

Computing for Science (CFS) Ltd.,
CCLRC Daresbury Laboratory.

Generalised Atomic and Molecular Electronic Structure System

G A M E S S - U K

USER'S GUIDE and REFERENCE MANUAL

Version 8.0 June 2008

PART 12. GAMESS-UK under UNIX

M.F. Guest, J. Kendrick, J.H. van Lenthe and P. Sherwood

Copyright (c) 1993-2008 Computing for Science Ltd.

This document may be freely reproduced provided that it is reproduced unaltered and in its entirety.

Contents

1 Introduction	2
2 Single Point SCF Calculation	4
3 Sequence of Calculations on Water	6
4 SCF Calculations on Cubane, Nitrobenzene and Trinitrotoluene	9
5 STO-3G Calculations on Na₇Mg⁺	11
6 Extended Basis Set Calculations of Na₇Mg⁺	13
7 ECP calculations of Na₇Mg⁺	16

<i>CONTENTS</i>	1
8 Graphical analysis of nickel tetracarbonyl	18
9 Two-Pair GVB Calculation on 1-imino-2,4-pentadiene	20
10 Direct-SCF Calculations	23
11 HCN/HNC Transition State Location	25
12 HSiP/HPSi Transition State Location	26
12.1 Numerical Force Constants	26
12.2 Analytic Force Constants	28
13 Use of Bond-centred Functions	30
14 SCF Analytic Force Constants for Ethylene	31
15 MP2 Analytic Force Constants for Ethylene	32
16 MP2 Polarisability for Ethylene	33
17 Direct-MP2 Calculation of Pyridine	34
18 CASSCF Geometry Optimisations	35
19 CASSCF + 2nd-order CI Calculations on BeO	38
20 MCSCF + 2nd-order CI Calculations on BeO	41
21 Table-CI calculations on the Ammonia Cation	44
22 ECP, CASSCF and Direct-CI Calculations on NiCCH₂	51
23 Table-CI Calculations of the Electronic Spectra of Pyridine	59
24 Full-CI calculations	68

1 Introduction

In the present section we consider initially execution of GAMESS–UK on a Linux workstation, although these notes are intended as a more general guide to running the code under the Unix operating system. Throughout this description we make the following assumptions:

- the user will in general submit jobs from a disk partition different to that where the direct access files used by GAMESS–UK will be cited: typically the latter will be striped. For the purpose of the present notes we assume that the various files involved will be routed to the partition `/scr1/user`, where the directory 'user' has been created prior to job submission (using the command `mkdir`), thus

```
mkdir /scr1/user
```

- that all job inputs reside in the user's home directory (or subdirectory thereof), and that all job output is to be routed back to that directory.
- We assume the user is submitting jobs directly to the background.
- In Part 13 we discuss execution of GAMESS–UK using the prepared script `rungames`
- all of the commands in these notes belong to the C shell.

Note that all data input for the Unix implementation of GAMESS–UK may be presented in either **upper** or **lower case**. In the examples below we have used *lower case* input throughout. Note that it is a trivial matter to convert data from under control of the `dd` command. Thus if upper case data input resides in the file **upper**, the following command

```
dd if=upper of=lower conv=lcase
```

will perform the necessary conversion to leave the required lower case input in the file **lower**. Note that the executable for GAMESS–UK is assumed to reside in the file `/scr1/wab/GAMESS-UK/games`. The following examples will be considered:

1. Single point SCF calculation of water using the default basis.
2. Sequence of calculations on water, including starting and restarting geometry optimisation of the neutral molecule, an RHF calculation on the 2B_1 cation, boys localisation and 2-pair GVB calculation of the neutral molecule.
3. Closed-shell SCF calculations on C_4F_4 , $C_6H_5NO_2$ and $C_6H_2(NO_2)_3CH_3$.
4. STO-3G calculation of Na_7Mg^+ , together with an RHF and UHF calculation of the triplet state.
5. Extended basis set calculation on Na_7Mg^+ , with SCF calculation of the singlet state preceding an RHF calculation of the triplet state.

6. ECP calculation on Na_7Mg^+ in a double-zeta valence basis, with SCF calculation of the singlet state preceding an RHF calculation of the triplet state.
7. 2-pair GVB calculation on 1-imino-2,4-pentadiene, $\text{CH}_2(\text{CH})_4\text{NH}_2^+$
8. Graphical analysis of the X^1A_1 state of $\text{Ni}(\text{CO})_4$.
9. STO-3G direct-SCF calculations on $\text{C}_{11}\text{O}_{10}\text{NPH}_{18}$ and the geometry optimisation of $\text{Be}(\text{C}_5\text{H}_5)_2$.
10. Determination of the transition state for the HCN/HNC isomerisation reaction. This example demonstrates usage of the three saddle point algorithms available, the default trust-region method plus the synchronous transit and Simons-Jorgensen algorithms.
11. Location of the transition state for the HPSi/HSiP isomerisation and subsequent force constant evaluation.
12. Specification of bond-centred functions, located at the midpoint of the C-N bond in the HCN/HNC transition state.
13. SCF geometry optimisation and analytic force constants of C_2H_4 .
14. MP2 geometry optimisation and analytic force constants of C_2H_4 .
15. MP2 geometry optimisation and polarisability of C_2H_4 .
16. Direct-MP2 calculation of $\text{C}_5\text{H}_5\text{N}$ in a 6-31G* basis.
17. CASSCF geometry optimisation of the X^1A_1 state of H_2O .
18. CASSCF + 2nd-order CI calculations of the $X^1\Sigma^+$ state of BeO .
19. MCSCF + 2nd-order CI calculations of the $X^1\Sigma^+$ state of BeO .
20. Table-CI calculation of the X^2A_1 and 1^2A_1 states of the ammonia cation, NH_3^+ cation.
21. ECP calculation on NiCCH_2 with CASSCF and Direct-CI calculations of the lowest triplet state wavefunction.
22. Table-CI calculations typical of those performed in the calculation of electronic spectra. In this case we are studying the disposition of the lowest 1A_1 and 1^1A_2 states of pyridine. The sequence of calculations involve the determination of the lowest 10 states of each category, performed in a DZ plus rydberg basis.
23. Full-CI calculations of the X^1A_1 state of H_2O .

2 Single Point SCF Calculation

Let us consider a simple SCF run for H₂O in a 3-21G basis, and describe the various mechanisms available for running the job in terms of the citing of direct access files involved and the routing of job output. Note at the outset that GAMESS–UK reads from *stdin* and writes to *stdout*, so that both input and output may be controlled by the standard means.

- Let us assume that the following lines reside in the file myjob,

```
/scr1/wab/GAMESS-UK/bin/gamess << EOF
title\h2o 3-21g scf
zmat angstrom\o\h 1 roh\h 1 roh 2 theta
variables\roh 0.956 hess 0.7\theta 104.5 hess 0.2 \end
enter
EOF
```

and are submitted to the background through the command

```
myjob >& myjob.log &
```

This will result in the files used by GAMESS–UK, in this case ED2, ED3 and ED7 being created in the user's own directory for the duration of the run, and deleted on job termination. The output from the job and any system diagnostics will be routed to the file myjob.log. Note that the user may assign execute attributes to the file myjob, using the *chmod* command, thus

```
chmod 700 myjob
```

- Note that it is also possible to read the data from a separate file, so that myjob would comprise the single line

```
/scr1/wab/GAMESS-UK/bin/gamess < datain
```

where datain contains just the GAMESS–UK data, thus

```
title\h2o 3-21g scf
zmat angstrom\o\h 1 roh\h 1 roh 2 theta
variables\roh 0.956 hess 0.7\theta 104.5 hess 0.2 \end
enter
```

In this case the job might equally well be submitted directly with the following command,

```
/scr1/wab/GAMESS-UK/bin/gamess < datain >& myjob.log &
```

- Now consider the changes to myjob required to route the direct access files from the user's own directory to the disk partition /scr1, in particular to the directory /scr1/user. Assuming this directory has been created by the user, thus

```
mkdir /scr1/user
```

this may be achieved either by using the `cd` command at the outset of myjob, so as execute the job in the required directory, thus

```
cd /scr1/user
/scr1/wab/GAMESS-UK/bin/gamess << EOF
title\h2o 3-21g scf
zmat angstrom\o\h 1 roh\h 1 roh 2 theta
variables\roh 0.956 hess 0.7\theta 104.5 hess 0.2 \end
enter
EOF
```

in which case the direct access files will be deleted on job termination, or through the `setenv` command, thus

```
#!/bin/csh -f
setenv ed2 /scr1/user/ed2
setenv ed3 /scr1/user/ed3
setenv ed7 /scr1/user/ed7
/scr1/wab/GAMESS-UK/bin/gamess << EOF
title\h2o 3-21g scf
zmat angstrom\o\h 1 roh\h 1 roh 2 theta
variables\roh 0.956 hess 0.7\theta 104.5 hess 0.2 \end
enter
EOF
```

In this case the files created in `/scr1/user` *will not* be deleted on job termination.

This provides, of course, the mechanism for keeping files between separate runs of the program, with the file names assigned though the `setenv` values. Thus to keep the mainfile and dumpfile with file names `h2omain` and `h2odump` would require the following job input:

```
#!/bin/csh -f
setenv ed2 /scr1/user/h2omain
setenv ed3 /scr1/user/h2odump
setenv ed7 /scr1/user/ed7
/scr1/wab/GAMESS-UK/bin/gamess << EOF
title\h2o 3-21g scf
zmat angstrom\o\h 1 roh\h 1 roh 2 theta
variables\roh 0.956 hess 0.7\theta 104.5 hess 0.2 \end
enter
EOF
```

or, if using the `cd` command,

```
#!/bin/csh -f
cd /scr1/user
setenv ed2 h2omain
setenv ed3 h2odump
```

```

/scri/wab/GAMESS-UK/bin/gamess << EOF
title\h2o 3-21g scf
zmat angstrom\o\h 1 roh\h 1 roh 2 theta
variables\roh 0.956 hess 0.7\theta 104.5 hess 0.2 \end
enter
EOF

```

with the scratchfile (ed7) omitted from the *setenv* commands.

Alternatively, instead of setting the names of the files through the *setenv* command, it is possible to use "file" pre-directives within the body of the GAMESS-UK input. Thus the following:

```

#!/bin/csh -f
cd /scri/user
/scri/wab/GAMESS-UK/bin/gamess << EOF
title\h2o 3-21g scf
file ed2 h2omain
file ed3 h2odump
zmat angstrom\o\h 1 roh\h 1 roh 2 theta
variables\roh 0.956 hess 0.7\theta 104.5 hess 0.2 \end
enter
EOF

```

achieves the same as using the *setenv* command. For all the following examples, either *setenv* commands run in the shell, or *file* directives in the GAMESS-UK input can be used interchangeably.

3 Sequence of Calculations on Water

In this example we include a sequence of job files for performing various calculations based on the H₂O example given above.

1. This run utilises the vectors made above. Both bond length and bond angle are to be optimised.

```

#!/bin/csh -f
setenv ed2 /scri/user/h2omain
setenv ed3 /scri/user/h2odump
setenv ed7 /scri/user/ed7
/scri/wab/GAMESS-UK/bin/gamess << EOF
restart new
title
water optimisation at scf level 3-21g basis set
zmat angstrom
o
h 1 oh
h 1 oh 2 hoh
variables
oh 0.956
hoh 104.5

```

```

end
runtype optimise
enter
EOF

```

2. This example would be used to complete, if necessary, the run started in 1.

```

#!/bin/csh -f
setenv ed2 /scr1/user/h2omain
setenv ed3 /scr1/user/h2odump
setenv ed7 /scr1/user/ed7
/scr1/wab/GAMESS-UK/bin/gamess << EOF
restart optimise
title
water optimisation at scf level 3-21g basis set
zmat angstrom
o
h 1 oh
h 1 oh 2 hoh
variables
oh 0.956
hoh 104.5
end
runtype optimise
enter
EOF

```

3. This example performs an open-shell RHF calculation at the optimised geometry from 2. (note the RESTART usage).

```

#!/bin/csh -f
setenv ed2 /scr1/user/h2omain
setenv ed3 /scr1/user/h2odump
setenv ed7 /scr1/user/ed7
/scr1/wab/GAMESS-UK/bin/gamess << EOF
restart
title
h2o+ doublet b1 state - ground state geometry
charge 1
mult 2
zmat angs
o
h 1 oh
h 1 oh 2 hoh
variables
oh 0.956
hoh 104.5
end
enter
EOF

```

4. The valence shell scf mos are to be localised. For the purpose of the example below it is assumed that orbitals 2 and 3 are the bond orbitals. The CHARGE and MULT directives are required to override the values set in the preceding job on the doublet cation.


```

#!/bin/csh -f
setenv ed2 /scr1/user/h2omain
setenv ed3 /scr1/user/h2odump
setenv ed7 /scr1/user/ed7
/scr1/wab/GAMESS-UK/bin/gamess << EOF
restart
title
lmos for h2o-- ground state geometry
charge 0
mult 1
zmat ang
o
h 1 oh
h 1 oh 2 hoh
variables
oh 0.956
hoh 104.5
end
runtype analyse
local
2 to 5
end
vectors 1
enter 5
EOF

```

5. The localised orbitals are restored from section 5 and the NOGEN facility used to generate the virtual pairs of the two bond orbitals. The SWAP directive has been used to move the localised bond orbitals to the top of the occupied orbital list. The NOGEN facility reorders the orbitals so that the GVB pairs occur together. Note the ADAPT OFF specification, now required when using localised orbitals as the input orbital set.

```

#!/bin/csh -f
setenv ed2 /scr1/user/h2omain
setenv ed3 /scr1/user/h2odump
setenv ed7 /scr1/user/ed7
/scr1/wab/GAMESS-UK/bin/gamess << EOF
restart
title
water gvb calculation using localised orbitals
adapt off
zmat ang
o
h 1 oh
h 1 oh 2 hoh
variables
oh 0.956
hoh 104.5
end
scftype gvb 2
vectors nogen 5
swap
2 5
3 4

```

```

end
enter
EOF

```

4 SCF Calculations on Cubane, Nitrobenzene and Trinitrotoluene

We show below the job files for three straightforward closed-shell SCF calculations, providing more examples of z-matrix specification and reliance on the default options in such calculations. In each case the direct access files will be deleted on job completion.

Closed shell SCF Job for C₄F₄

```

#!/bin/csh -f
cd /scr1/user
/scr1/wab/GAMESS-UK/bin/gamess << EOF
title
**** c4f4 3/21g ****
zmat angstrom
x
c 1 r1
c 1 r2 2 90.
c 1 r1 3 90. 2 180.
c 1 r2 4 90. 3 180.
x 2 1. 1 90. 3 0.
f 2 r3 6 90. 3 180.
x 4 1. 1 90. 3 0.
f 4 r3 8 90. 3 180.
x 3 1. 1 90. 4 0.
f 3 r3 10 90. 4 180.
x 5 1. 1 90. 4 0.
f 5 r3 12 90. 4 180.
variables
r1 1.2
r2 1.3
r3 1.313
end
enter
EOF

```

Closed shell SCF Job for C₆H₅NO₂

```

#!/bin/csh -f
cd /scr1/user
/scr1/wab/GAMESS-UK/bin/gamess << EOF
title
c6h5.no2 3-21g
accuracy 20 7
noprint
zmat angstrom
c

```

4 SCF CALCULATIONS ON CUBANE, NITROBENZENE AND TRINITROTOLUENE10

```
n 1 rcn
x 2 1.0 1 90.0
c 1 rcc1 2 t1 3 p1
c 1 rcc1 2 t1 3 -p1
c 4 rcc2 1 t2 2 p2
c 5 rcc2 1 t2 2 p2
c 7 rcc3 5 t3 1 p3
o 2 rno1 1 t5 3 -90.0
o 2 rno1 1 t5 3 90.0
h 4 rch1 1 t6 2 p5
h 5 rch1 1 t6 2 p5
h 6 rch2 4 t7 11 p6
h 7 rch2 5 t7 12 p6
h 8 rch3 7 t8 14 p7
variables
rcn 1.49
rcc1 1.37
rcc2 1.43
rcc3 1.37
rno1 1.21
rch1 1.084
rch2 1.084
rch3 1.084
t1 120.0
t2 120.0
t3 120.0
t5 120.0
t6 120.0
t7 120.0
t8 120.0
p1 90.0
p2 180.0
p3 0.0
p5 0.0
p6 0.0
p7 0.0
end
maxcyc 20
enter
EOF
```

Closed shell SCF Job for $C_6H_2(NO_2)_3CH_3$

```
#!/bin/csh -f
cd /scr1/user
/scr1/wab/GAMESS-UK/bin/gamess << EOF
title
2,4,6 tri-nitro-toluene. 3-21g basis.
noprnt distance basis vectors hessian
zmat angstrom
x
c 1 r1
c 1 r2 2 a1
c 1 r2 2 a1 3 180.
c 1 r3 2 a2 3 0.
```

```

c 1 r3 2 a2 3 180.
x 1 1. 2 90. 3 180.
c 1 r4 7 90. 2 180.
n 3 r5 2 a3 1 180.
o 9 r6 3 a4 2 0.
o 9 r7 3 a5 2 180.
n 4 r5 2 a3 1 180.
o 12 r6 4 a4 2 0.
o 12 r7 4 a5 2 180.
x 8 1. 1 90. 6 0.
n 8 r8 15 90. 1 180.
o 16 r9 8 a6 5 0.
o 16 r9 8 a6 5 180.
x 2 1. 1 90. 4 0.
c 2 r10 19 90. 1 180.
h 20 r11 2 a7 19 90.
h 20 r12 2 a8 21 120.
h 20 r12 2 a8 21 -120.
h 5 r13 8 a9 6 180.
h 6 r13 8 a9 5 180.
variables
r1 1.431\r2 1.367\r3 1.397\r4 1.395
a1 60.38\a2 120.67
r5 1.521\r8 1.505\r6 1.277\r7 1.278\r9 1.277
a3 123.52\a4 121.19\a5 116.17\a6 117.53
r10 1.529\r11 1.087\r12 1.082
a7 110.07\a8 109.7
r13 1.086\a9 121.26
end
enter
EOF

```

5 STO-3G Calculations on Na_7Mg^+

In this calculation we perform an STO-3G calculation on Na_7Mg^+ , followed by an RHF and then UHF calculation on the triplet state. Note the use of the SUPER directive to ensure an integral file format compatible with the use of BYPASS in the subsequent RHF and UHF calculations.

Closed shell SCF Job

```

#!/bin/csh -f
setenv ed2 /scr1/user/namgmain
setenv ed3 /scr1/user/namgdump
setenv ed7 /scr1/user/ed7
/scr1/wab/GAMESS-UK/bin/gamess << EOF
title
* na7mg+ * sto-3g * closed shell * scf-energy= -1314.828516
mult 1
super force
charge 1
zmat ang
mg

```

```

na 1 r1
na 1 r2 2 90.
na 1 r2 2 90. 3 72.
na 1 r2 2 90. 4 72.
na 1 r2 2 90. 5 72.
na 1 r2 2 90. 6 72.
na 1 r1 3 90. 2 180.
variables
r1 3.0286740
r2 3.194799
end
basis sto3g
level 1.5 10 1.0
maxcyc 40
enter
EOF

```

Open shell RHF Job

```

#!/bin/csh -f
setenv ed2 /scr1/user/namgmain
setenv ed3 /scr1/user/namgdump
setenv ed7 /scr1/user/ed7
/scr1/wab/GAMESS-UK/bin/gamess << EOF
restart
title
* na7mg+ * sto-3g * triplet * scf energy=-1314.900851
super force
bypass
mult 3
charge 1
zmat angs
mg
na 1 r1
na 1 r2 2 90.
na 1 r2 2 90. 3 72.
na 1 r2 2 90. 4 72.
na 1 r2 2 90. 5 72.
na 1 r2 2 90. 6 72.
na 1 r1 3 90. 2 180.
variables
r1 3.0286740
r2 3.194799
end
basis sto3g
maxcyc 40
enter
EOF

```

UHF Job

```

#!/bin/csh -f
setenv ed2 /scr1/user/namgmain
setenv ed3 /scr1/user/namgdump
setenv ed7 /scr1/user/ed7

```

```

/scr1/wab/GAMESS-UK/bin/gamess << EOF
restart
super force
title
* na7mg+ * sto-3g * triplet * uhf energy=-1314.901919
mult 3
charge 1
bypass
zmat angz
mg
na 1 r1
na 1 r2 2 90.
na 1 r2 2 90. 3 72.
na 1 r2 2 90. 4 72.
na 1 r2 2 90. 5 72.
na 1 r2 2 90. 6 72.
na 1 r1 3 90. 2 180.
variables
r1 3.0286740
r2 3.194799
end
basis sto3g
scftype uhf
vectors 5
enter
EOF

```

Note that we are using the energy ordered open-shell RHF eigenvectors to initiate the UHF calculation (as written to the default section 5 by the Open shell RHF Job). Had this section not been specified using the VECTORS directive, then the closed-shell SCF MOs would be used in default.

6 Extended Basis Set Calculations of Na_7Mg^+

In this example we use the STO-3G calculation on Na_7Mg^+ , performed above as a starting point for a more extensive basis set calculation. In particular the set of closed-shell vectors is restored under control of GETQ, with the STO-3G Dumpfile used as a 'foreign' Dumpfile. We then perform an RHF calculation on the open-shell singlet state of Na_7Mg^+ , using the integrals calculated in the closed-shell case. Note that the OPEN directive is now required for this low-spin state.

Closed shell SCF Job

```

#!/bin/csh -f
setenv ed2 /scr1/user/namgmain
setenv ed3 /scr1/user/namgdump
setenv ed7 /scr1/user/ed7
/scr1/wab/GAMESS-UK/bin/gamess << EOF
dumpfile ed3 500
title

```

```
* na7mg+ (4s3p//4s3p1d) scf energy=-1330.808742
mult 1
charge 1
super off
noprnt vectors
zmat angs
mg
na 1 r1
na 1 r2 2 90.
na 1 r2 2 90. 3 72.
na 1 r2 2 90. 4 72.
na 1 r2 2 90. 5 72.
na 1 r2 2 90. 6 72.
na 1 r1 3 90. 2 180.
variables
r1 3.0286740
r2 3.194799
end
basis
s mg
.005004 5609.67
.037083 841.969
.171495 191.263
.444597 53.2621
.480060 16.6003
s mg
.352170 2.97082
.692921 1.00728
s mg
1.00000 .113641
s mg
1.000000 .044678
p mg
.039884 50.9665
.223321 11.4364
.514536 3.21935
p mg
1.00000 0.914433
p mg
1.00000 0.16
d mg
1.00000 0.175
s na
.003064 6902.67
.022198 1059.04
.095576 255.445
.280448 77.3172
.452587 26.8224
.29313 10.0718
s na
1.000000 2.17902
s na
1.000000 .689482
s na
1.0 .040274
```

```

p na
  .042422  38.9438
  .229433  8.71012
  .509774  2.42053
p na
  1.00000  .661896
p na
  1.0      .065
end
maxcyc 40
vectors getq ed3 1 1
enter
EOF

```

Open shell RHF Job

```

#!/bin/csh -f
setenv ed2 /scr1/user/namgmain
setenv ed3 /scr1/user/namgdump
setenv ed7 /scr1/user/ed7
/scr1/wab/GAMESS-UK/bin/gamess << EOF
dumpfile ed3 500
restart
# open shell scf using closed shell vectors from above  *
# bypass integral evaluation                            *
title
* na7mg+ (4s3p//4s3p1d) triplet rhf * energy=-1330.766950
super off
bypass
mult 1
charge 1
zmat angs
mg
na 1 r1
na 1 r2 2 90.
na 1 r2 2 90. 3 72.
na 1 r2 2 90. 4 72.
na 1 r2 2 90. 5 72.
na 1 r2 2 90. 6 72.
na 1 r1 3 90. 2 180.
variables
r1 3.0286740
r2 3.194799
end
basis
s mg
  .005004  5609.67
  .037083  841.969
  .171495  191.263
  .444597  53.2621
  .480060  16.6003
s mg
  .352170  2.97082
  .692921  1.00728
s mg

```



```

1.00000 .113641
s mg
1.000000 .044678
p mg
.039884 50.9665
.223321 11.4364
.514536 3.21935
p mg
1.00000 0.914433
p mg
1.00000 0.16
d mg
1.00000 0.175
s na
.003064 6902.67
.022198 1059.04
.095576 255.445
.280448 77.3172
.452587 26.8224
.29313 10.0718
s na
1.000000 2.17902
s na
1.000000 .689482
s na
1.0 .040274
p na
.042422 38.9438
.229433 8.71012
.509774 2.42053
p na
1.00000 .661896
p na
1.0 .065
end
open 1 1 1 1
maxcyc 40
enter
EOF

```

7 ECP calculations of Na_7Mg^+

In this example on Na_7Mg^+ , we perform a local ECP calculation, using the Hay-Wadt ECP's, together with the associated double zeta basis sets, augmented by a d-function on Mg. Having carried out the closed-shell SCF calculation, we perform an RHF calculation on the singlet state of Na_7Mg^+ , using the integrals calculated in the closed-shell case. Note that we are re-using the files from the previous example.

Closed shell SCF Job

```
#!/bin/csh -f
```

```

setenv ed2 /scr1/user/namgmain
setenv ed3 /scr1/user/namgdump
setenv ed7 /scr1/user/ed7
/scr1/wab/GAMESS-UK/bin/gamess << EOF
title
na7mg+ ecp LANL ecp /closed shell singlet
charge 1
super off
zmat angS
mg
na 1 r1
na 1 r2 2 90.
na 1 r2 2 90. 3 72.
na 1 r2 2 90. 4 72.
na 1 r2 2 90. 5 72.
na 1 r2 2 90. 6 72.
na 1 r1 3 90. 2 180.
variables
r1 3.0286740
r2 3.194799
end
basis
ecpdz na
ecpdz mg
d mg
1.0 0.175
end
ecp
na na
mg mg
level 1.0
enter
EOF

```

Open shell RHF Job

```

#!/bin/csh -f
setenv ed2 /scr1/user/namgmain
setenv ed3 /scr1/user/namgdump
setenv ed7 /scr1/user/ed7
/scr1/wab/GAMESS-UK/bin/gamess << EOF
restart
title
na7mg+ ecp /open-shell singlet rhf
mult 1
charge 1
super off
bypass
zmat angS
mg
na 1 r1
na 1 r2 2 90.
na 1 r2 2 90. 3 72.
na 1 r2 2 90. 4 72.
na 1 r2 2 90. 5 72.

```

```

na 1 r2 2 90. 6 72.
na 1 r1 3 90. 2 180.
variables
r1 3.0286740
r2 3.194799
end
basis
ecpdz na
ecpdz mg
d mg
1.0 0.175
end
ecp
na na
mg mg
runtype scf
open 1 1 1 1
level 0.3 1.0
enter
EOF

```

8 Graphical analysis of nickel tetracarbonyl

The following example illustrates features of the Graphical Analysis module, in analysing the ground state SCF wavefunction of $\text{Ni}(\text{CO})_4$. Let us assume the following job has been used in constructing this wavefunction.

```

#!/bin/csh -f
setenv ed2 /scr1/user/nicomain
setenv ed3 /scr1/user/nicodump
setenv ed7 /scr1/user/ed7
/scr1/wab/GAMESS-UK/bin/gamess << EOF
title\ni(co)4 .. 3-21g / SCF total energy -1947.868687
zmat angstrom
ni
c 1 nic
c 1 nic 2 109.471
c 1 nic 2 109.471 3 120.0
c 1 nic 2 109.471 4 120.0
x 2 1.0 1 90.0 3 180.0
o 2 co 6 90.0 1 180.0
x 3 1.0 1 90.0 2 180.0
o 3 co 8 90.0 1 180.0
x 4 1.0 1 90.0 5 180.0
o 4 co 10 90.0 1 180.0
x 5 1.0 1 90.0 4 180.0
o 5 co 12 90.0 1 180.0
variables
nic 1.831
co 1.131
end
level 1.5

```

```
enter
EOF
```

Examination of the output reveals the following symmetry designation:

```
*****
MOLECULAR SYMMETRY
*****

MOLECULAR POINT GROUP   TD
ORDER OF PRINCIPAL AXIS 0

SYMMETRY POINTS :

POINT 1 :   0.000000   0.000000   0.000000
POINT 2 :   0.000000   0.000000   1.000000
POINT 3 :   0.000000   1.000000   0.000000
```

and the following atomic coordinates:

```
0.000000   0.000000   0.000000   NI
-1.9976836  1.9976836  -1.9976836   C
 1.9976836  -1.9976836  -1.9976836   C
-1.9976836  -1.9976836   1.9976836   C
 1.9976836   1.9976836   1.9976836   C
-3.2316433  3.2316433  -3.2316433   O
 3.2316433  -3.2316433  -3.2316433   O
-3.2316433  -3.2316433   3.2316433   O
 3.2316433   3.2316433   3.2316433   O
```

The following job may be used to construct a total density plot of the SCF wavefunction in a plane containing the Ni atom and two carbonyl groups, with the Ni at the centre of the plot: a contour plot will be generated on line printer output.

```
#!/bin/csh -f
setenv ed2 /scr1/user/nicomain
setenv ed3 /scr1/user/nicodump
setenv ed7 /scr1/user/ed7
/scr1/wab/GAMESS-UK/bin/gamess << EOF
restart
title\ni(co)4 .. 3-21g / SCF total energy -1947.868687
zmat angstrom
ni
c 1 nic
c 1 nic 2 109.471
c 1 nic 2 109.471 3 120.0
c 1 nic 2 109.471 4 120.0
x 2 1.0 1 90.0 3 180.0
o 2 co 6 90.0 1 180.0
x 3 1.0 1 90.0 2 180.0
o 3 co 8 90.0 1 180.0
x 4 1.0 1 90.0 5 180.0
o 4 co 10 90.0 1 180.0
```

```

x 5 1.0 1 90.0 4 180.0
o 5 co 12 90.0 1 180.0
variables
nic 1.831
co 1.131
end
runtype analyse
graphics
gdef
type 2d
title
square 2d grid ni(co)4 - total density
calc
type dens
title
ni(co)4 - total density
section 151
plot
type line
title
ni(co)4 - total density
vectors 1
enter
EOF

```

9 Two-Pair GVB Calculation on 1-imino-2,4-pentadiene

Closed shell SCF Job

```

#!/bin/csh -f
setenv ed2 /scr1/user/gvbmain
setenv ed3 /scr1/user/gvbdump
setenv ed7 /scr1/user/ed7
/scr1/wab/GAMESS-UK/bin/gamess << EOF
# open shell rhf sto3g *
# check super force *
title
1-imino-2,4-pentadiene * energy=-245.073477
super force nosym
mult 1
accuracy 20 7
charge 1
zmat angs
c
c 1 r1
c 2 r2 1 a1
c 3 r3 2 a2 1 cx
c 4 r4 3 a3 2 c2
n 1 r5 2 a4 3 c2
h 1 r6 2 a5 3 c1
h 2 r7 3 a6 7 c2
h 3 r8 4 a7 8 c2
h 4 r9 5 a8 9 c2

```

```

h 5 r10 4 a9 10 c1
h 5 r11 4 a10 11 c2
h 6 r12 1 a11 7 c1
h 6 r13 1 a12 13 c2
variables
r1      1.3463261
r2      1.4632685
r3      1.3961480
r4      1.3568062
r5      1.3416773
r6      1.0748794
r7      1.0669518
r8      1.0811641
r9      1.0707072
r10     1.0729928
r11     1.0747118
r12     0.9971261
r13     0.9985437
a1      118.2539432
a2      122.8419092
a3      119.3229511
a4      125.9857684
a5      119.9766875
a6      122.1120978
a7      116.3317717
a8      120.9014063
a9      121.5606571
a10     121.8124933
a11     120.9303349
a12     121.8324395
constants
c1 0.
c2 180.
cx 90.
end
basis sto3g
scftype rhf
open 1 1 1 1
enter
EOF

```

Two-Pair GVB Job

```

#!/bin/csh -f
setenv ed2 /scr1/user/gvbmain
setenv ed3 /scr1/user/gvbdump
setenv ed7 /scr1/user/ed7
/scr1/wab/GAMESS-UK/bin/gamess << EOF
# gvb-scf with two pairs *
# bypass integral evaluation *
restart
bypass
title
1-imino-2,4-pentadiene * energy=-245.1146628
mult 1

```

```
accuracy 20 7
super force nosym
charge 1
zmat angs
c
c 1 r1
c 2 r2 1 a1
c 3 r3 2 a2 1 cx
c 4 r4 3 a3 2 c2
n 1 r5 2 a4 3 c2
h 1 r6 2 a5 3 c1
h 2 r7 3 a6 7 c2
h 3 r8 4 a7 8 c2
h 4 r9 5 a8 9 c2
h 5 r10 4 a9 10 c1
h 5 r11 4 a10 11 c2
h 6 r12 1 a11 7 c1
h 6 r13 1 a12 13 c2
variables
r1 1.3463261
r2 1.4632685
r3 1.3961480
r4 1.3568062
r5 1.3416773
r6 1.0748794
r7 1.0669518
r8 1.0811641
r9 1.0707072
r10 1.0729928
r11 1.0747118
r12 0.9971261
r13 0.9985437
a1 118.2539432
a2 122.8419092
a3 119.3229511
a4 125.9857684
a5 119.9766875
a6 122.1120978
a7 116.3317717
a8 120.9014063
a9 121.5606571
a10 121.8124933
a11 120.9303349
a12 121.8324395
constants
c1 0.
c2 180.
cx 90.
end
basis sto3g
runtype scf
scftype gvb 2
enter
EOF
```

10 Direct-SCF Calculations

In the first example below we show a direct-SCF calculation in which the input geometry in cartesian coordinates is converted to z-matrix representation; the second calculation features geometry optimisation of $\text{Be}(\text{C}_5\text{H}_5)_2$ using the direct-SCF module.

```
#!/bin/csh -f
setenv ed3 /scr1/user/dscfdump
setenv ed7 /scr1/user/ed7
/scr1/wab/GAMESS-UK/bin/gamesss << EOF
# direct scf generate zmatrix sto3g-basis *
title
* test2a * energy=-1550.28679356
charge -2
geometry distance angles torsions all
-2.9512196 -0.1547624 -2.3287565 8.0 o
-1.0815728 -1.9700376 -1.5385361 6.0 c
-1.1603816 -3.5363478 -2.8467927 1.0 h
1.6367703 -0.8475562 -1.5624978 6.0 c
2.1566895 -0.4797763 -3.4976155 1.0 h
3.5011251 -2.6669663 -0.4827273 7.0 n
2.9474874 -3.6433853 1.0782554 1.0 h
1.7359097 1.7242063 -0.1090391 6.0 c
1.3150929 1.4125382 1.8702785 1.0 h
4.1957289 2.9182102 -0.4054688 8.0 o
-0.3417469 3.5022051 -1.1895255 6.0 c
0.0532604 3.8272799 -3.1681491 1.0 h
-0.3292201 5.9011224 0.0783133 8.0 o
-1.4442971 7.1126500 -0.6802213 1.0 h
-2.9721287 2.1997957 -0.9534701 6.0 c
-3.3279629 1.8049798 1.0197182 1.0 h
-5.1750163 3.9122805 -1.8751357 6.0 c
-4.8159917 4.4971112 -3.8035825 1.0 h
-6.8815215 2.7942026 -1.8646838 1.0 h
-5.4889849 6.1460386 -0.3379417 8.0 o
-7.5612331 6.0739323 1.4363625 6.0 c
-7.4278090 4.3945431 2.5896385 1.0 h
5.7357642 3.1285958 1.6502323 6.0 c
5.5713092 1.7094915 3.4875662 8.0 o
7.8017770 5.1679189 1.7463198 6.0 c
7.0224823 6.8328410 2.6479587 1.0 h
8.3530583 5.6784964 -0.1498644 1.0 h
5.9321304 -2.9668945 -1.2970693 6.0 c
6.7897779 -1.7121829 -3.0617741 8.0 o
7.7021385 -4.8380024 0.0564767 6.0 c
7.1302965 -6.7576698 -0.3499893 1.0 h
7.6050313 -4.5640081 2.0812894 1.0 h
-1.5715523 -2.9124352 0.9658559 8.0 o
-3.9184431 -4.8124121 0.9101853 15.0 p
-3.1659952 -7.1913356 -0.3438675 8.0 o
-6.0342521 -3.6456571 -0.4943459 8.0 o
-4.4900093 -5.1460285 3.8664887 8.0 o
9.4719556 -4.5440252 -0.5381892 1.0 h
9.3293820 4.5891096 2.6957586 1.0 h
```



```

-9.1872029    6.0381561    0.4734880    1.0    h
-7.5522104    7.5798978    2.5757500    1.0    h
end
basis sto3g
scftype direct
enter
EOF

```

Direct-SCF Geometry Optimisation of Be(C₅H₅)₂

```

#!/bin/csh -f
/scri/wab/GAMESS-UK/bin/gamess << EOF
title
be(c5h5)2 sto3g optimised total energy = -394.2789851 au
zmatrix angstrom
x
x 1 fxa
c 2 xc 1 xxc
c 2 xc 1 xxc 3 cxc
c 2 xc 1 xxc 4 cxc
c 2 xc 1 xxc 3 -cxc
c 2 xc 1 xxc 6 -cxc
x 2 xx 3 xxc 4 -xxc
h 2 hx 8 hxx 3 hcx
h 2 hx 8 hxx 4 hcx
h 2 hx 8 hxx 5 hcx
h 2 hx 8 hxx 6 hcx
h 2 hx 8 hxx 7 hcx
x 2 fxt 3 xxc 4 xxc
c 14 xc 1 xxc 3 cxxc
c 14 xc 1 xxc 15 cxc
c 14 xc 1 xxc 16 cxc
c 14 xc 1 xxc 15 -cxc
c 14 xc 1 xxc 18 -cxc
x 14 xx 15 xxc 16 -xxc
h 14 hx 20 hxx 15 hcx
h 14 hx 20 hxx 16 hcx
h 14 hx 20 hxx 17 hcx
h 14 hx 20 hxx 18 hcx
h 14 hx 20 hxx 19 hcx
be 2 fxa 3 xxc 4 xxc
variables
fxa 1.47
fxt 3.37
xc 1.22
hx 2.12
hxx 88.4
constants
cxc 72.0
cxxc 36.0
xxc 90.0
hcx 0.0
xx 1.0
end
basis sto3g

```

```

runtype optimize
scftype direct
level 2.0 10 1.4
enter
EOF

```

11 HCN/HNC Transition State Location

Transition state calculation for the HCN,HNC isomerisation process. The first job uses the default trust region algorithm, the second the synchronous transit algorithm, and the third the Jorgensen-Simons algorithm.

```

#!/bin/csh -f
cd /scr1/user
/scr1/wab/GAMESS-UK/bin/games 

```

Saddle point for HCN using the synchronous transit algorithm - note the definition of the minima required (on the variable definition lines) and the LSEARCH directive. The default saddle point method does not require minima definition (see above)

```

#!/bin/csh -f
cd /scr1/user
/scr1/wab/GAMESS-UK/bin/games 

```

```
basis 4-31g
runtype saddle
lsearch 0 4
enter
EOF
```

Saddle point for HCN using the Jorgensen-Simons algorithm.

```
#!/bin/csh -f
cd /scr1/user
/scr1/wab/GAMESS-UK/bin/gamess << EOF
title
hcn/hnc ts search . jorgensen-simons
zmat angz
c
x 1 1.0
n 1 cn 2 90.0
h 1 ch 2 90.0 3 hcn
variables
cn 1.1484 type 3
ch 1.5960 type 3
hcn 90.0 type 3
end
basis 4-31g
runtype saddle jorgensen
powell
maxjor 55
recalc off
rfo off
cutoffs
optprint on
xtol 0.0018
enter
EOF
```

12 HSiP/HPSi Transition State Location

This example is concerned with locating the transition state in the HPSi, HSiP isomerisation process, and calculating the associated vibrational frequencies. We provide sample jobs using both numerical and analytical techniques in the transition state location and subsequent force constant evaluation. Note that the latter example is computationally the most efficient, and should certainly be adopted for small-medium sized molecules.

12.1 Numerical Force Constants

In the first step we perform an initial SCF for subsequent use in the saddle point calculation.

Closed shell SCF Job

```
#!/bin/csh -f
```

```

setenv ed2 /scr1/user/hpsimain
setenv ed3 /scr1/user/hpsidump
setenv ed7 /scr1/user/ed7
/scr1/wab/GAMESS-UK/bin/gamesss << EOF
title
psih saddle point
zmat ang
P
x 1 1.0
si 1 psi 2 90.0
h 1 ph 2 90.0 3 hpsi
variables
psi 2.053 type 3
ph 2.44 type 3
hpsi 51.02 type 3
end
enter
EOF

```

In the subsequent location of the transition state, note the use of TYPE 3 which causes the program to calculate the complete force constant matrix numerically before commencing the search for the saddle point, and the use of XTOL to provide more stringent optimisation criteria in view of the subsequent force constant evaluation. LOCK is used to retain the initial SCF configuration throughout the search.

Transition State Job

```

#!/bin/csh -f
setenv ed2 /scr1/user/hpsimain
setenv ed3 /scr1/user/hpsidump
setenv ed7 /scr1/user/ed7
/scr1/wab/GAMESS-UK/bin/gamesss << EOF
restart new
bypass
title
psih <-> hpsi saddle point
zmat ang
P
x 1 1.0
si 1 psi 2 90.0
h 1 ph 2 90.0 3 hpsi
variables
psi 2.053 type 3
ph 2.44 type 3
hpsi 51.02 type 3
end
runtype saddle
lock
xtol 0.0005
enter 2
EOF

```

Finally we present the job for numerical evaluation of the force constants at the optimised geometry. Note the use of restart in requesting usage of the geometry from the Dumpfile, rather

than from the data file.

Numerical Force Constant Job

```
#!/bin/csh -f
setenv ed2 /scr1/user/hpsimain
setenv ed3 /scr1/user/hpsidump
setenv ed7 /scr1/user/ed7
/scr1/wab/GAMESS-UK/bin/gamesess << EOF
restart
title
psih <-> hpsi saddle point numerical fcm
zmat ang
P
x 1 1.0
si 1 psi 2 90.0
h 1 ph 2 90.0 3 hpsi
variables
psi 2.053 type 3
ph 2.44 type 3
hpsi 51.02 type 3
end
runtype force
vectors 2
lock
enter 3
EOF
```

12.2 Analytic Force Constants

In the first step we perform the computation of the trial hessian under RUNTYPE HESSIAN control for subsequent use in the saddle point calculation.

Computing the trial Hessian

```
#!/bin/csh -f
cd /scr1/user
setenv ed2 hpsimain
setenv ed3 hpsidump
/scr1/wab/GAMESS-UK/bin/gamesess << EOF
title
psih trial hessian / SCF
zmat ang
P
x 1 1.0
si 1 psi 2 90.0
h 1 ph 2 90.0 3 hpsi
variables
psi 2.053
ph 2.44
hpsi 51.02
end
```

```

runtype hessian
enter
EOF

```

In the subsequent location of the transition state, note the use of the FCM keyword on the RUNTYPE data line to restore the trial hessian computed in the first job and the use of XTOL to provide more stringent optimisation criteria in view of the subsequent force constant evaluation. LOCK is used to retain the initial SCF configuration throughout the search.

Transition State Job

```

#!/bin/csh -f
cd /scr1/user
setenv ed2 hpsimain
setenv ed3 hpsidump
/scr1/wab/GAMESS-UK/bin/gamess << EOF
restart new
title
psih <-> hpsi saddle point location / using trial hessian
zmat angS
P
x 1 1.0
si 1 psi 2 90.0
h 1 ph 2 90.0 3 hpsi
variables
psi 2.053
ph 2.44
hpsi 51.02
end
runtype saddle fcm
xtol 0.0005
vectors 1
lock
enter 2
EOF

```

Finally we present the job for analytic computation of the force constants at the optimised geometry under control of runtype hessian. Note the use of restart in requesting usage of the geometry from the Dumpfile, rather than from the data file.

Analytic Force Constant Job

```

#!/bin/csh -f
cd /scr1/user
setenv ed2 hpsimain
setenv ed3 hpsidump
/scr1/wab/GAMESS-UK/bin/gamess << EOF
restart
title
psih <-> hpsi saddle point / force constants
zmat angS
P

```

```

x 1 1.0
si 1 psi 2 90.0
h 1 ph 2 90.0 3 hpsi
variables
psi 2.053
ph 2.44
hpsi 51.02
end
runtype hessian
vectors 2
lock
enter 2
EOF

```

13 Use of Bond-centred Functions

In this example we demonstrate the use of bond-centred functions (s,p), cited at the mid-point of the C-N bond in the HCN, HNC transition state.

```

#!/bin/csh -f
cd /scr1/user
/scr1/wab/GAMESS-UK/bin/gamess << EOF
title
hcn-hnc basis - dunning (9s5p-3s2p) bond(s,p) + p(h)
zmat angstrom
c
bq 1 rcn2
x 2 1.0 1 90.0
n 2 rcn2 3 90.0 1 180.0
x 1 1.0 2 90.0 3 0.0
h 1 rch 5 90.0 4 phi
variables
rcn2 0.5991
rch 1.2128
phi 71.2
end
basis
sv h
p h
1.0 0.7
s bq
1.0 1.0
p bq
1.0 0.7
sv c
sv n
end
enter
EOF

```

14 SCF Analytic Force Constants for Ethylene

We consider below computing the analytic force constants for C₂H₄, initially optimising the molecule at the SCF level, followed by the force constant calculation. Note the use of the XTOL directive in the optimisation job to ensure a higher degree of optimisation than that derived using the default XTOL.

Geometry Optimisation

```
#!/bin/csh -f
cd /scr1/user
setenv ed2 c2h4main
setenv ed3 c2h4dump
/scr1/wab/GAMESS-UK/bin/gamess << EOF
title
ethylene 6-31g** geometry optimisation
zmatrix angstrom
c
c 1 cc
h 1 ch 2 hcc
h 1 ch 2 hcc 3 180.0
h 2 ch 1 hcc 3 0.0
h 2 ch 1 hcc 3 180.0
variables
cc 1.40
ch 1.10
hcc 118.0
end
basis 6-31g**
runtime optimize
xtol 0.0001
enter
EOF
```

Analytic Force Constants

```
#!/bin/csh -f
cd /scr1/user
setenv ed2 c2h4main
setenv ed3 c2h4dump
/scr1/wab/GAMESS-UK/bin/gamess << EOF
restart
title
ethylene 6-31g** ground state vibrational frequencies
zmatrix angstrom
c
c 1 cc
h 1 ch 2 hcc
h 1 ch 2 hcc 3 180.0
h 2 ch 1 hcc 3 0.0
h 2 ch 1 hcc 3 180.0
variables
cc 1.40
```



```
ch 1.10
hcc 118.0
end
basis 6-31g**
runtype hessian
enter
EOF
```

15 MP2 Analytic Force Constants for Ethylene

We consider below computing the analytic force constants for C_2H_4 , initially optimising the molecule at the MP2 level, followed by the force constant calculation. Note again the use of the XTOL directive in the optimisation job to ensure a higher degree of optimisation than that derived using the default XTOL.

MP2 Geometry Optimisation

```
#!/bin/csh -f
cd /scr1/user
setenv ed2 c2h4main
setenv ed3 c2h4dump
/scr1/wab/GAMESS-UK/bin/gamess << EOF
title
ethylene 6-31g** MP2/ optimised total energy = -78.3272309
zmatrix angstrom
c
c 1 cc
h 1 ch 2 hcc
h 1 ch 2 hcc 3 180.0
h 2 ch 1 hcc 3 0.0
h 2 ch 1 hcc 3 180.0
variables
cc 1.40
ch 1.10
hcc 118.0
end
basis 6-31g**
runtype optimize
scftype mp2
xtol 0.0001
enter
EOF
```

MP2 Analytic Force Constants

```
#!/bin/csh -f
cd /scr1/user
setenv ed2 c2h4main
setenv ed3 c2h4dump
/scr1/wab/GAMESS-UK/bin/gamess << EOF
restart
```

```

title
ethylene MP2/6-31g** ground state vibrational frequencies
#freq  847.7, 941.6, 994.1, 1091.6, 1267.4, 1414.5,
#freq  1525.2, 1729.7, 3241.3, 3259.2, 3336.6, 3359.8
zmatrix angstrom
c
c 1 cc
h 1 ch 2 hcc
h 1 ch 2 hcc 3 180.0
h 2 ch 1 hcc 3 0.0
h 2 ch 1 hcc 3 180.0
variables
cc 1.40
ch 1.10
hcc 118.0
end
basis 6-31g**
runtype hessian
scftype mp2
enter
EOF

```

16 MP2 Polarisability for Ethylene

We consider below computing the molecular polarisability of C_2H_4 , initially optimising the molecule at the MP2 level, followed by the property calculation. Note again the use of the XTOL directive in the optimisation job to ensure a higher degree of optimisation than that derived using the default XTOL.

MP2 Geometry Optimisation

```

#!/bin/csh -f
cd /scr1/user
setenv ed2 c2h4main
setenv ed3 c2h4dump
/scr1/wab/GAMESS-UK/bin/gamess << EOF
title
ethylene 6-31g** MP2/ optimised total energy = -78.3272309
zmatrix angstrom
c
c 1 cc
h 1 ch 2 hcc
h 1 ch 2 hcc 3 180.0
h 2 ch 1 hcc 3 0.0
h 2 ch 1 hcc 3 180.0
variables
cc 1.40
ch 1.10
hcc 118.0
end
basis 6-31g**
runtype optimize

```

```

scftype mp2
xtol 0.0001
enter
EOF

```

MP2 Polarisability

```

#!/bin/csh -f
cd /scr1/user
setenv ed2 c2h4main
setenv ed3 c2h4dump
/scr1/wab/GAMESS-UK/bin/gamess << EOF
restart
title
ethylene MP2/6-31g** ground state polarisability
zmatrix angstrom
c
c 1 cc
h 1 ch 2 hcc
h 1 ch 2 hcc 3 180.0
h 2 ch 1 hcc 3 0.0
h 2 ch 1 hcc 3 180.0
variables
cc 1.40
ch 1.10
hcc 118.0
end
basis 6-31g**
runtype polarisability
scftype mp2
enter
EOF

```

17 Direct-MP2 Calculation of Pyridine

We show below the data for performing a direct-MP2 calculation on the C₅H₅N molecule, conducted in a 6-31G* basis set. Note the use of the MEMORY pre-directive in requesting a memory allocation of 4 MWords.

```

#!/bin/csh -f
cd /scr1/user
setenv ed3 pyred3
/scr1/wab/GAMESS-UK/bin/gamess << EOF
title
pyridine 6-31g* direct-mp2
zmat angstrom
n
x 1 1.0
x 1 1.0 2 90.
x 1 1.0 2 90. 3 90.
c 1 c4n 3 90. 2 180.
x 5 1.0 1 90. 3 0.0

```

```

x 5 1.0 1 90. 4 0.0
h 5 ch4 6 90. 1 180.
c 1 c2n 2 c2nz 3 180.
c 1 c2n 2 c2nz 3 0.0
c 9 c2c3 1 ccn 2 180.
c 10 c2c3 1 ccn 2 180.
h 9 c2h6 1 nch2 2 0.0
h 10 c2h6 1 nch2 2 0.0
h 11 c3h5 9 c2c3h 1 180.
h 12 c3h5 10 c2c3h 1 180.
variables
c4n 2.7845546
ch4 1.0823078
c2n 1.3372389
c2nz 120.641858
c2c3 1.3944571
ccn 122.662269
c2h6 1.0814291
c3h5 1.0809550
nch2 116.400433
c2c3h 120.158516
end
basis 6-31g*
scftype direct mp2
enter
EOF

```

18 CASSCF Geometry Optimisations

We consider below a CASSCF calculation on the X^1A_1 state of H_2O , using a full valence criterion in specifying the active space so that the formally vacant SCF virtual MOs, $4a_1$ and $2b_2$, are permitted variable occupancy. This example utilises the vectors from the closed shell SCF calculation of Example 1.

```

#!/bin/csh -f
cd /scr1/user
setenv ed2 h2omain
setenv ed3 h2odump
/scr1/wab/GAMESS-UK/bin/gamess << EOF
restart new
title
water at casscf level 3-21g basis set
zmat angstrom
o
h 1 oh
h 1 oh 2 hoh
variables
oh 0.956
hoh 104.5
end
scftype casscf
config print

```

```

doc 1 to 5
uoc 6 7
end
superci 1 to 8
newton 9 to 20
hessian 9 to 20
simul 9 to 20
enter
EOF

```

The following points should be noted:

- It is not possible to use BYPASS in the above, given the data for the SCF job of Example 1. This would have resulted in generation of a P-supermatrix which is not usable in a CASSCF run (see Part 2, Table 1).
- CASSCF calculations require two scratch FORTRAN data sets, FT01 and FT02.

In the above we have assumed that the CASSCF calculation completes in the time allocated, with the associated direct-access files allocated in default scratch status. The following job is typical of that required if restarts of the CASSCF step are envisaged:

```

#!/bin/csh -f
cd /scr1/user
setenv ed1 h2oed1
setenv ed2 h2omain
setenv ed3 h2odump
setenv ed4 h2oed4
setenv ed6 h2oed6
setenv ed9 h2oed9
setenv ed10 h2oed10
/scr1/wab/GAMESS-UK/bin/gamess << EOF
restart new
title
water at casscf level 3-21g basis set
zmat angstrom
o
h 1 oh
h 1 oh 2 hoh
variables
oh 0.956
hoh 104.5
end
scftype casscf
config print
doc 1 to 5
uoc 6 7
end
superci 1 to 8
newton 9 to 20
hessian 9 to 20
simul 9 to 20
enter
EOF

```

Assuming the above job terminated prior to convergence, the calculation might be restarted as follows:

```
#!/bin/csh -f
cd /scr1/user
setenv ed1 h2oed1
setenv ed2 h2omain
setenv ed3 h2odump
setenv ed4 h2oed4
setenv ed6 h2oed6
setenv ed9 h2oed9
setenv ed10 h2oed10
/scr1/wab/GAMESS-UK/bin/gamess << EOF
restart scf
title
water at casscf level 3-21g basis set
zmat angstrom
o
h 1 oh
h 1 oh 2 hoh
variables
oh 0.956
hoh 104.5
end
scftype casscf
config bypass
doc 1 to 5
uoc 6 7
end
superci 1 to 2
newton 3 to 20
hessian 3 to 20
simul 3 to 20
vectors 6 7
enter 6 7
EOF
```

where the default sections housing the CASSCF vectors and ci coefficients (sections 6 and 7 respectively) created in the startup job are explicitly declared above, and CONFIG processing is bypass'ed. Having completed the single point calculation, the following might be used to perform a geometry optimisation at the CASSCF level. Note that it is now necessary to SAVE the data set associated with ED11 if restarts are envisaged.

```
#!/bin/csh -f
cd /scr1/user
setenv ed1 h2oed1
setenv ed2 h2omain
setenv ed3 h2odump
setenv ed4 h2oed4
setenv ed6 h2oed6
setenv ed9 h2oed9
setenv ed10 h2oed10
setenv ed11 h2oed11
```

```

/scr1/wab/GAMESS-UK/bin/gamess << EOF
restart new
title
water - geometry optimisation at casscf level
zmat angstrom
o
h 1 oh
h 1 oh 2 hoh
variables
oh 0.956
hoh 104.5
end
runtype optimise
scftype casscf
config bypass
doc 1 to 5
uoc 6 7
end
superci 1 to 5
newton 6 to 20
hessian 6 to 20
simul 6 to 20
enter
EOF

```

Again the default CASSCF vector and CI coefficient sections from the initial energy calculation will be used by default in the optimisation job.

19 CASSCF + 2nd-order CI Calculations on BeO

First, we consider below a CASSCF calculation on the $X^1\Sigma^+$ state of BeO, characterised by the configuration

$$1\sigma^2 2\sigma^2 3\sigma^2 4\sigma^2 1\pi^4 \quad (1)$$

The initial closed-shell SCF using a DZP basis was conducted with the following job:

```

#!/bin/csh -f
cd /scr1/user
setenv ed2 beomain
setenv ed3 beodump
/scr1/wab/GAMESS-UK/bin/gamess << EOF
super off nosym
title\beo .. dzp
zmat angstrom\be\o 1 beo
variables\beo 1.300 hessian 0.7\end
basis dzp
enter
EOF

```

An examination of the closed-shell SCF output reveals the following symmetry adapted basis information

```

=====
IRREP  NO. OF SYMMETRY ADAPTED
        BASIS FUNCTIONS
=====
  1         17
  2         6
  3         6
  4         2
=====

```

and the SCF MO ordering shown below:

```

=====
M.O.  IRREP  ORBITAL ENERGY  ORBITAL OCCUPANCY
=====
  1    1    -20.45769692    2.0000000
  2    1     -4.72825831    2.0000000
  3    1     -1.15792230    2.0000000
  4    1     -0.46629250    2.0000000
  5    3     -0.39257378    2.0000000
  6    2     -0.39257378    2.0000000
  7    1     -0.05704423    0.0000000
  8    2      0.09936415    0.0000000
  9    3      0.09936415    0.0000000
 10    1      0.15573442    0.0000000
 11    1      0.25156032    0.0000000
 12    3      0.29518660    0.0000000
 13    2      0.29518660    0.0000000
 14    1      0.57290305    0.0000000
 15    4      0.66957865    0.0000000
 16    1      0.66957865    0.0000000
 17    2      0.84348942    0.0000000
 18    3      0.84348942    0.0000000
 19    1      1.01733643    0.0000000
 20    2      1.05237116    0.0000000
 21    3      1.05237116    0.0000000
 22    1      1.24301610    0.0000000
 23    1      1.45883277    0.0000000
 24    1      1.80402496    0.0000000
 25    4      2.36534068    0.0000000
 26    1      2.36534068    0.0000000
 27    2      2.62307878    0.0000000
 28    3      2.62307878    0.0000000
 29    1      3.16009549    0.0000000
 30    1      4.37857805    0.0000000
 31    1     45.42979631    0.0000000
=====

```

We wish to perform a CASSCF calculation in which the inner shell and O2s orbitals (the $1\sigma-3\sigma$) remain doubly occupied, with the active space including the formally vacant SCF virtual MOs, the 5σ and 2π . This example utilises the vectors from the closed shell SCF calculation. We wish to perform the CASSCF calculation under RUNTYPE CI specification where, having performed the 6 electrons in 6 orbital CASSCF, we use the natural orbitals in carrying out a second-order CI using the Direct-CI module. Specifically we aim to use a reference space in the CI consisting

20 MCSCF + 2nd-order CI Calculations on BeO

First, we consider below a MCSCF calculation on the $X^1\Sigma^+$ state of BeO, characterised by the configuration

$$1\sigma^2 2\sigma^2 3\sigma^2 4\sigma^2 1\pi^4 \quad (2)$$

The initial closed-shell SCF using a DZP basis was conducted with the following job:

```
#!/bin/csh -f
cd /scr1/user
setenv ed2 beomain
setenv ed3 beodump
/scr1/wab/GAMESS-UK/bin/gamess << EOF
super off nosym
title\beo .. dzp
zmat angstrom\be\o 1 beo
variables\beo 1.300 hessian 0.7\end
basis dzp
enter
EOF
```

An examination of the closed-shell SCF output reveals the following symmetry adapted basis information

```
=====
IRREP  NO. OF SYMMETRY ADAPTED
        BASIS FUNCTIONS
=====
   1         17
   2          6
   3          6
   4          2
=====
```

and the SCF MO ordering shown below:

```
=====
M.O.  IRREP  ORBITAL ENERGY  ORBITAL OCCUPANCY
=====
   1    1   -20.45769692    2.0000000
   2    1    -4.72825831    2.0000000
   3    1    -1.15792230    2.0000000
   4    1    -0.46629250    2.0000000
   5    3    -0.39257378    2.0000000
   6    2    -0.39257378    2.0000000
   7    1    -0.05704423    0.0000000
   8    2     0.09936415    0.0000000
   9    3     0.09936415    0.0000000
  10    1     0.15573442    0.0000000
  11    1     0.25156032    0.0000000
  12    3     0.29518660    0.0000000
```

13	2	0.29518660	0.0000000
14	1	0.57290305	0.0000000
15	4	0.66957865	0.0000000
16	1	0.66957865	0.0000000
17	2	0.84348942	0.0000000
18	3	0.84348942	0.0000000
19	1	1.01733643	0.0000000
20	2	1.05237116	0.0000000
21	3	1.05237116	0.0000000
22	1	1.24301610	0.0000000
23	1	1.45883277	0.0000000
24	1	1.80402496	0.0000000
25	4	2.36534068	0.0000000
26	1	2.36534068	0.0000000
27	2	2.62307878	0.0000000
28	3	2.62307878	0.0000000
29	1	3.16009549	0.0000000
30	1	4.37857805	0.0000000
31	1	45.42979631	0.0000000

=====

We wish to perform a CASSCF calculation in which the inner shell and O2s orbitals (the 1σ – 3σ) remain doubly occupied, with the active space including the formally vacant SCF virtual MOs, the 5σ and 2π . This example utilises the vectors from the closed shell SCF calculation.

```
#!/bin/csh -f
cd /scr1/user
setenv ed2 beomain
setenv ed3 beodump
/scr1/wab/GAMESS-UK/bin/gamess << EOF
restart new
super off nosym
title\beo .. dzp
bypass
zmat angstrom\be\o 1 beo
variables\beo 1.300 hessian 0.7\end
basis dzp
scftype mcscf
thresh 4
mcscf
orbital\3cor1 doc1 doc3 doc2 uoc1 uoc2 uoc3 \end
enter
EOF
```

The following points should be noted:

- The MCSCF Natural orbitals will be routed to section 10 of the Dumpfile on convergence, the default section used for NO output.
- Integral evaluation has been bypassed as the initial SCF job specified the necessary integral format for the subsequent SCF.

In the above we have assumed that the MCSCF calculation completes in the time allocated, with the associated direct-access files allocated in default scratch status. The following job is typical of that required if restarts of the MCSCF step are envisaged:

```
#!/bin/csh -f
cd /scr1/user
setenv ed2 beomain
setenv ed3 beodump
setenv ed4 beoed4
setenv ed6 beoed6
setenv ed13 beoed13
/scr1/wab/GAMESS-UK/bin/gamess << EOF
restart new
super off nosym
title\beo .. dzp
bypass
zmat angstrom\be\o 1 beo\
variables\beo 1.300 hessian 0.7\end
basis dzp
scftype mcscf
thresh 4
mcscf
orbital\3cor1 doc1 doc3 doc2 uoc1 uoc2 uoc3 \end
enter
EOF
```

Note that the symmetry adapted list of integrals are sorted at the outset of processing to ED13, and this file should be preserved across restart jobs, given that the DONT SORT data line is presented to the restart job. Assuming the above job terminated prior to convergence, the calculation might be restarted as follows:

```
#!/bin/csh -f
cd /scr1/user
setenv ed2 beomain
setenv ed3 beodump
setenv ed4 beoed4
setenv ed6 beoed6
setenv ed13 beoed13
/scr1/wab/GAMESS-UK/bin/gamess << EOF
restart scf
super off nosym
title\beo .. dzp
zmat angstrom\be\o 1 beo\
variables\beo 1.300 hessian 0.7\end
basis dzp
scftype mcscf
thresh 4
mcscf
orbital\3cor1 doc1 doc3 doc2 uoc1 uoc2 uoc3 \end
dont sort
enter
/EOF
```

Now let us consider performing the MCSCF calculation under RUNTYPE CI specification where, having performed the 6 electrons in 6 orbital CASSCF, we use the natural orbitals in carrying out a second-order CI using the Direct-CI module. Specifically we aim to use a reference space in the CI consisting of all CSFs which can be generated by distributing 6 electrons in 6 MOs i.e. the CASSCF space. This may be achieved in a single run through the following job specification:

```
#!/bin/csh -f
cd /scr1/user
setenv ed2 beomain
setenv ed3 beodump
/scr1/wab/GAMESS-UK/bin/gamess << EOF
restart new
super off nosym
title\beo .. dzp mcscf+2nd-order ci (6 electrons in 6 mos)
zmat angstrom\be\o 1 beo
variables\beo 1.300 hessian 0.7\end
basis dzp
runtype ci
active\4 to 31\end
core\1 to 3\end
scftype mcscf
thresh 4
mcscf
orbital\3cor1 doc1 doc3 doc2 uoc1 uoc2 uoc3 \end
direct 6 6 22
conf
2 2 2 0 0 0
refgen
1 4 1 5 1 6 2 4 2 5 2 6 3 4 3 5 3 6
refgen
1 4 1 5 1 6 2 4 2 5 2 6 3 4 3 5 3 6
refgen
1 4 1 5 1 6 2 4 2 5 2 6 3 4 3 5 3 6
refgen
1 4 1 5 1 6 2 4 2 5 2 6 3 4 3 5 3 6
refgen
1 4 1 5 1 6 2 4 2 5 2 6 3 4 3 5 3 6
refgen
1 4 1 5 1 6 2 4 2 5 2 6 3 4 3 5 3 6
vectors 1\enter 20 21
EOF
```

Note that the vectors specification is requesting that the closed-shell SCF eigenvectors be used to initiate the MCSCF calculation. The MCSCF natural orbitals, routed to section 10 of the Dumpfile in default, will be used as the orbitals for the Direct-CI calculation.

21 Table-CI calculations on the Ammonia Cation

We consider below a Table-CI calculation of the X^2A_1 state and 1^2A_1 state of the ammonia cation. In the first instance we consider performing the calculation in two steps, initially the

open-shell SCF calculation followed by the MRD-CI 2-reference state calculation. We then subdivide the CI calculation into 5 separate steps, performing the symmetry adaption + integral transformation, followed by configuration selection, construction of the CI Hamiltonian, the diagonalisation and, finally, the subsequent analysis of the CI wavefunctions.

Open-shell SCF Job

```
#!/bin/csh -f
cd /scr1/user
setenv ed2 nh3main
setenv ed3 nh3dump
/scr1/wab/GAMESS-UK/bin/gamess << EOF
title
nh3+ * 3-21g * scf-energy=-55.53325817 hartree
super off nosym
charge 1
mult 2
zmat angstrom
n
h 1 roh
h 1 roh 2 theta
h 1 roh 2 theta 3 theta 1
variables
roh 1.03 hessian 0.7
theta 104.2 hessian 0.2
end
enter
EOF
```

Table-CI Job

```
#!/bin/csh -f
cd /scr1/user
setenv ed2 nh3main
setenv ed3 nh3dump
setenv table TABLE
/scr1/wab/GAMESS-UK/bin/gamess << EOF
restart
title
* nh3+ * 3-21g * mrdci-energies 1r -55.6393336 2r -55.4116210
bypass scf
charge 1
mult 2
zmat angstrom
n
h 1 roh
h 1 roh 2 theta
h 1 roh 2 theta 3 theta 1
variables
roh 1.03 hessian 0.7
theta 104.2 hessian 0.2
end
runtype ci
mrdci
```

```

adapt
tran
table
select
symmetry 1
spin 2
cntrl 9
conf
1 4 1 2 3 12
1 3 1 2 4 12
roots 2
thresh 5 5
ci
diag
extrap 3
dthr 0.0001 0.0001
natorb
cive 1 2
prop
cive 1 2
1 4 1 2 3 12
1 3 1 2 4 12
moment
36 1 36 2 1
enter
EOF

```

The orbitals employed in the CI calculation will be taken from the default section associated with the open-shell RHF module, section 5, that containing the energy-ordered canonicalised open-shell vectors written on termination of the SCF process. Note that the table keyword will activate generation of the Table-CI data base, to be used in the subsequent steps below. In this case the data base will be written to the file TABLE in /scr1 for subsequent use. A copy of this data base is available on the DEC PW433AU, and may be accessed directly, thus:

```
setenv table /scr1/wab/GAMESS-UK/libs/TABLE
```

Now let us consider dividing the above CI calculation. The following points should be noted in this division:

- The SETENV lines indicate those FORTRAN data sets that must be retained between separate runs of the program. We assume below that the TABLE data-base is available from the previous job, thus omitting the TABLE step.
- Note the use of the BYPASS keyword on the various steps comprising the Table-CI procedure. Such a keyword is required on *both* those steps already completed and those steps to be handled in a subsequent run of the program.

Table-CI Data I. Symmetry Adaption and Integral Transformation

```
#!/bin/csh -f
cd /scr1/user
```

```

setenv ed2 nh3main
setenv ed3 nh3dump
setenv table TABLE
setenv ftn031 nh3tran
/scr1/wab/GAMESS-UK/bin/games  $\ll$  EOF
restart
title
* nh3+ * 3-21g * mrdci-energies 1r -55.6393336 2r -55.4116210
bypass scf
charge 1
mult 2
zmat angstrom
n
h 1 roh
h 1 roh 2 theta
h 1 roh 2 theta 3 theta 1
variables
roh 1.03 hessian 0.7
theta 104.2 hessian 0.2
end
runtype ci
mrdci
adapt
tran
select bypass
symmetry 1
spin 2
cntrl 9
conf
1 4 1 2 3 12
1 3 1 2 4 12
roots 2
thresh 5 5
ci bypass
diag bypass
extrap 3
dthr 0.0001 0.0001
enter
EOF

```

Table-CI Job II. Configuration Selection

```

#!/bin/csh -f
cd /scr1/user
setenv ed2 nh3main
setenv ed3 nh3dump
setenv table TABLE
setenv ftn031 nh3tran
setenv ftn033 nh3sel01
setenv ftn034 nh3sel02
/scr1/wab/GAMESS-UK/bin/games  $\ll$  EOF
restart ci
title
* nh3+ * 3-21g * mrdci-energies 1r -55.6393336 2r -55.4116210
bypass scf

```



```
charge 1
mult 2
zmat angstrom
n
h 1 roh
h 1 roh 2 theta
h 1 roh 2 theta 3 theta 1
variables
roh 1.03 hessian 0.7
theta 104.2 hessian 0.2
end
runtype ci
mrdci
adapt bypass
tran bypass
select
symmetry 1
spin 2
cntrl 9
conf
1 4 1 2 3 12
1 3 1 2 4 12
roots 2
thresh 5 5
ci bypass
diag bypass
extrap 3
dthr 0.0001 0.0001
enter
EOF
```

Table-CI Job III. CI Hamiltonian Construction

```
#!/bin/csh -f
cd /scr1/user
setenv ed2 nh3main
setenv ed3 nh3dump
setenv table TABLE
setenv ftn031 nh3tran
setenv ftn033 nh3sel01
setenv ftn034 nh3sel02
setenv ftn035 nh3ham
/scr1/wab/GAMESS-UK/bin/gamess << EOF
restart ci
title
* nh3+ * 3-21g * mrdci-energies 1r -55.6393336 2r -55.4116210
bypass scf
charge 1
mult 2
zmat angstrom
n
h 1 roh
h 1 roh 2 theta
h 1 roh 2 theta 3 theta 1
variables
```

```

roh 1.03  hessian 0.7
theta 104.2  hessian 0.2
end
runtype ci
mrdci
adapt bypass
tran bypass
select bypass
symmetry 1
spin 2
cntrl 9
conf
1 4 1 2 3 12
1 3 1 2 4 12
roots 2
thresh 5 5
ci
diag bypass
extrap 3
dthr 0.0001 0.0001
enter
EOF

```

Table-CI Job IV. Diagonalisation

```

#!/bin/csh -f
cd /scr1/user
setenv ed2 nh3main
setenv ed3 nh3dump
setenv ftn035 nh3ham
setenv ftn036 nh3diag
/scr1/wab/GAMESS-UK/bin/gamess << EOF
restart ci
title
* nh3+ * 3-21g * mrdci-energies 1r -55.6393336 2r -55.4116210
bypass scf
charge 1
mult 2
zmat angstrom
n
h 1 roh
h 1 roh 2 theta
h 1 roh 2 theta 3 theta 1
variables
roh 1.03  hessian 0.7
theta 104.2  hessian 0.2
end
runtype ci
mrdci
adapt bypass
tran bypass
select bypass
symmetry 1
spin 2
cntrl 9

```

```
conf
1 4 1 2 3 12
1 3 1 2 4 12
roots 2
thresh 5 5
ci bypass
diag
extrap 3
dthr 0.0001 0.0001
enter
EOF
```

Table-CI Job V. CI Wavefunction Analysis

```
#!/bin/csh -f
cd /scr1/user
setenv ed2 nh3main
setenv ed3 nh3dump
setenv ftn036 nh3diag
/scr1/wab/GAMESS-UK/bin/gamess << EOF
restart ci
title
* nh3+ * 3-21g * mrdci-energies 1r -55.6393336 2r -55.4116210
bypass scf
charge 1
mult 2
zmat angstrom
n
h 1 roh
h 1 roh 2 theta
h 1 roh 2 theta 3 theta 1
variables
roh 1.03 hessian 0.7
theta 104.2 hessian 0.2
end
runtype ci
mrdci
adapt bypass
tran bypass
select bypass
symmetry 1
spin 2
cntrl 9
conf
1 4 1 2 3 12
1 3 1 2 4 12
roots 2
thresh 5 5
ci bypass
diag bypass
extrap 3
dthr 0.0001 0.0001
natorb
cive 1 2
prop
```

```

cive 1 2
1 4 1 2 3 12
1 3 1 2 4 12
moment
36 1 36 2 1
enter
EOF

```

22 ECP, CASSCF and Direct-CI Calculations on NiCCH₂

This example illustrates the use of CASSCF and Direct-CI calculations in the framework of ECP studies. The molecular system under investigation is NiCCH₂, with a 5-reference direct-CI calculation performed using a CASSCF wavefunction for the lowest triplet state. Five data files are presented below:

1. Start-up closed-shell SCF calculation for the ¹A₁ state. Note the SUPER directive for compatibility with the subsequent open-shell calculation. The ECP library file /scr1/wab/GAMESS-UK/libs/ecplib is allocated to LFN ed0, with the NIHAY and C non-local ECPs requested under control of the PSEUDO directive.
2. Restart SCF job, with appropriate use of the SWAP directive to converge the closed-shell SCF.
3. RHF calculation for the ³A₁ state.
4. CASSCF calculation for the ³A₁ state.
5. 5-reference Direct-CI calculation for the ³A₁ state.

Closed-shell SCF Start-up Job

```

#!/bin/csh -f
cd /scr1/user
setenv ed2 mainnips
setenv ed3 dumpnips
setenv ed0 /scr1/wab/GAMESS-UK/libs/ecplib
/scr1/wab/GAMESS-UK/bin/gamess << EOF
title
ni(cch2) 1a1 rhf ,hay's ni, bar's nm ecp's
mult 1
super force
zmat angstrom
ni
c 1 nica
x 2 1.0 1 90.0
c 2 cacb 3 90.0 1 180.0
x 4 1.0 2 90.0 3 0.0
h 4 hcb 2 hcc 5 90.0
h 4 hcb 2 hcc 5 -90.0
variables
nica 2.0895

```

```

cacb 1.3604
hcb 1.1047
hcc 122.646
end
basis
s h
0.032828      13.3615
0.231208      2.0133
0.817238      0.4538
s h
1.000000      0.1233
s c
1.000000      0.4962
s c
1.000000      0.1533
p c
0.018534      18.1557
0.115442      3.9864
0.386206      1.1429
0.640089      0.3594
p c
1.000000      0.1146
s ni
-0.4372528 0.6778
1.1889453 0.1116
s ni
1.0000000 0.0387
p ni
1.0000000 0.0840
p ni
1.0000000 0.0240
d ni
0.0360414 42.7200
0.1938645 11.7600
0.4596238 3.8170
0.5599305 1.1690
d ni
1.0000000 0.2836
end
pseudo nonlocal
nihay ni
c c
maxcyc 30
level 2.5 15 1.0
vectors hcore
enter
EOF

```

Closed-shell SCF Restart Data

```

#!/bin/csh -f
cd /scr1/user
setenv ed2 mainnips
setenv ed3 dumpnips
setenv ed0 /scr1/wab/GAMESS-UK/libs/ecplib

```

```
/scr1/wab/GAMESS-UK/bin/gamess << EOF
restart new
title
ni(cch2) 1a1 rhf restart ,hay's ni, bar's nm ecp's
mult 1
bypass
super force
zmat angstrom
ni
c 1 nica
x 2 1.0 1 90.0
c 2 cacb 3 90.0 1 180.0
x 4 1.0 2 90.0 3 0.0
h 4 hcb 2 hcc 5 90.0
h 4 hcb 2 hcc 5 -90.0
variables
nica 2.0895
cacb 1.3604
hcb 1.1047
hcc 122.646
end
basis
s h
0.032828      13.3615
0.231208      2.0133
0.817238      0.4538
s h
1.000000      0.1233
s c
1.000000      0.4962
s c
1.000000      0.1533
p c
0.018534      18.1557
0.115442      3.9864
0.386206      1.1429
0.640089      0.3594
p c
1.000000      0.1146
s ni
-0.4372528 0.6778
1.1889453 0.1116
s ni
1.0000000 0.0387
p ni
1.0000000 0.0840
p ni
1.0000000 0.0240
d ni
0.0360414 42.7200
0.1938645 11.7600
0.4596238 3.8170
0.5599305 1.1690
d ni
1.0000000 0.2836
```

```

end
pseudo nonlocal
nihay ni
c c
maxcyc 40
level 3.0 10 1.0
swap
4 5
6 8
8 10
10 11
end
enter
EOF

```

Open-shell SCF Job

```

#!/bin/csh -f
cd /scr1/user
setenv ed2 mainnips
setenv ed3 dumpnips
setenv ed0 /scr1/wab/GAMESS-UK/libs/ecplib
/scr1/wab/GAMESS-UK/bin/gamesss << EOF
restart new
title
ni(cch2) 3a1 rhf ,hay's ni, bar's nm ecp's
mult 3
super force
bypass
zmat angstrom
ni
c 1 nica
x 2 1.0 1 90.0
c 2 cacb 3 90.0 1 180.0
x 4 1.0 2 90.0 3 0.0
h 4 hcb 2 hcc 5 90.0
h 4 hcb 2 hcc 5 -90.0
variables
nica 2.0895
cacb 1.3604
hcb 1.1047
hcc 122.646
end
basis
s h
0.032828      13.3615
0.231208      2.0133
0.817238      0.4538
s h
1.000000      0.1233
s c
1.000000      0.4962
s c
1.000000      0.1533
p c

```

```

0.018534      18.1557
0.115442      3.9864
0.386206      1.1429
0.640089      0.3594
p c
1.000000      0.1146
s ni
-0.4372528 0.6778
1.1889453 0.1116
s ni
1.0000000 0.0387
p ni
1.0000000 0.0840
p ni
1.0000000 0.0240
d ni
0.0360414 42.7200
0.1938645 11.7600
0.4596238 3.8170
0.5599305 1.1690
d ni
1.0000000 0.2836
end
pseudo nonlocal
nihay ni
c c
scftype gvb
maxcyc 50
level 2.0 3.0 15 1.0 1.0
open 2 2
swap
11 12
14 15
end
enter
EOF

```

Eigenvector utilisation in the above job will drive off the default sections of the Dumpfile, with the open-shell SCF module using the closed-shell SCF vectors from section 1 to initiate the SCF process, and writing the SCF open-shell orbitals to sections 4 and 5 (the energy-ordered SCF MOs). These latter orbitals will be used below to instigate the CASSCF processing.

CASSCF Job

```

#!/bin/csh -f
cd /scr1/user
setenv ed2 mainnips
setenv ed3 dumpnips
setenv ed0 /scr1/wab/GAMESS-UK/libs/ecplib
setenv ed6 trannips
setenv ed4 lfornips
/scr1/wab/GAMESS-UK/bin/games << EOF
restart new
title

```



```
ni(cch2) 3a1 c2v cas at opt (3 2 2 0), hay's ni, bar's nm ecp's
mult 3
super off nosym
zmat angstrom
ni
c 1 nica
x 2 1.0 1 90.0
c 2 cacb 3 90.0 1 180.0
x 4 1.0 2 90.0 3 0.0
h 4 hcb 2 hcc 5 90.0
h 4 hcb 2 hcc 5 -90.0
variables
nica 2.0895
cacb 1.3604
hcb 1.1047
hcc 122.646
end
basis
s h
0.032828      13.3615
0.231208      2.0133
0.817238      0.4538
s h
1.000000      0.1233
s c
1.000000      0.4962
s c
1.000000      0.1533
p c
0.018534      18.1557
0.115442      3.9864
0.386206      1.1429
0.640089      0.3594
p c
1.000000      0.1146
s ni
-0.4372528 0.6778
1.1889453 0.1116
s ni
1.0000000 0.0387
p ni
1.0000000 0.0840
p ni
1.0000000 0.0240
d ni
0.0360414 42.7200
0.1938645 11.7600
0.4596238 3.8170
0.5599305 1.1690
d ni
1.0000000 0.2836
end
pseudo nonlocal
nihay ni
c c
```

```

scftype casscf
config print
fzc 1 to 7
doc 8 to 9
alp 10 to 11
uoc 12 to 14
end
superci 1 to 12
newton 13 to 20
hessian 13 to 20
simul 15 to 20
vectors 5
swap
14 15
end
enter
EOF

```

Direct-CI Job

```

#!/bin/csh -f
cd /scr1/user
setenv ed2 mainnips
setenv ed3 dumpnips
setenv ed0 /scr1/wab/GAMESS-UK/libs/ecplib
setenv ed5 cinips
setenv ed6 trannips
/scr1/wab/GAMESS-UK/bin/games  $\ll$  EOF
restart new
title
ni(cch2) 3a1 mrsdci (3 2 2 0) ,hay's ni, bar's nm ecp's
mult 3
super off nosym
bypass scf
zmat angstrom
ni
c 1 nica
x 2 1.0 1 90.0
c 2 cacb 3 90.0 1 180.0
x 4 1.0 2 90.0 3 0.0
h 4 hcb 2 hcc 5 90.0
h 4 hcb 2 hcc 5 -90.0
variables
nica 2.0895
cacb 1.3604
hcb 1.1047
hcc 122.646
end
basis
s h
0.032828      13.3615
0.231208      2.0133
0.817238      0.4538
s h
1.000000      0.1233

```

```
s c
1.000000      0.4962
s c
1.000000      0.1533
p c
0.018534     18.1557
0.115442     3.9864
0.386206     1.1429
0.640089     0.3594
p c
1.000000      0.1146
s ni
-0.4372528  0.6778
1.1889453  0.1116
s ni
1.0000000  0.0387
p ni
1.0000000  0.0840
p ni
1.0000000  0.0240
d ni
0.0360414  42.7200
0.1938645  11.7600
0.4596238  3.8170
0.5599305  1.1690
d ni
1.0000000  0.2836
end
pseudo nonlocal
nihay ni
c c
runtype ci
core
end
active
1 to 40
end
scftype casscf
config print
fzc 1 to 7
doc 8 to 9
alp 10 to 11
uoc 12 to 14
end
superci 1 to 12
newton 13 to 20
hessian 13 to 20
simul 15 to 20
direct 20 14 26
spin triplet
conf
2 2 2 2 2 2 2 2 2 1 1 0 0 0
2 2 2 2 2 2 2 2 1 2 0 0 1 0
2 2 2 2 2 2 2 2 1 1 1 0 1 0
2 2 2 2 2 2 2 2 0 1 1 0 2 0
```

```

2 2 2 2 2 2 2 1 2 2 0 1 0 0
2 2 2 2 2 2 2 1 2 1 1 1 0 0
vprint 100 0.01
maxcyc 10
enter
EOF

```

23 Table-CI Calculations of the Electronic Spectra of Pyridine

This example demonstrates the use of the Table-CI module in the calculation of the low-lying states of Pyridine. Specifically, we are involved in determining the disposition of the first ten 1A_1 and 1A_2 states, using a common set of orbitals (the X^1A_1 SCF-MOs) in a DZ plus Rydberg basis set of 91 functions. Five job files are presented below:

1. Start-up closed-shell SCF calculation for the X^1A_1 state. Note the SUPER directive for compatibility with the subsequent CI calculation. Note also the particular syntax for siting the DZ basis on H: the third and fourth data fields are to provide an unscaled hydrogen basis, since the default specification will scale the two components by 1.2 (the more contracted) and 1.15 (the more diffuse component)
2. 1M/1R Table-CI calculation of the X^1A_1 state.
3. 6M/1R Table-CI calculation of the X^1A_1 state.
4. 21M/10R Table-CI calculation of the ten lowest 1A_1 states.
5. 19M/10R Table-CI calculation of the ten lowest 1A_2 states.

1. Closed-shell SCF Job

```

#!/bin/csh -f
cd /scr1/user
setenv ed2 pyred2
setenv ed3 pyred3
/scr1/wab/GAMESS-UK/bin/gamess << EOF
title
pyridine dz+bond-centred functions
super off nosym
zmat angstrom
n
x 1 1.0
x 1 1.0 2 90.
x 1 1.0 2 90. 3 90.
c 1 c4n 3 90. 2 180.
x 5 1.0 1 90. 3 0.0
x 5 1.0 1 90. 4 0.0
h 5 ch4 6 90. 1 180.
c 1 c2n 2 c2nz 3 180.
c 1 c2n 2 c2nz 3 0.0

```

23 TABLE-CI CALCULATIONS OF THE ELECTRONIC SPECTRA OF PYRIDINE60

```

c 9 c2c3 1 ccn 2 180.
c 10 c2c3 1 ccn 2 180.
h 9 c2h6 1 nch2 2 0.0
h 10 c2h6 1 nch2 2 0.0
h 11 c3h5 9 c2c3h 1 180.
h 12 c3h5 10 c2c3h 1 180.
bq 1 1.39 3 90. 2 180.
variables
c4n 2.7845546
ch4 1.0823078
c2n 1.3372389
c2nz 120.641858
c2c3 1.3944571
ccn 122.662269
c2h6 1.0814291
c3h5 1.0809550
nch2 116.400433
c2c3h 120.158516
end
basis
dz h 1.0 1.0
dz n
dz c
s bq
1.0 0.021
s bq
1.0 0.008
s bq
1.0 0.0025
p bq
1.0 0.017
p bq
1.0 0.009
d bq
1.0 0.015
d bq
1.0 0.008
end
enter
EOF

```

2. 1M/1R Table-CI Job for the X¹A₁ State

An examination of the SCF output reveals the following symmetry adapted basis functions, given the C_{2v} geometry and DZ plus Rydberg basis set:

```

=====
IRREP  NO. OF SYMMETRY ADAPTED
        BASIS FUNCTIONS
=====
  1          45
  2          12
  3          28
  4           6

```

=====

Thus the orbital reordering performed by the Table-CI module will yield the sequence numbers 1–45 for the a_1 MOs, 46–57 for the b_1 MOs, 58–85 for the b_2 MOs and 86–91 for the a_2 MOs. We are both freezing and discarding orbitals in the subsequent CI calculations. Confining this to both a_1 and b_2 MOs, the first six orbitals of a_1 symmetry and first four orbitals of b_2 symmetry are to be frozen, and the eight highest energy orbitals of a_1 symmetry and six highest of b_2 are to be discarded. Thus the final sequence numbers for the active orbitals in the CI are 1–31 for the a_1 MOs, 32–43 for the b_1 MOs, 44–61 for the b_2 MOs and 62–68 for the a_2 MOs. The CONF data line specifying the reference configuration is based on the associated sequence numbers of these active orbitals.

```
#!/bin/csh -f
cd /scr1/user
setenv ed2 pyred2
setenv ed3 pyred3
setenv ftn031 pyrtran
setenv table /scr1/wab/GAMESS-UK/libs/TABLE
/scr1/wab/GAMESS-UK/bin/gamess << EOF
restart
title
pyridine dz+bond-centred functions
super off nosym
bypass scf
zmat angstrom
n
x 1 1.0
x 1 1.0 2 90.
x 1 1.0 2 90. 3 90.
c 1 c4n 3 90. 2 180.
x 5 1.0 1 90. 3 0.0
x 5 1.0 1 90. 4 0.0
h 5 ch4 6 90. 1 180.
c 1 c2n 2 c2nz 3 180.
c 1 c2n 2 c2nz 3 0.0
c 9 c2c3 1 ccn 2 180.
c 10 c2c3 1 ccn 2 180.
h 9 c2h6 1 nch2 2 0.0
h 10 c2h6 1 nch2 2 0.0
h 11 c3h5 9 c2c3h 1 180.
h 12 c3h5 10 c2c3h 1 180.
bq 1 1.39 3 90. 2 180.
variables
c4n 2.7845546
ch4 1.0823078
c2n 1.3372389
c2nz 120.641858
c2c3 1.3944571
ccn 122.662269
c2h6 1.0814291
c3h5 1.0809550
nch2 116.400433
c2c3h 120.158516
```

```

end
basis
dz h 1.0 1.0
dz n
dz c
s bq
1.0 0.021
s bq
1.0 0.008
s bq
1.0 0.0025
p bq
1.0 0.017
p bq
1.0 0.009
d bq
1.0 0.015
d bq
1.0 0.008
end
runtype ci
mrdci
adapt
tran freeze discard
6 0 4 0
1 to 6 1 to 4
8 0 6 0
38 to 45 23 to 28
select
cntrl 22
spin singlet
symmetry 1
conf
0 1 2 3 4 5 32 33 44 45 46 62
roots 1 1
thresh 30 10
ci
diag
title
pyridine 1m1r ground state dz + 3s2p2d rydberg basis
extrap 3
natorb
civec 1
putq aos 2
enter
EOF

```

3. 6M/1R Table-CI Job for the X^1A_1 State

```

#!/bin/csh -f
cd /scr1/user
setenv ed2 pyred2
setenv ed3 pyred3
setenv ftn031 pyrtran
setenv table /scr1/wab/GAMESS-UK/libs/TABLE

```

23 TABLE-CI CALCULATIONS OF THE ELECTRONIC SPECTRA OF PYRIDINE63

```
/scr1/wab/GAMESS-UK/bin/gamess << EOF
restart
title
pyridine dz+bond-centred functions
super off nosym
bypass scf
zmat angstrom
n
x 1 1.0
x 1 1.0 2 90.
x 1 1.0 2 90. 3 90.
c 1 c4n 3 90. 2 180.
x 5 1.0 1 90. 3 0.0
x 5 1.0 1 90. 4 0.0
h 5 ch4 6 90. 1 180.
c 1 c2n 2 c2nz 3 180.
c 1 c2n 2 c2nz 3 0.0
c 9 c2c3 1 ccn 2 180.
c 10 c2c3 1 ccn 2 180.
h 9 c2h6 1 nch2 2 0.0
h 10 c2h6 1 nch2 2 0.0
h 11 c3h5 9 c2c3h 1 180.
h 12 c3h5 10 c2c3h 1 180.
bq 1 1.39 3 90. 2 180.
variables
c4n 2.7845546
ch4 1.0823078
c2n 1.3372389
c2nz 120.641858
c2c3 1.3944571
ccn 122.662269
c2h6 1.0814291
c3h5 1.0809550
nch2 116.400433
c2c3h 120.158516
end
basis
dz h 1.0 1.0
dz n
dz c
s bq
1.0 0.021
s bq
1.0 0.008
s bq
1.0 0.0025
p bq
1.0 0.017
p bq
1.0 0.009
d bq
1.0 0.015
d bq
1.0 0.008
end
```


23 TABLE-CI CALCULATIONS OF THE ELECTRONIC SPECTRA OF PYRIDINE64

```

runtype ci
mrdci
adapt bypass
tran freeze discard bypass
6 0 4 0
1 to 6 1 to 4
8 0 6 0
38 to 45 23 to 28
select
cntrl 22
spin singlet
symmetry 1
conf
0 1 2 3 4 5 32 33 44 45 46 62
0 1 2 3 4 5 32 38 44 45 46 62
0 1 2 3 4 5 32 33 44 45 46 65
4 32 33 38 39 1 2 3 4 5 44 45 46 62
4 32 39 62 65 1 2 3 4 5 33 44 45 46
4 33 38 62 65 1 2 3 4 5 32 44 45 46
roots 1 1
thresh 30 10
ci
diag
title
pyridine 6m1r ground state dz + 3s2p2d rydberg basis
extrap 3
natorb
civec 1
putq aos 2
enter
EOF

```

4. 21M/10R Table-CI Job for the 1A_1 States

```

#!/bin/csh -f
cd /scr1/user
setenv ed2 pyred2
setenv ed3 pyred3
setenv ftn031 pyrtran
setenv table /scr1/wab/GAMESS-UK/libs/TABLE
/scr1/wab/GAMESS-UK/bin/gamess << EOF
restart
title
pyridine dz+rydberg basis
super off nosym
bypass scf
zmat angstrom
n
x 1 1.0
x 1 1.0 2 90.
x 1 1.0 2 90. 3 90.
c 1 c4n 3 90. 2 180.
x 5 1.0 1 90. 3 0.0
x 5 1.0 1 90. 4 0.0
h 5 ch4 6 90. 1 180.

```

23 TABLE-CI CALCULATIONS OF THE ELECTRONIC SPECTRA OF PYRIDINE65

```

c 1 c2n 2 c2nz 3 180.
c 1 c2n 2 c2nz 3 0.0
c 9 c2c3 1 ccn 2 180.
c 10 c2c3 1 ccn 2 180.
h 9 c2h6 1 nch2 2 0.0
h 10 c2h6 1 nch2 2 0.0
h 11 c3h5 9 c2c3h 1 180.
h 12 c3h5 10 c2c3h 1 180.
bq 1 1.39 3 90. 2 180.
variables
c4n 2.7845546
ch4 1.0823078
c2n 1.3372389
c2nz 120.641858
c2c3 1.3944571
ccn 122.662269
c2h6 1.0814291
c3h5 1.0809550
nch2 116.400433
c2c3h 120.158516
end
basis
dz h 1.0 1.0
dz n
dz c
s bq
1.0 0.021
s bq
1.0 0.008
s bq
1.0 0.0025
p bq
1.0 0.017
p bq
1.0 0.009
d bq
1.0 0.015
d bq
1.0 0.008
end
runtype ci
mrdci
adapt bypass
tran freeze discard bypass
6 0 4 0
1 to 6 1 to 4
8 0 6 0
38 to 45 23 to 28
select
cntrl 22
spin singlet
symmetry 1
conf
2 62 65 1 2 3 4 5 32 33 44 45 46
2 33 34 1 2 3 4 5 32 44 45 46 62

```

23 TABLE-CI CALCULATIONS OF THE ELECTRONIC SPECTRA OF PYRIDINE66

```

2 5 8 1 2 3 4 32 33 44 45 46 62
2 62 63 1 2 3 4 5 32 33 44 45 46
2 33 38 1 2 3 4 5 32 44 45 46 62
2 33 35 1 2 3 4 5 32 44 45 46 62
2 5 7 1 2 3 4 32 33 44 45 46 62
2 33 37 1 2 3 4 5 32 44 45 46 62
2 5 9 1 2 3 4 32 33 44 45 46 62
2 62 64 1 2 3 4 5 32 33 44 45 46
2 33 36 1 2 3 4 5 32 44 45 46 62
2 5 11 1 2 3 4 32 33 44 45 46 62
2 33 39 1 2 3 4 5 32 44 45 46 62
2 32 34 1 2 3 4 5 33 44 45 46 62
2 32 38 1 2 3 4 5 33 44 45 46 62
4 5 8 33 38 1 2 3 4 32 44 45 46 62
4 33 38 62 65 1 2 3 4 5 32 44 45 46
4 32 33 34 38 1 2 3 4 5 44 45 46 62
4 33 34 62 65 1 2 3 4 5 32 44 45 46
4 32 38 62 63 1 2 3 4 5 33 44 45 46
4 5 7 33 38 1 2 3 4 32 44 45 46 62
roots 10 1 2 3 4 5 6 7 8 9 10
thresh 30 10
ci
diag
title
pyridine 21m10r 1a1 dz + 3s2p2d rydberg basis
extrap 3
enter
EOF

```

5. 19M/10R Table-CI Job for the 1A_2 States

```

#!/bin/csh -f
cd /scr1/user
setenv ed2 pyred2
setenv ed3 pyred3
setenv ftn031 pyrtran
setenv table /scr1/wab/GAMESS-UK/libs/TABLE
/scr1/wab/GAMESS-UK/bin/gamess << EOF
restart
title
pyridine dz+rydberg basis
super off nosym
bypass scf
zmat angstrom
n
x 1 1.0
x 1 1.0 2 90.
x 1 1.0 2 90. 3 90.
c 1 c4n 3 90. 2 180.
x 5 1.0 1 90. 3 0.0
x 5 1.0 1 90. 4 0.0
h 5 ch4 6 90. 1 180.
c 1 c2n 2 c2nz 3 180.
c 1 c2n 2 c2nz 3 0.0
c 9 c2c3 1 ccn 2 180.

```

23 TABLE-CI CALCULATIONS OF THE ELECTRONIC SPECTRA OF PYRIDINE67

```

c 10 c2c3 1 ccn 2 180.
h 9 c2h6 1 nch2 2 0.0
h 10 c2h6 1 nch2 2 0.0
h 11 c3h5 9 c2c3h 1 180.
h 12 c3h5 10 c2c3h 1 180.
bq 1 1.39 3 90. 2 180.
variables
c4n 2.7845546
ch4 1.0823078
c2n 1.3372389
c2nz 120.641858
c2c3 1.3944571
ccn 122.662269
c2h6 1.0814291
c3h5 1.0809550
nch2 116.400433
c2c3h 120.158516
end
basis
dz h 1.0 1.0
dz n
dz c
s bq
1.0 0.021
s bq
1.0 0.008
s bq
1.0 0.0025
p bq
1.0 0.017
p bq
1.0 0.009
d bq
1.0 0.015
d bq
1.0 0.008
end
runtype ci
mrdci
adapt bypass
tran freeze discard bypass
6 0 4 0
1 to 6 1 to 4
8 0 6 0
38 to 45 23 to 28
select
cntrl 22
spin singlet
symmetry 4
conf
2 5 65 1 2 3 4 32 33 44 45 46 62
2 33 47 1 2 3 4 5 32 44 45 46 62
2 5 63 1 2 3 4 32 33 44 45 46 62
2 33 48 1 2 3 4 5 32 44 45 46 62
2 8 62 1 2 3 4 5 32 33 44 45 46

```

```

2 7 62 1 2 3 4 5 32 33 44 45 46
2 33 50 1 2 3 4 5 32 44 45 46 62
2 5 64 1 2 3 4 32 33 44 45 46 62
2 33 49 1 2 3 4 5 32 44 45 46 62
2 6 62 1 2 3 4 5 32 33 44 45 46
4 5 33 38 65 1 2 3 4 32 44 45 46 62
4 5 33 38 63 1 2 3 4 32 44 45 46 62
4 33 47 62 65 1 2 3 4 5 32 44 45 46
4 5 33 34 65 1 2 3 4 32 44 45 46 62
4 7 33 38 62 1 2 3 4 5 32 44 45 46
4 33 47 62 63 1 2 3 4 5 32 44 45 46
4 8 33 38 62 1 2 3 4 5 32 44 45 46
4 5 33 34 63 1 2 3 4 32 44 45 46 62
4 33 48 62 63 1 2 3 4 5 32 44 45 46
roots 10 1 2 3 4 5 6 7 8 9 10
thresh 30 10
ci
diag
title
pyridine 19m10r 1a2 dz + 3s2p2d rydberg basis
extrap 3
enter
EOF

```

24 Full-CI calculations

We consider below Full-CI calculations of the X^1A_1 state of the H_2O molecule. In the first instance we consider correlating all electrons. We then perform a valence-only calculation, freezing the $O1s$ orbital through the ACTIVE and CORE directives, specifying a total of 8 electrons on the FULLCI data line.

All-electron Job

```

#!/bin/csh -f
cd /scr1/user
setenv ed2 h2omain
setenv ed3 h2odump
setenv ed6 h2otran
setenv ftn008 file8
/scr1/wab/GAMESS-UK/bin/gamess << EOF
title
h2o - DZ basis - full-ci
super off nosym
zmat angstrom\o\h 1 roh\h 1 roh 2 theta
variables\roh 0.956 hess 0.7\theta 104.5 hess 0.2 \end
basis dz
runtype ci\fullci 14 5 5
enter
EOF

```

Assuming the above job did not complete in the time allocated, and dumped to disk in a controlled fashion, the following job would act to continue the processing, assuming that the FOR-

TRAN file file8 had been saved, along with the Mainfile, Dumpfile and Transformed integral file.

Restarting the Full-CI job

```
#!/bin/csh -f
cd /scr1/user
setenv ed2 h2omain
setenv ed3 h2odump
setenv ed6 h2otran
setenv ftn008 file8
/scr1/wab/GAMESS-UK/bin/gamess << EOF
restart ci
title
h2o - DZ basis - restart full-ci
super off nosym
zmat angstrom\o\h 1 roh\h 1 roh 2 theta
variables\roh 0.956 hess 0.7\theta 104.5 hess 0.2 \end
basis dz
runtype ci\fullci 14 5 5
enter
EOF
```

Valence-electron Job

```
#!/bin/csh -f
cd /scr1/user
setenv ed2 h2omain
setenv ed3 h2odump
setenv ftn008 file8
/scr1/wab/GAMESS-UK/bin/gamess << EOF
core 8000000
restart new
title
h2o - DZ basis - valence full-ci
super off nosym
bypass
zmat angstrom\o\h 1 roh\h 1 roh 2 theta
variables\roh 0.956 hess 0.7\theta 104.5 hess 0.2 \end
basis dz
runtype ci
active\2 to 14 end\core\1\end
fullci 13 4 4
enter
EOF
```

The following points should be noted:

- the use of setenv to allocate the FORTRAN stream ftn008;
- the use of the core pre-directive to specify memory requirements.