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Generalised Atomic and Molecular Electronic Structure System

G A M E S S - U K

USER'S GUIDE and REFERENCE MANUAL

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PART 9. TROUBLE SHOOTING

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Contents

1 Introduction	1
2 SCF Calculations	1
3 The role of the VECTORS and ENTER Directives	2
4 Transition State and Geometry Optimisation	5
4.1 Synchronous Transit Algorithm	9
5 Direct-CI Calculations	9
6 Table-CI Calculations	9

CONTENTS

ii

7 Known Bugs/Issues

10

1 Introduction

In this chapter we try to anticipate areas where the user may run into problems, either from lack of appreciation of the workings of the program, or from the author's failure to present a clear picture of requirements. The items below are presented in no real order, but reflect some of the known aspects of running the program that have given problems historically. Again users are welcome to use the EMAIL addresses given in Chapter 1 in trying to resolve matters not discussed herein. Note that the original use of error numbers has been replaced with textual messages designed to provide some insight into the problem causing the abort. If the user meets an error condition characterised only by a number in the log, please inform the author.

2 SCF Calculations

1. *The SCF aborts at the outset of processing*; this will almost certainly have arisen from supplying a two-electron file that is not in the format expected. Care must be taken in understanding the workings of the SUPER directive and the use of BYPASS.
2. *The SCF fails to converge, with violent oscillations in the total energy*; increase the LEVEL parameters, which should remove the problem.
3. *Large negative values for the energy*: the program assumes in constructing the Fock matrix that the density matrix transforms as the totally symmetric representation i.e. the wave function belongs to a non-degenerate representation of the molecular point group. If this is not the case, the energy may collapse to a meaningless value. If this occurs, the user should modify the TAGs in the z-matrix to lower the effective molecular point group.
4. *The SCF output reveals that the DIIS procedure has been initiated, but the energy still fluctuates, with DIIS appearing to push the energy up*; this may be indicative of trying to converge on an excited state, particularly in closed-shell calculations. If the TESTER is small, and the problem persists, it may be advantageous to suppress DIIS through the data line DIIS OFF.
5. *The two-electron integral file is lost or corrupted, say in the middle of an optimisation*, use the REGEN parameter on the RESTART directive.
6. *The error message ATTEMPTING TO RETRIEVE UNDEFINED DUMPFIL SECTIION appears during vector generation in a restart job*; this may have arisen from specifying an incorrect section on the VECTORS directive, but it is also indicative of the user having inadvertently omitted the RESTART directive, or incorrectly allocated the Dumpfile to the Job.
7. *Confusion over Multiple Section Specification*: When performing open shell or GVB calculations, the user should be aware that the final list of output vectors refers to the canonicalised set i.e. to the set of MOs residing in the *second* section specified on the ENTER directive. Confusion may arise when restoring MOs from the first section, and assigning, for example, orbital symmetries from the SCF output.

8. *Symmetry contaminated molecular orbitals*: the SCF modules are fairly demanding in their attempts to maintain the symmetry classification of the MOs. If the orbitals appear contaminated, the cause may lie in the choice of an inappropriate starting set used to initialise the SCF.

3 The role of the VECTORS and ENTER Directives

GAMESS is reporting an error when trying to restore vectors in a restart job after a startup step has completed successfully, referencing a section number unknown to the User

Consider the following data, that aims to first conduct an initial geometry optimisation, followed in a subsequent step by a direct-CI calculation at the optimised geometry.

```
TITLE
WATER
ZMAT ANGS
O
H 1 R
H 1 R 2 A
VARIABLES
R          0.9429786  HESSIAN    0.749526
A          105.9806454 HESSIAN    0.178413
END
BASIS 6-31G
RUNTYPE OPTIMIZE
ENTER 1
```

with the following data specified in the restart job;

```
RESTART
TITLE
WATER
ZMAT ANGS
O
H 1 R
H 1 R 2 A
VARIABLES
R          0.9429786  HESSIAN    0.749526
A          105.9806454 HESSIAN    0.178413
END
BASIS 6-31G
RUNTYPE CI
DIRECT
ENTER 1
```

This restart will fail, with the diagnostics shown below taken from the failing output:

```
MOLECULAR ORBITALS RESTORED FROM DUMPFIL
```

```

-A-  VECTORS RESTORED FROM SECTION 410 OF DUMPFILE ON ED3

*****
PROBLEM WITH SECTION
*****
MPOS, MTYPE, BLOCK  410   3*****
CURRENT INPUT LINE IS:
ENTER 1
#####
                                ERROR DETECTED
                                *****

                                ATTEMPTING TO RETRIEVE UNDEFINED DUMPFILE SECTION

#####

GAMESS-UK ERROR: ATTEMPTING TO RETRIEVE UNDEFINED DUMPFILE SECTION

```

Diagnosis

In the absence of section specification on the VECTORS and ENTER directive, GAMESS will use a default section (410) for keeping the current set of vectors. If the user specifies a section on the ENTER directive of the startup job (section 1) above, then that section MUST be specified in subsequent jobs, for GAMESS will not redefine the initial "ENTER" section in the first step as being the section for use of VECTORS in the second step. If no VECTORS directive is specified, its default choice is a function of the perceived status of the processing:

- in startup job, with no vectors available, it will assume "VECTORS ATOMS" and proceed from an atomic startup.
- in a restart job, it will assume that vectors are available, and that such vectors are to be restored from a section on the Dumpfile. If no such section is specified, it will try to input those from a default section, 410. This will lead to the diagnostic above.

Solution 1

Do not specify section numbers and let the programme defaults apply (this is somewhat limiting, since direct, data-driven access to the default section is not permitted by the user i.e. section 410 cannot be explicitly specified on a directive). However, in the present example the following data will suffice:

Data for Step 1

```

TITLE
WATER
ZMAT ANGS
0
H 1 R
H 1 R 2 A

```

```

VARIABLES
R          0.9429786  HESSIAN  0.749526
A          105.9806454 HESSIAN  0.178413
END
BASIS 6-31G
RUNTYPE OPTIMIZE
ENTER

```

Data for Step 2

```

RESTART
TITLE
WATER
ZMAT ANGS
0
H 1 R
H 1 R 2 A
VARIABLES
R          0.9429786  HESSIAN  0.749526
A          105.9806454 HESSIAN  0.178413
END
BASIS 6-31G
RUNTYPE CI
DIRECT
ENTER

```

Solution 2

Use section number for explicit control of vector placing. This will require use of the VECTORS directive in the second step to nominate section 1.

Data for Step 1

This is just the data specified in the startup job above:

```

TITLE
WATER
ZMAT ANGS
0
H 1 R
H 1 R 2 A
VARIABLES
R          0.9429786  HESSIAN  0.749526
A          105.9806454 HESSIAN  0.178413
END
BASIS 6-31G
RUNTYPE OPTIMIZE
ENTER 1

```

Data for Step 2

This now specifies the explicit section for the VECTORS the absence of which caused the problem in the restart job above:

```

RESTART
TITLE
WATER
ZMAT ANGS
O
H 1 R
H 1 R 2 A
VARIABLES
R          0.9429786  HESSIAN    0.749526
A          105.9806454 HESSIAN    0.178413
END
BASIS 6-31G
RUNTYPE CI
DIRECT
VECTORS 1
ENTER 1

```

4 Transition State and Geometry Optimisation

1. *ZMATRIX and Point Group Problems*: One of the constraints in the z-matrix formalism concerns potential problems in dealing with directly bonded angles of 180° . The use of dummy X-centres in circumventing these problems has been discussed in Part 3, §8.3. Consider below the data file for optimisation of the CaH_2 species, where we are starting the optimisation with a bond angle of 150° .

```

TITLE\CAH2 .. 3-21G
ZMAT ANGS\CA\H 1 CAH\H 1 CAH 2 HCAH
VARIABLES\CAH 2.148 HESS 0.7\HCAH 150.0 HESS 0.1\END
RUNTYPE OPTIMIZE
VECTORS EXTGUESS\ENTER 1

```

This job will fail, with the diagnostics shown below taken from the failing output:

```

=====
                                Z-MATRIX (ANGSTROMS AND DEGREES)
CD CENT ATOM  N1      LENGTH      N2      ALPHA      N3      BETA
-----
 1   1   CA
 2   2   H    1  2.148195 ( 1)
 3   3   H    1  2.148195 ( 2)  2  181.008 ( 3)
=====

=====
VARIABLE      VALUE      HESSIAN
=====
CAH           2.1481952 ANGS    0.699998
HCAH          181.0076613 DEGS    0.034888

ERROR ON Z-MATRIX CARD NUMBER      3

ANGLE ALPHA IS OUTSIDE THE VALID RANGE OF 0 TO 180

```

```

#####
                                ERROR DETECTED
                                *****

ERROR DETECTED IN CONVERTING Z-MATRIX TO CARTESIAN COORDINATES

#####

```

In most cases this can be avoided by using the half-angle and dummy centre specification, as shown below:

```

TIME 60
TITLE\CAH2 .. 3-21G
ZMAT ANGS\CA\X 1 1.0\ H 1 CAH 2 XCAH\H 1 CAH 2 XCAH 3 180.0
VARIABLES\CAH 2.148 HESSIAN 0.7\XCAH 75.0 HESSIAN 0.1\END
RUNTYPE OPTIMIZE
VECTORS EXTGUESS\ENTER 1

```

An additional constraint in the default optimisation algorithm is the inability to handle a change in point group during the optimisation pathway. This example has been chosen to illustrate this point: thus while the above data file avoids the angle problem, it will again fail because of the point group change, as shown below:

```

=====
                                Z-MATRIX (ANGSTROMS AND DEGREES)
CD CENT ATOM  N1      LENGTH      N2      ALPHA      N3      BETA
-----
  1   1   CA
  2     X   1   1.000000 ( 1)
  3   2   H   1   2.148105 ( 2)  2   89.998 ( 4)
  4   3   H   1   2.148105 ( 3)  2   89.998 ( 5)  3  180.000 ( 6)
=====

=====
VARIABLE          VALUE          HESSIAN
=====
CAH                2.1481048 ANGS          0.699995
XCAH               89.9978901 DEGS          0.156813

**** CHANGE IN POINT GROUP ****

          CNV          2          DNH          2

#####
                                ERROR DETECTED
                                POINT GROUP CHANGE DURING OPTIMISATION
#####

```

In such cases the optimisation may be completed by changing to the OPTXYZ algorithm, using the RESTART option to retrieve the partially converged geometry from the Dumpfile

as the starting point. Note that OPTXYZ will not suffer from either ZMATRIX or Point group problems.

```
RESTART
TITLE\CAH2 .. 3-21G
ZMAT ANGS\CA\X 1 1.0\ H 1 CAH 2 XCAH\H 1 CAH 2 XCAH 3 180.0
VARIABLES\CAH 2.148 HESSIAN 0.7\XCAH 75.0 HESSIAN 0.1\END
RUNTYPE OPTXY
VECTORS 1\ENTER 1
```

- Particular care should be taken when dealing with the ZMATRIX specification for cyclic systems. If this is specified such that a multiple bond is not explicitly defined, then the initial step taken in an optimisation with either a poor starting geometry or ill-defined Hessian can lead to unreasonable values for such a bond. In the worst case, the bond can become so compressed (with a disastrous effect on the total energy) that linear dependence will be (correctly) diagnosed! Certainly in such cases the starting hessian should be taken from a smaller basis calculation (STO-3G will do ..).
- PARAMETER ERRORS*: Possible errors may stem from the user not appreciating the workings of the optimisation modules (as loaded under RUNTYPE OPTIMIZE or RUNTYPE SADDLE). Both algorithms are based on the notion of a 'history' file, with any restart jobs working through the previous points along the optimisation pathway, prior to continuing execution at the interrupted point. Anything which perturbs this process, causing the 'history' file, as present on the Dumpfile, to appear at odds with that generated from the data input will lead to a 'PARAMETER ERROR', and termination of execution. Basically, once the optimisation has been initiated, the user should not modify the input data, other than through the introduction of the RESTART directive, modification of the VECTORS specification etc. Specifically, modifying the ZMATRIX data or optimisation controls (XTOL etc.) will lead to this error condition. Let us consider one example where this might occur. In the data files below we are using the results of a 3-21G optimisation as a basis for a larger TZVP optimisation. The 3-21G data might appear as follows:

```
TITLE
H2O -- 3-21G
ZMAT ANGSTROM
O
H 1 OH
H 1 OH 2 HOH
VARIABLES
OH 0.956 HESSIAN 1.1
HOH 109.05 HESSIAN 0.2
END
RUNTYPE OPTIMIZE
VECTORS EXTGUESS
ENTER 1
```

with the TZVP startup job below using the vectors and hessian from the split-valence calculation:

```

DUMPFIL ED3 300
TITLE
H2O -- TZVP -- RESTARTING FROM 3-21G
ZMAT ANGSTROM
O
H 1 OH
H 1 OH 2 HOH
VARIABLES
OH 0.956 HESSIAN 1.1
HOH 109.05 HESSIAN 0.2
END
BASIS TZVP
RUNTYPE OPTIMIZE ED3
VECTORS GETQ ED3 1 1
ENTER 1

```

Let us assume the above calculation terminated on time up: typical restart data is shown below. Note that the RUNTYPE directive is as before i.e. still restoring the 3-21G Hessian. If the ED3 specification is removed from this line, the job would fail immediately since the starting-Hessian will now be different from that resident on the 'history' file.

```

DUMPFIL ED3 300
RESTART OPTIMIZE
TITLE
H2O -- TZVP -- RESTARTING FROM 3-21G
ZMAT ANGSTROM
O
H 1 OH
H 1 OH 2 HOH
VARIABLES
OH 0.956 HESSIAN 1.1
HOH 109.05 HESSIAN 0.2
END
BASIS TZVP
RUNTYPE OPTIMIZE ED3
VECTORS 1
ENTER 1

```

4. *The optimisation appears to have converged but iterations continue;* if too small a value of XTOL is specified the energy is not sufficiently numerically accurate to justify using line searches. This is especially true when employing default accuracy integrals.
5. *The optimisation will not converge:*
 - Check that the starting guess is reasonable
 - In a SADDLE calculation the quality of the initial hessian is crucial, and the user should if possible generate this at the outset of the optimisation (ie. specify TYPE 3 for all the variables) - it should have only one negative eigenvalue if the starting point is reasonable.
 - If a large step is made it is possible for the wavefunction to change state. Usually this is manifested by the linear search returning to a previous point on the surface, or

by exceptionally large values in the hessian matrix. To avoid this reduce STEPMAX, and if dealing with a closed shell system use LOCK.

4.1 Synchronous Transit Algorithm

1. *Too many z-subspace iterations:* If many more than (n-1) iterations are performed in any one z-subspace minimisation then the parameter TOLMAX should be reduced.
2. *The optimisation will not converge:*
 - Check that the minima have been input correctly
 - Check that the starting guess is reasonable
 - Try calculating the full hessian (ie. specify TYPE 3 for all the variables) - it should have only one negative eigenvalue if the starting point is reasonable.
 - Sometimes the linear search along the polynomial for a maximum causes problems which result in very large rises in energy. Occasionally this may be overcome by increasing the VALUE parameter so that the linear search is not as rigorous (check also that STEPMAX is not too large).

5 Direct-CI Calculations

The internal symmetry manipulations within the Direct-CI module are largely hidden from the user, although the re-ordering performed to align both internal and external MOs into groups of common IRrep is recorded on the output. It is possible for incorrect CONF specification to lead to problems, and one of the best ways to monitor such effects is to look at the output from the 'pre-sorting' of the transformed integrals, a typical example of which is shown below.

```

**** TRANSFORMED INTEGRAL PRE-SORT CALLED AT   380.21 SECS

TRANSFORMED 1-ELECTRON INTEGRALS RESTORED FROM SECTION 466
OF DUMPFIL STARTING AT BLOCK           1 OF ED3

*** SYMMETRY CHECK / LARGEST FORBIDDEN H-INTEGRAL :  39  2 -0.40457E-12

```

If there are inconsistencies between the ACTIVE and CONF specification, this will almost certainly lead to a large value in the symmetry check, in which case the diagonalisation results are probably meaningless.

6 Table-CI Calculations

In previous releases of the code, failing to allocate, or pre-compute the Table-CI data base lead to an operand range, or related error, at the outset of selection mode processing. This situation has now been addressed, with the program checking for correct assignment of the data base in the absence of the table directive.

7 Known Bugs/Issues

The list of know bugs, as well as a list of feature requests, is maintained on the GAMESS-UK CCPForge site at:

http://ccpforge.cse.rl.ac.uk/tracker/?group_id=14

If you think you have encountered a bug that is not listed there, please send an email to the gamess-uk-users list at:

<http://ccpforge.cse.rl.ac.uk/mailman/listinfo/gamess-uk-users>