

---

# Introduction to Q-CHEM and QCMAGIC

*A brief tutorial*

©Thom Group Cambridge, 2019

Maintainer: Bang C. Huynh ([cbh31\[at\]cam.ac.uk](mailto:cbh31@cam.ac.uk))

---

## Contents

<b>1</b>	<b>Single-Point Calculations</b>	<b>2</b>		<b>1.2</b>	<b>Unrestricted Hartree–Fock (UHF)</b>	<b>4</b>
	1.1	Restricted Hartree–Fock (UHF)	2			

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 (UHF)

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 the existence and meaningfulness of its  $S$  value 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  $1 \times 10^{-13}$  (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

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`

```
UNRESTRICTED true
```

### Task 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 that in the RHF case? If it is, explain the origin of the identity.

## 1.3 Effects of the Basis Set