Introduction to Q-Chem and QCMagic

A brief tutorial

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Before we begin, make sure that you have a copy of Q-Chem 5.2 compiled with parallelisation on your workstation and that you are sufficiently familiar with Unix shell commands to navigate around and perform various day-to-day tasks. This tutorial assumes that you already know how to carry out such tasks and focuses entirely on Q-Chem and QCMagic.

1 Single-Point Calculations

1.1 Restricted Hartree–Fock (RHF)

We begin with a simple Hartree–Fock (HF) calculation for the simplest closed-shell system, a He atom, to familiarise ourselves with the syntax of Q-CHEM. Every Q-CHEM run requires an input file in which the molecular configuration and all relevant calculation parameters are specified. Listing 1 gives an example of such an input file.

Listing 1: `codesnippets/singlepoint/He.RHF.STO-3G.inp`

```
1    $molecule
2        0 1
3        He   0    0    0
4    $end
5    $rem
6        BASIS STO-3G
7        EXCHANGE hf
8        CORRELATION none
9        UNRESTRICTED false
10       SCF_GUESS CORE
11       SCF_ALGORITHM DIIS
12       SCF_CONVERGENCE 13
13       SCF_MAX_CYCLES 1000
14       MOM_START 1
15       SCF_PRINT 1
16       PRINT_ORBITALS true
17   $end
```

We observe the following in Listing 1:

1. There are two sections in this file: `$molecule` specifies the molecular configuration of the system and `$rem` specifies the parameters to be used in the calculation.

2. The system of interest consists of a single He nucleus located at the origin (line 3).

3. The overall charge of the system is zero (first number on line 2), so there are two electrons in total.

4. The "spin multiplicity" of the system is supposed to be 1 (second number on line 2). However, one cannot in general constrain the value of S in a conventional HF calculation. Therefore, the "multiplicity" specified here is actually equal to $2M_S + 1$ instead of $2S + 1$. This system thus has $M_S = 0$, but whether or

not S is a "good" quantum number for the system is dependent upon the HF method and the solutions obtained.

5. A self-consistent-field (SCF) restricted HF (RHF) calculation will be run on this system in the STO-3G basis set using the DIIS converging algorithm starting from the guess molecular orbital (MO) coefficients obtained by diagonalising the one-electron Hamiltonian matrix (lines 6–11).

6. The convergence criterion is when the maximum DIIS error becomes smaller than 1×10^{-13} (line 12). This is a very tight criterion.

7. The maximum number of SCF cycles is 1000 (line 13). This is more than enough here because convergence can be reached very quickly in this particular example.

8. During each SCF cycle, the code maximises overlap with the orbitals from the previous cycle. This behaviour starts from cycle 1 (line 14) where the code maximises overlap with the guess orbitals.

9. After each cycle, the code prints out only the minimal and useful output together with the component breakdown of SCF electronic energy (line 15).

10. After convergence, the code prints out the occupied orbitals plus five virtual orbitals (line 16).

To carry out the above Q-CHEM calculation, copy Listing 1 from the `git` repository to a location of your choice and then execute the following command in a shell:

```
$  qchem -nt 6 He.RHF.STO-3G.inp He.RHF.STO-3G.out
```

which instructs Q-CHEM to run a calculation with the input parameters specified in `He.RHF.STO-3G.inp` using six OpenMP threads and write the outputs to `He.RHF.STO-3G.out`.

Task 1.1

Examine the output file and determine the following:

   (a) the DIIS error at convergence;
   (b) the SCF energy of the converged solution;
   (c) the contributing components of the SCF energy;
   (d) the MO energies; and
   (e) the MO coefficients in terms of the atomic orbital (AO) basis functions.

What is the value of $\langle \hat{S}^2 \rangle$ of the converged solution and why? Assign a term symbol to this solution.

1.2 Unrestricted Hartree–Fock (UHF)

Duplicate `He.RHF.STO-3G.inp` and give it a different name such as `He.UHF.STO-3G.inp`. Then, change the value of UNRESTRICTED on line 9 to `true` as shown in Listing 2 and run Q-Chem on this new file as above to produce a new output file, say, `He.UHF.STO-3G.out`.

Listing 2: `codesnippets/singlepoint/He.UHF.STO-3G.inp`

```
9    UNRESTRICTED true
```

Task 1.2

Examine `He.UHF.STO-3G.out` and compare the following with those in the RHF case:

(a) the SCF energy of the converged solution;
(b) the contributing components of the SCF energy;
(c) the value of $\langle \hat{S}^2 \rangle$;
(d) the structure of the MO coefficients;
(e) the MO energies; and
(f) the MO coefficients in terms of the atomic orbital (AO) basis functions.

Is this converged solution identical to the RHF one? If so, explain the origin of the identicality.

1.3 Effects of Basis Sets

Choosing an appropriate basis set is an important aspect of electronic structure calculation: a suitable basis set not only gives sensible and sufficiently accurate results but also saves computation time and storage space. To investigate basis set effects on the solutions obtained so far, duplicate `He.RHF.STO-3G.inp` and `He.UHF.STO-3G.inp` to `He.RHF.6-31GSTAR.inp` and `He.UHF.6-31GSTAR.inp`, respectively, then change the value of BASIS on line 6 to `6-31G*` as shown in Listings 3 and 4. Run Q-Chem on these files as above to produce `He.RHF.6-31GSTAR.out` and `He.UHF.6-31GSTAR.out`.

Listing 3: `codesnippets/singlepoint/He.RHF.6-31GSTAR.inp`

```
6    BASIS 6-31G*
```

Listing 4: `codesnippets/singlepoint/He.UHF.6-31GSTAR.inp`

```
6    BASIS 6-31G*
```

> **Task 1.3**
>
> Examine `He.RHF.6-31GSTAR.out` and `He.UHF.6-31GSTAR.out` and answer the following:
>
> (a) Are the RHF and UHF solutions located in 6-31G* identical to each other?
>
> (b) Can these solutions be assigned to the same term as those in STO-3G? If so, are they a better description of this term and why?

But how exactly does 6-31G* differ from STO-3G for a He atom? One possible way to determine this is to ask Q-CHEM to print out the basis set definition. This is achieved by setting `PRINT_GENERAL_BASIS` to `true` in the `$rem` section. Another way is to look it up on `https://www.basissetexchange.org/`.

Shown in Listing 5 is the 6-31G* basis set definition for a He atom as printed by Q-CHEM. This tells us that, in 6-31G*, each electron in a He atom is described by two *s* shells. The radial part of the first shell is constructed by contracting three primitive Gaussian functions whereas the radial part of the second shell is constructed by contracting only a single primitive Gaussian function. The Gaussian primitive exponents and the contraction coefficients are given by the first and second columns respectively within each shell. Since both of these shells are of angular momentum *s*, their angular parts are simply 1.

Listing 5: `codesnippets/singlepoint/He.RHF.6-31GSTAR.withbasis.out`

```
122  Basis set in general basis input format:
123  ----------------------------------------------------------------------
124  $basis
125  He    0
126  S    3     1.000000
127      3.84216340E+01     2.37660000E-02
128      5.77803000E+00     1.54679000E-01
129      1.24177400E+00     4.69630000E-01
130  S    1     1.000000
131      2.97964000E-01     1.00000000E+00
132  ****
133  $end
134  ----------------------------------------------------------------------
```

5

Task 1.4

(a) In 6-31G*, how many basis functions are used to describe each orbital of He?

(b) How does STO-3G differ from 6-31G* for He?

6-31G** is another small basis set for He in which each electron is described by two s shells and one p shell. Run an RHF calculation in this basis and answer the following:

(c) How many basis functions are used to describe each orbital of He in this basis set? Why is this number different from the number of shells in this basis set?

(d) Examine the orbital coefficient matrix carefully. Why does it have a very particular block-diagonal form?

(e) Does 6-31G** offer any improvement over 6-31G* for the ground RHF solution of He?