

CHAPTER 4

DETAIL OF CALCULATIONS

In this chapter, detail of the investigations regarding first part of the semi-automatic Fortran program have been given. These focus on how to generate complex configurations.

The selected configurations are used by the Gaussian 98 program [24], which is one of well known programs for quantum chemical calculations, to calculate total energy of the complex as well as those of individual molecules or ions. The outputs of the Gaussian program are extracted automatically in order to get interaction energy of the pair.

The program name is “**GENERATE**” version 1.0. The source code was written in FORTRAN-77 running in the UNIX system. See the manual of the program in appendix. The program was separated into three parts:

1. Reading initial input file,
2. Selection of representative geometries of the pairs,
3. The *ab initio* calculations.

The flowchart of the **GENERATE** program is shown in Figure 4.1.

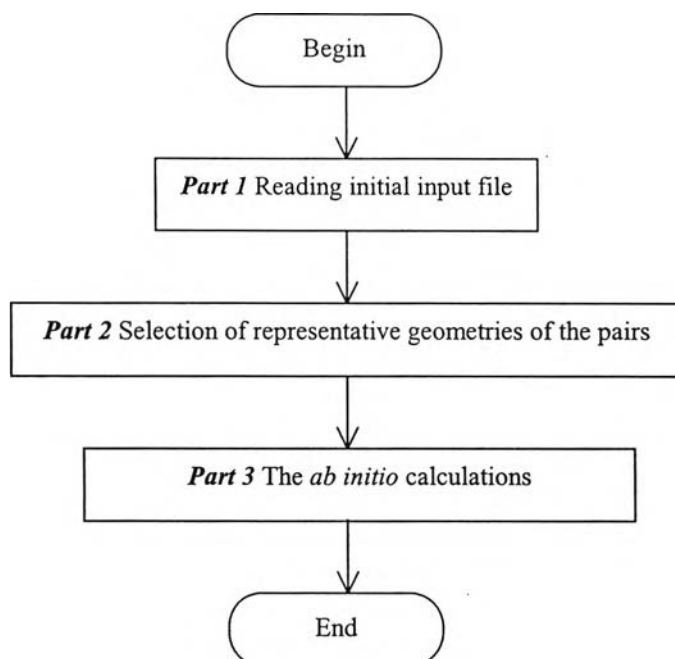


Figure 4.1 The sequence of *GENERATE* program version 1.0.

4.1 Reading initial input file

Subroutine Read_Input

This routine reads all information from the input file and keep them for processing. The initial input file structure is shown in Figure 4.2. And the example initial input file for $\text{NH}_3\text{-Li}^+$ system is shown in Figure 4.3.

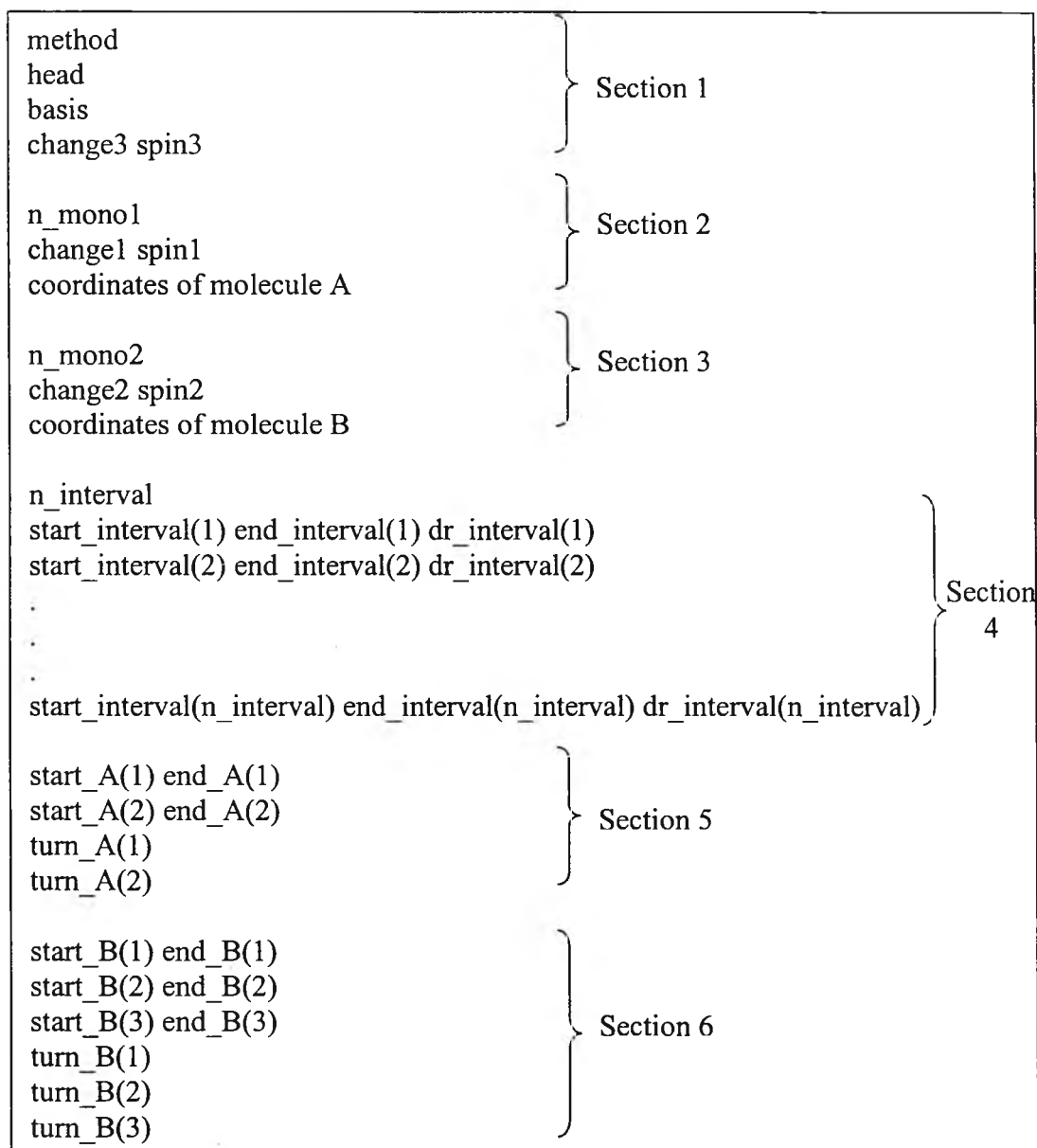


Figure 4.2 The initial input file structure.

```
3
#RHF
d95**
1 1

4
0 1
N      0.000000      0.000000      0.000000
H      0.937760      0.000000     -0.381470
H     -0.468880     -0.812120     -0.381470
H     -0.468880      0.812120     -0.381470

1
1 1
Li     0.000000      0.000000      0.000000

4
1.5  1.7  0.1
1.7  3.0  0.05
3.0  6.0  0.5
6.0 10.0  2.0

0  180
0  60
30
30

0  0
0  0
0  0
0
0
0
```

Figure 4.3 Initial input file for $\text{NH}_3\text{-Li}^+$ system.

The initial input file is separated into six sections. First section contains parameters necessary for Gaussian 98 program, number of cases for calculated the interaction energies, namely the SCF method and names of the basis set, and the line giving the charge and spin multiplicity of complex. Second section is details of monomer A, that are number of atoms of monomer A and followed by the molecular. The molecular specification section begins with a line giving the charge and spin multiplicity of the molecule: charge = 0 (neutral molecule) and spin multiplicity = 1 (single) in this case. The next lines describe location of each atom in the molecule using Cartesian coordinates. The third section is the same as section 2 but it is for monomer B, Li^+ for this example. The first 3 sections are required for the Gaussian 98 program in order to calculation total energies of the super-system and sub-systems, and hence interaction energy of the systems. The last three sections contain parameters required for generating complex configurations. More details are given in 4.2.

The flowchart of part 1 is shown in Figure 4.4.

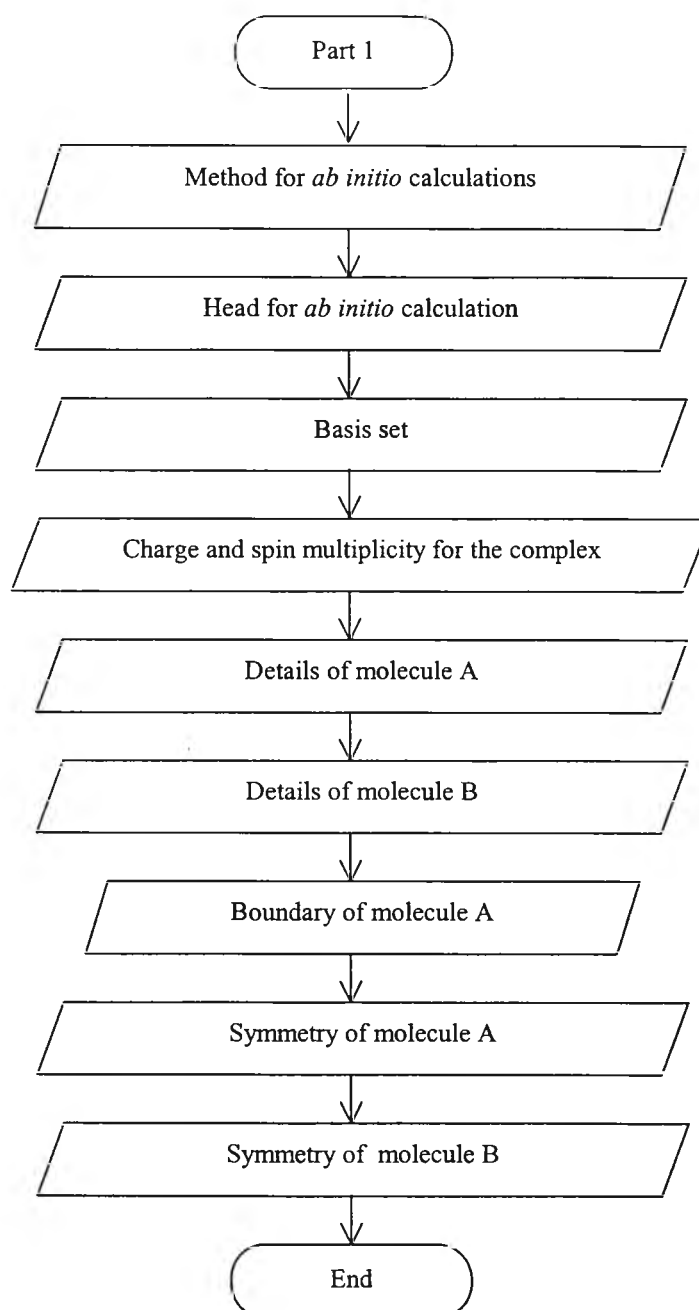


Figure 4.4 The flowchart of part 1; Reading initial input file.

4.2 Selection of representative geometries of the pairs

Subroutine Generate_Configuration

The input that this subroutine requires is the last three sections of the initial input file structure shown in Figure 4.2.

Details of the related parameters are:

$n_interval$: number of interval of r

$start_interval(1)$: minimum value of interval 1

$end_interval(1)$: maximum value of interval 1

$dr_interval(1)$: Δr of interval 1

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$start_interval(n_interval)$: minimum value of interval $n_interval$

$end_interval(n_interval)$: maximum value of interval $n_interval$

$dr_interval(n_interval)$: Δr of interval $n_interval$

$start_A(1)$: lower bound of θ

$end_A(1)$: upper bound of θ

$start_A(2)$: lower bound of ϕ

$end_A(2)$: upper bound of ϕ

$turn_A(1)$: $\Delta\theta$

$turn_A(2)$: $\Delta\phi$

start_B(1) : lower bound of α

end_B(1) : upper bound of α

start_B(2) : lower bound of β

end_B(2) : upper bound of β

start_B(1) : lower bound of γ

end_B(1) : upper bound of γ

turn_B(1) : $\Delta\alpha$

turn_B(2) : $\Delta\beta$

turn_B(2) : $\Delta\gamma$

The flowchart of this subroutine is shown in figure 4.5.

This routine gets the input from subroutine *Read_Input*. Then, numerous position of molecule **B** around A can be automatically generated.

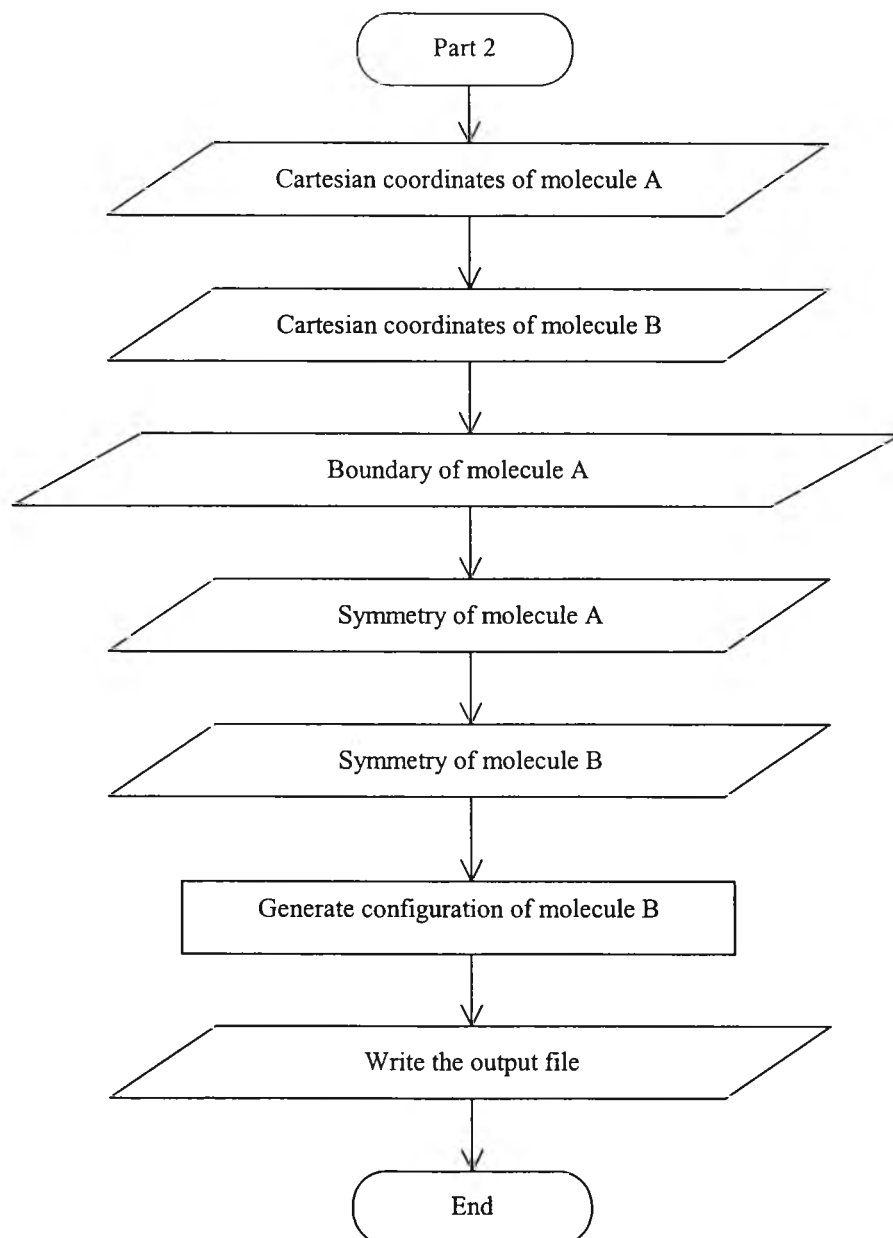


Figure 4.5 The flowchart of subroutine `Generate_Configuration`.

4.3 The *ab initio* calculations

In this step, quantum chemical calculations have been performed for the aforementioned configurations using Subroutine *Calculate_energy*. All calculations are run using Gaussian 98 program with the parameters selected from Figure 4.2.

Subroutine Calculate_energy

The routine is designed to calculate interaction energy for the following 3 choices: either with or without BSSE corrections or both.

Part I Calculated interaction energies without BSSE corrections.

To calculate interaction energy of the complex without BSSE corrections, the total energies (in atomic units) of the sub-systems were calculated once and were kept constant throughout the computation. Then the total energies of super-systems were calculated with respect to each configuration of B, which are generated from subroutine *Generate_Configuration*. Then ΔE_{SCF} has been computed using equation (3.1).

Part II Calculated interaction energies with BSSE corrections.

With the BSSE corrections, the total energies of the two subsystems and of the complex have to be calculated for all configurations. That means that time requirement for this procedure is almost twice of those calculations without BSSE corrections. The ΔE_{SCF} has been computed using equation (3.10). The example input file for Gaussian 98 program shown in Figure 4.7.

The flowchart of this subroutine is shown in Figure 4.6.

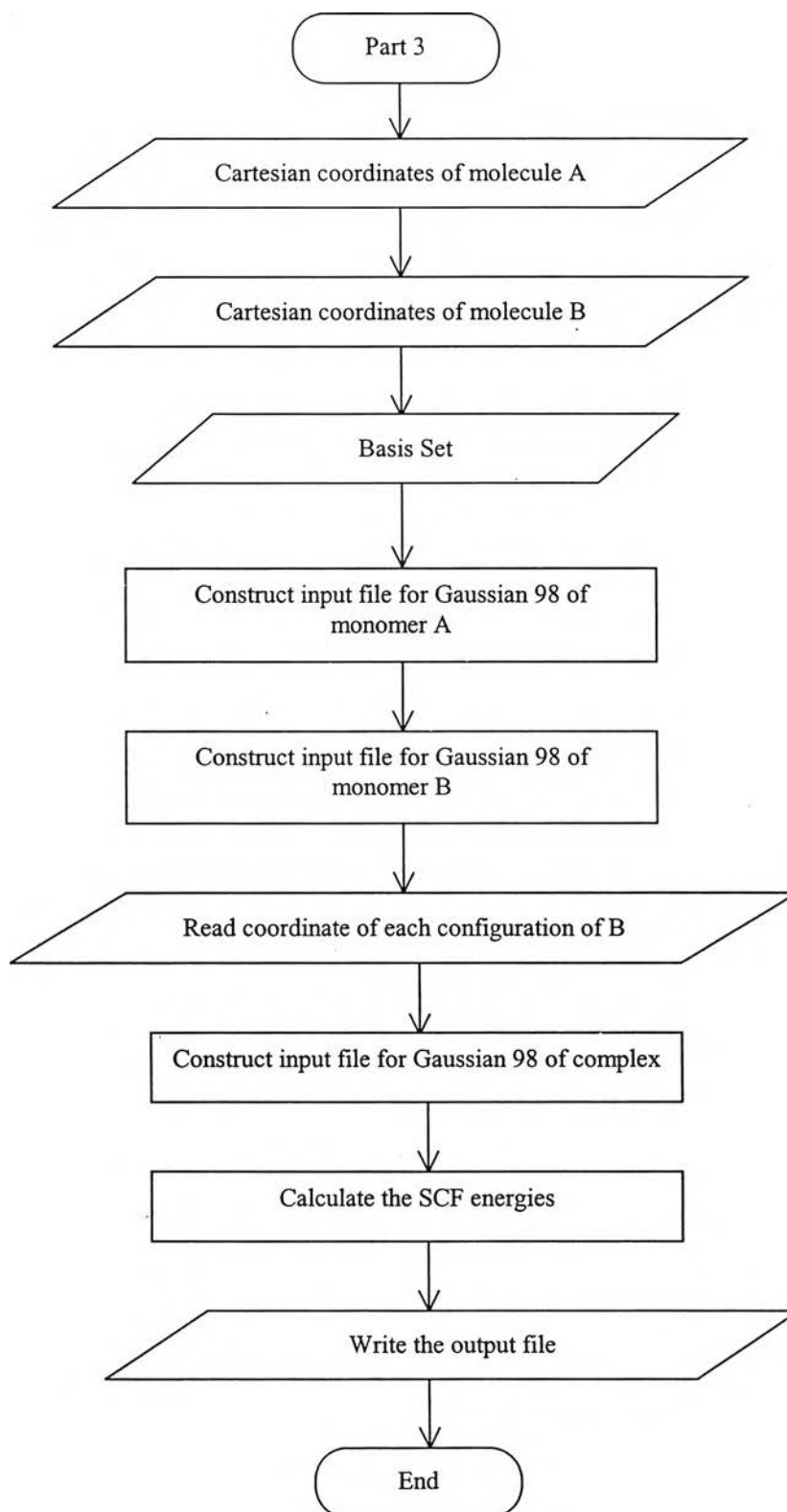


Figure 4.6 The flowchart of subroutine Calculate_energy.

```
#RHF/d95**      Message

g98

0 1
N      0.000000      0.000000      0.000000
H      0.937760      0.000000     -0.381470
H     -0.468880     -0.812120     -0.381470
H     -0.468880      0.812120     -0.381470
N      0.000000      0.000000     10.000000
H     -0.083072      0.985721     10.215327
H      0.119957     -0.069259      8.997144
H     -0.895193     -0.420918     10.215324

5 0 0.0
6 0 0.0
7 0 0.0
8 0 0.0
```

Figure 4.7 The input file for Gaussian 98 program for calculate with BSSE corrections.