Quantum Package tutorial
User mode

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Quantum package documentation: Link
QP git: Link
Associated talk: Link

(This document is a first version. Don't hesitate to report any errors to improve it !)

Exercise 1

This exercise proposes to discover QP through the computation of Hartree-Fock and FCI[1] energies for the singlet and triplet states of CH_2. The geometries are from Ref. [1].

1.1 Singlet CH_2

1.1.1 Creation of xyz file and script file for master

1. Create a file, `CH2_singlet.xyz`, that contains the geometry (xyz file) with coordinates in Angström.
   ```
   3
   #Singlet state
   C 0. 0. 0.1734
   H 0. 0.8623 -0.5202
   H 0. -0.8623 -0.5202
   ```

In this tutorial, we show how to properly run calculations in `master`. However, Quantum Package offers a `shell` mode. More informations are available on the Quick-start guide on the QP website.

Download the `master_template.txt` file on Slack (or my website) and copy it to `ch2_singlet.txt`.

In Appendix 1, the output of `qp create_ezfio -h` shows you how to define the EZFIO directory that contains all needed informations for the calculations and outputs. We start by defining the needed parameters. According to the manual, the mandatory parameters are the basis-set[2], `-b`, and `FILE`, the xyz file)

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[1]For a system of this size, $E_{\text{CIPSI}} \simeq E_{\text{FCI}}$.

[2]The list of available basis is available in the data/basis folder of the program. If interested by basis-set definitions, have a look at the references available on the basis-set exchange website.

2. Define variables for the basis-set and the xyz file in `ch2_singlet.txt`.
   ```
   basis=sto-3g
   xyz_file=CH2_singlet.xyz
   ```

3. Add the following command line to create the EZFIO directory.
   ```
   qp create_ezfio -b ${basis} ${xyz_file}
   ```

1.1.2 Generate molecular orbitals through SCF calculation

The first step of any electronic structure calculation is the definition of the (one-electron) molecular orbitals generated from the basis-set[3]. This is done by the SCF program (info). A great introduction to the SCF procedure is provided on Ref. [2].

4. Add the following command in the script file:
   ```
   qp run scf | tee scf.out
   ```

5. Save the script, close it, and enter
   ```
   qsub ch2_singlet.txt
   ```

Appendix 2 gives you an extract of the output. At this stage, do not hesitate to go through the `CH2_singlet.ezfio` folder to see the other available informations.

> **To visualize the wave-function**
> It is possible to visualize the generated orbitals using `molden`. For that, you need to add `qp run molden` after the calculations command (here after the scf calculation). However, you will need to copy the .mol file on your own computer as no visualization are possible on master.

From the set of generated molecular orbitals, QP will generate determinants from which you can get:

- the Hartree-Fock determinant : determinant with the lowest energy.

- configuration interaction states : CIS (HF + singly excited determinants), CISD (HF + Singly and doubly excited determinants).

- selected configuration interaction states : CIPSI.

- perturbation theory calculations.

- ... [4]

1.1.3 Configuration interaction using single excited determinants (CIS)

We start by launching a CIS calculation and print the determinants.

6. Add the following command in the script file:
   ```
   qp run cis | tee cis.out
   qp run print_ci_vectors | tee ci_vectors.out
   ```

7. Save the script, close it, and enter
   ```
   qsub ch2_singlet.txt
   ```

---

[3]See slides of the presentation
[4]A non-exhaustiv list of available programs: A non-exhaustive list of available programs

In the `cis.out` file (Appendix 3) you found at the very end, the energy of the state asked (1 = ground state) and the S^2 value. The later being 0, you have a singlet state. Next exercise shows you how to treat the triplet state.

If you go back in the file, you find for example the number of determinants generated for the CIS: 4. I invite you to explore this output file and come discuss the informations you found on it ! (And don't forget to go through the ezfio folder for more data.)

In the `ci_vectors.out`, you can found a representation of the CIS determinants. You should recognize the singly excited determinants showed in the presentation slide. The coefficients under each determinants are the c_a^r coefficients.

8. Replace the `qp run cis` command by any other CI method. For CIPSI, you should write `qp run fci`.

1.2 Triplet CH$_2$

1. Create a file, `CH2_triplet.xyz`, that contains the geometry (xyz file) with coordinates in Angström.
   ```
   3
   #Triplet state
   C 0. 0. 0.1027
   H 0. 1.0042 -0.3081
   H 0. -1.0042 -0.3081
   ```

2. Copy the `master_template.txt` to `ch2_triplet.txt`

3. Define variables for the basis-set, the xyz file and the multiplicity.
   ```
   basis=sto-3g
   xyz_file=CH2_triplet.xyz multiplicity=3
   ```

4. Replace the `qp create_ezfio` line by
   ```
   qp create_ezfio -b ${basis} -m ${multiplicity} ${xyz_file}
   ```

5. Continue following Sec. 1.1 steps.

References

[1] Diptarka Hait and Martin Head-Gordon. "How Accurate Is Density Functional Theory at Predicting Dipole Moments? An Assessment Using a New Database of 200 Benchmark Values." In: *Journal of Chemical Theory and Computation* 14.4 (2018), pp. 1969–1981.

[2] Attila Szabo and Neil S. Ostlund. *Modern Quantum Chemistry: Introduction to Advanced Electronic Structure Theory*. Dover Publications, Inc., 1996.

Appendix 1 : qp create_ezfio

qp_create_ezfio – Quantum Package command

Usage :

```
qp_create_ezfio [-a] -b <string> [-c <int>] [-d <float>] [-h] [-m <int>]
    [-o EZFIO_DIR] [-p <string>] [-x] [--] FILE
```

Arguments :

```
FILE                       Input file in xyz format or z-matrix.
```

Options :

```
-a  --au                   Input geometry is in atomic units.
-b  --basis=<string>       Name of basis set file. Searched in
                           ${QP_ROOT}/data/basis if not found.
-c  --charge=<int>         Total charge of the molecule. Default is
                           0. For negative values, use m instead of
                           -, for ex m1
-d  --dummy=<float>        Add dummy atoms. x * (covalent radii of the
                           atoms).
-h  --help                 Prints the help message.
-m  --multiplicity=<int>   Spin multiplicity (2S+1) of the molecule.
                           Default is 1.
-o  --output=EZFIO_DIR     Name of the created EZFIO directory.
-p  --pseudo=<string>      Name of the pseudopotential.
-x  --cartesian            Compute AOs in the Cartesian basis set (6d,
                           10f, ...).
```

Description :

Creates an EZFIO directory from a standard xyz file or from a z-matrix
file in Gaussian format. The basis set is defined as a single string
if all the atoms are taken from the same basis set, otherwise specific
elements can be defined as follows :

```
-b "cc-pcvdz | H:cc-pvdz | C:6-31g"
-b "cc-pvtz | 1,H:sto-3g | 3,H:6-31g"
```

If a file with the same name as the basis set exists, this file will
be read. Otherwise, the basis set is obtained from the database.

Appendix 2 : Extract of the scf output

(... Some informations ...)
Nuclear Coordinates (Angstroms)
===============================

Atom	Charge	X	Y	Z
C	6.000000	0.000000	0.000000	0.102700
H	1.000000	0.000000	1.004200	−0.308100
H	1.000000	0.000000	−1.004200	−0.308100

Minimal interatomic distance found: 1.0850 Angstrom
(... Some informations ...)
 Sorting the map
 AO integrals provided:
  Size of AO map :   3.0746459960937500E−003 MB
  Number of AO integrals :   228
  cpu time :   9.4378000000000073E−002 s
  wall time :   3.3013001084327698E−002 s (x   2.8588131009029731   )
(... Some informations ...)
* Nuclear repulsion energy   6.116259241920639
(... Some informations ...)
 Energy of the guess =   −38.015316679210912

N	Energy	Energy diff	DIIS error	Level shift
1	−38.2425624010	−0.2272457218	0.0976236469	0.0000000000
2	−38.2517729674	−0.0092105664	0.0282267669	0.0000000000
3	−38.2525900189	−0.0008170515	0.0008631741	0.0000000000
4	−38.2525904529	−0.0000004340	0.0000942094	0.0000000000
5	−38.2525904612	−0.0000000082	0.0000241018	0.0000000000
6	−38.2525904618	−0.0000000006	0.0000069361	0.0000000000
7	−38.2525904618	−0.0000000001	0.0000020686	0.0000000000

(... Some informations ...)
MOs are now ** Canonical **
Eigenvalues

1	−10.9140592647
2	−0.7667912911
3	−0.5284443025
4	−0.2169219909
5	0.1972411625
6	0.6490463494
7	0.8731104237

(... Some informations ...)
* SCF energy   −38.25259046182742

Appendix 3 : Extract of the cis output

```
(...Some informations...)
* Number of active    MOs                                               7
  Active MOs:
              1           2          3         4         5         6         7
* Number of virtual   MOs                                               0
* Number of inactive MOs                                                0
(...Some informations...)
  Energies   of  the  states:
              1   −38.332936001869150
* Saved determinants                                                    4
  Diagonalization of H using Lapack


* Energy of state    1                              −38.33293600186915
* S^2 of state     1                         0.1028753506498722E−25
```

Appendix 4 : Extract of the print_ci_vector output

```
Determinant                 1
000000000000000F|0000000000000017
|++++----------------------------------------------------------|
|+++-+----------------------------------------------------------|
−0.700442179783E+00



Determinant                 2
0000000000000017|000000000000000F
|+++-+----------------------------------------------------------|
|++++----------------------------------------------------------|
−0.700442179783E+00



Determinant                 3
000000000000000F|0000000000000027
|++++----------------------------------------------------------|
|+++--+----------------------------------------------------------|
−0.968542863326E−01



Determinant                 4
0000000000000027|000000000000000F
|+++--+----------------------------------------------------------|
|++++----------------------------------------------------------|
−0.968542863325E−01
```