
```

```
-118.529 -10.883  8.43788      -0      -0
 -10.883 -210.487      -0      -0      -0
  8.43788      -0 -189.295      -0      -0
      -0      -0      -0 -189.295      -0
```

-0 -0 -0 -0 -189.295

SCF Cycle: 1

Starting Densities:

0 0 0 0 0
0 0 0 0 0
0 0 0 0 0
0 0 0 0 0
0 0 0 0 0
0 0 0 0 0

0 0 0 0 0
0 0 0 0 0
0 0 0 0 0
0 0 0 0 0
0 0 0 0 0
0 0 0 0 0

Fock Matrices:

-118.529	-10.883	8.43788	-0	-0
-10.883	-210.487	-0	-0	-0
8.43788	-0	-189.295	-0	-0
-0	-0	-0	-189.295	-0
-0	-0	-0	-0	-189.295

-118.529	-10.883	8.43788	-0	-0
-10.883	-210.487	-0	-0	-0
8.43788	-0	-189.295	-0	-0
-0	-0	-0	-189.295	-0
-0	-0	-0	-0	-189.295

End of SCF Cycle: 1

Change in density: 4

Ca:

0.119784	0.108018	0	0	0.986906
0.991784	-0.0579848	0	0	-0.11403
-0.0449083	-0.992457	0	0	0.114076
0	0	1	0	0
0	0	0	1	0

Cb:

0.119784	0.108018	0	0	0.986906
0.991784	-0.0579848	0	0	-0.11403
-0.0449083	-0.992457	0	0	0.114076

0	0	1	0	0
0	0	0	1	0

Ea:

-7.78365
-6.99029
-6.95654
-6.95654
-4.27385

Eb:

-7.78365
-6.99029
-6.95654
-6.95654
-4.27385

Ending Densities:

0.0260161	0.112537	-0.112582	0	0
0.112537	0.986997	0.013008	0	0
-0.112582	0.013008	0.986987	0	0
0	0	0	1	0
0	0	0	0	1

0.0260161	0.112537	-0.112582	0	0
0.112537	0.986997	0.013008	0	0
-0.112582	0.013008	0.986987	0	0
0	0	0	1	0
0	0	0	0	1

Nuclear Repulsion Energy is 110.742

Electron Energy is -859.473

Total Energy=-748.731

SCF Cycle: 2

Starting Densities:

0.0260161	0.112537	-0.112582	0	0
0.112537	0.986997	0.013008	0	0
-0.112582	0.013008	0.986987	0	0
0	0	0	1	0
0	0	0	0	1

0.0260161	0.112537	-0.112582	0	0
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0.112537	0.986997	0.013008	0	0
-0.112582	0.013008	0.986987	0	0
0	0	0	1	0
0	0	0	0	1

Fock Matrices:

-3.51395	-12.5038	10.0593	-0	-0
-12.5038	-34.3072	-0.327828	-0	-0
10.0593	-0.327828	-13.115	-0	-0
-0	-0	-0	-13.4429	-0
-0	-0	-0	-0	-13.4429

-3.51395	-12.5038	10.0593	-0	-0
-12.5038	-34.3072	-0.327828	-0	-0
10.0593	-0.327828	-13.115	-0	-0
-0	-0	-0	-13.4429	-0
-0	-0	-0	-0	-13.4429

End of SCF Cycle: 2
Change in density: 1.10611

...
...
...

SCF Cycle: 17

Starting Densities:

0.387878	0.202796	-0.443061	0	0
0.202796	0.932814	0.146786	0	0
-0.443061	0.146786	0.679308	0	0
0	0	0	1	0
0	0	0	0	1

0.387878	0.202796	-0.443061	0	0
0.202796	0.932814	0.146786	0	0
-0.443061	0.146786	0.679308	0	0
0	0	0	1	0
0	0	0	0	1

Fock Matrices:

-6.30974	-13.8037	14.8188	-0	-0
-13.8037	-40.7579	-3.69929	-0	-0

14.8188	-3.69929	-13.1771	-0	-0
-0	-0	-0	-21.2591	-0
-0	-0	-0	-0	-21.2591
-6.30974	-13.8037	14.8188	-0	-0
-13.8037	-40.7579	-3.69929	-0	-0
14.8188	-3.69929	-13.1771	-0	-0
-0	-0	-0	-21.2591	-0
-0	-0	-0	-0	-21.2591

End of SCF Cycle: 17
Change in density: 8.09833e-07

Ca:

0.347792	-0.516642	0	0	0.782382
0.936128	0.237653	0	0	-0.259203
-0.0520206	0.822558	0	0	0.566297
0	0	1	0	0
0	0	0	1	0

Cb:

0.347792	-0.516642	0	0	0.782382
0.936128	0.237653	0	0	-0.259203
-0.0520206	0.822558	0	0	0.566297
0	0	1	0	0
0	0	0	1	0

Ea:

-1.67876
-0.865586
-0.78127
-0.78127
0.330361

Eb:

-1.67876
-0.865586
-0.78127
-0.78127
0.330361

Ending Densities:

0.387878	0.202796	-0.443061	0	0
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0.202796	0.932814	0.146786	0	0
-0.443061	0.146786	0.679308	0	0
0	0	0	1	0
0	0	0	0	1
0.387878	0.202796	-0.443061	0	0
0.202796	0.932814	0.146786	0	0
-0.443061	0.146786	0.679308	0	0
0	0	0	1	0
0	0	0	0	1

Nuclear Repulsion Energy is 110.742
Electron Energy is -873.141
Total Energy=-762.399

This matches very closely to the given output! The final energies are slightly off, I think this is because I am using Eigen but the sample output is solving with armadillo. Our coefficient matrices and eigenvectors are ever so slightly off from each other. I suspect this is also why my calculation takes a few more cycles to converge. Here is an example of how close the eigenvectors are:

My Output:

Ea:
-45.6807
-23.5535 *
-21.2591 *
-21.2591 *
8.98945 *

Eb:
-45.6807
-23.5535 *
-21.2591 *
-21.2591 *
8.98945 *

Given Output:

Ea
-45.6807
-23.5536 *
-21.2592 *
-21.2592 *
8.9896 *

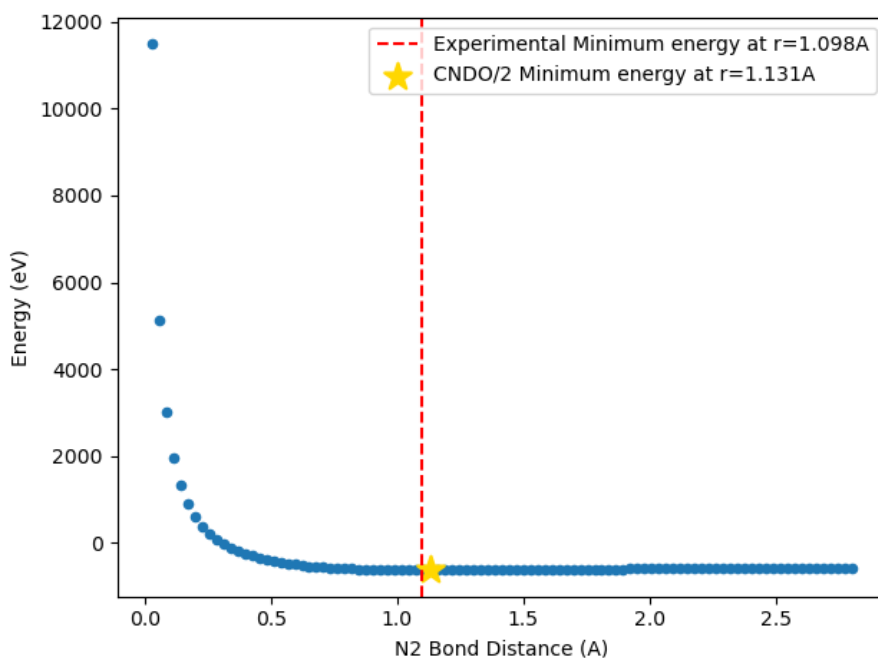
Eb
-45.6807

```
-23.5536 *  
-21.2592 *  
-21.2592 *  
8.9896 *
```

Obviously we are only seeing however many significant digits are configured to print. But, the differences in rounding suggest to me there are very small differences between the two solvers that slightly affect the final energies.

To run all the provided tests, a script `run_samples.sh`. This will save all the outputs to `my_output`.

N2 Bond scan: ** BONUS ** To experiment with my CNDO/2 code I wanted to try calculating the equilibrium bond distance of N₂. I created 100 input geometries scanning from 0 to 3 Angstroms between the two N atoms. I then re-worked the program above to take in multiple xyz files instead of a single file. The output is written to console in csv format. So, I piped it into a file. From there, I plotted the results in python.



The curve matches the *general* expected bond dissociation curve! Although, the minimum energy is not very much lower in energy than the two elements far separated. This can be somewhat expected since CNDO/2 doesn't take into account the more complex pi bonding occurring in N₂'s triple bond. Nevertheless, despite the well being shallow, the distance itself is remarkably close at 1.131A

compared to the experimental 1.098Å. This certainly shows why semi-empirical methods can be really useful for geometry optimization before re-calculating the energies at higher levels of theory!