Documentation and User Guide

Hartree-Fock and MP2 energy calculation program

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Version 1.0

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1 The program

This program calculates the Hartree-Fock (HF) and Møller–Plesset perturbation theory (MP2) energies from data and integrals stored in HDF5 format. In particular, the number of molecular orbitals, number of spin-up electrons, nuclear repulsion energy, one-electron integrals and two-electron integrals are read from a HDF5 file using the TREXIO library. The program then calculates and outputs the one-electron and two-electron contribution to the Hartree-Fock energy as well as the MP2 energy correction.

2 Installation

2.1 Prerequisites

Ensure you have the following installed on your system.

```
gcc
make
trexio
```

2.2 Installation

1. Clone the repository:

```
git clone https://github.com/pauline-schtt/tccm-homeworks/tree/master/project1
cd project1
```

2. Compile the program using `make`:

```
make
```

3. Then, run the program:

```
./HF_and_MP2 <path_to_the_input_file>
```

Installation instructions can also be found in the `INSTALL.md` file.

3 Usage

To calculate the Hartree-Fock and MP2 energies, provide the full path to the HDF5 file containing the molecular data and integrals as an argument to the program. Important notice: this program works exclusively with the file in HDF5 format, other formats will not produce any results.

Example:

```
./HF_and_MP2 data/h2o.h5
```

If no file is provided, the program is going to ask the user to enter the path to the file on the command line before starting the calculation.

4 Expected output

The expected output from the Hartree-Fock and MP2 energy calculation for water (using the HDF5-file provided in `data/h20.h5`) is pasted below.

```
  ___  ___  ________      _____ ______   ________    _______
|\  \|\  \|\  _____\    |\   _ \  _   \|\   __  \  /  ___  \
 \ \  \\\  \ \  \__/     \ \  \\\__\ \  \ \  \|\  \/__/|_/  /|
  \ \   __  \ \   __\     \ \  \\|__| \  \ \   ____\__|//  / /
   \ \  \ \  \ \  \_|      \ \  \    \ \  \ \  \___|   /  /_/__
    \ \__\ \__\ \__\        \ \__\    \ \__\ \__\     |\________\
     \|__|\|__|\|__|         \|__|     \|__|\|__|      \|_______|

Welcome to the Hartree-Fock and MP2 energy calculation program.

Calculating the Hartree-Fock energy...
Done!

Calculating the MP2 energy correction...
Done!

################## Energy Summary ##################

Nuclear repulsion energy:             9.194966
One-electron energy:               -123.151186
Two-electron energy:                37.929422
Hartree-Fock energy:               -76.026799
MP2 energy correction:              -0.203960
Total energy (HF + MP2):           -76.230759

################ System Information ################

Number of occupied orbitals:         5
Number of molecular orbitals:        24
Number of two-electron integrals:    13458

################ Timing Information ################
HF calculation time:                 0.000032 seconds
MP2 calculation time:                0.008758 seconds
I/O and setup time:                  0.004182 seconds
Total execution time:                0.012972 seconds

Your calculation is done.
Thank you for using the program!
```

5 Tests

The program was tested on MacOS Sequoia 15.2 and Ubuntu 24.04. To test whether the installation was succesful, you could calculate the Hartree-Fock and MP2 energies on the set of molecules provided in the `data` folder. The reference values are given in the `README.org` file. The expected output for the set of test molecules is provided in the `test` folder.

6 Cleaning up

To clean up the compiled files, run:

```
make clean
```

7 Troubleshooting

If you encounter any issues during the installation, ensure that your versions of the prerequisites meet the required versions mentioned above. In case you're still facing issues, feel free to reach out to any of the contributors or opening an issue on GitHub.

8 License

9 Acknowledgments

This project is based on data and instructions provided by Abdallah Ammar, Yann Damour, Peter Reinhardt and Anthony Scemama, available at https://github.com/scemama/tccm-homeworks.

Appendix

Detailed documentation on the file contents, functions and variables in the code are provided in the documentation as generated using Doxygen (https://www.doxygen.nl/) in the appendix.

Hartree-Fock and MP2 energy calculation

1.0

Generated by Doxygen 1.9.8

Chapter 1

File Index

1.1 File List

Here is a list of all files with brief descriptions:

Chapter 2

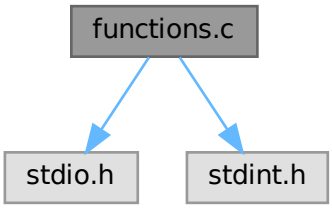
File Documentation

2.1 functions.c File Reference

Contains the functions associated with the HF and MP2 energy calculation.

```
#include <stdio.h>
#include <stdint.h>
```

Include dependency graph for functions.c:



Functions

- double one_electron_energy (double *data, int32_t n_up, int32_t mo_num)

  Calculates the one-electron energy contribution to the Hartree-Fock energy.
- double two_electron_energy (int32_t *index, double *value, int32_t n_up, int64_t n_integrals)

  Calculates the two-electron energy contribution to the Hartree-Fock energy.
- double hartree_fock_energy (double nuc_repul, double one_el_energy, double two_el_energy)

  Calculates the total Hartree-Fock energy.
- double get_integral (int i, int j, int k, int l, const int32_t *index, const double *value, int64_t n_integrals)

  Retrieves integral value.
- double MP2_energy_correction (int32_t *index, double *value, double *mo_energy, int32_t n_up, int64_t n_integrals)

  MP2 energy correction calculation.

2.1.1 Detailed Description

Contains the functions associated with the HF and MP2 energy calculation.

2.1.2 Function Documentation

2.1.2.1 get_integral()

```
double get_integral (
            int i,
            int j,
            int k,
            int l,
            const int32_t * index,
            const double * value,
            int64_t n_integrals )
```

Retrieves integral value.

Parameters

i	First index
j	Second index
k	Third index
l	Fourth index
index	Array containing four-index combinations
value	Array containing integral values
n_integrals	Total number of integrals

Returns

Value of the requested integral or 0.0 if not found

2.1.2.2 hartree_fock_energy()

```
double hartree_fock_energy (
            double nuc_repul,
            double one_el_energy,
            double two_el_energy )
```

Calculates the total Hartree-Fock energy.

Parameters

nuc_repul	Nuclear repulsion energy
one_el_energy	One-electron energy contribution
two_el_energy	Two-electron energy contribution

Returns

Total Hartree-Fock energy

2.1.2.3 MP2_energy_correction()

```
double MP2_energy_correction (
            int32_t * index,
            double * value,
            double * mo_energy,
            int32_t n_up,
            int64_t n_integrals )
```

MP2 energy correction calculation.

Parameters

index	Array containing four-index combinations
value	Array containing integral values
mo_energy	Array of molecular orbital energies
n_up	Number of occupied orbitals
n_integrals	Total number of integrals

Returns

MP2 energy correction

2.1.2.4 one_electron_energy()

```
double one_electron_energy (
            double * data,
            int32_t n_up,
            int32_t mo_num )
```

Calculates the one-electron energy contribution to the Hartree-Fock energy.

Parameters

data	Array containing one-electron integrals
n_up	Number of occupied orbitals
mo_num	Total number of molecular orbitals

Returns

One-electron energy contribution

2.1.2.5 two_electron_energy()

```
double two_electron_energy (
            int32_t * index,
```

```
double * value,
int32_t n_up,
int64_t n_integrals )
```

Calculates the two-electron energy contribution to the Hartree-Fock energy.

Parameters

index	Array containing four-index combinations for two-electron integrals
value	Array containing values of two-electron integrals
n_up	Number of occupied orbitals
n_integrals	Total number of two-electron integrals

Returns

Two-electron energy contribution

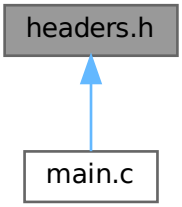
Iterate over the stored integrals

Substract the exchange integral, ∗2 for permutational symmetry

2.2 headers.h File Reference

Contains the function headers.

This graph shows which files directly or indirectly include this file:



Functions

- double one_electron_energy (double ∗data, int32_t n_up, int32_t mo_num)
  Calculates the one-electron energy contribution to the Hartree-Fock energy.
- double two_electron_energy (int32_t ∗index, double ∗value, int32_t n_up, int64_t n_integrals)
  Calculates the two-electron energy contribution to the Hartree-Fock energy.
- double hartree_fock_energy (double nuc_repul, double one_el_energy, double two_el_energy)
  Calculates the total Hartree-Fock energy.
- double get_integral (int i, int j, int k, int l, const int32_t ∗index, const double ∗value, int64_t n_integrals)
  Retrieves integral value.
- double MP2_energy_correction (int32_t ∗index, double ∗value, double ∗mo_energy, int32_t n_up, int64_t n_integrals)
  MP2 energy correction calculation.

2.2.1 Detailed Description

Contains the function headers.

2.2.2 Function Documentation

2.2.2.1 get_integral()

```
double get_integral (
            int i,
            int j,
            int k,
            int l,
            const int32_t * index,
            const double * value,
            int64_t n_integrals )
```

Retrieves integral value.

Parameters

i	First index
j	Second index
k	Third index
l	Fourth index
index	Array containing four-index combinations
value	Array containing integral values
n_integrals	Total number of integrals

Returns

Value of the requested integral or 0.0 if not found

2.2.2.2 hartree_fock_energy()

```
double hartree_fock_energy (
            double nuc_repul,
            double one_el_energy,
            double two_el_energy )
```

Calculates the total Hartree-Fock energy.

Parameters

nuc_repul	Nuclear repulsion energy
one_el_energy	One-electron energy contribution
two_el_energy	Two-electron energy contribution

Returns

Total Hartree-Fock energy

2.2.2.3 MP2_energy_correction()

```
double MP2_energy_correction (
            int32_t * index,
            double * value,
            double * mo_energy,
            int32_t n_up,
            int64_t n_integrals )
```

MP2 energy correction calculation.

Parameters

index	Array containing four-index combinations
value	Array containing integral values
mo_energy	Array of molecular orbital energies
n_up	Number of occupied orbitals
n_integrals	Total number of integrals

Returns

MP2 energy correction

2.2.2.4 one_electron_energy()

```
double one_electron_energy (
            double * data,
            int32_t n_up,
            int32_t mo_num )
```

Calculates the one-electron energy contribution to the Hartree-Fock energy.

Parameters

data	Array containing one-electron integrals
n_up	Number of occupied orbitals
mo_num	Total number of molecular orbitals

Returns

One-electron energy contribution

2.2.2.5 two_electron_energy()

```
double two_electron_energy (
            int32_t * index,
```

```
            double * value,
            int32_t n_up,
            int64_t n_integrals )
```

Calculates the two-electron energy contribution to the Hartree-Fock energy.

Parameters

index	Array containing four-index combinations for two-electron integrals
value	Array containing values of two-electron integrals
n_up	Number of occupied orbitals
n_integrals	Total number of two-electron integrals

Returns

Two-electron energy contribution

Iterate over the stored integrals

Substract the exchange integral, ∗2 for permutational symmetry

2.3 headers.h

Go to the documentation of this file.

```
00001
00006 #ifndef FUNCTIONS_H
00007 #define FUNCTIONS_H
00008
00009 double one_electron_energy(double* data, int32_t n_up, int32_t mo_num);
00010 double two_electron_energy(int32_t* index, double* value, int32_t n_up, int64_t n_integrals);
00011 double hartree_fock_energy(double nuc_repul, double one_el_energy, double two_el_energy);
00012
00013 double get_integral(int i, int j, int k, int l, const int32_t* index, const double* value, int64_t
      n_integrals);
00014 double MP2_energy_correction(int32_t* index, double* value, double* mo_energy, int32_t n_up, int64_t
      n_integrals);
00015
00016 #endif
00017
```

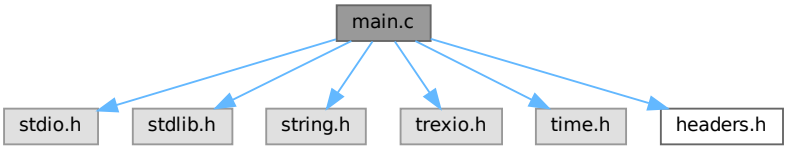
2.4 main.c File Reference

Contains the main program.

```
#include <stdio.h>
#include <stdlib.h>
#include <string.h>
#include <trexio.h>
#include <time.h>
```

```
#include "headers.h"
```

Include dependency graph for main.c:



Functions

- int main (int argc, char ∗argv[ ])

2.4.1 Detailed Description

Contains the main program.

2.4.2 Function Documentation

2.4.2.1 main()

```
int main (
             int argc,
             char * argv[] )
```

2.4.3 Variables

- `char* filename`: Name of the HDF5 file.
- `trexio_exit_code rc`: TREXIO output.
- `trexio_t* trexio_file`: TREXIO file handler.
- `double nuc_repul`: Nuclear repulsion energy.
- `int32_t n_up`: Number of spin-up electrons.
- `int32_t mo_num`: Number of molecular orbitals.
- `double* mo_energy`: Array of molecular orbital energies.
- `int64_t elements`: Number of elements in the data array.
- `double* data`: Array of one-electron integrals.
- `int64_t n_integrals`: Number of non-zero two-electron integrals.
- `int32_t* index`: Array of indices of the two-electron integrals.
- `double* value`: Array of values of the two-electron integrals.
- `int64_t buffer_size`: Buffer size for reading, initially equal to number of two-electron integrals.
- `double one_el_energy`: One-electron energy contribution.
- `double two_el_energy`: Two-electron energy contribution.
- `double HF_energy`: Hartree-Fock energy.
- `double MP2_energy`: MP2 energy correction.

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