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CCLRC Daresbury Laboratory.

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 6. TABLE-CI CALCULATIONS

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

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Contents

1 Introduction	1
1.1 Sub-Module Structure of Conventional Table-CI	1
2 Directives Controlling Conventional Table-CI Calculations	2
2.1 MRDCI	2
3 Data for Conventional Table-CI Symmetry Adaptation	2
3.1 ADAPT	3
4 Data for Conventional Table-CI Transformation	3
4.1 TRAN	3

5	Data for Conventional Table-CI Data-base Generation	8
5.1	TABLE	8
6	Data for Conventional Table-CI Selection	8
6.1	SELECT	9
6.2	CNTRL	9
6.3	SPIN	9
6.4	SYMMETRY	10
6.5	SINGLES	10
6.6	CONF	11
6.7	ROOTS	23
6.8	THRESH	24
7	Data for Conventional Table-CI H-Matrix Construction	25
7.1	CI	25
8	Data for Conventional Table-CI Diagonalisation	25
8.1	DIAG	26
8.2	EXTRAP	26
8.3	ACCURACY	26
8.4	MAXD	27
8.5	TRIAL	27
8.6	PRINT	27
9	Data for Conventional Table-CI Natural Orbitals	28
9.1	Natural Orbital Data - NATORB	28
9.2	Natural Orbital Data - CIVEC	28
9.3	Natural Orbital Data - PUTQ	29
10	Data for Conventional Table-CI One-electron Properties	29
10.1	PROP	29
10.2	CIVEC	30
10.3	AOPR	30
10.4	MOPR	30
10.5	Configuration Data Lines	31

11 Data for Conventional Table-CI Transition Moments	32
11.1 TM	32
12 Calculating the 1A_1 states of H₂O	33
13 Iterative Natural Orbital Calculations	41
14 Table-CI Calculations Using MCSCF Orbitals	46
15 The Semi-direct Table-CI Module	51
15.1 Sub-Module Structure of Semi-direct Table-CI	52
16 Directives Controlling Semi-direct Table-CI Calculations	53
16.1 MRDCI	53
17 Data for Semi-direct Table-CI Integral Transformation	53
18 Data for Semi-direct Table-CI Data-base Generation	57
18.1 TABLE	58
19 Data for Semi-direct Table-CI Selection	58
19.1 SELECT	58
19.2 CNTRL	59
19.3 SPIN	59
19.4 SYMMETRY	59
19.5 SINGLES	60
19.6 CONF	60
19.7 ROOTS	75
19.8 THRESH	76
20 Data for Semi-direct Table-CI Eigen Solution	77
20.1 CI	77
20.2 ACCURACY	77
20.3 PRINT	78
21 Data for Semi-direct Table-CI Natural Orbitals	78
21.1 Natural Orbital Data - NATORB	78

21.2	Natural Orbital Data - CIVEC	79
21.3	Natural Orbital Data - PUTQ	79
22	Data for Semi-direct Table-CI One-electron Properties	80
22.1	PROP	80
22.2	CIVEC	80
22.3	AOPR	81
22.4	MOPR	81
22.5	Configuration Data Lines	81
23	Data for Semi-direct Table-CI Transition Moments	82
23.1	TM	83
24	Semi-direct Table-CI - Using Default Options	84
24.1	Calculations on the Formaldehyde Ground State	84
24.2	Calculations on the Formaldehyde Cations	86
25	Memory Specification for the Semi-direct Table-CI Module	90
26	Calculating the 1A_1 states of H_2O	92
27	Iterative Natural Orbital Calculations	100
28	Table-CI Calculations Using MCSCF Orbitals	105
29	Iterative MRDCI Calculations	110
29.1	The ITERATE Directive and Associated Options	111
29.1.1	The MAXITER Directive	111
29.1.2	The WEIGHT Directive	112
29.1.3	The C**2 Directive	112
29.1.4	The Ethylene Ground state Wavefunction	112
29.2	The Algorithm for Controlling Multi-root Calculations	114
29.2.1	The MAXROOT Directive	115
29.2.2	The SROOT Directive	115
29.2.3	The DROOT Directive	116
29.2.4	The RETAIN Directive	116

29.3 Examples of Excited State Generation	118
29.3.1 Calculating the 1A_1 states of Formaldehyde	118
29.3.2 Calculating the Excited States of the Formyl Radical	119
29.3.3 The $^2A'$ States	119
29.3.4 The $^2A''$ States	120

1 Introduction

In this chapter we describe the data requirements of Table-CI, a conventional configuration-driven CI module featuring configuration selection and energy extrapolation. The methods used in the package are described in [1]. Note that Version 6.2 of GAMESS-UK also contains a new, more efficient semi-direct version of the Table-CI module that is capable of performing significantly larger calculations. At this stage both "old" (Conventional) and "new" (Semi-direct) modules are available, and are described in detail below. To maintain compatibility with previous documentation, we first describe below the data input and file requirements of the older version. This is then followed by a description of the new code.

1.1 Sub-Module Structure of Conventional Table-CI

An outline of the sub-module structure and philosophy behind Table-CI have already been given in Part 2, material that should be taken in conjunction with the present chapter. As pointed out previously, the module comprises a set of 9 sub-modules, which must be user-driven (either implicitly or explicitly, see below) through data input. These sub modules are as follows:

- ADAPT: generation of a symmetry adapted list of integrals, derived by a pseudo-transformation from the list of 'raw' integrals;
- TRAN: integral transformation, using the list of adapted integrals generated above together with a molecular orbital coefficient array nominated by the user. Note that in contrast to the Direct-CI module, transformation is an integral part of the Table-CI module;
- TABLE: generation of the data base of pattern matrix elements required by both the SELECT and CI sub-modules (see below – this data base will have usually been made available on a given machine, but may be generated by the user using this sub-module);
- SELECT: configuration generation and subsequent selection based on a user-specified set of reference configurations and appropriate thresholds;
- CI: generation of the CI-Hamiltonian based on the set of selected configurations from SELECT and integrals from TRAN;
- DIAG: calculation of one or more CI eigenfunctions of the Hamiltonian generated under CI.

The remaining modules are optional, and may be used to analyse one or more of the CI eigenvectors:

- NATORB: to generate the spin-free natural orbitals for one or more of the calculated CI eigenvectors.
- PROP: to compute various 1-electron properties of the CI wavefunctions. Note that the natural orbitals generated above may be routed to the Dumpfile and examined by the other analysis modules of GAMESS-UK in a subsequent job.

- TM: to compute the transition moments between nominated CI eigenvectors.

In addition to the Mainfile, Dumpfile and Scratchfile, the following data sets will be used by the program.

- The Tablefile: A dataset normally assigned using the local file name (LFN) TABLE will be used as a source of pattern symbolic matrix elements in the SELECT and CI phases of the Table-CI procedure. The space requirements of the Tablefile are about 2 MBytes.
- The Sortfile: A dataset normally assigned using the LFN SORT will be used as a scratchfile in the generation of symmetry adapted and transformed integrals. The maximum space requirements of the Sortfile are about twice that of the Mainfile, although this will be much reduced in high symmetry.
- In contrast to the other post-Hartree Fock modules of GAMESS-UK, the Table-CI routines make extensive use of unformatted sequential FORTRAN data sets (or *interfaces*). The data set reference numbers and associated LFNs of these files have been given in Table 6 of Part 2.

2 Directives Controlling Conventional Table-CI Calculations

Data input characterising conventional Table-CI calculation commences with the MRDCI data line, and is typically followed by a sequence of directives, terminated by presenting a valid *Class 2* directive, such as VECTORS or ENTER. An overview of the data structure has been given in Part 2: we provide additional detail on the directives associated with each sub-module below.

2.1 MRDCI

The Table-CI data initiator consists of a single line containing the character string MRDCI in the first data field. It acts to transfer control to those routines responsible for inputting all data relevant to the MRDCI calculation. Termination of this data is achieved by presenting a valid *Class 2* directive that is not recognised by the Table-CI input routines, for example, VECTORS or ENTER.

3 Data for Conventional Table-CI Symmetry Adaptation

The Symmetry Adaptation module generates the list of symmetry adapted 1- and 2-electron integrals using as input the full list of integrals in the basis function representation. It is assumed that this latter list is not skeletonised, but has been generated with the SUPER OFF NOSYM specification in effect. The list of generated two-electron integrals is routed to the FORTRAN *interface* FTN021, the one-electron integrals to the Dumpfile.

3.1 ADAPT

The ADAPT directive is used to control the symmetry adapted integral generator, and comprises a single data line read to the variables TEXT, TEXTF and TEXTB using format (3A).

- TEXT should be set to the character string ADAPT.
- TEXTF is an optional parameter that may be used to control the quantity of printed output produced by the module. Valid settings include the strings,
 - NOPRINT, to suppress output from the module;
 - IPRINT, to produce an intermediate level of output, charactering for example the symmetry adapted functions;
 - FPRINT, to produce output suitable for debugging purposes.
- TEXTB is an optional parameter that should be set to the string BYPASS if the user wishes to bypass generation of the symmetry adapted integrals. Such usage is typically associated with restarting Table-CI calculations.

Example

```
ADAPT BYPASS
```

is a valid data line to bypass the module in a Table-CI restart job.

4 Data for Conventional Table-CI Transformation

4.1 TRAN

The TRAN directive is used to control the integral transformation module, and comprises one or more data lines. The first data line is read to the variables TEXT, ISECV, TEXTF, TEXTC, TEXTD and TEXTB using format (A,I,4A).

- TEXT should be set to the character string TRAN.
- ISECV is an optional integer parameter used to specify the section number on the Dumpfile wherein lies the set of eigenvectors to be used as the molecular orbital coefficient array in the integral transformation. If ISECV is omitted, the MOs will be either be taken from the section nominated on the ENTER directive, or from the default eigenvector section deemed to be in effect through the associated SCFTYPE. Note that examples of restoring orbitals from both MCSCF and CASSCF calculations are given below.
- TEXTF is an optional parameter that may be used to control the quantity of printed output produced by the module. Valid settings include the strings,
 - NOPRINT, to suppress output from the module;

- IPRINT, to produce an intermediate level of output;
- FPRINT, to produce output suitable for debugging purposes.
- TEXTB is an optional parameter that should be set to the string BYPASS if the user wishes to bypass generation of the transformed integrals. Such usage is typically associated with restarting Table-CI calculations.
- TEXTC is an optional parameter that should be set to one of the strings CORE or FREEZE if orbitals are to be frozen in the transformation.
- TEXTD is an optional parameter that should be set to one of the strings DISCARD or DELETE if orbitals are to be discarded in the transformation.

Additional data lines for the TRAN directive are triggered by the presence of the CORE and/or DISCARD keywords on the first line above.

1. If the CORE keyword has been presented, two additional data lines are now required to define the number (*Line 1*) and the sequence numbers (*Line 2*) of the orbitals to be frozen. *Line 1* is read in I-format to the variables (NOCORE(I), I=1, NIRREP), where NOCORE(I) specifies the number of orbitals of irreducible representation (IRrep) I that are to be frozen. NIRREP is the number of irreducible representations characterising the associated Abelian point-group in use containing more than zero orbitals. Note again that each IRrep has an associated sequence number (see Table 1) and that the input orbital set will be reordered such that
 - IRreps having zero orbitals are discarded, and
 - orbitals of common IRrep are grouped together, these groups being arranged in order of increasing IRrep number, and
 - orbitals of common IRrep are ordered according to their relative disposition in the input orbital set e.g., by eigenvalue ordering if SCF MOs.

Line 2 line is also read in I-format and specifies the sequence numbers of the frozen orbitals, in the spirit of the re-ordered sequence above. Thus the first NOCORE(1) integers specify the frozen orbitals of IRrep₁, the next NOCORE(2) integers the frozen orbitals of IRrep₂, and so on until all IRreps have been specified. Note that the integer specification within each IRrep refers to the relative ordering within that IRrep, and not within the total orbital manifold (see below).

2. If the DISCARD keyword has been presented, two additional data lines are now required to define the number (*Line 1*) and the sequence numbers (*Line 2*) of the orbitals to be discarded. *Line 1* is read in I-format to the variables (NODISC(I), I=1, NIRREP), where NODISC(I) specifies the number of orbitals of irreducible representation (IRrep) I that are to be discarded. *Line 2* is also read in I-format and specifies the sequence numbers of the discarded orbitals, in the spirit of the re-ordered sequence above. Thus the first NODISC(1) integers specify

the discarded orbitals of IRrep₁, the next NODISC(2) integers the discarded orbitals of IRrep₂, and so on until all IRreps (with more than zero orbitals) have been specified. Note that the integer specification within each IRrep again refers to the relative ordering within that IRrep, and not within the total orbital manifold (see below).

Example 1

In this example we wish to perform a valence-CI calculation on the H₂CO molecule using a DZ basis of 24 gtos, looking to freeze both the oxygen and carbon 1s orbitals, and to discard the inner-shell complement orbitals. An examination of the SCF output reveals the following orbital analysis.

```

=====
IRREP  NO. OF SYMMETRY ADAPTED
        BASIS FUNCTIONS
=====
   1           14
   2            4
   3            6
=====

```

with the following orbital assignments from the closed shell SCF:

```

=====
M.O.  IRREP  ORBITAL ENERGY  ORBITAL OCCUPANCY
=====
   1     1  -20.58952765      2.0000000
   2     1  -11.35779935     2.0000000
   3     1   -1.43525479     2.0000000
   4     1   -0.87463564     2.0000000
   5     3   -0.70990765     2.0000000
   6     1   -0.64751394     2.0000000
   7     2   -0.53989416     2.0000000
   8     3   -0.44423257     2.0000000
   9     2    0.10853108     0.0000000
  10     1    0.25726604     0.0000000
  11     1    0.28106873     0.0000000
  12     3    0.38903939     0.0000000
  13     3    0.40966861     0.0000000
  14     2    0.46216570     0.0000000
  15     1    0.65466944     0.0000000
  16     1    0.82879998     0.0000000
  17     2    0.98111608     0.0000000
  18     1    0.98701051     0.0000000
  19     3    1.07064863     0.0000000
  20     1    1.16621340     0.0000000
  21     3    1.29856111     0.0000000
  22     1    1.82320845     0.0000000
  23     1   23.76352004     0.0000000
  24     1   43.36689896     0.0000000
=====

```

Thus the orbitals of interest are of common IRrep (a_1), with sequence numbers 1,2 (core) and 13,14 (complement MOs) within the re-ordered a_1 set. The following TRAN data would freeze and discard these MOs:

```
TRAN 1 CORE DISCARD
2 0 0 0
1 2
2 0 0 0
13 14
```

or, assuming the default eigenvector specification is in effect, simply

```
TRAN CORE DISCARD
2 0 0 0
1 2
2 0 0 0
13 14
```

The following sequence would be used to simply freeze the orbitals while retaining the complete virtual manifold:

```
TRAN CORE
2 0 0 0
1 2
```

Example 2

In this example we wish to perform a valence-CI calculation on the N_2 molecule using a TZVP basis. While the molecular symmetry is $D_{\infty h}$, the symmetry adaptation and subsequent CI will be conducted in the D_{2h} point group. The resolution of the $D_{\infty h}$ into the D_{2h} orbital species is given below in Table 2. An examination of the SCF output reveals the following orbital analysis.

IRREP	NO. OF SYMMETRY ADAPTED BASIS FUNCTIONS
1	11
2	4
3	4
4	1
5	11
6	4
7	4
8	1

and the following orbital assignments from the converged closed shell SCF:

```

=====
M.O.  IRREP  ORBITAL ENERGY  ORBITAL OCCUPANCY
=====
  1    1   -15.66716423    2.0000000
  2    5   -15.66241865    2.0000000
  3    1   -1.51005217    2.0000000
  4    5   -0.76128176    2.0000000
  5    1   -0.63704931    2.0000000
  6    3   -0.63448705    2.0000000
  7    2   -0.63448705    2.0000000
  8    6    0.17408343    0.0000000
  9    7    0.17408343    0.0000000
 10    5    0.30302673    0.0000000
 11    3    0.38747796    0.0000000
 12    2    0.38747796    0.0000000
 13    1    0.42599317    0.0000000
 14    1    0.49515007    0.0000000
 15    7    0.57046706    0.0000000
 16    6    0.57046706    0.0000000
 17    5    0.92638361    0.0000000
 18    5    1.12927523    0.0000000
 19    1    1.83974927    0.0000000
 20    3    2.01160646    0.0000000
 21    2    2.01160646    0.0000000
 22    5    2.01683641    0.0000000
 23    4    2.08974396    0.0000000
 24    1    2.08974396    0.0000000
 25    7    2.16718057    0.0000000
 26    6    2.16718057    0.0000000
 27    1    2.16945852    0.0000000
 28    3    2.20023738    0.0000000
 29    2    2.20023738    0.0000000
 30    8    2.67650248    0.0000000
 31    5    2.67650248    0.0000000
 32    5    2.98166352    0.0000000
 33    1    3.57616884    0.0000000
 34    7    3.58056531    0.0000000
 35    6    3.58056531    0.0000000
 36    5    4.37707106    0.0000000
 37    1    6.02043977    0.0000000
 38    5    6.12816913    0.0000000
 39    1   35.89673292    0.0000000
 40    5   35.91926868    0.0000000
=====

```

Thus the inner-shell N1s orbitals, the $1\sigma_g$ and $1\sigma_u$ transform as a_g and b_{1u} respectively in D_{2h} symmetry, with IRrep numbers 1 and 5. Both correspond of course to the first orbital in the appropriate IRrep. The following sequence would be used to simply freeze the orbitals while retaining the complete virtual manifold:

```

TRAN CORE
1 0 0 0 1 0 0 0
1 1

```

Turning to the inner-shell complement orbitals, we again find the corresponding IRreps, 1 and 5, with the orbitals the highest lying member in each case, with relative sequence number of 11. Thus the following TRAN data would act to both freeze and discard the inner-shells and their complement MOs:

```
TRAN CORE DISCARD
1 0 0 0 1 0 0 0
1 1
1 0 0 0 1 0 0 0
11 11
```

Further examples of TRAN data will be discussed below in the section discussing Reference Function specification within the SELECT data.

5 Data for Conventional Table-CI Data-base Generation

The 'data-base' of pattern symbolic matrix elements required by both the Selection and CI modules may be generated by the user in the course of any Table-CI calculation. It is not envisaged that this step will be necessary, since the data base will in general be already installed on those machines on which GAMESS-UK is available, the data set being allocated to the program with LFN TABLE.

5.1 TABLE

The TABLE directive is used to request and control the data-base generator, and comprises a single data line read to the variables TEXT, TEXTF using format (2A).

- TEXT should be set to the character string TABLE.
- TEXTF is an optional parameter that may be used to control the quantity of printed output produced by the module. Valid settings include the strings,
 - NOPRINT, to suppress output from the module;
 - IPRINT, to produce an intermediate level of output;
 - FPRINT, to produce output suitable for debugging purposes.

6 Data for Conventional Table-CI Selection

Data for the configuration selection module is initiated with the SELECT directive, followed by those directives characterising the symmetry of the state(s) of interest and reference configurations (CNTRL, SPIN, SYMMETRY, CONF etc.) and terminated by data (ROOTS, THRESH) controlling the process of selection.

6.1 SELECT

The SELECT directive is used to control the configuration selection module, and comprises a single data line read to the variables TEXT, TEXTF and TEXTB using format (3A).

- TEXT should be set to the character string SELECT.
- TEXTF is an optional parameter that may be used to control the quantity of printed output produced by the module. Valid settings include the strings,
 - NOPRINT, to suppress the major part of the output from the module, in particular all details of the perturbative energy lowerings associated with the initial set of configurations;
 - IPRINT, to produce an intermediate level of output;
 - FPRINT, to produce output suitable for debugging purposes. This includes the energy lowerings associated with the complete configuration list.
- TEXTB is an optional parameter that should be set to the string BYPASS if the user wishes to bypass SELECT processing. Such usage is typically associated with restarting Table-CI calculations.

6.2 CNTRL

This directive consists of one line read to variables TEXT, NELEC using format (A,I).

- TEXT should be set to the character string CNTRL.
- NELEC is used to specify the total number of 'active' electrons in the CI calculation. Note that any inner shell electrons frozen out under control of the TRAN directive should not be included.

The CNTRL directive may be omitted, when the program will set NELEC to the value characterising the SCF process implicit within the RUNTYPE CI processing, subtracting out those electrons nominated through the CORE parameter of the TRAN data.

6.3 SPIN

This directive consists of one line read to variables TEXT, NSPIN using format (A,I).

- TEXT should be set to the character string SPIN.
- NSPIN is used to specify the spin degeneracy of the CI wavefunction of the electronic eigenstate(s) of interest, using the values 1,2,3 etc. for singlet, doublet, triplet states etc. respectively. It is also possible to use one of the character strings SINGLET, DOUBLET, TRIPLET, QUARTET and QUINTET to specify NSPIN.

The SPIN directive may be omitted, when the program will set NSPIN to the value specified on the MULTIPLICITY directive (see section 4.6.2)

Example

```
SPIN 3
SPIN TRIPLET
```

are equivalent; the wavefunction will be three-fold spin degenerate.

6.4 SYMMETRY

This directive consists of one line read to variables TEXT, NSYM using format (A,I).

- TEXT should be set to the character string SYMMETRY.
- NSYM is an integer parameter used to specify the spatial symmetry of the CI wavefunction, and is set to the appropriate sequence number of the required irreducible representation (see Table 1).

The SYMMETRY directive may be omitted, when the program will set NSYM to 1 i.e., the totally symmetric representation. (see section 4.6.2)

Example

In a system of C_{2v} symmetry, the data line

```
SYMMETRY 3
```

would be required when performing calculations on states of B_2 symmetry. Failure to present the directive in such cases will lead to the default A_1 symmetry.

6.5 SINGLES

This directive consists of one line read to variables TEXT, NREF using format (A,I).

- TEXT should be set to the character string SINGLES.
- NREF is an integer parameter used to nominate a particular configuration within the set of reference functions. The selection module will then retain in the final CI all single excitations with respect to the nominated function *regardless* of their computed energy lowerings.

Table 1: Resolution of the $C_{\infty v}$ Species into the C_{2v} Species

Orbital		IRrep
$C_{\infty v}$	C_{2v}	Sequence No.
σ	a_1	1
$\delta_{x^2-y^2}$		
π_x	b_1	2
π_y	b_2	3
δ_{xy}	a_2	4

Table 2: Resolution of the $D_{\infty h}$ Species into the D_{2h} Species

Orbital		IRrep
$D_{\infty h}$	D_{2h}	Sequence No.
σ_g	a_g	1
δ_{g,x^2-y^2}		
$\pi_{u,x}$	b_{3u}	2
$\pi_{u,y}$	b_{2u}	3
$\delta_{g,xy}$	b_{1g}	4
σ_u	b_{1u}	5
δ_{u,x^2-y^2}		
$\pi_{g,x}$	b_{2g}	6
$\pi_{g,y}$	b_{3g}	7
$\delta_{u,xy}$	a_u	8

The SINGLES directive may be omitted, when the program will use the energy lowerings as the sole criteria for including configurations in the final CI.

Example

Presenting the data line

```
SINGLES 1
```

in a Table-CI calculation of a closed-shell system, where the SCF configuration is the first in the CONF list, will lead to the inclusion of all single excitations with respect to the SCF function in the final CI. Such inclusion leads, of course, to a marked improvement in the quality of one-electron properties computed from the CI wavefunction.

6.6 CONF

The CONF directive is used to specify the reference CSFs for the CI expansion. The first line of the CONF directive is set to the character string CONF. Each subsequent line defines a

reference CSF by specifying the sequence numbers of the component active orbitals in l-format. A given reference CSF is defined by

1. the number of open-shell orbitals (NOPEN). NOPEN includes any unpaired orbitals together with those non-identical spin-coupled pairs open to substitution.
2. NOPEN integers specifying the sequence numbers of these orbitals
3. the (NELEC-NOPEN)/2 sequence numbers of the doubly-occupied orbitals i.e., the identically spin-coupled orbitals

where the sequence-numbers refers to the symmetry ordered orbitals performed at the outset of processing. Within the set of open- and doubly-occupied orbitals, the MOs are presented in groups of common IRrep, with the groups presented in order of increasing IRrep sequence number. Note that all reference function nominated by CONF *must* be of the same symmetry as that nominated on the SYMMETRY directive. A few examples will help clarify this order of presentation.

Example 1

Consider performing a valence-CI calculation on the PH₃ molecule using a 6-31G(*) basis. While the molecular symmetry is C_{3v}, the symmetry adaptation and subsequent CI will be conducted in the C_s point group. An examination of the SCF output reveals the following orbital analysis.

```

=====
IRREP  NO. OF SYMMETRY ADAPTED
        BASIS FUNCTIONS
=====
   1           18
   2           7
=====

```

and the following orbital assignments characterising the closed-shell SCF configuration:

$$1a_1^2 2a_1^2 1e^4 3a_1^2 4a_1^2 2e^4 5a_1^2 \quad (1)$$

or, in the C_s symmetry representation:

$$1a'^2 2a'^2 1a''^2 3a'^2 4a'^2 5a'^2 6a'^2 2a''^2 7a'^2 \quad (2)$$

```

=====
M.O.  IRREP  ORBITAL ENERGY  ORBITAL OCCUPANCY
=====
   1     1    -79.93661395      2.0000000
   2     1     -7.48916431      2.0000000
   3     1     -5.38319410      2.0000000
   4     2     -5.38319405      2.0000000
=====

```

5	1	-5.38149104	2.0000000
6	1	-0.85610769	2.0000000
7	1	-0.52191424	2.0000000
8	2	-0.52191424	2.0000000
9	1	-0.38579686	2.0000000
10	1	0.16819544	0.0000000
11	2	0.16819544	0.0000000
12	1	0.26587776	0.0000000
13	1	0.46072690	0.0000000
14	2	0.46072690	0.0000000
15	1	0.47871033	0.0000000
16	1	0.56106989	0.0000000
17	1	0.89229884	0.0000000
18	2	0.89229885	0.0000000
19	2	0.91131383	0.0000000
20	1	0.91131383	0.0000000
21	1	0.93118300	0.0000000
22	1	1.17900613	0.0000000
23	2	1.45058658	0.0000000
24	1	1.45058658	0.0000000
25	1	3.78674557	0.0000000

=====

Based on the above output, the CONF data lines may be deduced from the following table, where we assume that we wish to freeze the five inner shell orbitals:

$$1a'^2 2a'^2 1a''^2 3a'^2 4a'^2 \quad (3)$$

IRrep	IRrep No.	No. of Basis Functions	Frozen MOs	Active MOs	Sequence Nos.
a'	1	18	4	14	1-14
a''	2	7	1	6	15-20

To perform an 8-electron valence-CI calculation, involving the SCF configuration and two degenerate (1e)' to (2e)' doubly-excited configurations

$$5a'^2 8a'^2 2a''^2 7a'^2 \quad (4)$$

and

$$5a'^2 6a'^2 3a''^2 7a'^2 \quad (5)$$

would require the following CONF data:

```
CONF
0 1 2 3 15
0 1 3 4 15
0 1 2 3 16
```

The complete data file for performing the SCF and subsequent CI would then be as follows:

```

TITLE
PH3 * 6-31G* VALENCE-CI 3M/1R
SUPER OFF NOSYM
ZMAT
P
H 1 RPH
H 1 RPH 2 THETA
H 1 RPH 2 THETA 3 THETA 1
VARIABLES
RPH 2.685
THETA 93.83
END
BASIS 6-31G*
RUNTYPE CI
MRDCI
TRAN CORE
4 1
1 TO 4 1
SELECT
SINGLES 1
CONF
0 1 2 3 15
0 1 3 4 15
0 1 2 3 16
NATORB
ENTER

```

Example 2

In this example we wish to perform a valence-CI calculation on the CuCl molecule using a 3-21G basis. While the molecular symmetry is $C_{\infty v}$, the symmetry adaptation and subsequent CI will be conducted in the C_{2v} point group. The resolution of the $C_{\infty v}$ into the C_{2v} orbital species is given in Table 2. An examination of the SCF output reveals the following orbital analysis.

```

=====
IRREP  NO. OF SYMMETRY ADAPTED
        BASIS FUNCTIONS
=====
1           22
2           9
3           9
4           2
=====

```

and the following orbital assignments from the converged closed shell SCF:

```

=====
M.O.  IRREP  ORBITAL ENERGY  ORBITAL OCCUPANCY
=====
1      1     -326.84723972      2.0000000
2      1     -104.02836336      2.0000000
3      1     -40.71695637       2.0000000

```

4	1	-35.46377378	2.0000000
5	3	-35.45608069	2.0000000
6	2	-35.45608068	2.0000000
7	1	-10.42193940	2.0000000
8	1	-7.88512031	2.0000000
9	2	-7.88222844	2.0000000
10	3	-7.88222844	2.0000000
11	1	-5.07729175	2.0000000
12	1	-3.38247056	2.0000000
13	3	-3.35978308	2.0000000
14	2	-3.35978307	2.0000000
15	1	-1.01099628	2.0000000
16	3	-0.53702948	2.0000000
17	2	-0.53702947	2.0000000
18	4	-0.49640067	2.0000000
19	1	-0.49640067	2.0000000
20	1	-0.44715317	2.0000000
21	3	-0.39988537	2.0000000
22	2	-0.39988537	2.0000000
23	1	-0.35127248	2.0000000
24	1	0.00023285	0.0000000
25	3	0.06300102	0.0000000
26	2	0.06300102	0.0000000
27	1	0.12855448	0.0000000
28	1	0.19287013	0.0000000
29	3	0.25729975	0.0000000
30	2	0.25729975	0.0000000
31	1	0.39720201	0.0000000
32	1	0.86197727	0.0000000
33	2	0.88942618	0.0000000
34	3	0.88942618	0.0000000
35	1	1.01877167	0.0000000
36	1	2.16694989	0.0000000
37	3	3.96181512	0.0000000
38	2	3.96181512	0.0000000
39	4	3.98212497	0.0000000
40	1	3.98212497	0.0000000
41	1	4.08851360	0.0000000
42	1	24.51368240	0.0000000

=====

Based on the above output, the CONF data lines may be deduced from the following table, where we assume that we wish to freeze the first 14 inner shell orbitals:

$$1\sigma^2 2\sigma^2 3\sigma^2 4\sigma^2 1\pi^4 5\sigma^2 6\sigma^2 2\pi^4 7\sigma^2 8\sigma^2 3\pi^4 \quad (6)$$

IRrep	IRrep No.	No. of Basis Functions	Frozen MOs	Active MOs	Sequence Nos.
a ₁	1	22	8	14	1-14
b ₁	2	9	3	6	15-20
b ₂	3	9	3	6	21-26
a ₂	4	2	0	2	27-28

To perform an 18-electron valence-CI calculation, based on the SCF configuration

$$9\sigma^2 4\pi^4 1\delta^4 10\sigma^2 5\pi^4 11\sigma^2 \quad (7)$$

would require the following CONF data:

```
CONF
0 1 2 3 4 15 16 21 22 27
```

The complete data file for performing the SCF and subsequent CI would then be as follows:

```
TITLE\CUCL .. 3-21G
ZMAT ANGSTROM\CU\CL 1 CUCL\
VARIABLES\CUCL 2.093 \END
BASIS 3-21G
RUNTYPE CI
MRDCI
TRAN CORE
8 3 3 0
1 TO 8 1 TO 3 1 TO 3
SELECT
SINGLES 1
CONF
0 1 2 3 4 15 16 21 22 27
NATORB
ENTER
```

The inclusion of a second reference configuration corresponding to the doubly excited configuration

$$9\sigma^2 4\pi^4 1\delta^4 10\sigma^2 5\pi^4 12\sigma^2 \quad (8)$$

would require the following CONF data;

```
CONF
0 1 2 3 4 15 16 21 22 27
0 1 2 3 5 15 16 21 22 27
```

Example 3

Consider performing a valence-CI calculation on the SiH_4 molecule using a 6-31G(*) basis. While the molecular symmetry is T_d , the symmetry adaptation and subsequent CI will be conducted in the C_{2v} point group. An examination of the SCF output reveals the following orbital analysis.

```
=====
IRREP NO. OF SYMMETRY ADAPTED
      BASIS FUNCTIONS
=====
  1           9
  2           6
  3           6
  4           6
=====
```

and the following orbital assignments from the converged closed shell SCF:

```

=====
M.O.  IRREP  ORBITAL ENERGY  ORBITAL OCCUPANCY
=====
  1    1   -68.77130710      2.0000000
  2    1    -6.12943325      2.0000000
  3    2    -4.23503117      2.0000000
  4    3    -4.23503117      2.0000000
  5    4    -4.23503117      2.0000000
  6    1    -0.73046864      2.0000000
  7    4    -0.48480821      2.0000000
  8    3    -0.48480821      2.0000000
  9    2    -0.48480821      2.0000000
 10    2     0.16291387      0.0000000
 11    3     0.16291387      0.0000000
 12    4     0.16291387      0.0000000
 13    1     0.25681257      0.0000000
 14    1     0.33606346      0.0000000
 15    3     0.37087856      0.0000000
 16    2     0.37087856      0.0000000
 17    4     0.37087856      0.0000000
 18    1     0.79946861      0.0000000
 19    1     0.79946861      0.0000000
 20    4     0.86232544      0.0000000
 21    3     0.86232544      0.0000000
 22    2     0.86232544      0.0000000
 23    1     1.23833149      0.0000000
 24    4     1.44033091      0.0000000
 25    3     1.44033091      0.0000000
 26    2     1.44033091      0.0000000
 27    1     3.13181655      0.0000000
=====

```

Based on the above output, the CONF data lines may be deduced from the following table, where we assume that we wish to freeze the first 5 silicon inner shell orbitals:

IRrep	IRrep No.	No. of Basis Functions	Frozen MOs	Active MOs	Sequence Nos.
a ₁	1	9	2	7	1-7
b ₁	2	6	1	5	8-12
b ₂	3	6	1	5	13-17
a ₂	4	6	1	5	18-22

To perform a 8-electron valence-CI calculation, based on the SCF configuration would require the following CONF data:

```

CONF
0 1 8 13 18

```

The complete data file for performing the SCF and subsequent CI would then be as follows:

```

TITLE
SIH4 * 6-31G* MRDCI VALENCE-CI 1M/1R
ZMAT
SI
H 1 SIH
H 1 SIH 2 109.471
H 1 SIH 2 109.471 3 120.0
H 1 SIH 2 109.471 4 120.0
VARIABLES
SIH 2.80
END
BASIS 6-31G*
RUNTYPE CI
MRDCI
TRAN CORE
2 1 1 1
1 2 1 1 1
SELECT
CONF
0 1 8 13 18
SINGLES 1
NATORB
ENTER

```

Example 4

In this example we wish to perform a valence-CI calculation on the N_2 molecule using a 4-31G(*) basis. While the molecular symmetry is $D_{\infty h}$, the symmetry adaptation and subsequent CI will be conducted in the D_{2h} point group. The resolution of the $D_{\infty h}$ into the D_{2h} orbital species is given in Table 2. An examination of the SCF output reveals the following orbital analysis.

```

=====
IRREP  NO. OF SYMMETRY ADAPTED
        BASIS FUNCTIONS
=====
  1         8
  2         3
  3         3
  4         1
  5         8
  6         3
  7         3
  8         1
=====

```

and the following orbital assignments from the converged closed shell SCF:

```

=====
M.O.  IRREP  ORBITAL ENERGY  ORBITAL OCCUPANCY
=====
  1    1    -15.65951533    2.0000000
  2    5    -15.65474750    2.0000000

```

3	1	-1.50615941	2.0000000
4	5	-0.75782277	2.0000000
5	1	-0.63244925	2.0000000
6	3	-0.63135826	2.0000000
7	2	-0.63135826	2.0000000
8	6	0.20154861	0.0000000
9	7	0.20154861	0.0000000
10	5	0.63883097	0.0000000
11	1	0.82491489	0.0000000
12	3	0.89634343	0.0000000
13	2	0.89634343	0.0000000
14	1	0.91812387	0.0000000
15	7	1.10036132	0.0000000
16	6	1.10036132	0.0000000
17	5	1.17625689	0.0000000
18	5	1.66995008	0.0000000
19	4	1.70518236	0.0000000
20	1	1.70518236	0.0000000
21	3	1.91001614	0.0000000
22	2	1.91001614	0.0000000
23	8	2.29436539	0.0000000
24	5	2.29436539	0.0000000
25	1	2.84356916	0.0000000
26	7	3.00847817	0.0000000
27	6	3.00847817	0.0000000
28	5	3.37447679	0.0000000
29	1	3.71753400	0.0000000
30	5	4.09917273	0.0000000

=====

Based on the above output, the CONF data lines may be deduced from the following table, where we assume that we wish to freeze the two N1s inner shell orbitals:

IRrep	IRrep No.	No. of Basis Functions	Frozen MOs	Active MOs	Sequence Nos.
σ_g	1	8	1	7	1-7
$\pi_{u,x}$	2	3	0	3	8-10
$\pi_{u,y}$	3	3	0	3	11-13
$\delta_{g,xy}$	4	1	0	1	14
σ_u	5	8	1	7	15-21
$\pi_{g,x}$	6	3	0	3	22-24
$\pi_{g,y}$	7	3	0	3	25-27
$\delta_{u,xy}$	8	1	0	1	28

To perform a 10-electron valence-CI calculation, based on the SCF configuration

$$2\sigma_g^2 2\sigma_u^2 3\sigma_g^2 1\pi_u^4 \quad (9)$$

and associated π to π^* excitations

$$2\sigma_g^2 2\sigma_u^2 3\sigma_g^2 1\pi_{u,y}^2 2\pi_{u,x}^2 \quad (10)$$

$$2\sigma_g^2 2\sigma_u^2 3\sigma_g^2 1\pi_{u,x}^2 2\pi_{u,y}^2 \quad (11)$$

$$2\sigma_g^2 2\sigma_u^2 3\sigma_g^2 (1\pi_{u,x} 2\pi_{u,x}) (1\pi_{u,y} 2\pi_{u,y}) \quad (12)$$

would require the following CONF data:

```
CONF
0 1 2 8 11 15
0 1 2 11 15 22
0 1 2 8 15 25
4 8 11 22 25 1 2 15
```

The complete data file for performing the SCF and subsequent CI would then be as follows:

```
TITLE\N2 .. 4-31G*
SUPER OFF NOSYM
ZMAT ANG\N\N 1 NN
VARIABLES\NN 1.05 \END
BASIS 4-31G*
RUNTYPE CI
MRDCI
TRAN CORE
1 0 0 0 1 0 0 0
1 1
SELECT
SINGLES 1
CONF
0 1 2 8 11 15
0 1 2 11 15 22
0 1 2 8 15 25
4 8 11 22 25 1 2 15
NATORB IPRIN
ENTER
```

Now consider the corresponding calculation performed in a smaller 3-21G basis. An examination of the SCF output reveals the following orbital analysis.

```
=====
IRREP  NO. OF SYMMETRY ADAPTED
        BASIS FUNCTIONS
=====
  1          5
  2          2
  3          2
  5          5
  6          2
  7          2
=====
```

and the following orbital assignments from the converged closed shell SCF:

```

=====
M.O.  IRREP  ORBITAL ENERGY  ORBITAL OCCUPANCY
=====
  1    1   -15.59983859    2.0000000
  2    5   -15.59796932    2.0000000
  3    1    -1.54485796    2.0000000
  4    5    -0.74550130    2.0000000
  5    2    -0.63373069    2.0000000
  6    3    -0.63373069    2.0000000
  7    1    -0.62012170    2.0000000
  8    6     0.20546760    0.0000000
  9    7     0.20546760    0.0000000
 10    5     0.79186362    0.0000000
 11    1     1.16445455    0.0000000
 12    2     1.26826720    0.0000000
 13    3     1.26826720    0.0000000
 14    7     1.43237859    0.0000000
 15    6     1.43237859    0.0000000
 16    5     1.55279124    0.0000000
 17    1     1.83635478    0.0000000
 18    5     2.63677794    0.0000000
=====

```

Note that there are now *no* MOs of IRREP 4 or 8. Based on the above output, the CONF data lines may be deduced from the following table, where we again assume that we wish to freeze the two N1s inner shell orbitals:

IRrep	IRrep No.	No. of Basis Functions	Frozen MOs	Active MOs	Sequence Nos.
σ_g	1	5	1	4	1-4
$\pi_{u,x}$	2	2	0	2	5-6
$\pi_{u,y}$	3	2	0	2	7-8
σ_u	5	5	1	4	9-12
$\pi_{g,x}$	6	2	0	2	13-14
$\pi_{g,y}$	7	2	0	2	15-16

To perform an 10-electron valence-CI calculation, based on the SCF configuration would require the following CONF data:

```

CONF
0 1 2 5 7 9

```

The complete data file for performing the SCF and subsequent CI would then be as follows:

```

TITLE\N2 .. 3-21G
SUPER OFF NOSYM
ZMAT ANGS\N\N 1 NN
VARIABLES\NN 1.05 \END
BASIS 3-21G
RUNTYPE CI

```

```

MRDCI
TRAN CORE
1 0 0 1 0 0
1      1
SELECT
SINGLES 1
CONF
0 1 2 5 7 9
NATORB IPRIN
ENTER

```

Example 5

In this example we wish to perform a valence-CI calculation on the CaH_2 molecule using a 3-21G basis. While the molecular symmetry is $D_{\infty h}$, the symmetry adaptation and subsequent CI will be conducted in the D_{2h} point group. An examination of the SCF output reveals the following orbital analysis.

```

=====
IRREP  NO. OF SYMMETRY ADAPTED
        BASIS FUNCTIONS
=====
  1          7
  2          4
  3          4
  5          6
=====

```

and the following orbital assignments from the converged closed shell SCF:

```

=====
M.O.  IRREP  ORBITAL ENERGY  ORBITAL OCCUPANCY
=====
  1    1   -148.37173884    2.0000000
  2    1   -16.76521275    2.0000000
  3    3   -13.55586861    2.0000000
  4    2   -13.55586861    2.0000000
  5    5   -13.55460610    2.0000000
  6    1    -2.26357685    2.0000000
  7    3    -1.36160958    2.0000000
  8    2    -1.36160958    2.0000000
  9    5    -1.35089927    2.0000000
 10    1    -0.34923025    2.0000000
 11    5    -0.31649941    2.0000000
 12    2     0.02334207    0.0000000
 13    3     0.02334207    0.0000000
 14    1     0.04980631    0.0000000
 15    5     0.09478404    0.0000000
 16    1     0.12395484    0.0000000
 17    3     0.13549605    0.0000000
 18    2     0.13549605    0.0000000
 19    5     0.28345574    0.0000000

```

```

20    1    1.32404002    0.0000000
21    5    1.45900204    0.0000000
=====

```

Based on the above output, the CONF data lines may be deduced from the following table, where we assume that we wish to freeze the nine Ca inner shell orbitals:

	IRrep	IRrep	No. of Basis	Frozen	Active	Sequence
		No.	Functions	MOs	MOs	Nos.
σ_g	1		7	3	4	1-4
$\pi_{u,x}$	2		4	2	2	5-6
$\pi_{u,y}$	3		4	2	2	7-8
σ_u	5		6	2	4	9-12

To perform an 4-electron valence-CI calculation, based on the SCF configuration would require the following CONF data:

```

CONF
0 1 9

```

The complete data file for performing the SCF and subsequent CI would then be as follows:

```

TITLE\CAH2 .. 3-21G
SUPER OFF NOSYM
ZMAT ANGS\CA\X 1 1.0\ H 1 CAH 2 90.0\H 1 CAH 2 90.0 3 THETA
VARIABLES\CAH 2.148 \THETA 180.0 \END
BASIS 3-21G
RUNTYPE CI
MRDCI
TRAN CORE
3 2 2 2
1 2 3 1 2 1 2 1 2
SELECT
SINGLES 1
CONF
0 1 9
NATORB IPRIN
ENTER

```

6.7 ROOTS

The ROOTS directive is used to specify those eigenvectors of the 'root' secular problem to be used in the process of selection, with the energy contributions of the configurations computed with respect to the nominated vectors. The directive consists of a single data line with the character string ROOTS in the first data field. Subsequent data comprises integer variables used to specify the *number* of root eigenstates (NROOT) and the *sequence numbers* of these vectors within the matrix of zero-order eigenvectors, (IROOT(I),I=1,NROOT). Two formats may be used in this specification:

1. If the lowest NROOT vectors are to be used, then the data line is read to the variables TEXT, NROOT using format (A,I);
 - TEXT is set to the character string ROOTS;
 - NROOT is an integer specifying the number of roots to be used, where the sequence numbers of the roots will be 1–NROOT.
2. If the NROOT vectors to be used are not the lowest in the root eigenvector matrix, then the sequence numbers within this matrix must be specified. The data line is then read to the variables TEXT, NROOT, (IROOT(I), I=1,NROOT), using format (A, (NROOT+1) I):
 - TEXT and NROOT are defined as above;
 - NROOT integers are read to the array IROOT defining the vectors of the zero-order matrix to be used in selection.

We now provide some further notes on the directive:

- the ROOTS directive may be omitted, when the energy contributions are calculated with reference to the lowest eigenstate of the root problem only. Omission of the directive is thus equivalent to presenting the data line

```
ROOTS 1
```

- The number of root eigenstates to be specified will depend on the number of states required in the final CI. Thus if NVEC roots of the final CI matrix are to be subsequently generated in DIAG processing, the user should ideally perform selection with respect to at least the corresponding NVEC roots of the root secular problem to ensure a consistent treatment of each of the required states. The choice of the reference set will clearly prove crucial and should be such as to ensure a one to one correspondence between each of the final CI vectors and a certain vector of the root problem. Indeed the whole process of extrapolation to zero threshold is meaningless if this condition is not obeyed.

6.8 THRESH

This directive defines the threshold factors to be used in the process of configuration selection, and consists of a single line read to variables TEXT, TMIN, TINC using format (A,2F).

- TEXT should be set to the character string THRESH.
- TMIN should be set to the minimum threshold factor (in units of micro-hartree, μH) to be used in selection. Any CSF with a computed energy lowering greater than TMIN will be retained in the final list of selected configurations.
- TINC should be set to the threshold increment to be used in the process of extrapolation. This process involves solution of the final secular problem at a range of increasing thresholds defined by TMIN, TMIN + TINC, TMIN + 2 × TINC, ..., TMIN + (NEXTRP-1) × TINC, TMIN + NEXTRP × TINC where NEXTRP is the number of extrapolation passes requested under control of the EXTRAP directive (see the DIAG directives).

The THRESH directive may be omitted, when TMIN will be set to 30.0 and TINC to 10.0. With the default EXTRAP setting, this would lead to the solution of the T=50, 40 and 30 μ H secular problem.

Example

```
THRESH 5.0 5.0
```

```
THRESH 5 5
```

are equivalent, causing T_{min} and T_{inc} to be set to 5 microhartree.

7 Data for Conventional Table-CI H-Matrix Construction

7.1 CI

The CI directive comprises a single data line read to the variables TEXT, TEXTF and TEXTB using format (3A).

- TEXT should be set to the character string CI.
- TEXTF is an optional parameter that may be used to control the quantity of printed output produced by the module. Valid settings include the strings,
 - NOPRINT, to suppress the major part of the output from the module;
 - IPRINT, to produce an intermediate level of output;
 - FPRINT, to produce output suitable for debugging purposes.
- TEXTB is an optional parameter that should be set to the string BYPASS if the user wishes to bypass CI processing. Such usage is typically associated with restarting Table-CI calculations.

8 Data for Conventional Table-CI Diagonalisation

Data input controlling the diagonalisation of the final CI Hamiltonian is introduced by the DIAG directive. The process of extrapolation to zero selection threshold involves the diagonalisation module solving not just one, but several secular problems corresponding to a range of selection thresholds. The number of so called 'extrapolation passes' is specified by the EXTRAP directive. In default, the module will generate NROOT eigenvectors of the CI matrix on each pass, where NROOT is the number of roots specified by the ROOTS directive at selection time. Thus the solutions of the zero-order Hamiltonian will be used through a maximum overlap criterion in deriving the final CI eigenvectors. Additional data may be specified to override this default and provide various convergence and printing controls.

8.1 DIAG

The DIAG directive comprises a single data line read to the variables TEXT, TEXTF and TEXTB using format (3A)

- TEXT should be set to the character string DIAG
- TEXTF is an optional parameter that may be used to control the quantity of printed output produced by the module. Valid settings include the strings,
 - NOPRINT, to suppress the major part of the output from the module;
 - IPRINT, to produce an intermediate level of output;
 - FPRINT, to produce output suitable for debugging purposes.
- TEXTB is an optional parameter that should be set to the string BYPASS if the user wishes to bypass DIAG processing. Such usage is typically associated with restarting Table-CI calculations.

8.2 EXTRAP

This directive consists of one line read to variables TEXT, MAXE using format (A,I).

- TEXT should be set to the character string EXTRAP.
- MAXE specifies the maximum number of extrapolation cycles to be carried out by the Davidson diagonalizer.

The directive may be omitted, when MAXE will take the default value 2.

8.3 ACCURACY

This directive may be used to define the diagonalisation thresholds for the extrapolation passes and for the final secular problem (at the threshold T_{min}), and consists of a single line read to variables TEXT, THRESH0, THRESHF using format (A,2F).

- TEXT should be set to the character string ACCURACY or DTHRESH;
- THRESH0: On the NEXTRP extrapolation passes, the diagonalization is converged to a threshold THRESH0;
- THRESHF: On the final diagonalisation, solving the secular problem corresponding to the threshold T_{min} , the diagonalization is converged to a threshold THRESHF.

The THRESH directive may be omitted, when THRESH0 will be set to 0.005 and THRESHF to 0.001.

Example

Assuming the default selection thresholds ($T_{min}=10$, $T_{inc}=10$) and the default number of extrapolation passes (NEXTRP=2), then presenting the data line

```
ACCURACY 0.005 0.0005
```

will result in a diagonalisation threshold of 0.005 for the two extrapolation passes (corresponding to solving the secular problem at selection thresholds of 20 and 30 microhartree), and a threshold of 0.0005 for the final secular problem, that corresponding to the 10 microhartree selection.

8.4 MAXD

This directive consists of one line read to variables TEXT, MAXD using format (A,I).

- TEXT should be set to the character string MAXD.
- MAXD specifies the maximum number of iterative cycles to be carried out by the Davidson diagonalizer.

The directive may be omitted, when MAXD will take the default value 50.

8.5 TRIAL

This directive may be used to define a trial CI wavefunction by diagonalising a sub-Hamiltonian obtained by sampling the diagonal elements of the CI-Hamiltonian, and selecting the lowest energy terms. The directive may be used to define the number of such elements to be included in the sub-Hamiltonian, and is read to the variables TEXT, NTRIAL using format (A,I).

- TEXT should be set to the character string TRIAL;
- NTRIAL should be set to the number of lowest-energy configurations in the CI list to be used in constructing the sub-Hamiltonian.

The TRIAL directive may be omitted, when NTRIAL will be set to the maximum allowed value of 80.

8.6 PRINT

The PRINT directive may be used to control the printing of CI coefficients and weights throughout the extrapolation passes and in the final analysis. This directive consists of a single data line read to variables TEXT, PTHR, PTHRCC, IFLAG using format (A,2F,I).

- TEXT should be set to the character string PRINT.
- CI coefficients less than PTHR in absolute magnitude will not be printed during the extrapolation passes.
- CI weights (coefficients²) less than PTHRCC in absolute magnitude will not be printed in the final analysis of the CI wavefunctions.
- IFLAG may be used to control the printing of the CI wavefunctions in the event that the diagonalisation does not converge. Setting IFLAG=1 will cause a detailed print of the CI vectors corresponding to each root.

This directive may be omitted, when the defaults PTHR=0.05 and PTHRCC=0.002 will be taken.

9 Data for Conventional Table-CI Natural Orbitals

9.1 Natural Orbital Data - NATORB

The NATORB directive is used to request Natural Orbital (NO) generation, and comprises a single data line read to the variables TEXT, TEXTF and TEXTB using format (3A).

- TEXT should be set to the character string NATORB.
- TEXTF is an optional parameter that may be used to control the quantity of printed output produced by the module. Valid settings include the strings,
 - NOPRINT, to suppress the major part of the output from the module;
 - IPRINT, to produce an intermediate level of output. This option should be set to generate a print of the natural orbital coefficient array(s);
 - FPRINT, to produce output suitable for debugging purposes.
- TEXTB is an optional parameter that should be set to the string BYPASS if the user wishes to bypass NATORB processing. Such usage is typically associated with restarting Table-CI calculations.

9.2 Natural Orbital Data - CIVEC

The CIVEC directive is used to specify those eigenvectors of the CI-matrix to be analysed. The directive consists of a single data line with the character string CIVEC in the first data field. If natural orbitals associated with NVEC eigenvectors of the secular problem are to be generated, subsequent data fields should contain NVEC integers, the integers specifying the numbering of the CI-eigenvectors on the FORTRAN *interface*, FTN036, as generated by the DIAG sub-module. If the CIVEC directive is omitted under NATORB processing the natural orbitals of the first CI-vector will be generated.

Example

```
CIVEC 1 3
```

The above data line may be used to generate natural orbitals from the first and third CI-eigenvector generated by the DIAG sub-module.

9.3 Natural Orbital Data - PUTQ

The PUTQ directive may be used to route spin-free natural orbitals to the Dumpfile, and consists of a single dataline with the first two fields read to variables TEXT, TYPE using format (2A).

- TEXT should be set to the character string PUTQ.
- TYPE should be set to one of the character strings AOS, A.O. or SABF, defining the basis representation required for the output NOs. The character string AOS and A.O. will yield the NOs in the basis function representation, suitable for subsequent input to the other analysis modules of GAMESS-UK. The string SABF will result in the NO expansion in the symmetry adapted basis representation, and should be used when performing iterative natural orbital calculations (see section 6.13 below)

The remaining data consists of a sequence of NVEC integers, (between 0 and 350 inclusive) specifying the section number of the Dumpfile where the spin-free NOs derived from the NVEC CI-vectors nominated by the CIVEC directive are to be placed.

Example

```
PUTQ AOS 100 120
```

The spin-free NOs in the basis-set representation are output to sections 100 and 120 respectively of the Dumpfile. A section setting of 0 on the PUTQ directive will act to suppress natural orbital output to the Dumpfile.

10 Data for Conventional Table-CI One-electron Properties**10.1 PROP**

The PROP directive is used to request the computation of one-electron properties and comprises a single data line read to the variables TEXT, TEXTF and TEXTB using format (3A).

- TEXT should be set to the character string PROP.
- TEXTF is an optional parameter that may be used to control the quantity of printed output produced by the module. Valid settings include the strings,

- NOPRINT, to suppress the major part of the output from the module;
 - IPRINT, to produce an intermediate level of output;
 - FPRINT, to produce output suitable for debugging purposes.
- TEXTB is an optional parameter that should be set to the string BYPASS if the user wishes to bypass PROP processing. Such usage is typically associated with restarting Table-CI calculations.

10.2 CIVEC

The CIVEC directive is used to specify those eigenvectors of the CI-matrix to be analysed. The directive consists of a single data line with the character string CIVEC in the first data field. If the properties associated with NVEC eigenvectors of the secular problem are to be generated, subsequent data fields should contain NVEC integers, the integers specifying the numbering of the CI-eigenvectors on the FORTRAN *interface*, FTN036. If the CIVEC directive is omitted under PROP processing an analysis of the first CI-vector will be performed.

Example

The data line

```
CIVEC 1 3
```

may be used to analyse the first and third CI-eigenvector generated by the DIAG sub-module.

10.3 AOPR

The AOPR directive may be used to request printing of the property integrals in the basis function (AO) representation. If specified, the directive consists of a single data line with the character string AOPR in the first data field. Subsequent data fields are used to specify those integrals to be printed. Valid character strings include S, T, X, Y, Z, XX, YY, ZZ, XY, XZ and YZ, requesting in obvious notation printing of the components of the overlap, kinetic energy, dipole and quadrupole moments respectively.

Example

```
AOPR X Y Z
```

would result in printing of integrals of the x-, y- and z-components of the dipole moment.

10.4 MOPR

The MOPR directive may be used to request printing of the property integrals in the molecular orbital (MO) basis. If specified, the directive consists of a single data line with the character

string MOPR in the first data field. Subsequent data fields are used to specify those integrals to be printed. Valid character strings include S, T, X, Y, Z, XX, YY, ZZ, XY, XZ and YZ, requesting in obvious notation printing of the components of the overlap, kinetic energy, dipole and quadrupole moments respectively.

Example

```
MOPR XX YY ZZ
```

would result in printing of integrals of the diagonal components of the quadrupole moment.

10.5 Configuration Data Lines

In addition to evaluating the properties of a given CI-vector, the module will also look to evaluating the corresponding properties of a nominated single configuration, typically the leading term in the CI-vector: the idea here of course is to provide a guide to the effect of the CI treatment on the property, with the nominated CSF being typically the corresponding SCF configuration. Thus the final data for the properties module comprises a sequence of NVEC data lines, each line a sequence of integers defining the single configuration for the CI-vector under consideration. The format of these lines is identical to that of the CONF data used in nominating the reference functions, and in most instances will be a repeat of that data.

Example

Consider the valence-CI calculation on PH₃ described in example 1 of the CONF directive. Considering just the CI data,

```
MRDCI
TRAN 1 CORE
4 1
1 TO 4 1
SELECT
SINGLES 1
CONF
0 1 2 3 15
0 1 3 4 15
0 1 2 3 16
NATORB
```

then the first data line of the CONF directive specifies the SCF configuration, and it is this configuration that should be nominated in the PROP data. Thus the CI data including the property analysis would appear as follows,

```
MRDCI
TRAN 1 CORE
4 1
```

```

1 TO 4 1
SELECT
SINGLES 1
CONF
0 1 2 3 15
0 1 3 4 15
0 1 2 3 16
NATORB
PROP
CIVEC 1
0 1 2 3 15

```

where one such data line is required given the specification of CIVEC.

11 Data for Conventional Table-CI Transition Moments

This Table-CI module will calculate both electrical and magnetic dipole moments as well as oscillator strengths and lifetimes of excited states. The module will look to calculate the moment between a specific state (typically the ground state) and a set of additional states (typically the excited states). It is assumed that the CI eigen-vectors have been generated and are available on the appropriate FORTRAN *interfaces*. While in most cases the ground and excited state CI-vectors will reside on the same *interface*, FTN036, the module will allow the use of differing data sets for these vectors, a situation most likely to occur when the ground and excited states are of different symmetry.

11.1 TM

The TM directive is used to request Transition Moment analysis, and comprises two data lines. The first line is read to the variables TEXT, TEXTF and TEXTB using format (3A).

- TEXT should be set to the character string TM.
- TEXTF is an optional parameter that may be used to control the quantity of printed output produced by the module. Valid settings include the strings,
 - NOPRINT, to suppress the major part of the output from the module;
 - IPRINT, to produce an intermediate level of output;
 - FPRINT, to produce output suitable for debugging purposes.
- TEXTB is an optional parameter that should be set to the string BYPASS if the user wishes to bypass TM processing. Such usage is typically associated with restarting Table-CI calculations.

The second data line of the TM directive is used to specify the location of the CI-vectors, and the number of excited state vectors involved in the subsequent analysis. The line is read to the variables IFTNX, ISECX, IFTNE, ISECE, NSTATE using format (5I);

- IFTNX defines the FORTRAN data set reference number of the *interface* holding the CI-vector of the first state. Normally this vector will reside on FTN036, with IFTNX=36.
- ISECX defines the position of this first vector on the *interface* defined by IFTNX. Typically, for the first state of a given symmetry, the vector will be located first on the data set i.e., ISECX=1.
- IFTNE defines the FORTRAN data set reference number of the *interface* holding the CI-vector(s) of the set of additional states. Assuming these states are of the same symmetry as the first, then we would expect all the states involved to lie on the same *interface* i.e., IFTNE will also be set to 36. If, however, the set of states is of different symmetry to the first, then their vectors will almost certainly reside on a different *interface*, which we will assume reside on FTN037 i.e., IFTNE should be set to 37.
- ISECE defines the position of the first of the excited state vectors on the *interface* defined by IFTNE. Typically, if all the states involved are of the same symmetry, residing on the same data set (IFTNX=IFTNE), then the first excited state vector will be located second on the data set i.e., ISECE=2. When the first and excited states are of different symmetry, then different data sets will be involved, and the first of the excited state vectors will be the first on IFTNE.
- NSTATE - defines the number of excited state vectors involved, and is usually equal to the number of transition moment calculations to be performed. Thus if we wished to calculate the transition moment between the two lowest states of H_2O , then NSTATE would equal 1, and the TM data would appear as follows:

```

      TM
      36 1 36 2 1

```

12 Calculating the 1A_1 states of H_2O

To clarify our discussion of the Table-CI module, we work through a typical example of using the Table-CI method in calculating the energetics and properties of the three low lying 1A_1 states of the H_2O molecule. The basis set employed is the TZVP triple-zeta plus polarisation set; this is augmented with a diffuse s- and p-orbital on the oxygen to provide a reasonable description of the known Rydberg character of the states of interest. The computation is split into four separate jobs, in which we,

1. perform the initial SCF;
2. carry out an initial CI, where the reference set employed acts to provide at least a qualitative description of the states of interest;
3. based on the output from the initial CI, we augment the reference set to provide a quantitative description of the first three states;

4. finally, having generated the CI vectors for the three states, we carry out in the final job an analysis of each vector in terms of natural orbitals and one-electron properties, and generate the transition moments between the ground and two excited states.

We now consider various aspects of each job in turn.

Job 1: The SCF

```

TITLE
**** H2O TZVP + DIFFUSE S,P MRDCI *
SUPER OFF NOSYM
ZMAT ANGSTROM
O
H 1 0.951
H 1 0.951 2 104.5
END
BASIS
TZVP O
TZVP H
S 0
1.0 0.02
P 0
1.0 0.02
END
ENTER

```

The only points to note here are (i) the use of the SUPER directive in suppressing skeletonisation, and (ii) use of the default section for eigenvector output (section 1 for the closed-shell SCF).

Job 2: The Initial 3M/3R CI

An examination of the SCF output reveals the following orbital analysis.

```

=====
IRREP  NO. OF SYMMETRY ADAPTED
        BASIS FUNCTIONS
=====
  1         18
  2         6
  3        10
  4         2
=====

```

and the following orbital assignments characterising the closed-shell SCF configuration:

$$1a_1^2 2a_1^2 1b_2^2 3a_1^2 1b_1^2 \quad (13)$$

```

=====
M.O.  IRREP  ORBITAL ENERGY  ORBITAL OCCUPANCY
=====

```

1	1	-20.56084959	2.0000000
2	1	-1.35696939	2.0000000
3	3	-0.72200122	2.0000000
4	1	-0.58247942	2.0000000
5	2	-0.50858566	2.0000000
6	1	0.02724259	0.0000000
7	3	0.04894440	0.0000000
8	2	0.05589681	0.0000000
9	1	0.06133571	0.0000000
10	1	0.20403420	0.0000000
11	3	0.22824210	0.0000000
12	3	0.53700802	0.0000000
13	1	0.56235022	0.0000000
14	2	0.58645643	0.0000000
15	1	0.66887228	0.0000000
16	3	0.74805617	0.0000000
17	1	1.07690608	0.0000000
18	1	1.88545053	0.0000000
19	4	1.92243836	0.0000000
20	2	2.12944874	0.0000000
21	3	2.20541910	0.0000000
22	1	2.34202871	0.0000000
23	3	2.39946430	0.0000000
24	3	2.69788310	0.0000000
25	1	2.72651832	0.0000000
26	2	2.73832720	0.0000000
27	1	3.07664215	0.0000000
28	3	3.26840142	0.0000000
29	2	3.54616570	0.0000000
30	1	3.58631019	0.0000000
31	4	3.59701772	0.0000000
32	1	3.84174131	0.0000000
33	1	4.84610143	0.0000000
34	3	5.14220270	0.0000000
35	1	7.73115986	0.0000000
36	1	47.56758932	0.0000000

=====

Based on the above output, the CONF data lines may be deduced from the following table, where we assume that we wish to freeze the O1s inner shell orbitals and discard the inner shell complement orbital:

IRrep	IRrep No.	No. of Basis Functions	Frozen MOs	Active MOs	Sequence Nos.
a ₁	1	18	1	16	1-16
b ₁	2	6	0	6	17-22
b ₂	3	10	0	10	23-32
a ₂	4	2	0	2	33-34

Note that the virtual SCF MOs dominated by the diffuse oxygen basis functions are the 4a₁, the 2b₂, the 2b₁ and the 5a₁, with SCF sequence numbers 6,7,8 and 9 respectively. The symmetry

re-ordered sequence numbers, allowing for the effective removal of the two a_1 orbitals, are 3, 24, 18 and 5 respectively. To perform a three-root 8-electron valence-CI calculation, based on the SCF configurations of the ground and excited Rydberg states, involving the single excitations ($1b_1$ to $2b_1$) and ($3a_1$ to $4a_1$) would require the following CONF data:

```
CONF
0      1 2 17 23
2 2 3 1 17 23
2 17 18 1 2 23
```

The following data will perform this three root-CI, where

- the SCF computation is BYPASS'ed;
- both CORE and DISCard are specified on the TRAN data line flagging the freezing and discarding of the two a_1 MOs;
- the default sub-module specifications are in effect, with no specific need to reference ADAPT, CI or DIAG activity; we also assume that the TABLE data set is available to the job;
- the ROOT directive is specifying selection with respect to the first 3 roots of the zero order problem, which we assume will correspond to the states of interest.

```
RESTART NEW
TITLE
****          H2O  TZVP + DIFFUSE S,P TABLE-CI 3M/3R*
SUPER OFF NOSYM
BYPASS SCF
ZMAT ANGSTROM
O
H 1 0.951
H 1 0.951 2 104.5
END
BASIS
TZVP O
TZVP H
S 0
1.0 0.02
P 0
1.0 0.02
END
RUNTYPE CI
MRDCI
TRAN CORE DISC
1 0 0 0
1
1 0 0 0
18
SELECT
CONF
0      1 2 17 23
```

```

2 2 3 1 17 23
2 17 18 1 2 23
THRE 10 10
ROOT 3
ENTER

```

Job 3: The Final 12M/3R CI

An examination of the output from the initial CI reveals that the dominant configurations have, as expected, been included. We show below the final CI vectors for each of the states: not surprisingly the ground state is more accurate, by virtue of its SCF MOs having been employed. Augmenting the reference set to improve the description of the two excited states follows straightforwardly from the statistics below:

Description of the X^1A_1 state

EXTRAPOLATED ENERGY = -76.2724087+/-0.0000790

```

=====
CSF NO.          C*C          CONFIGURATION
=====
(  1-   1)M      0.94952507      1  2 17 23
( 118- 118)M     0.00002448      2  3  1 17 23
( 129- 129)M     0.00016368     17 18  1  2 23

```

SUM OF MAIN REFERENCE C*C = 0.94971323

Description of the 1^1A_1 state

EXTRAPOLATED ENERGY = -75.9009069+/-0.0002121

```

=====
CSF NO.          C*C          CONFIGURATION
=====
(  1-   1)M      0.00020304      1  2 17 23
(  71-  71)M     0.00284448      1  2 18 23
( 118- 118)M     0.06411957      2  3  1 17 23
( 120- 120)M     0.00757395      2  5  1 17 23
( 129- 129)M     0.84004197     17 18  1  2 23
( 130- 130)M     0.00261567     17 19  1  2 23
( 363- 363)M     0.01150383     18 19  1  2 23
(  886- 887)M     0.00221466      1  5 17 18  2 23
( 1226- 1227)M    0.00227863      2  5 17 18  1 23
( 1236- 1237)M    0.00441966      2  6 17 18  1 23
( 1246- 1247)M    0.00550738      2  7 17 18  1 23
( 1640- 1641)M    0.00666055     17 18 23 25  1  2
( 1644- 1645)M    0.00664455     17 18 23 27  1  2

```

SUM OF MAIN REFERENCE C*C = 0.90436458

Description of the 2^1A_1 state

EXTRAPOLATED ENERGY = -75.8825335+/-0.0002079

CSF NO.	C*C	CONFIGURATION
(1- 1)M	0.00017134	1 2 17 23
(118- 118)M	0.78352745	2 3 1 17 23
(119- 119)	0.00620129	2 4 1 17 23
(120- 120)	0.05602432	2 5 1 17 23
(129- 129)M	0.07076103	17 18 1 2 23
(211- 211)	0.00236797	3 5 1 17 23
(212- 212)	0.00343646	3 6 1 17 23
(213- 213)	0.00493434	3 7 1 17 23
(1212- 1213)	0.00870751	2 3 17 19 1 23
(1372- 1373)	0.00638562	2 3 23 25 1 17
(1376- 1377)	0.00600107	2 3 23 27 1 17

SUM OF MAIN REFERENCE C*C = 0.85445982

Taking as the criterion for inclusion a weight of 0.005, the final 12 reference set-CI is shown below. We have assumed that the FORTRAN *interface* FTN031 has been saved from the second job, enabling us to bypass the transformation. Note also the specific appearance now of ADAPT in the data to enable bypassing.

```

RESTART CI
TITLE
**** H2O TZVP + DIFFUSE S,P TABLE-CI 12M/3R *
SUPER OFF NOSYM
BYPASS SCF
ZMAT ANGSTROM
O
H 1 0.951
H 1 0.951 2 104.5
END
BASIS
TZVP O
TZVP H
S O
1.0 0.02
P O
1.0 0.02
END
RUNTYPE CI
MRDCI
ADAPT BYPASS
TRAN CORE DISC BYPASS
1 0 0 0
1
1 0 0 0
18
SELECT

```

```

CONF
0      1 2 17 23
2 2 3 1 17 23
2 2 4 1 17 23
2 2 5 1 17 23
2 17 18 1 2 23
2 18 19 1 2 23
4 17 18 23 25 1 2
4 17 18 23 27 1 2
4 2 7 17 18 1 23
4 2 3 17 19 1 23
4 2 3 23 25 1 17
4 2 3 23 27 1 17
THRE 10 10
ROOT 3
ENTER

```

Job 4: The Analysis

Assuming that the diagonalisation *interface*, FTN036, had been saved above, then the final analysis job is straightforward: again bypassing of the various sub-modules involves explicit mention of the ADAPT, CI and DIAG modules, in addition to flagging the previous TRAN and SELECT data lines with the BYPASS keyword. We have routed the natural orbitals from the 3 A_1 states to the Dumpfile using the PUTQ directive.

```

RESTART CI
TITLE
**** H2O TZVP + DIFFUSE S,P TABLE-CI / ANALYSIS *
SUPER OFF NOSYM
BYPASS SCF
ZMAT ANGSTROM
0
H 1 0.951
H 1 0.951 2 104.5
END
BASIS
TZVP 0
TZVP H
S 0
1.0 0.02
P 0
1.0 0.02
END
RUNTYPE CI
MRDCI
ADAPT BYPASS
TRAN CORE DISC BYPASS
1 0 0 0
1
1 0 0 0
18
SELECT BYPASS
CONF

```

```

0          1 2 17 23
2  2  3  1   17 23
2  2  4  1   17 23
2  2  5  1   17 23
2 17 18  1 2 23
2 18 19  1 2 23
4 17 18 23 25 1 2
4 17 18 23 27 1 2
4  2  7 17 18  1 23
4  2  3 17 19  1 23
4  2  3 23 25  1 17
4  2  3 23 27  1 17
THRE 10 10
ROOT 3
CI BYPASS
DIAG BYPASS
NATORB IPRIN
CIVE 1 2 3
PUTQ AOS 50 51 52
PROP
CIVE 1 2 3
0          1 2 17 23
2 17 18  1 2 23
2  2  3  1   17 23
MOMENT
36 1 36 2 2
ENTER

```

Description of the Output for MRDCI Moments

The MRDCI module calculates the oscillator strength using both the dipole length formalism:

$$f(\mathbf{r}) = 2/3 \langle \Psi' | \mathbf{r} | \Psi'' \rangle^2 / \Delta E$$

and the dipole velocity formalism:

$$f(\nabla) = 2/3 | \langle \Psi' | \nabla | \Psi'' \rangle |^2 / \Delta E$$

The most significant contributions due to individual molecular orbitals are printed out as a table containing the largest coefficients of the transition density matrix and the following corresponding integrals.

$$\langle \psi_i | x | \psi_j \rangle$$

$$\langle \psi_i | y | \psi_j \rangle$$

$$\langle \psi_i | z | \psi_j \rangle$$

$$\langle \psi_i | \nabla(x) | \psi_j \rangle$$

$$\langle \psi_i | \nabla(y) | \psi_j \rangle$$

$$\langle \psi_i | \nabla(z) | \psi_j \rangle$$

The $f(\mathbf{r})$ and $f(\nabla)$ values are printed out in x,y,z components and the expectation values for $\langle \psi | \sum_i x_i, y_i, z_i | \psi \rangle$ are also printed.

13 Iterative Natural Orbital Calculations

We work through an example of using the natural orbitals generated by the module in a subsequent CI calculation. We consider a DZ calculation on the ground state of C_2H_4 , with the computation split into four separate jobs, in which we,

1. perform the initial SCF;
2. carry out an initial CI, where the reference set employed comprises just the SCF configuration, using the SCF MOs; of interest;
3. based on the output from the initial CI, we augment the reference set to include the leading secondary configuration, generating the resulting natural orbitals;
4. carry out the 2-reference CI based on the natural orbitals generated in the previous step.

We now consider various aspects of each job in turn.

Job 1: The SCF

```
TITLE
ETHYLENE DZ GROUND STATE SCF
SUPER OFF NOSYM
ZMATRIX ANGSTROM
C
C 1 1.4
H 1 1.1 2 120.0
H 1 1.1 2 120.0 3 180.0
H 2 1.1 1 120.0 3 0.0
H 2 1.1 1 120.0 3 180.0
END
BASIS DZ
ENTER
```

The only points to note here is the use of the SUPER directive in suppressing skeletonisation, and use of the default eigenvector section (section 1) for storage of the closed-shell eigenvectors.

Job 2: The Initial 1M/1R CI

An examination of the SCF output reveals the following orbital analysis.

```
=====
IRREP  NO. OF SYMMETRY ADAPTED
        BASIS FUNCTIONS
=====
  1           8
  2           2
  3           4
  5           8
  6           2
```

```

      7          4
=====

```

and the following orbital assignments characterising the closed-shell SCF configuration:

$$1a_g^2 1b_{1u}^2 2a_g^2 2b_{1u}^2 1b_{2u}^2 3a_g^2 1b_{3g}^2 1b_{3u}^2 \quad (14)$$

```

=====
M.O.  IRREP  ORBITAL ENERGY  ORBITAL OCCUPANCY
=====
  1    1   -11.25533463    2.0000000
  2    5   -11.25413119    2.0000000
  3    1   -1.02052567    2.0000000
  4    5   -0.79195744    2.0000000
  5    3   -0.64152856    2.0000000
  6    1   -0.57038928    2.0000000
  7    7   -0.51438205    2.0000000
  8    2   -0.36388693    2.0000000
  9    6    0.13190687    0.0000000
 10    5    0.25441028    0.0000000
 11    1    0.25558269    0.0000000
 12    3    0.33918097    0.0000000
 13    5    0.36641681    0.0000000
 14    1    0.41844853    0.0000000
 15    3    0.45487336    0.0000000
 16    7    0.49648833    0.0000000
 17    2    0.49708917    0.0000000
 18    6    0.60222488    0.0000000
 19    7    0.64242537    0.0000000
 20    1    0.76465797    0.0000000
 21    5    0.82560838    0.0000000
 22    5    1.10140194    0.0000000
 23    1    1.20630804    0.0000000
 24    3    1.30189632    0.0000000
 25    5    1.35219192    0.0000000
 26    7    1.50761510    0.0000000
 27    1   23.76609415    0.0000000
 28    5   24.01493168    0.0000000
=====

```

Based on the above output, the CONF data lines may be deduced from the following table, where we assume that we wish to freeze the C1s inner shell orbitals:

IRrep	IRrep No.	No. of Basis Functions	Frozen MOs	Active MOs	Sequence Nos.
a_g	1	8	1	7	1-7
b_{3u}	2	2	0	2	8-9
b_{2u}	3	4	0	4	10-13
b_{1u}	5	8	1	7	14-20
b_{2g}	6	2	0	2	21-22
b_{3g}	7	4	0	4	23-26

Note that within the DZ basis employed, there are no basis functions of b_{1g} (IRrep 4) or a_u (IRrep 8) symmetry. The symmetry re-ordered sequence numbers of the ground state orbitals, allowing for the effective removal of the $1a_g$ and $1b_{1u}$ orbitals, are 1, 14, 10, 2, 23 and 8 respectively. To perform a single reference 12-electron valence-CI calculation, based on the SCF configuration would require the following CONF data:

```
CONF
0 1 2 8 10 14 23
```

The following data will perform this CI, where

- the SCF computation is BYPASS'ed;
- CORE is specified on the TRAN data line flagging the freezing and discarding of the $1a_g$ and $1b_{1u}$ MOs. The default section for retrieval of the closed-shell eigenvectors is assumed;
- the default sub-module specifications are in effect, with no specific need to reference ADAPT, CI or DIAG activity; we also assume that the TABLE data set is available to the job;

```
RESTART
TITLE
ETHYLENE CI GROUND STATE SCF-MOS
BYPASS SCF
ZMATRIX ANGSTROM
C
C 1 1.4
H 1 1.1 2 120.0
H 1 1.1 2 120.0 3 180.0
H 2 1.1 1 120.0 3 0.0
H 2 1.1 1 120.0 3 180.0
END
BASIS DZ
RUNTYPE CI
MRDCI
TRAN CORE
1 0 0 1 0 0
1 1
SELECT
SYMMETRY 1
SPIN 1
SINGLES 1
CONF
0 1 2 8 10 14 23
ENTER
```

Job 3: The 2M/1R CI

We show below the final CI vector for the ground state.

Description of the X^1A_g state

EXTRAPOLATED ENERGY = -78.1944869+/-0.0001635

CSF NO.	C*C	CONFIGURATION
(1- 1)M	0.90889665	1 2 8 10 14 23
(43- 43)	0.01645740	1 2 10 14 21 23
(142- 142)	0.00543252	21 22 1 2 10 14 23
(374- 375)	0.00328957	2 8 17 21 1 10 14 23

Taking as the criterion for inclusion a weight of 0.01, the 2 reference set-CI job is shown below. We have assumed that the FORTRAN *interface* FTN031 has been saved from the second job, enabling us to bypass the transformation. Note also the specific appearance now of ADAPT in the data to enable bypassing. The natural orbitals are routed to section 200 of the Dumpfile. Note that subsequent usage of the NOs by the Conventional Table-CI module requires the SABF specification on the PUTQ directive.

```

RESTART NEW
TITLE
ETHYLENE CI GROUND STATE 2M SCF-MOS
BYPASS SCF
ZMATRIX ANGSTROM
C
C 1 1.4
H 1 1.1 2 120.0
H 1 1.1 2 120.0 3 180.0
H 2 1.1 1 120.0 3 0.0
H 2 1.1 1 120.0 3 180.0
END
BASIS DZ
RUNTYPE CI
MRDCI
ADAPT BYPASS
TRAN CORE BYPASS
1 0 0 1 0 0
1 1
SELECT
SYMMETRY 1
SPIN 1
SINGLES 1
CONF
0 1 2 8 10 14 23
0 1 2 10 14 21 23
NATORB IPRINT
PUTQ SABF 200
ENTER

```

Job 4: The Natural Orbital CI

We show below the data for using the NOs from the 2-reference CI, where the orbitals routed to section 200 are now restored by specification on the TRAN directive. The following points should be noted:

- We assume that the adaptation *interface* FTN022 has been saved from the initial CI job, allowing the BYPASS specification on the ADAPT directive.
- Restoring the NOs *must* be controlled via TRAN specification; an attempt to restore such orbitals through VECTORS and ENTER specification will lead to an error condition.
- The resulting NOs from the natural orbital CI are now routed to section 210, and could be used in a subsequent CI in obvious fashion.

```

RESTART NEW
TITLE
ETHYLENE CI GROUND STATE 2M NOS
BYPASS SCF
ZMATRIX ANGSTROM
C
C 1 1.4
H 1 1.1 2 120.0
H 1 1.1 2 120.0 3 180.0
H 2 1.1 1 120.0 3 0.0
H 2 1.1 1 120.0 3 180.0
END
BASIS DZ
RUNTYPE CI
MRDCI
ADAPT BYPASS
TRAN 200 CORE
1 0 0 1 0 0
1 1
SELECT
SYMMETRY 1
SPIN 1
SINGLES 1
CONF
0 1 2 8 10 14 23
0 1 2 10 14 21 23
NATORB IPRINT
PUTQ SABF 210
ENTER

```

We show below the final CI vector from the natural orbital CI

Description of the X^1A_g state

EXTRAPOLATED ENERGY = -78.2021125+/-0.0002347

```

=====
CSF NO.          C*C          CONFIGURATION

```

```

=====
(   1-   1)M   0.89795112   1  2  8 10 14 23
(  29-  29)M   0.03202257   1  2 10 14 21 23
( 194- 195)   0.00279273   1  8 15 21  2 10 14 23
( 308- 309)   0.00499259   2  8 15 21  1 10 14 23
( 430- 431)   0.00259858   3  8 14 21  1  2 10 23
( 514- 515)   0.00297122  10 11 23 24  1  2  8 14

```

SUM OF MAIN REFERENCE C*C = 0.92993884

14 Table-CI Calculations Using MCSCF Orbitals

To conclude our discussion of the Conventional Table-CI module, we work through an example of using the natural orbitals generated from the MCSCF module in a subsequent CI calculation. We consider a calculation on the ground state of H_2CO , with the computation split into three separate jobs, in which we,

1. perform an initial SCF;
2. carry out the MCSCF calculation;
3. perform the MRDCI calculation using the MCSCF natural orbitals.

We now consider various aspects of each job in turn.

Job 1: The SCF

```

TITLE
H2CO - DZP + F
SUPER OFF NOSYM
ZMATRIX ANGSTROM
C
O 1 1.203
H 1 1.099 2 121.8
H 1 1.099 2 121.8 3 180.0
END
BASIS
DZP O
DZP C
DZP H
F C
1 1.0
F 0
1.0 1.0
END
ENTER

```

The only points to note here is the use of the SUPER directive in suppressing skeletonisation, and use of the default eigenvector section (section 1) for storage of the closed-shell eigenvectors. An examination of the SCF output reveals the following orbital analysis.

```

=====
IRREP  NO. OF SYMMETRY ADAPTED
        BASIS FUNCTIONS
=====
  1         28
  2         13
  3         16
  4          5
=====

```

and the following orbital assignments characterising the closed-shell SCF configuration:

```

=====
M.O.  IRREP  ORBITAL ENERGY  ORBITAL OCCUPANCY
=====
  1    1    -20.57768533      2.0000000
  2    1    -11.34457777      2.0000000
  3    1     -1.40746540    2.0000000
  4    1     -0.87003449    2.0000000
  5    3     -0.69591811    2.0000000
  6    1     -0.65109519    2.0000000
  7    2     -0.53687971    2.0000000
  8    3     -0.44174805    2.0000000
  9    2      0.11697212    0.0000000
 10    1      0.26220763    0.0000000
 11    1      0.27217357    0.0000000
 12    3      0.38931080    0.0000000
 13    3      0.41757152    0.0000000
 14    2      0.46526352    0.0000000
 15    1      0.60968525    0.0000000
 16    1      0.75001014    0.0000000
 17    2      0.86980119    0.0000000
 18    1      0.89167074    0.0000000
 19    3      0.93051881    0.0000000
 20    1      1.07098621    0.0000000
 21    3      1.18616042    0.0000000
 22    1      1.35370640    0.0000000
 23    4      1.52221224    0.0000000
 24    2      1.68895841    0.0000000
 25    1      1.88480823    0.0000000
 26    3      1.97392259    0.0000000
 27    4      2.13452238    0.0000000
 28    1      2.13982211    0.0000000
 29    3      2.19187925    0.0000000
 30    1      2.34994146    0.0000000
 31    2      2.36355601    0.0000000
 32    4      2.67698155    0.0000000
 33    1      2.82812279    0.0000000
 34    2      2.84696649    0.0000000
 35    3      2.97321688    0.0000000
 36    1      3.14466153    0.0000000
 37    1      3.33275225    0.0000000
 38    3      3.51306001    0.0000000
 39    1      3.51697350    0.0000000
 40    2      3.52974692    0.0000000
=====

```

41	3	3.68500148	0.0000000
42	1	3.79236483	0.0000000
43	3	3.83958499	0.0000000
44	4	3.85444369	0.0000000
45	2	3.87171104	0.0000000
46	2	4.14123645	0.0000000
47	3	4.16304613	0.0000000
48	1	4.16535425	0.0000000
49	2	4.16620625	0.0000000
50	2	4.32796704	0.0000000
51	3	4.47390388	0.0000000
52	1	4.49325977	0.0000000
53	1	4.68584478	0.0000000
54	4	4.89513471	0.0000000
55	3	5.13208791	0.0000000
56	1	5.14756255	0.0000000
57	2	5.85901984	0.0000000
58	1	5.92954017	0.0000000
59	3	6.06228738	0.0000000
60	1	8.35480844	0.0000000
61	1	27.71561806	0.0000000
62	1	45.72664766	0.0000000

=====

Job 2: The MCSCF

The following data performs a 10 electron in 9 orbital CASSCF calculation using the MCSCF module, with the natural orbitals routed to section 10 of the Dumpfile under control of the CANONICAL directive. In the absence of the VECTORS directive, the SCF MOs will be used as the starting orbitals.

```

RESTART
TITLE
H2CO - MCSCF (10E IN 9 M.O.)
SUPER OFF NOSYM
NOPRINT
BYPASS
ZMATRIX ANGSTROM
C
O 1 1.203
H 1 1.099 2 121.8
H 1 1.099 2 121.8 3 180.0
END
BASIS
DZP O
DZP C
DZP H
F C
1 1.0
F 0
1.0 1.0
END
SCFTYPE MCSCF

```

```

MCSCF
ORBITAL
COR1 COR1 COR1 DOC1 DOC3 DOC1 DOC2 DOC3 UOC2 UOC1 UOC3 UOC1
END
PRINT ORBITALS VIRTUALS NATORB
CANONICAL 10 FOCK DENSITY FOCK
ENTER

```

Job 3: The Table-CI Job

Performing a Table-CI calculation using the natural orbitals generated in the previous step is fairly straightforward. The following points should be noted:

- The MCSCF data presented in the preceding step must remain as part of the input data set, with that computation now BYPASS'ed.
- Specification of the input orbital set must be driven through section specification on the TRAN directive; without such specification, the default MCSCF sections will be used which are not appropriate as input to the subsequent CI. In the data below this is achieved through the data line "TRAN 10", where the section specified is just that nominated on the CANONICAL directive.
- With no frozen or discarded orbital, the orbital indices specified on the CONF directive follow in obvious fashion from the list of IRREPs given above. We are performing a simple 16 electron, 3 reference calculation, deriving just the first root, and using a 2 micro-hartree threshold.

```

RESTART
TITLE
H2CO - MCSCF (10E IN 9 M.O.) MRDCI FROM MCSCF NOS
SUPER OFF NOSYM
BYPASS SCF
ZMAT ANGSTROM
C
O 1 1.203
H 1 1.099 2 121.8
H 1 1.099 2 121.8 3 180.0
END
BASIS
DZP O
DZP C
DZP H
F C
1 1.0
F O
1.0 1.0
END
RUNTYPE CI
SCFTYPE MCSCF
MCSCF
ORBITAL

```

```

COR1 COR1 COR1 DOC1 DOC3 DOC1 DOC2 DOC3 UOC2 UOC1 UOC3 UOC1
END
PRINT ORBITALS VIRTUALS NATORB
CANONICAL 10 FOCK DENSITY FOCK
MRDCI
ADAPT
TRAN 10
SELECT
SYMMETRY 1
SPIN 1
CNTRL 16
SINGLES 1
CONF
0 1 2 3 4 5 29 42 43
0 1 2 3 4 5 30 42 43
0 1 2 3 4 5 29 42 44
ROOTS 1
THRESH 2 2
CI
DIAG
ENTER

```

Finally, we consider the data for performing exactly the same calculation as above, but now freezing the oxygen and carbon 1s core orbitals in the Table-CI calculation. The following points should be noted:

- The TRAN directive now appends the CORE descriptor after the section specification, with the following 2 data lines requesting that the first two orbitals of symmetry 1 be removed from the Table-CI calculation.
- The orbital indices specified on the CONF data lines reflect the removal of these two orbitals, with the CNTRL directive now pointing to a 12-electron CI calculation, as distinct from the 16 electron calculation above.

```

RESTART
TITLE
H2CO - MRDCI FROM MCSCF NOS - FREEZE 1S MOS
SUPER OFF NOSYM
BYPASS SCF
ZMAT ANGSTROM
C
0 1 1.203
H 1 1.099 2 121.8
H 1 1.099 2 121.8 3 180.0
END
BASIS
DZP 0
DZP C
DZP H
F C
1 1.0
F 0
1.0 1.0

```

```

END
RUNTYPE CI
SCFTYPE MCSCF
MCSCF
ORBITAL
COR1 COR1 COR1 DOC1 DOC3 DOC1 DOC2 DOC3 UOC2 UOC1 UOC3 UOC1
END
PRINT ORBITALS VIRTUALS NATORB
CANONICAL 10 FOCK DENSITY FOCK
MRDCI
ADAPT
TRAN 10 CORE
2 0 0 0
1 2
SELECT
SYMMETRY 1
SPIN 1
CNTRL 12
SINGLES 1
CONF
0 1 2 3 27 40 41
0 1 2 3 28 40 41
0 1 2 3 27 40 42
ROOTS 1
THRESH 2 2
CI
DIAG
ENTER

```

15 The Semi-direct Table-CI Module

We now consider the data requirements and file structure of the new, semi-direct version of the Table-CI module that is capable of performing significantly larger calculations. The main differences as far as the user is concerned include the following.

- The original adapt and transformation modules of the Conventional Table-CI module have now been replaced by the standard 4-index transformation module of GAMESS-UK.
- Semi-direct Table-CI calculations require at least two reference configurations i.e. CISD calculations based on a single reference configuration are not possible with this module. However we do not consider this to be a major disadvantage given that the process of configuration choice and specification has been simplified through the use of automated configuration generation (see below).
- The original CI and Diagonalisation modules have now been condensed into a single CI module.
- The formal limits that apply to conventional calculations are significantly extended in the semi-direct module. There is now a limit of 800,000 selected configurations derived from an initial list of configurations generated by single plus double excitations from a

user-specified list of reference functions, the number of which may not exceed 256. The selection and extrapolation procedure may now be applied on up to thirty roots of a given secular problem.

- The memory requirements of the semi-direct module may be significantly greater than those associated with the conventional algorithm. While the default memory allocations will prove adequate for "small-medium" cases, the user should use the MEMORY pre-directive to request at least 8 MWords in calculations with, say, more than 20 active electrons.
- The overall filespace requirements are significantly reduced compared to the Conventional module; note that the FORTRAN unit numbers for some the key data sets have been modified compared to the original settings.
- An automatic procedure for obtaining a number of excited states within a single given run of the program is now possible under control of the ITERATE directive. This is designed to remove much of the labour involved in generating, for example, vertical excitation spectra.

15.1 Sub-Module Structure of Semi-direct Table-CI

An outline of the sub-module structure and philosophy behind the semi-direct Table-CI module has already been given in Part 2, material that should be taken in conjunction with the present chapter. As pointed out previously, this module comprises a reduced set of 6 sub-modules, which must be user-driven (either implicitly or explicitly, see below) through data input. These sub modules are as follows:

- TABLE: generates an input a 'data-base' of pattern symbolic matrix elements for use in both the selection process and in solving the secular problem. This data base is written to a file with LFN *table-ci* (note the name change compared to the LFN TABLE employed in the Conventional module).
- SELECT: configuration generation and subsequent selection based on a user-specified set of reference configurations and appropriate thresholds;
- CI: provides pre-processing prior to the semi-direct evaluation of the CI eigenfunctions, followed by the calculation, in semi-direct fashion, of one or more CI eigenfunctions of the secular problem. In contrast to the conventional module, just two secular problems are solved as part of the extrapolation process, one at the lowest threshold (T_{min}) and one at the threshold ($T_{min} + T_{inc}$).
- NATORB: generates the spin-free natural orbitals for one or more of the calculated CI eigenvectors. Note that this module is now executed in default.

AS with the original code, the remaining modules are optional, and may be used to further analyse one or more of the CI eigenvectors:

- PROP: to compute various 1-electron properties of the CI wavefunctions. Note that the natural orbitals generated above may be routed to the Dumpfile and examined by the other analysis modules of GAMESS-UK in a subsequent job.
- TM: to compute the transition moments between nominated CI eigenvectors.

In addition to the Mainfile, Dumpfile, Scratchfile and Transformed Integral File (ED6), the following data sets will be used by the program.

- The Tablefile: A dataset normally assigned using the local file name "table-ci" will be used as a source of pattern symbolic matrix elements in the SELECT and CI phases of the Table-CI procedure. The space requirements of the Tablefile are now about 6 MBytes.
- In contrast to the other post-Hartree Fock modules of GAMESS-UK, the Table-CI routines make extensive use of unformatted sequential FORTRAN data sets (or *interfaces*). The data set reference numbers and associated LFNs of these files have been given in Table 8 of Part 2.

16 Directives Controlling Semi-direct Table-CI Calculations

Data input characterising the Semi-direct Table-CI calculation commences with the MRDCI data line, and is typically followed by a sequence of directives, terminated by presenting a valid *Class 2* directive, such as VECTORS or ENTER. A fairly thorough overview of the data structure has been given in Part 2: we provide additional detail on the directives associated with each sub-module below.

16.1 MRDCI

The Table-CI data initiator for the semi-direct module consists of a single line containing the character string MRDCI in the first data field, and the string DIRECT in the second. It acts to transfer control to those routines responsible for inputting all data relevant to the MRDCI calculation. Termination of this data is achieved by presenting a valid *Class 2* directive that is not recognised by the Table-CI input routines, for example, VECTORS or ENTER.

17 Data for Semi-direct Table-CI Integral Transformation

In contrast to the Conventional Table-CI code, integral transformation is now performed under control of the conventional transformation code of GAMESS-UK. Control of the transformation is now carried out under the ACTIVE and CORE directives described previously in Part 5 of the manual. The following points should be noted:

1. The MOs to be used in the transformation process will be taken from the section as nominated on the ENTER directive, or the default section in effect if explicit section specification is omitted.

2. The transformation may be bypassed under control of the BYPASS directive. Such usage is typically associated with restarting Table-CI calculations.
3. The freezing and discarding of orbitals in the transformation is controlled by a combination of the CORE and ACTIVE directives.
4. Users of the old module will be familiar with the ordering of the MOs required within the Table-CI module, namely in terms of irreducible representation (IRrep) and numbering within each IRrep. While this ordering is still the preferred means of driving the CI module and associated specification of the reference functions etc., it is no longer necessary to adhere to this numbering scheme when specifying CORE and ACTIVE orbitals, for the code will automatically generate the appropriate numbering of these MOS. This is best illustrated by considering the same examples used at the beginning of the chapter.
5. Note again that the input orbital set will be reordered by the transformation module such that
 - IRreps having zero orbitals are discarded, and
 - orbitals of common IRrep are grouped together, these groups being arranged in order of increasing IRrep number, and
 - orbitals of common IRrep are ordered according to their relative disposition in the input orbital set e.g., by eigenvalue ordering if SCF MOs.
6. Generation of the Transformed Integral Interface (to FTN031) is carried out on completion of the integral transformation, using the integrals written to the Transformed Integral File (ED6). This conversion is triggered by the appearance of the "MRDCI DIRECT" data line in the job input; any attempt to use the Transformed Integral File produced, say, during a run of the Direct-CI module (see Part 5) as input to a subsequent semi-direct Table-CI calculation will lead to an error condition, as the generation of FTN031 would have not have attempted by the previous run of the transformation module.

Example 1

In this example we wish to perform a valence-CI calculation on the H₂CO molecule using a DZ basis of 24 gtos, looking to freeze both the oxygen and carbon 1s orbitals, and to discard the inner-shell complement orbitals. An examination of the SCF output reveals the following orbital analysis.

```

=====
IRREP  NO. OF SYMMETRY ADAPTED
        BASIS FUNCTIONS
=====
   1           14
   2            4
   3            6
=====

```

with the following orbital assignments from the closed shell SCF:

```

=====
M.O.  IRREP  ORBITAL ENERGY  ORBITAL OCCUPANCY
=====
  1    1   -20.58952765    2.0000000
  2    1   -11.35779935   2.0000000
  3    1    -1.43525479    2.0000000
  4    1    -0.87463564    2.0000000
  5    3    -0.70990765    2.0000000
  6    1    -0.64751394    2.0000000
  7    2    -0.53989416    2.0000000
  8    3    -0.44423257    2.0000000
  9    2     0.10853108    0.0000000
 10    1     0.25726604    0.0000000
 11    1     0.28106873    0.0000000
 12    3     0.38903939    0.0000000
 13    3     0.40966861    0.0000000
 14    2     0.46216570    0.0000000
 15    1     0.65466944    0.0000000
 16    1     0.82879998    0.0000000
 17    2     0.98111608    0.0000000
 18    1     0.98701051    0.0000000
 19    3     1.07064863    0.0000000
 20    1     1.16621340    0.0000000
 21    3     1.29856111    0.0000000
 22    1     1.82320845    0.0000000
 23    1    23.76352004    0.0000000
 24    1    43.36689896    0.0000000
=====

```

Thus the orbitals of interest are of common IRrep (a_1), with sequence numbers 1,2 (core) and 23,24 (complement MOs) within the SCF orbital set. The following ACTIVE and CORE data would freeze and discard these MOs:

```

ACTIVE
3 TO 22 END
CORE
1 2
END

```

The following sequence would be used to simply freeze the orbitals while retaining the complete virtual manifold:

```

ACTIVE
3 TO 24 END
CORE
1 2
END

```

Note that if no orbitals are to be discarded, as in the example above, the user may omit the ACTIVE directive, with the CORE specification acting to define this set. Thus the above data sequence is equivalent to merely presenting the sequence:

```

CORE
1 2
END

```

Example 2

In this example we wish to perform a valence-CI calculation on the N_2 molecule using a TZVP basis. While the molecular symmetry is $D_{\infty h}$, the symmetry adaptation and subsequent CI will be conducted in the D_{2h} point group. The resolution of the $D_{\infty h}$ into the D_{2h} orbital species has been given in Table 2. An examination of the SCF output reveals the following orbital analysis.

```

=====
IRREP  NO. OF SYMMETRY ADAPTED
        BASIS FUNCTIONS
=====
  1         11
  2          4
  3          4
  4          1
  5         11
  6          4
  7          4
  8          1
=====

```

and the following orbital assignments from the converged closed shell SCF:

```

=====
M.O.  IRREP  ORBITAL ENERGY  ORBITAL OCCUPANCY
=====
  1     1    -15.66716423      2.0000000
  2     5    -15.66241865      2.0000000
  3     1    -1.51005217      2.0000000
  4     5    -0.76128176      2.0000000
  5     1    -0.63704931      2.0000000
  6     3    -0.63448705      2.0000000
  7     2    -0.63448705      2.0000000
  8     6     0.17408343      0.0000000
  9     7     0.17408343      0.0000000
 10     5     0.30302673      0.0000000
 11     3     0.38747796      0.0000000
 12     2     0.38747796      0.0000000
 13     1     0.42599317      0.0000000
 14     1     0.49515007      0.0000000
 15     7     0.57046706      0.0000000
 16     6     0.57046706      0.0000000
 17     5     0.92638361      0.0000000
 18     5     1.12927523      0.0000000
 19     1     1.83974927      0.0000000
 20     3     2.01160646      0.0000000
 21     2     2.01160646      0.0000000

```

22	5	2.01683641	0.0000000
23	4	2.08974396	0.0000000
24	1	2.08974396	0.0000000
25	7	2.16718057	0.0000000
26	6	2.16718057	0.0000000
27	1	2.16945852	0.0000000
28	3	2.20023738	0.0000000
29	2	2.20023738	0.0000000
30	8	2.67650248	0.0000000
31	5	2.67650248	0.0000000
32	5	2.98166352	0.0000000
33	1	3.57616884	0.0000000
34	7	3.58056531	0.0000000
35	6	3.58056531	0.0000000
36	5	4.37707106	0.0000000
37	1	6.02043977	0.0000000
38	5	6.12816913	0.0000000
39	1	35.89673292	0.0000000
40	5	35.91926868	0.0000000

=====

Thus the inner-shell N1s orbitals, the $1\sigma_g$ and $1\sigma_u$ transform as a_g and b_{1u} respectively in D_{2h} symmetry, with IRrep numbers 1 and 5. Both correspond of course to the first orbital in the appropriate IRrep. The following sequence would be used to simply freeze the orbitals while retaining the complete virtual manifold:

```
CORE
1 2 END
```

Turning to the inner-shell complement orbitals, we again find the corresponding IRreps, 1 and 5, with the orbitals the highest lying member in each case, with relative sequence number of 11. Thus the following ACTIVE and CORE data would act to both freeze and discard the inner-shells and their complement MOs:

```
ACTIVE
3 TO 38
END
CORE
1 2 END
```

Further examples of transformation data will be discussed below in the section discussing Reference Function specification within the SELECT data.

18 Data for Semi-direct Table-CI Data-base Generation

The 'data-base' of pattern symbolic matrix elements required by both the Selection and CI modules may be generated by the user in the course of any Table-CI calculation. In contrast to the Conventional module, we envisage that this step will be executed in each run of the module rather than the user allocating a previously generated version.

18.1 TABLE

The TABLE directive is used to request and control the data-base generator, and comprises a single data line read to the variables TEXT, TEXTF, TEXTB using format (3A).

- TEXT should be set to the character string TABLE.
- TEXTF is an optional parameter that may be used to control the quantity of printed output produced by the module. Valid settings include the strings,
 - NOPRINT, to suppress output from the module;
 - IPRINT, to produce an intermediate level of output;
 - FPRINT or DEBUG, to produce output suitable for debugging purposes.
- TEXTB is a further optional parameter that should be set to the string BYPASS if the user wishes to bypass generation of the Table-CI data base. Such usage assumes that the data set "table-ci" is resident in the directory in which the calculation is preceding, having been generated there is some previous run of the direct-CI module. Such usage is typically associated with restarting Table-CI calculations.

19 Data for Semi-direct Table-CI Selection

Data for the configuration selection module is initiated with the SELECT directive, followed by those directives characterising the symmetry of the state(s) of interest and reference configurations (CNTRL, SPIN, SYMMETRY, CONF etc.) and terminated by data (ROOTS, THRESH) controlling the process of selection.

19.1 SELECT

The SELECT directive is used to control the configuration selection module, and comprises a single data line read to the variables TEXT, TEXTF and TEXTB using format (3A).

- TEXT should be set to the character string SELECT.
- TEXTF is an optional parameter that may be used to control the quantity of printed output produced by the module. Valid settings include the strings,
 - NOPRINT, to suppress the major part of the output from the module, in particular all details of the perturbative energy lowerings associated with the initial set of configurations;
 - IPRINT, to produce an intermediate level of output;
 - FPRINT or DEBUG, to produce output suitable for debugging purposes. This includes the energy lowerings associated with the complete configuration list.
- TEXTB is an optional parameter that should be set to the string BYPASS if the user wishes to bypass SELECT processing. Such usage is typically associated with restarting Table-CI calculations.

19.2 CNTRL

This directive consists of one line read to variables TEXT, NELEC using format (A,I).

- TEXT should be set to the character string CNTRL or NELEC.
- NELEC is used to specify the total number of 'active' electrons in the CI calculation. Note that any inner shell electrons frozen out under control of the CORE directive should not be included.

19.3 SPIN

This directive consists of one line read to variables TEXT, NSPIN using format (A,I).

- TEXT should be set to the character string SPIN.
- NSPIN is used to specify the spin degeneracy of the CI wavefunction of the electronic eigenstate(s) of interest, using the values 1,2,3 etc. for singlet, doublet, triplet states etc. respectively. It is also possible to use one of the character strings SINGLET, DOUBLET, TRIPLET, QUARTET and QUINTET to specify NSPIN.

Example

```
SPIN 3
SPIN TRIPLET
```

are equivalent; the wavefunction will be three-fold spin degenerate.

19.4 SYMMETRY

This directive consists of one line read to variables TEXT, NSYM using format (A,I).

- TEXT should be set to the character string SYMMETRY.
- NSYM is an integer parameter used to specify the spatial symmetry of the CI wavefunction, and is set to the appropriate sequence number of the required irreducible representation (see Table 1).

Example

In a system of C_{2v} symmetry, the data line

```
SYMMETRY 3
```

would be required when performing calculations on states of B_2 symmetry. Failure to present the directive in such cases will lead to the default A_1 symmetry.

19.5 SINGLES

This directive consists of one line read to variables TEXT, TEXTS using format 2A.

- TEXT should be set to the character string SINGLES.
- TEXTS may be set to one of the following character strings:
 - ALL; The selection module will retain in the final CI all single excitations with respect to ALL nominated reference functions (specified under the CONF directive) *regardless* of their computed energy lowerings.
 - OFF; The selection module will use the computed energy lowerings as the sole criteria for including configurations in the final CI, with no automatic inclusion of single excitations.

Note that this usage differs from that described in the Conventional module. An alternative form of the SINGLES directive is also possible, comprising a single data line read to variables TEXT, NREF using format (A,I).

- TEXT should be set to the character string SINGLES.
- NREF is an integer parameter used to nominate a particular configuration within the set of reference functions. The selection module will then retain in the final CI all single excitations with respect to the nominated function *regardless* of their computed energy lowerings.

The SINGLES directive may be omitted, when the program will include all single excitations with respect to ALL nominated reference functions (i.e. SINGLES ALL).

Example

Presenting the data line

```
SINGLES 1
```

in a Table-CI calculation of a closed-shell system, where the SCF configuration is the first in the CONF list, will lead to the inclusion of all single excitations with respect to the SCF function in the final CI. Such inclusion leads, of course, to a marked improvement in the quality of one-electron properties computed from the CI wavefunction.

19.6 CONF

The CONF directive is used to specify the reference CSFs for the CI expansion. The first line of the CONF directive is set to the character string CONF. In contrast to CONF specification in the conventional module, the last line of the directive, the directive terminator, now consists of the

text END in the first data field. Lines between the initiator and terminator define the reference configuration set; each line defines a reference CSF by specifying the sequence numbers of the component active orbitals in I-format. A given reference CSF is defined by

1. the number of open-shell orbitals (NOPEN). NOPEN includes any unpaired orbitals together with those non-identical spin-coupled pairs open to substitution.
2. NOPEN integers specifying the sequence numbers of these orbitals
3. the $(\text{NELEC}-\text{NOPEN})/2$ sequence numbers of the doubly-occupied orbitals i.e., the identically spin-coupled orbitals

where the sequence-numbers refers to the symmetry ordered orbitals performed at the outset of processing. Within the set of open- and doubly-occupied orbitals, the MOs are presented in groups of common IRrep, with the groups presented in order of increasing IRrep sequence number. A few examples below will help clarify this order of presentation. Note again that:

- all reference function nominated by CONF *must* be of the same symmetry as that nominated on the SYMMETRY directive.
- at least two reference functions must be specified; it is not possible to conduct simple CISD calculations with the semi-direct module.
- note again the requirement for a directive terminator.

Example 1

Consider performing a valence-CI calculation on the PH₃ molecule using a 6-31G(*) basis. While the molecular symmetry is C_{3v}, the symmetry adaptation and subsequent CI will be conducted in the C_s point group. An examination of the SCF output reveals the following orbital analysis.

```

=====
IRREP  NO. OF SYMMETRY ADAPTED
        BASIS FUNCTIONS
=====
    1          18
    2           7
=====

```

and the following orbital assignments characterising the closed-shell SCF configuration:

$$1a_1^2 2a_1^2 1e^4 3a_1^2 4a_1^2 2e^4 5a_1^2 \quad (15)$$

or, in the C_s symmetry representation:

$$1a'^2 2a'^2 1a''^2 3a'^2 4a'^2 5a'^2 6a'^2 2a''^2 7a'^2 \quad (16)$$

```

=====
M.O.  IRREP  ORBITAL ENERGY  ORBITAL OCCUPANCY
=====
  1    1   -79.93661395    2.0000000
  2    1   -7.48916431    2.0000000
  3    1   -5.38319410    2.0000000
  4    2   -5.38319405    2.0000000
  5    1   -5.38149104    2.0000000
  6    1   -0.85610769    2.0000000
  7    1   -0.52191424    2.0000000
  8    2   -0.52191424    2.0000000
  9    1   -0.38579686    2.0000000
 10    1    0.16819544    0.0000000
 11    2    0.16819544    0.0000000
 12    1    0.26587776    0.0000000
 13    1    0.46072690    0.0000000
 14    2    0.46072690    0.0000000
 15    1    0.47871033    0.0000000
 16    1    0.56106989    0.0000000
 17    1    0.89229884    0.0000000
 18    2    0.89229885    0.0000000
 19    2    0.91131383    0.0000000
 20    1    0.91131383    0.0000000
 21    1    0.93118300    0.0000000
 22    1    1.17900613    0.0000000
 23    2    1.45058658    0.0000000
 24    1    1.45058658    0.0000000
 25    1    3.78674557    0.0000000
=====

```

Based on the above output, the CONF data lines may be deduced from the following table, where we assume that we wish to freeze the five inner shell orbitals:

$$1a'^2 2a'^2 1a''^2 3a'^2 4a'^2 \quad (17)$$

	IRrep	IRrep	No. of Basis	Frozen	Active	Sequence
		No.	Functions	MOs	MOs	Nos.
a'	1		18	4	14	1-14
a''	2		7	1	6	15-20

To perform an 8-electron valence-CI calculation, involving the SCF configuration and two degenerate $(1e)'$ to $(2e)'$ doubly-excited configurations

$$5a'^2 8a'^2 2a''^2 7a'^2 \quad (18)$$

and

$$5a'^2 6a'^2 3a''^2 7a'^2 \quad (19)$$

would require the following CONF data:

```

CONF
0 1 2 3 15
0 1 3 4 15
0 1 2 3 16
END

```

The complete data file for performing the SCF and subsequent semi-direct CI would then be as follows:

```

TITLE
PH3 * 6-31G* VALENCE-CI 3M/1R
SUPER OFF NOSYM
ZMAT
P
H 1 RPH
H 1 RPH 2 THETA
H 1 RPH 2 THETA 3 THETA 1
VARIABLES
RPH 2.685
THETA 93.83
END
BASIS 6-31G*
RUNTYPE CI
CORE
1 TO 5 END
MRDCI DIRECT
TABLE
SELECT
CNTRL 8
SPIN 1
SYMMETRY 1
SINGLES ALL
CONF
0 1 2 3 15
0 1 3 4 15
0 1 2 3 16
END
CI
NATORB
ENTER

```

Example 2

In this example we wish to perform a valence-CI calculation on the CuCl molecule using a 3-21G basis. While the molecular symmetry is $C_{\infty v}$, the symmetry adaptation and subsequent CI will be conducted in the C_{2v} point group. The resolution of the $C_{\infty v}$ into the C_{2v} orbital species is given in Table 2. An examination of the SCF output reveals the following orbital analysis.

```

=====
IRREP NO. OF SYMMETRY ADAPTED
      BASIS FUNCTIONS
=====
1          22

```

```

2          9
3          9
4          2
=====

```

and the following orbital assignments from the converged closed shell SCF:

```

=====
M.O.  IRREP  ORBITAL ENERGY  ORBITAL OCCUPANCY
=====
  1    1   -326.84723972    2.0000000
  2    1   -104.02836336    2.0000000
  3    1    -40.71695637    2.0000000
  4    1   -35.46377378    2.0000000
  5    3   -35.45608069    2.0000000
  6    2   -35.45608068    2.0000000
  7    1   -10.42193940    2.0000000
  8    1    -7.88512031    2.0000000
  9    2    -7.88222844    2.0000000
 10    3    -7.88222844    2.0000000
 11    1    -5.07729175    2.0000000
 12    1    -3.38247056    2.0000000
 13    3    -3.35978308    2.0000000
 14    2    -3.35978307    2.0000000
 15    1    -1.01099628    2.0000000
 16    3    -0.53702948    2.0000000
 17    2    -0.53702947    2.0000000
 18    4    -0.49640067    2.0000000
 19    1    -0.49640067    2.0000000
 20    1    -0.44715317    2.0000000
 21    3    -0.39988537    2.0000000
 22    2    -0.39988537    2.0000000
 23    1    -0.35127248    2.0000000
 24    1     0.00023285     0.0000000
 25    3     0.06300102     0.0000000
 26    2     0.06300102     0.0000000
 27    1     0.12855448     0.0000000
 28    1     0.19287013     0.0000000
 29    3     0.25729975     0.0000000
 30    2     0.25729975     0.0000000
 31    1     0.39720201     0.0000000
 32    1     0.86197727     0.0000000
 33    2     0.88942618     0.0000000
 34    3     0.88942618     0.0000000
 35    1     1.01877167     0.0000000
 36    1     2.16694989     0.0000000
 37    3     3.96181512     0.0000000
 38    2     3.96181512     0.0000000
 39    4     3.98212497     0.0000000
 40    1     3.98212497     0.0000000
 41    1     4.08851360     0.0000000
 42    1    24.51368240     0.0000000
=====

```

Based on the above output, the CONF data lines may be deduced from the following table, where we assume that we wish to freeze the first 14 inner shell orbitals:

$$1\sigma^2 2\sigma^2 3\sigma^2 4\sigma^2 1\pi^4 5\sigma^2 6\sigma^2 2\pi^4 7\sigma^2 8\sigma^2 3\pi^4 \quad (20)$$

IRrep	IRrep No.	No. of Basis Functions	Frozen MOs	Active MOs	Sequence Nos.
a ₁	1	22	8	14	1-14
b ₁	2	9	3	6	15-20
b ₂	3	9	3	6	21-26
a ₂	4	2	0	2	27-28

To perform an 18-electron valence-CI calculation, based on the SCF configuration

$$9\sigma^2 4\pi^4 1\delta^4 10\sigma^2 5\pi^4 11\sigma^2 \quad (21)$$

and the doubly excited configuration

$$9\sigma^2 4\pi^4 1\delta^4 10\sigma^2 5\pi^4 12\sigma^2 \quad (22)$$

would require the following CONF data:

```
CONF
0 1 2 3 4 15 16 21 22 27
0 1 2 3 5 15 16 21 22 27
END
```

The complete data file for performing the SCF and subsequent CI would then be as follows:

```
TITLE\CUCL .. 3-21G
ZMAT ANGSTROM\CU\CL 1 CUCL\
VARIABLES\CUCL 2.093 \END
BASIS 3-21G
RUNTYPE CI
CORE
1 TO 14 END
MRDCI DIRECT
TABLE
SELECT
CNTRL 18
SPIN 1
SYMM 1
SINGLES 1
CONF
0 1 2 3 4 15 16 21 22 27
0 1 2 3 5 15 16 21 22 27
END
CI
NATORB
ENTER
```

Example 3

Consider performing a valence-CI calculation on the SiH_4 molecule using a 6-31G(*) basis. While the molecular symmetry is T_d , the symmetry adaptation and subsequent CI will be conducted in the C_{2v} point group. An examination of the SCF output reveals the following orbital analysis.

```

=====
IRREP  NO. OF SYMMETRY ADAPTED
        BASIS FUNCTIONS
=====
  1         9
  2         6
  3         6
  4         6
=====

```

and the following orbital assignments from the converged closed shell SCF:

```

=====
M.O.  IRREP  ORBITAL ENERGY  ORBITAL OCCUPANCY
=====
  1    1    -68.77130710    2.0000000
  2    1     -6.12943325    2.0000000
  3    2     -4.23503117    2.0000000
  4    3     -4.23503117    2.0000000
  5    4     -4.23503117    2.0000000
  6    1     -0.73046864    2.0000000
  7    4     -0.48480821    2.0000000
  8    3     -0.48480821    2.0000000
  9    2     -0.48480821    2.0000000
 10    2      0.16291387    0.0000000
 11    3      0.16291387    0.0000000
 12    4      0.16291387    0.0000000
 13    1      0.25681257    0.0000000
 14    1      0.33606346    0.0000000
 15    3      0.37087856    0.0000000
 16    2      0.37087856    0.0000000
 17    4      0.37087856    0.0000000
 18    1      0.79946861    0.0000000
 19    1      0.79946861    0.0000000
 20    4      0.86232544    0.0000000
 21    3      0.86232544    0.0000000
 22    2      0.86232544    0.0000000
 23    1      1.23833149    0.0000000
 24    4      1.44033091    0.0000000
 25    3      1.44033091    0.0000000
 26    2      1.44033091    0.0000000
 27    1      3.13181655    0.0000000
=====

```

Based on the above output, the CONF data lines may be deduced from the following table, where we assume that we wish to freeze the first 5 silicon inner shell orbitals:

IRrep	IRrep No.	No. of Basis Functions	Frozen MOs	Active MOs	Sequence Nos.
a ₁	1	9	2	7	1-7
b ₁	2	6	1	5	8-12
b ₂	3	6	1	5	13-17
a ₂	4	6	1	5	18-22

To perform a 4-reference, 8-electron valence-CI calculation, based on the SCF configuration and configurations arising from the $2t_2$ to $3t_2$ would require the following CONF data:

```
CONF
0 1 8 13 18
0 1 8 13 19
0 1 8 14 18
0 1 9 13 18
END
```

The complete data file for performing the SCF and subsequent CI would then be as follows (note that we are retaining all single excitations with respect to each reference function in the final CI):

```
TITLE
SIH4 * 6-31G* DIRECT-TABLE-CI VALENCE-CI 4M/1R
ZMAT
SI
H 1 SIH
H 1 SIH 2 109.471
H 1 SIH 2 109.471 3 120.0
H 1 SIH 2 109.471 4 120.0
VARIABLES
SIH 2.80
END
BASIS 6-31G*
RUNTYPE CI
CORE
1 TO 5 END
MRDCI DIRECT
TABLE
SELECT
CNTRL 8
SYMM 1
SPIN 1
CONF
0 1 8 13 18
0 1 8 13 19
0 1 8 14 18
0 1 9 13 18
END
SINGLES ALL
CI
NATORB
ENTER
```


Example 4

In this example we wish to perform a valence-CI calculation on the N_2 molecule using a 4-31G(*) basis. While the molecular symmetry is $D_{\infty h}$, the symmetry adaptation and subsequent CI will be conducted in the D_{2h} point group. The resolution of the $D_{\infty h}$ into the D_{2h} orbital species is given in Table 2. An examination of the SCF output reveals the following orbital analysis.

```

=====
IRREP  NO. OF SYMMETRY ADAPTED
        BASIS FUNCTIONS
=====
  1         8
  2         3
  3         3
  4         1
  5         8
  6         3
  7         3
  8         1
=====

```

and the following orbital assignments from the converged closed shell SCF:

```

=====
M.O.  IRREP  ORBITAL ENERGY  ORBITAL OCCUPANCY
=====
  1     1   -15.65953319     2.0000000
  2     5   -15.65476539     2.0000000
  3     1    -1.50616872     2.0000000
  4     5    -0.75782843     2.0000000
  5     1    -0.63245667     2.0000000
  6     2    -0.63136574     2.0000000
  7     3    -0.63136574     2.0000000
  8     7     0.20154120     0.0000000
  9     6     0.20154120     0.0000000
 10     5     0.63882720     0.0000000
 11     1     0.82490877     0.0000000
 12     2     0.89633728     0.0000000
 13     3     0.89633728     0.0000000
 14     1     0.91811776     0.0000000
 15     6     1.10035435     0.0000000
 16     7     1.10035436     0.0000000
 17     5     1.17624961     0.0000000
 18     5     1.66993831     0.0000000
 19     4     1.70516525     0.0000000
 20     1     1.70516525     0.0000000
 21     2     1.91000364     0.0000000
 22     3     1.91000364     0.0000000
 23     8     2.29434948     0.0000000
 24     5     2.29434948     0.0000000
 25     1     2.84353563     0.0000000
 26     6     3.00847612     0.0000000
 27     7     3.00847612     0.0000000

```

28	5	3.37444027	0.0000000
29	1	3.71749475	0.0000000
30	5	4.09916047	0.0000000

=====

Based on the above output, the CONF data lines may be deduced from the following table, where we assume that we wish to freeze the two N1s inner shell orbitals:

	IRrep	IRrep	No. of Basis	Frozen	Active	Sequence
		No.	Functions	MOs	MOs	Nos.
	σ_g	1	8	1	7	1-7
	$\pi_{u,x}$	2	3	0	3	8-10
	$\pi_{u,y}$	3	3	0	3	11-13
	$\delta_{g,xy}$	4	1	0	1	14
	σ_u	5	8	1	7	15-21
	$\pi_{g,x}$	6	3	0	3	22-24
	$\pi_{g,y}$	7	3	0	3	25-27
	$\delta_{u,xy}$	8	1	0	1	28

To perform a 10-electron valence-CI calculation, based on the SCF configuration

$$2\sigma_g^2 2\sigma_u^2 3\sigma_g^2 1\pi_u^4 \quad (23)$$

and associated π to π^* excitations

$$2\sigma_g^2 2\sigma_u^2 3\sigma_g^2 1\pi_{u,y}^2 1\pi_{g,x}^2 \quad (24)$$

$$2\sigma_g^2 2\sigma_u^2 3\sigma_g^2 1\pi_{u,x}^2 1\pi_{g,y}^2 \quad (25)$$

$$2\sigma_g^2 2\sigma_u^2 3\sigma_g^2 (1\pi_{u,x} 1\pi_{g,x}) (1\pi_{u,y} 1\pi_{g,y}) \quad (26)$$

would require the following CONF data:

```
CONF
0 1 2 8 11 15
0 1 2 11 15 22
0 1 2 8 15 25
4 8 11 22 25 1 2 15
END
```

The complete data file for performing the SCF and subsequent CI would then be as follows:

```
TITLE\N2 .. 4-31G*
SUPER OFF NOSYM
ZMAT ANGS\N\N 1 NN
VARIABLES\NN 1.05 \END
BASIS 4-31G*
```

```

RUNTYPE CI
CORE
1 2 END
MRDCI DIRECT
TABLE
SELECT
CNTRL 10
SYMM 1
SPIN 1
SINGLES 1
CONF
0 1 2 8 11 15
0 1 2 11 15 22
0 1 2 8 15 25
4 8 11 22 25 1 2 15
END
CI
NATORB IPRIN
ENTER

```

Now consider the corresponding calculation performed in a larger CC-PVTZ basis. An examination of the SCF output reveals the following orbital analysis.

```

=====
IRREP  NO. OF SYMMETRY ADAPTED
        BASIS FUNCTIONS
=====
  1         16
  2          8
  3          8
  4          3
  5         16
  6          8
  7          8
  8          3
=====

```

and the following orbital assignments from the converged closed shell SCF:

```

=====
M.O.  IRREP  ORBITAL ENERGY  ORBITAL OCCUPANCY
=====
  1    1    -15.66553669    2.0000000
  2    5    -15.66076870    2.0000000
  3    1     -1.50580210    2.0000000
  4    5     -0.76246663    2.0000000
  5    1     -0.63737662    2.0000000
  6    2     -0.63425262    2.0000000
  7    3     -0.63425262    2.0000000
  8    7     0.18426391    0.0000000
  9    6     0.18426391    0.0000000
 10    1     0.40582614    0.0000000
 11    5     0.42020784    0.0000000
 12    2     0.51942385    0.0000000

```

13	3	0.51942385	0.0000000
14	1	0.53416038	0.0000000
15	6	0.71767715	0.0000000
16	7	0.71767715	0.0000000
17	5	0.74113094	0.0000000
18	4	1.04543157	0.0000000
19	1	1.04543157	0.0000000
20	5	1.15104310	0.0000000
21	2	1.37114036	0.0000000
22	3	1.37114036	0.0000000
23	8	1.53065438	0.0000000
24	5	1.53065438	0.0000000
25	1	1.58044223	0.0000000
26	5	1.89387038	0.0000000
27	6	1.93835376	0.0000000
28	7	1.93835376	0.0000000
29	1	2.02899399	0.0000000
30	5	2.38397418	0.0000000
31	2	2.58126398	0.0000000
32	3	2.58126398	0.0000000
33	1	3.03473543	0.0000000
34	6	3.21032541	0.0000000
35	7	3.21032541	0.0000000
36	4	3.84680067	0.0000000
37	1	3.84680067	0.0000000
38	3	3.93355912	0.0000000
39	2	3.93355912	0.0000000
40	2	4.03730269	0.0000000
41	3	4.03730269	0.0000000
42	7	4.48707133	0.0000000
43	6	4.48707133	0.0000000
44	1	4.52955492	0.0000000
45	5	4.56413770	0.0000000
46	6	4.76466065	0.0000000
47	7	4.76466065	0.0000000
48	4	4.78192405	0.0000000
49	1	4.78192405	0.0000000
50	8	4.91469244	0.0000000
51	5	4.91469244	0.0000000
52	5	5.11932527	0.0000000
53	8	5.42107737	0.0000000
54	5	5.42107737	0.0000000
55	2	5.42155085	0.0000000
56	3	5.42155085	0.0000000
57	2	5.53491607	0.0000000
58	3	5.53491607	0.0000000
59	1	5.70188467	0.0000000
60	6	6.24854532	0.0000000
61	7	6.24854532	0.0000000
62	5	6.31686796	0.0000000
63	6	7.07828789	0.0000000
64	7	7.07828789	0.0000000
65	1	7.42407537	0.0000000
66	1	8.86035408	0.0000000
67	5	11.17202050	0.0000000

68	1	11.65153449	0.0000000
69	5	12.12852685	0.0000000
70	5	25.31135299	0.0000000
=====			

Based on the above output, the CONF data lines may be deduced from the following table, where we again assume that we wish to freeze the two N1s inner shell orbitals:

IRrep	IRrep No.	No. of Basis Functions	Frozen MOs	Active MOs	Sequence Nos.
σ_g	1	16	1	15	1-15
$\pi_{u,x}$	2	8	0	8	16-23
$\pi_{u,y}$	3	8	0	8	24-31
$\delta_{g,xy}$	4	3	0	3	32-34
σ_u	5	16	1	15	35-49
$\pi_{g,x}$	6	8	0	8	50-57
$\pi_{g,y}$	7	8	0	8	58-65
$\delta_{u,xy}$	8	3	0	3	66-68

To perform a 10-electron valence-CI calculation, based on the SCF configuration

$$2\sigma_g^2 2\sigma_u^2 3\sigma_g^2 1\pi_u^4 \quad (27)$$

and associated π to π^* excitations

$$2\sigma_g^2 2\sigma_u^2 3\sigma_g^2 1\pi_{u,y}^2 1\pi_{g,x}^2 \quad (28)$$

$$2\sigma_g^2 2\sigma_u^2 3\sigma_g^2 1\pi_{u,x}^2 1\pi_{g,y}^2 \quad (29)$$

$$2\sigma_g^2 2\sigma_u^2 3\sigma_g^2 (1\pi_{u,x} 1\pi_{g,x}) (1\pi_{u,y} 1\pi_{g,y}) \quad (30)$$

based on the SCF configuration would require the following CONF data:

```
CONF
0 1 2 16 24 35
0 1 2 24 35 50
0 1 2 16 35 38
4 16 24 50 58 1 2 35
END
```

The complete data file for performing the SCF and subsequent CI would then be as follows:

```
TITLE\N2 .. CC-PVTZ
SUPER OFF NOSYM
ZMAT ANG5\N\N 1 NN
VARIABLES\NN 1.05 \END
```

```

BASIS CC-PVTZ
RUNTYPE CI
CORE
1 2 END
MRDCI DIRECT
TABLE
SELECT
CNTRL 10
SYMM 1
SPIN 1
SINGLES 1
CONF
0 1 2 16 24 35
0 1 2 24 35 50
0 1 2 16 35 58
4 16 24 50 58 1 2 35
END
CI
NATORB IPRIN
ENTER

```

Example 5

In this example we wish to perform a valence-CI calculation on the CaH_2 molecule using a 6-31G** basis. While the molecular symmetry is $D_{\infty h}$, the symmetry adaptation and subsequent CI will be conducted in the D_{2h} point group. An examination of the SCF output reveals the following orbital analysis.

```

=====
IRREP  NO. OF SYMMETRY ADAPTED
        BASIS FUNCTIONS
=====
  1         11
  2          5
  3          5
  4          1
  5          7
  6          2
  7          2
=====

```

and the following orbital assignments from the converged closed shell SCF:

```

=====
M.O.  IRREP  ORBITAL ENERGY  ORBITAL OCCUPANCY
=====
  1     1   -149.34279776    2.0000000
  2     1   -16.81835576    2.0000000
  3     2   -13.62701326    2.0000000
  4     3   -13.62701326    2.0000000
  5     5   -13.62532936    2.0000000
  6     1    -2.24495780    2.0000000

```

7	3	-1.34937153	2.0000000
8	2	-1.34937153	2.0000000
9	5	-1.33498314	2.0000000
10	1	-0.35141213	2.0000000
11	5	-0.31217469	2.0000000
12	3	0.02646555	0.0000000
13	2	0.02646555	0.0000000
14	1	0.04279408	0.0000000
15	5	0.11107022	0.0000000
16	1	0.11631297	0.0000000
17	2	0.20535510	0.0000000
18	3	0.20535510	0.0000000
19	4	0.30735852	0.0000000
20	1	0.30735852	0.0000000
21	7	0.32858094	0.0000000
22	6	0.32858094	0.0000000
23	5	0.36615374	0.0000000
24	1	0.47836712	0.0000000
25	1	0.49656774	0.0000000
26	1	1.18797119	0.0000000
27	5	1.30595420	0.0000000
28	3	2.42553536	0.0000000
29	2	2.42553536	0.0000000
30	7	2.45164750	0.0000000
31	6	2.45164750	0.0000000
32	5	2.50399980	0.0000000
33	1	2.74252653	0.0000000

=====

Based on the above output, the CONF data lines may be deduced from the following table, where we assume that we wish to freeze the nine Ca inner shell orbitals:

IRrep	IRrep No.	No. of Basis Functions	Frozen MOs	Active MOs	Sequence Nos.
σ_g	1	11	3	8	1-8
$\pi_{u,x}$	2	5	2	3	9-11
$\pi_{u,y}$	3	5	2	3	12-14
$\delta_{g,xy}$	4	1	0	1	15
σ_u	5	7	2	5	16-20
$\pi_{g,x}$	6	2	0	2	21-22
$\pi_{g,y}$	7	2	0	2	23-24

To perform an 4-electron valence-CI calculation, based on the SCF configuration

$$4\sigma_g^2 3\sigma_u^2 \quad (31)$$

and associated σ to σ^* excitations,

$$5\sigma_g^2 3\sigma_u^2 \quad (32)$$

$$4\sigma_g^2 4\sigma_u^2 \quad (33)$$

would require the following CONF data:

```
CONF
0 1 16
0 2 16
0 1 17
END
```

The complete data file for performing the SCF and subsequent CI (in which all singles are retained) would then be as follows:

```
TITLE\CAH2 .. 6-31G** 3M/1R
SUPER OFF NOSYM
ZMAT ANGS\CA\X 1 1.0\ H 1 CAH 2 90.0\H 1 CAH 2 90.0 3 THETA
VARIABLES\CAH 2.148 \THETA 180.0 \END
BASIS 6-31G**
RUNTYPE CI
CORE
1 TO 9 END
MRDCI DIRECT
TABLE
SELECT
CNTRL 4
SPIN 1
SYMMETRY 1
SINGLES ALL
CONF
0 1 16
0 2 16
0 1 17
END
THRESH 2.0 2.0
CI
NATORB IPRIN
ENTER
```

19.7 ROOTS

The ROOTS directive is used to specify those eigenvectors of the 'root' secular problem to be used in the process of selection, with the energy contributions of the configurations computed with respect to the nominated vectors. The directive consists of a single data line with the character string ROOTS in the first data field. Subsequent data comprises integer variables used to specify the *number* of root eigenstates (NROOT) and the *sequence numbers* of these vectors within the matrix of zero-order eigenvectors, (IROOT(I),I=1,NROOT). Two formats may be used in this specification:

1. If the lowest NROOT vectors are to be used, then the data line is read to the variables TEXT, NROOT using format (A,I);
 - TEXT is set to the character string ROOTS;

- NROOT is an integer specifying the number of roots to be used, where the sequence numbers of the roots will be 1–NROOT.
2. If the NROOT vectors to be used are not the lowest in the root eigenvector matrix, then the sequence numbers within this matrix must be specified. The data line is then read to the variables TEXT, NROOT, (IROOT(I), I=1,NROOT), using format (A, (NROOT+1) I):
- TEXT and NROOT are defined as above;
 - NROOT integers are read to the array IROOT defining the vectors of the zero-order matrix to be used in selection.

We now provide some further notes on the directive:

- the ROOTS directive may be omitted, when the energy contributions are calculated with reference to the lowest eigenstate of the root problem only. Omission of the directive is thus equivalent to presenting the data line

ROOTS 1

- The number of root eigenstates to be specified will depend on the number of states required in the final CI. Thus if NVEC roots of the final CI matrix are to be subsequently generated in DIAG processing, the user should ideally perform selection with respect to at least the corresponding NVEC roots of the root secular problem to ensure a consistent treatment of each of the required states. The choice of the reference set will clearly prove crucial and should be such as to ensure a one to one correspondence between each of the final CI vectors and a certain vector of the root problem. Indeed the whole process of extrapolation to zero threshold is meaningless if this condition is not obeyed.

19.8 THRESH

This directive defines the threshold factors to be used in the process of configuration selection, and consists of a single line read to variables TEXT, TMIN, TINC using format (A,2F).

- TEXT should be set to the character string THRESH.
- TMIN should be set to the minimum threshold factor (in units of micro-hartree, μH) to be used in selection. Any CSF with a computed energy lowering greater than TMIN will be retained in the final list of selected configurations.
- TINC should be set to the threshold increment to be used in the process of extrapolation. This process now involves solution of the final secular problem at just two thresholds, defined by TMIN, and TMIN + TINC. Note the restricted number of calculations here compared to the conventional module.

The THRESH directive may be omitted, when TMIN will be set to 10.0 and TINC to 10.0, leading to the solution of the T=10 and 20 μH secular problem.

Example

```
THRESH 5.0 5.0
```

```
THRESH 5 5
```

are equivalent, causing T_{min} and T_{inc} to be set to 5 microhartree.

20 Data for Semi-direct Table-CI Eigen Solution

Data input controlling the semi-direct construction and diagonalisation of the CI Hamiltonian is introduced by the CI directive. The process of extrapolation to zero selection threshold involves the CI module solving two secular problems, the first corresponding to the selection threshold TMIN, the second to the threshold (TMIN+TINC). In default, the module will generate NROOT eigenvectors of the CI matrix on both passes, where NROOT is the number of roots specified by the ROOTS directive at selection time. Thus the solutions of the zero-order Hamiltonian will be used through a maximum overlap criterion in deriving the final CI eigenvectors. Additional data may be specified to provide various convergence and printing controls.

20.1 CI

The CI directive comprises a single data line read to the variables TEXT, TEXTF and TEXTB using format (3A).

- TEXT should be set to the character string CI.
- TEXTF is an optional parameter that may be used to control the quantity of printed output produced by the module. Valid settings include the strings,
 - NOPRINT, to suppress the major part of the output from the module;
 - IPRINT, to produce an intermediate level of output;
 - FPRINT or DEBUG, to produce output suitable for debugging purposes.
- TEXTB is an optional parameter that should be set to the string BYPASS if the user wishes to bypass CI processing. Such usage is typically associated with restarting Table-CI calculations.

20.2 ACCURACY

This directive may be used to define the diagonalisation thresholds for the two extrapolation passes, consists of a single line read to variables TEXT, THRESHE using format (A,F).

- TEXT should be set to the character string ACCURACY or DTHRESH;
- THRESHE: On both extrapolation passes, the diagonalization is converged to an energy threshold THRESHE.

The THRESH directive may be omitted, when THRESHE will be set to 0.000001

Example

Presenting the data line

```
ACCURACY 0.0000001
```

will result in a diagonalisation threshold of 0.0000001 for the two extrapolation passes.

20.3 PRINT

The PRINT directive may be used to control the printing of CI coefficients and weights throughout the extrapolation passes and in the final analysis. This directive consists of a single data line read to variables TEXT, PTHR, PTHRCC, IFLAG using format (A,2F,I).

- TEXT should be set to the character string PRINT.
- CI coefficients less than PTHR in absolute magnitude will not be printed during the extrapolation passes.
- CI weights (coefficients²) less than PTHRCC in absolute magnitude will not be printed in the final analysis of the CI wavefunctions.
- IFLAG may be used to control the printing of the CI wavefunctions in the event that the diagonalisation does not converge. Setting IFLAG=1 will cause a detailed print of the CI vectors corresponding to each root.

This directive may be omitted, when the defaults PTHR=0.05 and PTHRCC=0.002 will be taken.

21 Data for Semi-direct Table-CI Natural Orbitals

21.1 Natural Orbital Data - NATORB

The NATORB directive is used to request Natural Orbital (NO) generation, and comprises a single data line read to the variables TEXT, TEXTF and TEXTB using format (3A).

- TEXT should be set to the character string NATORB.
- TEXTF is an optional parameter that may be used to control the quantity of printed output produced by the module. Valid settings include the strings,
 - NOPRINT, to suppress the major part of the output from the module;

- IPRINT, to produce an intermediate level of output. This option should be set to generate a print of the natural orbital coefficient array(s);
- FPRINT or DEBUG, to produce output suitable for debugging purposes.
- TEXTB is an optional parameter that should be set to the string BYPASS if the user wishes to bypass NATORB processing. Such usage is typically associated with restarting Table-CI calculations.

21.2 Natural Orbital Data - CIVEC

The CIVEC directive is used to specify those eigenvectors of the CI-matrix to be analysed. The directive consists of a single data line with the character string CIVEC in the first data field. If natural orbitals associated with NVEC eigenvectors of the secular problem are to be generated, subsequent data fields should contain NVEC integers, the integers specifying the numbering of the CI-eigenvectors on the FORTRAN *interface*, FTN036, as generated by the CI sub-module. If the CIVEC directive is omitted under NATORB processing the natural orbitals of the first CI-vector will be generated.

Example

```
CIVEC 1 3
```

The above data line may be used to generate natural orbitals from the first and third CI-eigenvector generated by the CI sub-module.

21.3 Natural Orbital Data - PUTQ

The PUTQ directive may be used to route spin-free natural orbitals to the Dumpfile, and consists of a single dataline with the first two fields read to variables TEXT, TYPE using format (2A).

- TEXT should be set to the character string PUTQ.
- TYPE should be set to one of the character strings AOS, A.O. or SABF, defining the basis representation required for the output NOs. The character string AOS and A.O. will yield the NOs in the basis function representation, suitable for subsequent input to the other analysis modules of GAMESS-UK. The string SABF will result in the NO expansion in the symmetry adapted basis representation, and should be used when performing iterative natural orbital calculations (see section 6.13 below)

The remaining data consists of a sequence of NVEC integers, (between 0 and 350 inclusive) specifying the section number of the Dumpfile where the spin-free NOs derived from the NVEC CI-vectors nominated by the CIVEC directive are to be placed.

Example

```
PUTQ AOS 100 120
```

The spin-free NOs in the basis-set representation are output to sections 100 and 120 respectively of the Dumpfile. A section setting of 0 on the PUTQ directive will act to suppress natural orbital output to the Dumpfile.

22 Data for Semi-direct Table-CI One-electron Properties

22.1 PROP

The PROP directive is used to request the computation of one-electron properties and comprises a single data line read to the variables TEXT, TEXTF and TEXTB using format (3A).

- TEXT should be set to the character string PROP.
- TEXTF is an optional parameter that may be used to control the quantity of printed output produced by the module. Valid settings include the strings,
 - NOPRINT, to suppress the major part of the output from the module;
 - IPRINT, to produce an intermediate level of output;
 - FPRINT or DEBUG, to produce output suitable for debugging purposes.
- TEXTB is an optional parameter that should be set to the string BYPASS if the user wishes to bypass PROP processing. Such usage is typically associated with restarting Table-CI calculations.

22.2 CIVEC

The CIVEC directive is used to specify those eigenvectors of the CI-matrix to be analysed. The directive consists of a single data line with the character string CIVEC in the first data field. If the properties associated with NVEC eigenvectors of the secular problem are to be generated, subsequent data fields should contain NVEC integers, the integers specifying the numbering of the CI-eigenvectors on the FORTRAN *interface*, FTN036. If the CIVEC directive is omitted under PROP processing an analysis of the first CI-vector will be performed.

Example

The data line

```
CIVEC 1 3
```

may be used to analyse the first and third CI-eigenvector generated by the CI sub-module.

22.3 AOPR

The AOPR directive may be used to request printing of the property integrals in the basis function (AO) representation. If specified, the directive consists of a single data line with the character string AOPR in the first data field. Subsequent data fields are used to specify those integrals to be printed. Valid character strings include S, T, X, Y, Z, XX, YY, ZZ, XY, XZ and YZ, requesting in obvious notation printing of the components of the overlap, kinetic energy, dipole and quadrupole moments respectively.

Example

```
AOPR X Y Z
```

would result in printing of integrals of the x-, y- and z-components of the dipole moment.

22.4 MOPR

The MOPR directive may be used to request printing of the property integrals in the molecular orbital (MO) basis. If specified, the directive consists of a single data line with the character string MOPR in the first data field. Subsequent data fields are used to specify those integrals to be printed. Valid character strings include S, T, X, Y, Z, XX, YY, ZZ, XY, XZ and YZ, requesting in obvious notation printing of the components of the overlap, kinetic energy, dipole and quadrupole moments respectively.

Example

```
MOPR XX YY ZZ
```

would result in printing of integrals of the diagonal components of the quadrupole moment.

22.5 Configuration Data Lines

In addition to evaluating the properties of a given CI-vector, the module will also look to evaluating the corresponding properties of a nominated single configuration, typically the leading term in the CI-vector: the idea here of course is to provide a guide to the effect of the CI treatment on the property, with the nominated CSF being typically the corresponding SCF configuration. Thus the final data for the properties module comprises a sequence of NVEC data lines, each line a sequence of integers defining the single configuration for the CI-vector under consideration. The format of these lines is identical to that of the CONF data used in nominating the reference functions, and in most instances will be a repeat of that data.

Example

Consider the valence-CI calculation on PH_3 described in example 1 of the CONF directive. Considering just the CI data,

```

MRDCI DIRECT
TABLE
SELECT
CNTRL 8
SPIN 1
SYMMETRY 1
SINGLES 1
CONF
0 1 2 3 15
0 1 3 4 15
0 1 2 3 16
END
CI
NATORB

```

then the first data line of the CONF directive specifies the SCF configuration, and it is this configuration that should be nominated in the PROP data. Thus the CI data including the property analysis would appear as follows,

```

MRDCI DIRECT
TABLE
SELECT
CNTRL 8
SPIN 1
SYMMETRY 1
SINGLES 1
CONF
0 1 2 3 15
0 1 3 4 15
0 1 2 3 16
END
CI
NATORB
PROP
CIVEC 1
0 1 2 3 15

```

where one such data line is required given the specification of CIVEC.

23 Data for Semi-direct Table-CI Transition Moments

This Table-CI module will calculate both electrical and magnetic dipole moments as well as oscillator strengths and lifetimes of excited states. The module will look to calculate the moment between a specific state (typically the ground state) and a set of additional states (typically the excited states). It is assumed that the CI eigen-vectors have been generated and are available on the appropriate FORTRAN *interfaces*. While in most cases the ground and excited state CI-vectors will reside on the same *interface*, FTN036, the module will allow the use of differing data sets for these vectors, a situation most likely to occur when the ground and excited states are of different symmetry.

23.1 TM

The TM directive is used to request Transition Moment analysis, and comprises two data lines. The first line is read to the variables TEXT, TEXTF and TEXTB using format (3A).

- TEXT should be set to the character string TM.
- TEXTF is an optional parameter that may be used to control the quantity of printed output produced by the module. Valid settings include the strings,
 - NOPRINT, to suppress the major part of the output from the module;
 - IPRINT, to produce an intermediate level of output;
 - FPRINT or DEBUG, to produce output suitable for debugging purposes.
- TEXTB is an optional parameter that should be set to the string BYPASS if the user wishes to bypass TM processing. Such usage is typically associated with restarting Table-CI calculations.

The second data line of the TM directive is used to specify the location of the CI-vectors, and the number of excited state vectors involved in the subsequent analysis. The line is read to the variables IFTNX, ISECX, IFTNE, ISECE, NSTATE using format (5I);

- IFTNX defines the FORTRAN data set reference number of the *interface* holding the CI-vector of the first state. Normally this vector will reside on FTN036, with IFTNX=36.
- ISECX defines the position of this first vector on the *interface* defined by IFTNX. Typically, for the first state of a given symmetry, the vector will be located first on the data set i.e., ISECX=1.
- IFTNE defines the FORTRAN data set reference number of the *interface* holding the CI-vector(s) of the set of additional states. Assuming these states are of the same symmetry as the first, then we would expect all the states involved to lie on the same *interface* i.e., IFTNE will also be set to 36. If, however, the set of states is of different symmetry to the first, then their vectors will almost certainly reside on a different *interface*, which we will assume reside on FTN037 i.e., IFTNE should be set to 37.
- ISECE defines the position of the first of the excited state vectors on the *interface* defined by IFTNE. Typically, if all the states involved are of the same symmetry, residing on the same data set (IFTNX=IFTNE), then the first excited state vector will be located second on the data set i.e., ISECE=2. When the first and excited states are of different symmetry, then different data sets will be involved, and the first of the excited state vectors will be the first on IFTNE.
- NSTATE - defines the number of excited state vectors involved, and is usually equal to the number of transition moment calculations to be performed. Thus if we wished to calculate the transition moment between the two lowest states of H₂O, then NSTATE would equal 1, and the TM data would appear as follows:

```

TM
36 1 36 2 1

```


24 Semi-direct Table-CI - Using Default Options

In order to simplify the process of configuration specification and data preparation, the semi-direct module now provides a set of default options that require little or no data input. While these defaults are not expected to cover most in-depth requirements, they do provide a starting point for users, and a route to subsequent, more extensive calculations. To illustrate this default working of the module, we consider below a number of example calculations.

24.1 Calculations on the Formaldehyde Ground State

A Semi-direct Table-CI calculation is to be performed on the formaldehyde molecule in a TZVP basis. Given the following data sequence:

```
TITLE
H2CO - TZVP X1A1 DEFAULT TABLE-CI OPTIONS
ZMAT ANGSTROM
C
O 1 1.203
H 1 1.099 2 121.8
H 1 1.099 2 121.8 3 180.0
END
BASIS TZVP
RUNTYPE CI
MRDCI DIRECT
ENTER
```

then the calculation undertaken will be based on the following;

1. Integral transformation will use the set of orbitals from section 1, the integer specified on the ENTER directive i.e. the closed shell SCF orbitals.
2. The table-ci data base will be generated rather than restored from a pre-existing *table-ci* data set.
3. The symmetry, spin and number of active electrons will be taken from the corresponding SCF wavefunction. In the present case this involves:
 - A CI wavefunction of A_1 symmetry (i.e. SYMMETRY 1).
 - A singlet CI wavefunction (i.e. SPIN 1).
 - The number of active electrons in the CI will be set to be those involved in the SCF calculation (i.e. CNTRL 16).
4. Singly excited configurations with respect to each of the default reference configurations (SINGLES ALL) will be included, regardless of their computed energy lowerings.
5. The set of reference configurations to be employed will include the SCF configuration, plus those generated from this configuration by including (i) for each symmetry IRREP, the doubly excited configuration arising from excitation of the highest occupied DOMO

of that symmetry to the lowest virtual orbital (VMO) of the same symmetry, and (ii) the lowest singly excited configuration, again arising from the highest occupied DOMO to the lowest VMO of the same symmetry. In the present example, this will correspond to the SCF configuration, the double and single excitation arising from the DOMO 5a₁ to VMO 6a₁, the double and single excitation arising from the DOMO 1b₁ to VMO 2b₁, and the double and single excitation arising from the DOMO 2b₂ to VMO 3b₂. No reference configurations will be included involving orbitals of a₂ symmetry given the absence of such orbitals involved in the occupied manifold. This results in a total reference set of 7 functions, as shown thus in the job output:

numbers of open shells and corresponding main configurations

```

0          1  2  3  4  5 28 37 38      .. SCF configuration
0          1  2  3  4  6 28 37 38      .. 5a1 -> 6a1 double
2          5  6  1  2  3  4 28 37 38 .. 5a1 -> 6a1 single
0          1  2  3  4  5 29 37 38      .. 1b1 -> 2b1 double
2          28 29  1  2  3  4  5 37 38 .. 1b1 -> 2b1 single
0          1  2  3  4  5 28 37 39      .. 2b2 -> 3b2 double
2          38 39  1  2  3  4  5 28 37 .. 2b2 -> 3b2 single

```

6. The default selection process subsequently undertaken is equivalent to the following ROOTS and THRESH directives.

```

THRESH 10 10
ROOTS 1

```

Thus this default selection process involves construction of an explicit zero-order Hamiltonian H_0 (over the reference functions described above) followed by perturbative selection of configurations with respect to the lowest root of H_0 . The minimum threshold to be used in selection (T_{min}) is 10 micro-Hartree, with an increment of 10 uH to be used in defining the higher-threshold case to be solved in the process of extrapolation [1].

7. In default the module will, having solved the secular problem for the lowest root of the CI secular problem, generate the spinfree natural orbitals from the associated CI eigenfunction.

The sequence of data lines defining the Semi-direct Table-CI calculation is terminated by the ENTER directive. Note at this stage that the full data specification corresponding to the defaults generated from the above data file is as follows:

```

TITLE
H2CO - TZVP - EXPLICIT DATA FOR DEFAULT MRDCI SETTINGS
SUPER OFF NOSYM
ZMAT ANGSTROM
C
O 1 1.203
H 1 1.099 2 121.8
H 1 1.099 2 121.8 3 180.0

```

```

END
BASIS TZVP
RUNTYPE CI
ACTIVE
1 TO 52 END
MRDCI DIRECT
TABLE
SELECT
CNTRL 16
SPIN 1
SYMM 1
SINGLES ALL
CONF
  0   1   2   3   4   5 28 37 38
  0   1   2   3   4   6 28 37 38
  2   5   6   1   2   3   4 28 37 38
  0   1   2   3   4   5 29 37 38
  2 28 29   1   2   3   4   5 37 38
  0   1   2   3   4   5 28 37 39
  2 38 39   1   2   3   4   5 28 37
END
THRESH 10 10
ROOTS 1
CI
NATORB
CIVEC 1
ENTER

```

24.2 Calculations on the Formaldehyde Cations

Let us now consider a Semi-direct Table-CI calculation on the 2B_2 state of H_2CO^+ , again using default options available within the module. A valid data sequence for performing such a calculation is shown below, where we are still performing all the computation in a single job.

```

TITLE
H2CO+ 2B2 TZVP - DEFAULT MRDCI SETTINGS -113.06446075
MULT 2
CHARGE 1
ZMAT ANGSTROM
C
O 1 1.203
H 1 1.099 2 121.8
H 1 1.099 2 121.8 3 180.0
END
BASIS TZVP
RUNTYPE CI
MRDCI DIRECT
ENTER

```

Considering the changes to the closed-shell run, the following points should be noted:

- The set of vectors used in the Table-CI transformation will be restored from the default eigenvector section of the Dumpfile (given that no section is specified on the ENTER

directive). This will be section 5, the section used to store the energy-ordered canonicalised orbitals from the open-shell SCF calculation.

- The symmetry and spin of the CI wavefunction will be deduced from the preceding SCF calculation i.e. a CI wavefunction of B_2 symmetry (corresponding to SYMMETRY 3), and a doublet CI wavefunction (corresponding to SPIN 2).
- The number of active electrons in the CI will be set to be those involved in the SCF calculation (i.e. CNTRL 15).
- Singly excited configurations with respect to each of the default reference configurations (SINGLES ALL) will be included, regardless of their computed energy lowerings.
- The set of reference configurations to be employed will follow the same algorithm used in the closed shell case above i.e. the SCF configuration, plus those generated from this configuration by including (i) for each symmetry IRREP, the doubly excited configuration arising from excitation of the highest occupied DOMO of that symmetry to the lowest virtual orbital (VMO) of the same symmetry, and (ii) the lowest singly excited configuration, again arising from the highest occupied DOMO to the lowest VMO of the same symmetry. In the present example, this will correspond to the SCF configuration, the double and single excitation arising from the DOMO $5a_1$ to VMO $6a_1$, the double and single excitation arising from the DOMO $1b_1$ to VMO $2b_1$, and the double and single excitation arising from the DOMO $1b_2$ to VMO $3b_2$. Note that the DOMO involved in the latter configurations is now the $1b_2$ given that the $2b_2$ is now singly occupied, and again the absence of excitations involving a_2 MOs given the absence of such orbitals involved in the occupied manifold. This again results in a total reference set of 7 functions, as shown thus in the job output:

numbers of open shells and corresponding main configurations

```

1  38  1  2  3  4  5  28  37      ..  SCF configuration
1  38  1  2  3  4  6  28  37      ..  5a1 -> 6a1 double
3   5  6 38  1  2  3  4  28  37    ..  5a1 -> 6a1 single
1  38  1  2  3  4  5  29  37      ..  1b1 -> 2b1 double
3  28 29 38  1  2  3  4  5  37    ..  1b1 -> 2b1 single
1  38  1  2  3  4  5  28  39      ..  1b2 -> 3b2 double
3  37 38 39  1  2  3  4  5  28    ..  1b2 -> 3b2 single

```

The sequence of data lines defining the Semi-direct Table-CI calculation is again terminated by the ENTER directive. Note at this stage that the full data specification corresponding to the defaults generated from the above data file is as follows

```

TITLE
H2CO+ 2B2 TZVP - EXPLICIT DATA FOR DEFAULTS
MULT 2
CHARGE 1
SUPER OFF NOSYM
ZMAT ANGSTROM
C

```

```

O 1 1.203
H 1 1.099 2 121.8
H 1 1.099 2 121.8 3 180.0
END
BASIS TZVP
RUNTYPE CI
OPEN 1 1
ACTIVE
1 TO 52 END
MRDCI DIRECT
TABLE
SELECT
CNTRL 15
SPIN 2
SYMM 3
SINGLES ALL
CONF
1 38 1 2 3 4 5 28 37
1 38 1 2 3 4 6 28 37
3 5 6 38 1 2 3 4 28 37
1 38 1 2 3 4 5 29 37
3 28 29 38 1 2 3 4 5 37
1 38 1 2 3 4 5 28 39
3 37 38 39 1 2 3 4 5 28
END
THRESH 10 10
ROOTS 1
CI
NATORB
CIVEC 1
VECTORS ATOMS
ENTER 4 5

```

Let us now consider a Semi-direct Table-CI calculation on the 2B_1 state of H_2CO^+ , again using default options available within the module. A valid data sequence for performing such a calculation is shown below, where we are still performing all the computation in a single job.

```

TITLE
H2CO+ 2B1 TZVP - DEFAULT MRDCI SETTINGS
MULT 2
CHARGE 1
ZMAT ANGSTROM
C
O 1 1.203
H 1 1.099 2 121.8
H 1 1.099 2 121.8 3 180.0
END
BASIS TZVP
RUNTYPE CI
MRDCI DIRECT
SWAP
7 8
END
ENTER

```

Considering the changes to the closed-shell run, the following points should be noted:

- The OPEN directive is now present, specified prior to the Table-CI data.
- In the absence of section specification on the ENTER directive, the set of vectors used in the Table-CI transformation will be restored from the default open-shell SCF section containing the energy ordered eigenvectors (section 5). The SWAP directive is to generate initial starting MOs for the B₁ state.
- The symmetry and spin of the CI wavefunction will be deduced from the preceding SCF calculation i.e. a CI wavefunction of B₁ symmetry (corresponding to SYMMETRY 2). and a doublet CI wavefunction (corresponding to SPIN 2).
- The number of active electrons in the CI will be set to be those involved in the SCF calculation (i.e. CNTRL 15).
- Singly excited configurations with respect to each of the default reference configurations (SINGLES ALL) will be included, regardless of their computed energy lowerings.
- The set of reference configurations to be employed will be generated using the same algorithm used in the open shell case above i.e. the SCF configuration, plus those generated from this configuration by including (i) for each symmetry IRREP, the doubly excited configuration arising from excitation of the highest occupied DOMO of that symmetry to the lowest virtual orbital (VMO) of the same symmetry, and (ii) the lowest singly excited configuration, again arising from the highest occupied DOMO to the lowest VMO of the same symmetry. In the present example, this will correspond to the SCF configuration, the double and single excitation arising from the DOMO 5a₁ to VMO 6a₁, and the double and single excitation arising from the DOMO 2b₂ to VMO 3b₂. Note that there no excitations involving a₂ or b₁ MOS, given the absence of such orbitals in the doubly occupied manifold. This now results in a total reference set of just 5 functions, as shown thus in the job output:

```

numbers of open shells and corresponding main configurations

1          28  1  2  3  4  5  37  38      ..  SCF configuration
1          28  1  2  3  4  6  37  38      ..  5a1 -> 6a1 double
3           5  6 28  1  2  3  4  37  38      ..  5a1 -> 6a1 single
1          28  1  2  3  4  5  37  39      ..  2b2 -> 3b2 double
3          28 38 39  1  2  3  4  5  37      ..  2b2 -> 3b2 single

```

The sequence of data lines defining the Semi-direct Table-CI calculation is again terminated by the ENTER directive. Note that the full data specification corresponding to the defaults generated from the above data file is as follows

```

TITLE
H2CO+ 2B1 TZVP - EXPLICIT DATA FOR DEFAULTS
MULT 2
CHARGE 1
SUPER OFF NOSYM

```

```

ZMAT ANGSTROM
C
O 1 1.203
H 1 1.099 2 121.8
H 1 1.099 2 121.8 3 180.0
END
BASIS TZVP
RUNTYPE CI
OPEN 1 1
ACTIVE
1 TO 52 END
MRDCI DIRECT
TABLE
SELECT
CNTRL 15
SPIN 2
SYMM 2
SINGLES ALL
CONF
1 28 1 2 3 4 5 37 38
1 28 1 2 3 4 6 37 38
3 5 6 28 1 2 3 4 37 38
1 28 1 2 3 4 5 37 39
3 28 38 39 1 2 3 4 5 37
END
THRESH 10 10
ROOTS 1
CI
NATORB
CIVEC 1
VECTORS ATOMS
SWAP
7 8
END
ENTER 4 5

```

25 Memory Specification for the Semi-direct Table-CI Module

The memory requirements of the semi-direct module are typically greater than those associated with the conventional algorithm. While the default memory allocations will prove adequate for "small-medium" cases, the user should use the MEMORY pre-directive to increase this allocation in more demanding cases e.g. at least 8 MWords in calculations with, say, more than 20 active electrons. In this section we outline the main demands on memory, and the mechanisms for increasing this allocation should the default allocations prove inadequate.

The overall memory required is determined by four integer quantities, namely;

1. NTEINT, the number of transformed two-electron integrals. The default value is 3,500,001.
2. IOTM, the field length for the selected configurations. The default value is 2,000,000.

3. NEDIM, the dimension of internal arrays required by the direct-CI algorithm. The default value is 2,000,000.
4. MDI, the maximum dimension of the hamiltonian. The default value is 1,000,001.

In practice the code will attempt to use these default values and computes the overall memory requirement based on the settings above. If this memory is not available, each of the above values will be halved until the calculation can proceed within the memory allocated to the job. The latter is 4 MWords in default, a value which will not be sufficient to accommodate the above settings. Thus an examination of the semi-direct Table-CI output will typically reveal the following:

```

+++++
+ Insufficient memory for default allocations +
+ reduce parameters as follows +
+++++
+ nteint from 3500001 to 1750001 +
+ mdi from 1000001 to 500001 +
+ iotm from 2000000 to 1000000 +
+ nedim from 2000000 to 1000000 +
+++++

```

```

+++++
+ Insufficient memory for default allocations +
+ reduce parameters as follows +
+++++
+ nteint from 3500001 to 875001 +
+ mdi from 1000001 to 250001 +
+ iotm from 2000000 to 500000 +
+ nedim from 2000000 to 500000 +
+++++

```

This is usually not a problem, as the default values are such to accommodate quite demanding applications. Should the decreased settings prove inadequate (the code should inform the user accordingly), then the first action is to increase the memory for the job using the MEMORY pre-directive. Typically a pre-directive setting of 14 MWords will enable the default settings to apply.

If these defaults prove inadequate, the user must resort to specifying the parameter to be increased through data input, while increasing the MEMORY setting to compensate for this increase. This data-driven allocation is achieved under control of the CORE directive, which should be presented immediately after the "MRDCI DIRECT" data line. The directive consists of a single line with the character string CORE in the first data field. Subsequent data fields are read in pairs to variables (TEXTM, IMEMM) in format (A,I), each such pair indicating the parameter which is to be modified, followed by an integer defining the revised value. Valid data fields are thus:

- TEXTM may be set to one of the character strings, NTEINT, IOTM, NEDIM or MDI.

- IMEMM is an integer parameter used to specify the required value to be used in determining the memory.

Example

Presenting the data line

```
MRDCI DIRECT
CORE NTEINT 5000000
..
..
```

will act to increase the memory allocation for holding the transformed two-electron integrals.

26 Calculating the 1A_1 states of H_2O

To clarify our discussion of the Semi-direct Table-CI module, we work through a typical example of using the Table-CI method in calculating the energetics and properties of the three low lying 1A_1 states of the H_2O molecule. The basis set employed is the TZVP triple-zeta plus polarisation set; this is augmented with a diffuse s- and p-orbital on the oxygen to provide a reasonable description of the known Rydberg character of the states of interest.

The computation is split into four separate jobs, in which we,

1. perform the initial SCF;
2. carry out an initial CI, where the reference set employed acts to provide at least a qualitative description of the states of interest;
3. based on the output from the initial CI, we augment the reference set to provide a quantitative description of the first three states;
4. finally, having generated the CI vectors for the three states, we carry out in the final job an analysis of each vector in terms of natural orbitals and one-electron properties, and generate the transition moments between the ground and two excited states.

We now consider various aspects of each job in turn.

Job 1: The SCF

```
TITLE
**** H2O TZVP + DIFFUSE S,P MRDCI *
SUPER OFF NOSYM
ZMAT ANGSTROM
O
H 1 0.951
```

```

H 1 0.951 2 104.5
END
BASIS
TZVP 0
TZVP H
S 0
1.0 0.02
P 0
1.0 0.02
END
ENTER

```

The only points to note here is the use of the SUPER directive in suppressing skeletonisation and, in the absence of section specification on the ENTER directive, the use of the default section for output of the SCF eigenvectors (section 1).

Job 2: The Initial 3M/3R CI

An examination of the SCF output reveals the following orbital analysis.

```

=====
IRREP  NO. OF SYMMETRY ADAPTED
        BASIS FUNCTIONS
=====
  1          18
  2           6
  3          10
  4           2
=====

```

and the following orbital assignments characterising the closed-shell SCF configuration:

$$1a_1^2 2a_1^2 1b_2^2 3a_1^2 1b_1^2 \quad (34)$$

```

=====
M.O.  IRREP  ORBITAL ENERGY  ORBITAL OCCUPANCY
=====
  1    1    -20.56084959    2.0000000
  2    1    -1.35696939    2.0000000
  3    3    -0.72200122    2.0000000
  4    1    -0.58247942    2.0000000
  5    2    -0.50858566    2.0000000
  6    1     0.02724259    0.0000000
  7    3     0.04894440    0.0000000
  8    2     0.05589681    0.0000000
  9    1     0.06133571    0.0000000
 10    1     0.20403420    0.0000000
 11    3     0.22824210    0.0000000
 12    3     0.53700802    0.0000000
 13    1     0.56235022    0.0000000
 14    2     0.58645643    0.0000000

```

15	1	0.66887228	0.0000000
16	3	0.74805617	0.0000000
17	1	1.07690608	0.0000000
18	1	1.88545053	0.0000000
19	4	1.92243836	0.0000000
20	2	2.12944874	0.0000000
21	3	2.20541910	0.0000000
22	1	2.34202871	0.0000000
23	3	2.39946430	0.0000000
24	3	2.69788310	0.0000000
25	1	2.72651832	0.0000000
26	2	2.73832720	0.0000000
27	1	3.07664215	0.0000000
28	3	3.26840142	0.0000000
29	2	3.54616570	0.0000000
30	1	3.58631019	0.0000000
31	4	3.59701772	0.0000000
32	1	3.84174131	0.0000000
33	1	4.84610143	0.0000000
34	3	5.14220270	0.0000000
35	1	7.73115986	0.0000000
36	1	47.56758932	0.0000000

=====

Based on the above output, the CONF data lines may be deduced from the following table, where we assume that we wish to freeze the O1s inner shell orbitals and discard the inner shell complement orbital:

IRrep	IRrep No.	No. of Basis Functions	Frozen MOs	Active MOs	Sequence Nos.
a ₁	1	18	1	16	1-16
b ₁	2	6	0	6	17-22
b ₂	3	10	0	10	23-32
a ₂	4	2	0	2	33-34

Note that the virtual SCF MOs dominated by the diffuse oxygen basis functions are the 4a₁, the 2b₂, the 2b₁ and the 5a₁, with SCF sequence numbers 6,7,8 and 9 respectively. The symmetry re-ordered sequence numbers, allowing for the effective removal of the two a₁ orbitals, are 3, 24, 18 and 5 respectively. To perform a three-root 8-electron valence-CI calculation, based on the SCF configurations of the ground and excited Rydberg states, involving the single excitations (1b₁ to 2b₁) and (3a₁ to 4a₁) would require the following CONF data:

```
CONF
0      1 2 17 23
2 2 3 1 17 23
2 17 18 1 2 23
END
```

The following data will perform this three root-CI, where

- the SCF computation is BYPASS'ed;
- the freezing and discarding of the two a_1 MOs is accomplished using the CORE and ACTIVE directives;
- the default sub-module specifications are in effect, with no specific need to reference CI or NATORB activity; we assume that the table-ci data set is not available to the job, and is to be generated in this run;
- the ROOTS directive is specifying selection with respect to the first 3 roots of the zero order problem, which we assume will correspond to the states of interest.

```

RESTART NEW
TITLE
H2O TZVP + DIFFUSE S,P TABLE-CI 3M/3R*
SUPER OFF NOSYM
BYPASS SCF
ZMAT ANGSTROM
0
H 1 0.951
H 1 0.951 2 104.5
END
BASIS
TZVP 0
TZVP H
S 0
1.0 0.02
P 0
1.0 0.02
END
RUNTYPE CI
ACTIVE
2 TO 35
END
CORE
1 END
MRDCI DIRECT
SELECT
CNTRL 8
CONF
0      1 2 17 23
2 2 3 1 17 23
2 17 18 1 2 23
END
THRE 10 10
ROOTS 3
ENTER

```

Job 3: The Final 12M/3R CI

An examination of the output from the initial CI reveals that the dominant configurations have, as expected, been included. We show below the final CI vectors for each of the states: not

surprisingly the ground state is more accurate, by virtue of its SCF MOs having been employed. Augmenting the reference set to improve the description of the two excited states follows straightforwardly from the statistics below:

Description of the X^1A_1 state

EXTRAPOLATED ENERGY = -76.27252960

```
*****
* CONFIGURATION WEIGHTS *
*****
**** ROOT 1 ****
=====
          C*C      CONFIGURATION
          =====
M  0.94942   1   2  17  23
    0.00141   1   2  19  23
    0.00112   2   7  17  19   1  23
    0.00125   2   7  23  27   1  17
    0.00147  17  19  23  27   1   2
```

SUM OF MAIN REFERENCE C*C = 0.949613377982042

Description of the 1^1A_1 state

EXTRAPOLATED ENERGY = -75.90090942

```
*****
* CONFIGURATION WEIGHTS *
*****
**** ROOT 2 ****
=====
          C*C      CONFIGURATION
          =====
    0.00283   1   2  18  23
M  0.06414   2   3   1  17  23
    0.00758   2   5   1  17  23
M  0.84001  17  18   1   2  23
    0.00263  17  19   1   2  23
    0.01150  18  19   1   2  23
    0.00221   1   5  17  18   2  23
    0.00136   1   8  17  18   2  23
    0.00226   2   5  17  18   1  23
    0.00444   2   6  17  18   1  23
    0.00550   2   7  17  18   1  23
    0.00667  17  18  23  25   1   2
    0.00664  17  18  23  27   1   2
```

SUM OF MAIN REFERENCE C*C = 0.904355147296805

Description of the 2^1A_1 state

EXTRAPOLATED ENERGY = -75.88256073

```

*****
* CONFIGURATION WEIGHTS *
*****
**** ROOT 3 ****
=====
          C*C      CONFIGURATION
=====
M  0.78360  2  3  1  17  23
    0.00618  2  4  1  17  23
    0.05594  2  5  1  17  23
M  0.07077 17 18  1  2  23
    0.00236  3  5  1  17  23
    0.00344  3  6  1  17  23
    0.00494  3  7  1  17  23
    0.00132  1  2  3  5  17  23
    0.00191  2  3  17 18  1  23
    0.00872  2  3  17 19  1  23
    0.00639  2  3  23 25  1  17
    0.00600  2  3  23 27  1  17

```

SUM OF MAIN REFERENCE C*C = 0.854543160127212

Taking as the criterion for inclusion a weight of 0.005, the final 12 reference set-CI is shown below. We have assumed that the FORTRAN *interface* FTN031, plus the TABLE data base, table-ci, has been saved from the second job, enabling us to bypass the transformation and data base generation.

```

RESTART CI
TITLE
H2O TZVP + DIFFUSE S,P TABLE-CI 12M/3R *
SUPER OFF NOSYM
BYPASS SCF TRAN
ZMAT ANGSTROM
O
H 1 0.951
H 1 0.951 2 104.5
END
BASIS
TZVP O
TZVP H
S O
1.0 0.02
P O
1.0 0.02
END
RUNTYPE CI
ACTIVE
2 TO 35
END
CORE
1 END

```

```

MRDCI DIRECT
TABLE BYPASS
SELECT
CNTRL 8
CONF
0      1 2 17 23
2 2 3 1 17 23
2 2 4 1 17 23
2 2 5 1 17 23
2 17 18 1 2 23
2 18 19 1 2 23
4 17 18 23 25 1 2
4 17 18 23 27 1 2
4 2 7 17 18 1 23
4 2 3 17 19 1 23
4 2 3 23 25 1 17
4 2 3 23 27 1 17
END
THRE 10 10
ROOT 3
ENTER

```

Job 4: The Analysis

Assuming that the diagonalisation *interface*, FTN036, had been saved above, then the final analysis job is straightforward: again bypassing of the various sub-modules involves explicit mention of the TABLE, and CI modules, in addition to flagging the previous SELECT data lines with the BYPASS keyword. We have routed the natural orbitals from the 3 A_1 states to the Dumpfile using the PUTQ directive.

```

RESTART CI
TITLE
**** H2O TZVP + DIFFUSE S,P TABLE-CI / ANALYSIS *
SUPER OFF NOSYM
BYPASS SCF TRAN
ZMAT ANGSTROM
0
H 1 0.951
H 1 0.951 2 104.5
END
BASIS
TZVP 0
TZVP H
S 0
1.0 0.02
P 0
1.0 0.02
END
ACTIVE
2 TO 35
END
CORE
1 END

```

```

RUNTYPE CI
MRDCI DIRECT
TABLE BYPASS
SELECT BYPASS
CNTRL 8
CONF
0      1 2 17 23
2 2 3 1 17 23
2 2 4 1 17 23
2 2 5 1 17 23
2 17 18 1 2 23
2 18 19 1 2 23
4 17 18 23 25 1 2
4 17 18 23 27 1 2
4 2 7 17 18 1 23
4 2 3 17 19 1 23
4 2 3 23 25 1 17
4 2 3 23 27 1 17
END
THRE 10 10
ROOT 3
CI BYPASS
NATORB IPRIN
CIVE 1 2 3
PUTQ AOS 50 51 52
PROP
CIVE 1 2 3
0      1 2 17 23
2 17 18 1 2 23
2 2 3 1 17 23
MOMENT
36 1 36 2 2
ENTER

```

Description of the Output for MRDCI Moments

The MRDCI module calculates the oscillator strength using both the dipole length formalism:

$$f(\mathbf{r}) = 2/3 \langle \Psi' | \mathbf{r} | \Psi'' \rangle^2 / \Delta E$$

and the dipole velocity formalism:

$$f(\nabla) = 2/3 | \langle \Psi' | \nabla | \Psi'' \rangle |^2 / \Delta E$$

The most significant contributions due to individual molecular orbitals are printed out as a table containing the largest coefficients of the transition density matrix and the following corresponding integrals.

$$\begin{array}{ccc}
 \langle \psi_i | x | \psi_j \rangle & \langle \psi_i | y | \psi_j \rangle & \langle \psi_i | z | \psi_j \rangle \\
 \langle \psi_i | \nabla(x) | \psi_j \rangle & \langle \psi_i | \nabla(y) | \psi_j \rangle & \langle \psi_i | \nabla(z) | \psi_j \rangle
 \end{array}$$

The $f(\mathbf{r})$ and $f(\nabla)$ values are printed out in x,y,z components and the expectation values for $\langle \psi | \sum_i x_i, y_i, z_i | \psi \rangle$ are also printed.

27 Iterative Natural Orbital Calculations

We now work through an example of using the natural orbitals generated by the module in a subsequent CI calculation. We consider a DZ calculation on the ground state of C_2H_4 , with the computation split into four separate jobs, in which we,

1. perform the initial SCF;
2. carry out an initial CI, where the reference set employed comprises just the SCF configuration, using the SCF MOs; of interest;
3. based on the output from the initial CI, we augment the reference set to include the leading secondary configuration, generating the resulting natural orbitals;
4. carry out the 2-reference CI based on the natural orbitals generated in the previous step.

We now consider various aspects of each job in turn.

Job 1: The SCF

```
TITLE
ETHYLENE DZ GROUND STATE SCF
SUPER OFF NOSYM
ZMATRIX ANGSTROM
C
C 1 1.4
H 1 1.1 2 120.0
H 1 1.1 2 120.0 3 180.0
H 2 1.1 1 120.0 3 0.0
H 2 1.1 1 120.0 3 180.0
END
BASIS DZ
ENTER
```

The only points to note here is the use of the SUPER directive in suppressing skeletonisation.

Job 2: The 2M/1R CI

An examination of the SCF output reveals the following orbital analysis.

```
=====
IRREP  NO. OF SYMMETRY ADAPTED
        BASIS FUNCTIONS
=====
      1          8
```

```

      2      2
      3      4
      5      8
      6      2
      7      4
=====

```

and the following orbital assignments characterising the closed-shell SCF configuration:

$$1a_g^2 1b_{1u}^2 2a_g^2 2b_{1u}^2 1b_{2u}^2 3a_g^2 1b_{3g}^2 1b_{3u}^2 \quad (35)$$

```

=====
M.O.  IRREP  ORBITAL ENERGY  ORBITAL OCCUPANCY
=====
  1    1   -11.25533463    2.0000000
  2    5   -11.25413119    2.0000000
  3    1    -1.02052567    2.0000000
  4    5    -0.79195744    2.0000000
  5    3    -0.64152856    2.0000000
  6    1    -0.57038928    2.0000000
  7    7    -0.51438205    2.0000000
  8    2    -0.36388693    2.0000000
  9    6     0.13190687    0.0000000
 10    5     0.25441028    0.0000000
 11    1     0.25558269    0.0000000
 12    3     0.33918097    0.0000000
 13    5     0.36641681    0.0000000
 14    1     0.41844853    0.0000000
 15    3     0.45487336    0.0000000
 16    7     0.49648833    0.0000000
 17    2     0.49708917    0.0000000
 18    6     0.60222488    0.0000000
 19    7     0.64242537    0.0000000
 20    1     0.76465797    0.0000000
 21    5     0.82560838    0.0000000
 22    5     1.10140194    0.0000000
 23    1     1.20630804    0.0000000
 24    3     1.30189632    0.0000000
 25    5     1.35219192    0.0000000
 26    7     1.50761510    0.0000000
 27    1    23.76609415    0.0000000
 28    5    24.01493168    0.0000000
=====

```

Based on the above output, the CONF data lines may be deduced from the following table, where we assume that we wish to freeze the C1s inner shell orbitals:

IRrep	IRrep No.	No. of Basis Functions	Frozen MOs	Active MOs	Sequence Nos.
a_g	1	8	1	7	1-7
b_{3u}	2	2	0	2	8-9
b_{2u}	3	4	0	4	10-13
b_{1u}	5	8	1	7	14-20
b_{2g}	6	2	0	2	21-22
b_{3g}	7	4	0	4	23-26

Note that within the DZ basis employed, there are no basis functions of b_{1g} (IRrep 4) or a_u (IRrep 8) symmetry. The symmetry re-ordered sequence numbers of the ground state orbitals, allowing for the effective removal of the $1a_g$ and $1b_{1u}$ orbitals, are 1, 14, 10, 2, 23 and 8 respectively. To perform a two reference, 12-electron valence-CI calculation, based on the SCF configuration

$$2a_g^2 2b_{1u}^2 1b_{2u}^2 3a_g^2 1b_{3g}^2 1b_{3u}^2 \quad (36)$$

and the doubly excited configuration:

$$2a_g^2 2b_{1u}^2 1b_{2u}^2 3a_g^2 1b_{3g}^2 1b_{2g}^2 \quad (37)$$

would require the following CONF data:

```
CONF
0 1 2 8 10 14 23
0 1 2 10 14 21 23
END
```

The following data will perform this CI, where

- The SCF computation is BYPASS'ed;
- The freezing and discarding of the $1a_g$ and $1b_{1u}$ MOs is accomplished using the CORE and ACTIVE directives;
- The default sub-module specifications are in effect, with no specific need to reference TABLE or CI activity i.e. the table-ci data set is to be constructed in the job;
- The natural orbitals are routed to section 200 of the Dumpfile. Note that subsequent usage of the NOs by the Table-CI module requires the SABF specification on the PUTQ directive.

```
RESTART NEW
TITLE
ETHYLENE CI GROUND STATE 2M SCF-MOS
BYPASS SCF
```

```

ZMATRIX ANGSTROM
C
C 1 1.4
H 1 1.1 2 120.0
H 1 1.1 2 120.0 3 180.0
H 2 1.1 1 120.0 3 0.0
H 2 1.1 1 120.0 3 180.0
END
BASIS DZ
CORE
1 2 END
ACTIVE
3 TO 28 END
RUNTYPE CI
MRDCI DIRECT
SELECT
SYMMETRY 1
CNTRL 12
SPIN 1
SINGLES 1
CONF
0 1 2 8 10 14 23
0 1 2 10 14 21 23
END
THRESH 30 10
NATORB IPRINT
PUTQ SABF 200
ENTER

```

Job 3: The Natural Orbital CI

We show below the data for using the NOs from the 2-reference CI, where the orbitals routed to section 200 are now restored by specification on the ENTER directive. The following points should be noted:

- We assume that the Table-CI data base, table-ci, been saved from the initial CI job, allowing the BYPASS specification on the TABLE directive.
- In contrast to the conventional Table-CI module, restoring the NOs *must* now be controlled through VECTORS and ENTER specification; in the conventional module this was input through TRAN specification within the Table-CI transformation module.
- The resulting NOs from the natural orbital CI are now routed to section 210, and could be used in a subsequent CI in obvious fashion.

```

RESTART NEW
TITLE
ETHYLENE CI GROUND STATE 2M NOS
BYPASS SCF
ZMATRIX ANGSTROM
C
C 1 1.4

```

```

H 1 1.1 2 120.0
H 1 1.1 2 120.0 3 180.0
H 2 1.1 1 120.0 3 0.0
H 2 1.1 1 120.0 3 180.0
END
BASIS DZ
3 TO 28 END
CORE
1 2 END
RUNTYPE CI
MRDCI DIRECT
TABLE BYPASS
SELECT
CNTRL 12
SYMMETRY 1
SPIN 1
SINGLES 1
CONF
0 1 2 8 10 14 23
0 1 2 10 14 21 23
END
THRESH 30 10
NATORB IPRINT
PUTQ SABF 210
VECTORS 200
ENTER 200

```

We show below the final CI vector from the natural orbital CI

Description of the X^1A_g state

EXTRAPOLATED ENERGY = -78.20206451

```

*****
* CONFIGURATION WEIGHTS *
*****
***** ROOT 1 *****
=====
          C*C      CONFIGURATION
=====
M  0.89794  1  2  8  10  14  23
    0.00125  1  8  10  14  15  23
M  0.03203  1  2  10  14  21  23
    0.00100  1  2  8  11  14  23
    0.00102  1  2  8  10  11  14
    0.00279  1  8  15  21  2  10  14  23
    0.00106  1  3  14  16  2  8  10  23
    0.00499  2  8  15  21  1  10  14  23
    0.00143  2  8  16  21  1  10  14  23
    0.00186  2  3  14  16  1  8  10  23
    0.00119  2  11  16  23  1  8  10  14
    0.00101  8  9  10  11  1  2  14  23
    0.00144  8  10  21  24  1  2  14  23

```

```

0.00260  3  8 14 21  1  2 10 23
0.00110  8  9 23 24  1  2 10 14
0.00104  8 12 21 23  1  2 10 14
0.00117  3 10 16 23  1  2  8 14
0.00297 10 11 23 24  1  2  8 14
0.00125  3 11 14 23  1  2  8 10

```

SUM OF MAIN REFERENCE C*C = 0.929973257309359

28 Table-CI Calculations Using MCSCF Orbitals

To conclude our discussion of the semi-direct Table-CI module, we work through an example of using the natural orbitals generated from the MCSCF module in a subsequent CI calculation. We consider a calculation on the ground state of H₂CO, with the computation split into three separate jobs, in which we,

1. perform an initial SCF;
2. carry out the MCSCF calculation;
3. perform the MRDCI calculation using the MCSCF natural orbitals.

We now consider various aspects of each job in turn, and note that several changes will be required to the corresponding data sets shown above for the Conventional Table-CI study.

Job 1: The SCF

```

TITLE
H2CO - DZP + F
SUPER OFF NOSYM
ZMATRIX ANGSTROM
C
O 1 1.203
H 1 1.099 2 121.8
H 1 1.099 2 121.8 3 180.0
END
BASIS
DZP O
DZP C
DZP H
F C
1 1.0
F 0
1.0 1.0
END
ENTER

```

The only points to note here again is the use of the SUPER directive in suppressing skeletonisation, and use of the default eigenvector section (section 1) for storage of the closed-shell eigenvectors. An examination of the SCF output reveals the following orbital analysis.

```

=====
IRREP  NO. OF SYMMETRY ADAPTED
        BASIS FUNCTIONS
=====
  1         28
  2         13
  3         16
  4          5
=====

```

and the following orbital assignments characterising the closed-shell SCF configuration:

```

=====
M.O.  IRREP  ORBITAL ENERGY  ORBITAL OCCUPANCY
=====
  1    1    -20.57768533    2.0000000
  2    1    -11.34457777    2.0000000
  3    1     -1.40746540    2.0000000
  4    1     -0.87003449    2.0000000
  5    3     -0.69591811    2.0000000
  6    1     -0.65109519    2.0000000
  7    2     -0.53687971    2.0000000
  8    3     -0.44174805    2.0000000
  9    2      0.11697212    0.0000000
 10    1      0.26220763    0.0000000
 11    1      0.27217357    0.0000000
 12    3      0.38931080    0.0000000
 13    3      0.41757152    0.0000000
 14    2      0.46526352    0.0000000
 15    1      0.60968525    0.0000000
 16    1      0.75001014    0.0000000
 17    2      0.86980119    0.0000000
 18    1      0.89167074    0.0000000
 19    3      0.93051881    0.0000000
 20    1      1.07098621    0.0000000
 21    3      1.18616042    0.0000000
 22    1      1.35370640    0.0000000
 23    4      1.52221224    0.0000000
 24    2      1.68895841    0.0000000
 25    1      1.88480823    0.0000000
 26    3      1.97392259    0.0000000
 27    4      2.13452238    0.0000000
 28    1      2.13982211    0.0000000
 29    3      2.19187925    0.0000000
 30    1      2.34994146    0.0000000
 31    2      2.36355601    0.0000000
 32    4      2.67698155    0.0000000
 33    1      2.82812279    0.0000000
 34    2      2.84696649    0.0000000
 35    3      2.97321688    0.0000000
 36    1      3.14466153    0.0000000
 37    1      3.33275225    0.0000000
 38    3      3.51306001    0.0000000
 39    1      3.51697350    0.0000000
 40    2      3.52974692    0.0000000

```

41	3	3.68500148	0.0000000
42	1	3.79236483	0.0000000
43	3	3.83958499	0.0000000
44	4	3.85444369	0.0000000
45	2	3.87171104	0.0000000
46	2	4.14123645	0.0000000
47	3	4.16304613	0.0000000
48	1	4.16535425	0.0000000
49	2	4.16620625	0.0000000
50	2	4.32796704	0.0000000
51	3	4.47390388	0.0000000
52	1	4.49325977	0.0000000
53	1	4.68584478	0.0000000
54	4	4.89513471	0.0000000
55	3	5.13208791	0.0000000
56	1	5.14756255	0.0000000
57	2	5.85901984	0.0000000
58	1	5.92954017	0.0000000
59	3	6.06228738	0.0000000
60	1	8.35480844	0.0000000
61	1	27.71561806	0.0000000
62	1	45.72664766	0.0000000

=====

Job 2: The MCSCF

The following data performs a 10 electron in 9 orbital CASSCF calculation using the MCSCF module, with the natural orbitals routed to section 10 of the Dumpfile under control of the CANONICAL directive. In the absence of the VECTORS directive, the SCF MOs will be used as the starting orbitals. This data set is just that provided in the conventional Table-CI case shown above.

```

RESTART
TITLE
H2CO - MCSCF (10E IN 9 M.O.)
SUPER OFF NOSYM
NOPRINT
BYPASS
ZMATRIX ANGSTROM
C
O 1 1.203
H 1 1.099 2 121.8
H 1 1.099 2 121.8 3 180.0
END
BASIS
DZP O
DZP C
DZP H
F C
1 1.0
F O
1.0 1.0
END

```



```

SCFTYPE MCSCF
MCSCF
ORBITAL
COR1 COR1 COR1 DOC1 DOC3 DOC1 DOC2 DOC3 UOC2 UOC1 UOC3 UOC1
END
PRINT ORBITALS VIRTUALS NATORB
CANONICAL 10 FOCK DENSITY FOCK
ENTER

```

Job 3: The Table-CI Job

Performing a semi-direct Table-CI calculation using the natural orbitals generated in the previous step is fairly straightforward. The following points should be noted:

- The MCSCF data presented in the preceding step must remain as part of the input data set, with that computation now BYPASS'ed.
- While specification of the input orbital set in the conventional Table-CI calculation requires use of the TRAN directive, it is assumed in the present case that the orbital set required is that nominated on the CANONICAL directive. i.e. no explicit section specification is required.
- With no frozen or discarded orbital, the orbital indices specified on the CONF directive follow in obvious fashion from the list of IRREPs given above. We are performing a simple 16 electron, 3 reference calculation, deriving just the first root, and using a 2 micro-hartree threshold.

```

RESTART
TITLE
H2CO - MCSCF (10E IN 9 M.O.) DIRECT-MRDCI FROM MCSCF NOS (SEC.10)
SUPER OFF NOSYM
BYPASS SCF
ZMAT ANGSTROM
C
O 1 1.203
H 1 1.099 2 121.8
H 1 1.099 2 121.8 3 180.0
END
BASIS
DZP O
DZP C
DZP H
F C
1 1.0
F O
1.0 1.0
END
RUNTYPE CI
SCFTYPE MCSCF
MCSCF
ORBITAL

```

```

COR1 COR1 COR1 DOC1 DOC3 DOC1 DOC2 DOC3 UOC2 UOC1 UOC3 UOC1
END
PRINT ORBITALS VIRTUALS NATORB
CANONICAL 10 FOCK DENSITY FOCK
MRDCI DIRECT
TABLE
SELECT
SYMMETRY 1
SPIN 1
CNTRL 16
SINGLES 1
CONF
0 1 2 3 4 5 29 42 43
0 1 2 3 4 5 30 42 43
0 1 2 3 4 5 29 42 44
END
ROOTS 1
THRESH 2 2
CI
NATORB
ENTER

```

Finally, we consider the data for performing exactly the same calculation as above, but now freezing the oxygen and carbon 1s core orbitals in the Table-CI calculation. The following points should be noted:

- Unlike the conventional Table-CI data, specification of the frozen orbitals now requires use of the ACTIVE and CORE directives. the CORE directive below specifying MOs 1 and 2, the ACTIVE directive specifying orbitals 3 to 62.
- The orbital indices specified on the CONF data lines reflect the removal of these two orbitals, with the CNTRL directive now pointing to a 12-electron CI calculation, as distinct from the 16 electron calculation above.

```

RESTART
TITLE
H2CO - DIRECT-MRDCI FROM MCSCF NOS (SEC.10) - FREEZE 1S
SUPER OFF NOSYM
BYPASS SCF
ZMAT ANGSTROM
C
0 1 1.203
H 1 1.099 2 121.8
H 1 1.099 2 121.8 3 180.0
END
BASIS
DZP 0
DZP C
DZP H
F C
1 1.0
F 0
1.0 1.0

```

```

END
RUNTYPE CI
ACTIVE
3 TO 62
END
CORE
1 TO 2
END
SCFTYPE MCSCF
MCSCF
ORBITAL
COR1 COR1 COR1 DOC1 DOC3 DOC1 DOC2 DOC3 UOC2 UOC1 UOC3 UOC1
END
PRINT ORBITALS VIRTUALS NATORB
CANONICAL 10 FOCK DENSITY FOCK
MRDCI DIRECT
TABLE
SELECT
SYMMETRY 1
SPIN 1
CNTRL 12
SINGLES 1
CONF
0 1 2 3 27 40 41
0 1 2 3 28 40 41
0 1 2 3 27 40 42
END
ROOTS 1
THRESH 2 2
CI
NATORB
ENTER
EOF

```

29 Iterative MRDCI Calculations

All of the MRDCI examples presented to date involve a single run of the module in which a number of excited states of specified symmetry are typically generated based on a user specified list of main configurations. Generating the entire sequence of states required for example in simulating the vertical electronic spectra of a given species is often a labour intensive exercise, requiring the repeated refinement of reference configurations. The ITERATE directive is designed to shorten this process by allowing for an iterative sequence of MRDCI calculations in which the initial reference set and associated eigenstates are iteratively refined with the minimum level of user intervention. This *modus operandi* is designed such that the user:

1. need present no explicit configuration (CONF) data;
2. may iteratively improve the quality of the CI wavefunction of a single eigen state by specifying the desired value of c^{*2} (coefficients²) of the main reference configurations.
3. may generate up to 30 eigen states of a specified spin and spatial symmetry in a single

run of the module with no prior knowledge of the composition of these states.

This iterative treatment is requested and controlled by the user through a number of options specified by the ITERATE directive. Before detailing these options, we would point to the following aspect of ITERATE usage;

- When specifying higher angular functions in the basis set to describe either Rydberg or Polarisation functions, the user is strongly recommended to use the HARMONIC directive to conduct all MRDCI calculations in a spherical harmonic rather than cartesian basis.
- As described previously, the memory requirements of the semi-direct module may be significantly greater than those associated with the conventional algorithm. As the iterative cycles of the ITERATE algorithm proceed, each energy calculation will become more demanding in memory as the number of associated reference configurations and overall size of the selected configuration space increases. While the default memory allocations may prove adequate at the outset of ITERATE processing, they are unlikely to prove so throughout, and the user should use the MEMORY pre-directive to request at least 20 MWords in calculations with, say, more than 20 active electrons. The user should try and avoid the onset of multi-passing of the eigenstate generation, a consequence of running with restrictive memory in the later stages of the iterative processing.

29.1 The ITERATE Directive and Associated Options

The role of the ITERATE directive is twofold, (i) to trigger a sequence of iterative MRDCI calculations rather a single calculation and (ii) to provide a mechanism for overriding the default MRDCI settings. The latter is achieved by specifying the ITERATE options described below on one or more data lines, each containing the character string ITERATE in the first data field; the user may present as many data lines as desired in specifying these options, providing the mechanism for presenting long option lists over several lines. Note that the ITERATE data lines should be the last of the MRDCI options presented, being typically followed by e.g. the VECTORS or ENTER directive.

29.1.1 The MAXITER Directive

This directive may be used to specify the maximum number of iterative MRDCI calculations to be undertaken. The directive consists of two data fields, read to the variables TEXT, MXITER using format (A,I);

- TEXT should be set to the character string MAXITER;
- MXITER is an integer used to specify the maximum number of MRDCI calculations to be performed.

The directive may be omitted when MXITER will be set to the default value of 8.

Example

```
ITERATE MAXITER 20
```

29.1.2 The WEIGHT Directive

This directive may be used to establish the criterion whereby a secondary configuration will be elevated to the status of a reference function in all subsequent iterative calculations. The directive consists of two data fields, read to the variables TEXT, CWEIGHT using format (A,F);

- TEXT should be set to the character string WEIGHT;
- All configurations with a CI weight (coefficients²) greater than CWEIGHT in magnitude in any of the derived CI wavefunctions will, in all subsequent MRDCI iterations, be treated as a reference function.

The directive may be omitted when CWEIGHT will be set to the default value of 0.005.

Example

```
ITERATE WEIGHT 0.003
```

29.1.3 The C**2 Directive

Limited to the treatment of a single CI wavefunction, this directive may be used to define the required level of accuracy of the final wavefunction, as reflected by the sum of the weights (C**2) of the main reference configurations. The directive consists of two data fields, read to the variables TEXT, WEIGHTM using format (A,F);

- TEXT should be set to the character string C**2;
- The reference set will continue to be augmented with secondary configurations until the final value of C**2 (coefficients²) for the CI wavefunction equals or exceeds the value specified by WEIGHTM. This is accomplished by reducing the default level of CWEIGHT for the secondary coefficients in consecutive MRDCI iterations.

The directive may be omitted when WEIGHTM will be set to the default value of 0.95.

Example

```
ITERATE C**2 0.95
```

29.1.4 The Ethylene Ground state Wavefunction

```
TITLE  
ETHYLENE CI GROUND STATE ITERATE to C*2=0.95
```

```

ZMATRIX ANGSTROM
C
C 1 1.4
H 1 1.1 2 120.0
H 1 1.1 2 120.0 3 180.0
H 2 1.1 1 120.0 3 0.0
H 2 1.1 1 120.0 3 180.0
END
BASIS DZ
CORE
1 2 END
RUNTYPE CI
MRDCI DIRECT
SELECT
SYMMETRY 1
CNTRL 12
SPIN 1
CONF
0 1 2 8 10 14 23
0 1 2 10 14 21 23
END
THRESH 3 3
ITERATE MAXI 20 C**2 0.95 WEIGHT 0.002
ENTER

```

The initial CI calculation concludes with the following analysis:

```

=====
==          Current Energies from MRDCI Iterations          ==
=====
== State   c**2      Energy      Energy      Davidson   ==
==                (T= 3, a.u.)  (T=0, a.u.)  (a.u.)     ==
=====
== 1       0.922      -78.199076   -78.199862   -78.213624 ==
=====

```

Five iterations of the MRDCI module are subsequently required to increase the initial value of c^{**2} from 0.922 to the requested level of 0.950, involving the addition of 35 secondary configurations as reference functions, and a final c^{**2} value of 0.957. The following analysis appears on completion of these iterations.

```

=====
== State   c**2      Energy      Energy      Davidson   ==
==                (T= 3, a.u.)  (T=0, a.u.)  (a.u.)     ==
=====
== 1       0.957      -78.200915   -78.207284   -78.211994 ==
=====

```

Note that merely presenting the data line:

```
ITERATE
```

would lead to refinement of the ground state wavefunction to the point where all secondary coefficients with c^2 greater than 0.005 are included in the reference state, at which point iterations would cease.

29.2 The Algorithm for Controlling Multi-root Calculations

The ITERATE sub-directives described above provide for control over the iterative treatment of single CI wavefunctions. This however is not the main purpose of ITERATE; controlling the treatment of multi root calculations with a view to the automatic handling of e.g. excitation spectrum requires a far greater level of control that is provided by a number of sub-directives - MAXROOT, SROOT, DROOT and RETAIN - that are described below.

Before considering these directives in detail, we first outline the algorithm that is used in controlling what is a relatively complex procedure. This has involved a number of prototyping exercises that have culminated in a final design criteria dominated by the desire to make the usage and specification as simple as possible, while providing the necessary level of robustness to deliver the required solution in a reasonable number of iterations. Users who have driven the MRDCI module in the search for excited states will be aware of the typical sequence of calculations that are performed manually. This involves starting with a number of reference configurations, and obtaining one or more CI wavefunctions under control of the ROOTS directive whereby selection is carried out with respect to NROOT roots of the 'root' secular problem to be used in process of configuration selection. Typically the same number of roots are then generated in the final secular problem. The user will then augment the reference set and increase the value of NROOT based on an examination of earlier calculations until the desired number of eigenstates are obtained.

The current implementation is an attempt to automate the above process. Initially the user must specify certain of the SELECT data fields; the fundamental decision taken here was that he/she should NOT have to specify any CONF data i.e. any explicit configuration data in the entire process. The consequences of this decision are twofold:

1. the following SELECT directives - CNTRL, SYMMETRY, SPIN - must be presented, together typically with THRESH and ROOTS;
2. the user is responsible for ensuring that the set of input orbitals (restored under control of the VECTORS directive) are consistent with the specifications given under SYMMETRY and SPIN. We shall clarify this requirement below; note that the code will check for this consistency and abort if it is not obeyed.

The initial calculation will be carried out using an internally constructed set of main configurations from which NROOT states will be generated (as specified by the ROOTS directive. Experience suggests that setting NROOT to 5 is generally quite reasonable. Subsequent calculations will iteratively generate a number of higher states as specified under control of the MAXROOT, SROOT, DROOT and RETAIN directives.

29.2.1 The MAXROOT Directive

This directive may be used to specify the number of states to be obtained from the sequence of iterative MRDCI calculations. The directive consists of two data fields, read to the variables TEXT, MXSTATE using format (A,I);

- TEXT should be set to the character string MAXROOT;
- MXSTATE is an integer used to specify the maximum number of eigenstates to be generated from the MRDCI treatment.

The directive may be omitted when MXSTATE will be set to the default value of 8.

Example

```
ITERATE MAXROOT 12
```

Thus the iterative procedure will, from an initial point of generating NROOT roots of the secular problem, attempt to generate roots (NROOT+1) up to and including root MAXROOT.

29.2.2 The SROOT Directive

This directive may be used to establish the criterion whereby the number of roots to be used in selection is increased from that in effect (NROOTS) during the preceding MRDCI iteration. The directive consists of two data fields, read to the variables TEXT, ROOTDEL using format (A,F);

- TEXT should be set to the character string SROOT;
- Selection will be extended from the NROOTS of the zero-order problem to (NROOTS+1) if the difference in the zero-order eigenvalues,

$$ABS[EIGVAL(NROOTS + 1) - EIGVAL(NROOTS)] \leq ROOTDEL \quad (38)$$

The directive may be omitted when ROOTDEL will be set to the default value of 0.0 i.e. no increase in NROOTS will be undertaken during the MRDCI iteration process.

Example

```
SROOT 0.20
```


29.2.3 The DROOT Directive

This directive should be used to confirm that the number of eigenstates derived from the diagonalisation process is to be increased during the iterative MRDCI cycles until the number specified by the MAXROOT directive has been derived, at which point the iterative process will terminate. The DROOT directive will typically appear together with the SROOT directive in controlling the energetics of this process; clearly the user may have little interest in deriving the final CI vector of an eigenstate whose zero-order description is separated by a large energy gap from the zero-order vector of the preceding state. Rejecting such a solution, and terminating the MRDCI process, is controlled by the value specified by SROOT.

Example

```
SROOT 0.20 DROOT
```

Given the above data sequence, the iterative MRDCI process will continue until either, (a) MXSTATE eigenvectors of the CI matrix have been obtained, or (b) having obtained N roots of the CI eigen vector, the (N+1)th root of the zero-order problem lies more than 0.20 a.u. above the Nth root.

The following points should be noted:

- The strategy behind the iterative sequence follows from an appreciation of the quantities defined by the MAXROOT, SROOT and DROOT directives. In practice three criteria are used in deciding whether to continue the sequence of MRDCI calculations:
 1. has the number of main configurations requested using WEIGHT changed from the preceding pass.
 2. does the eigen value spectra of the zero order problem justify expanding the no. of roots, NROOTS, to be used in selection?
i.e $ABS[EIGVAL(NROOTS+1)-EIGVAL(NROOTS)] \leq ROOTDEL$.
 3. based on 2., should we increase the no. of eigenstates (roots) to be extracted from the Davidson procedure (requested by DROOT).

Note that these criteria are executed *such that 3. is not invoked before 2. is satisfied, and 2. is not invoked before 1. is satisfied.*

- This approach is designed to ensure approximate convergence in the structure of the lower eigenstates before attempting to extract solutions for higher states in the spectrum.

29.2.4 The RETAIN Directive

This is the most complex of the ITERATE directives in terms of appreciating the role it plays in ensuring that all the states of interest are obtained by the iterative procedure outlined above. The key to obtaining these states is that at some point the associated leading configuration is identified as a reference species and is incorporated as a main configuration in the zero-order

space. While the process outlined above has been found to be extremely effective when all eigenstates are of similar character (e.g. Rydberg States), this is not always true when the derived eigenstates are of quite different character e.g. valence and Rydberg states. In such cases it is quite common for such a valence configuration not be included in the generated set of reference configurations at the outset, and while low-lying in energy, to have an extremely low value of c^2 in, for example, each of the derived Rydberg states i.e. it will never be incorporated in the set of main configurations, and hence never appear as one of the derived states.

A key to this behavior can be found from examining the nature of the configurations tagged as 'r' ('retain') in the output from the selection module. Initial attempts to implement an ITERATE strategy revealed that such configurations often remain isolated from the selected set of reference configurations throughout the iterative cycles, even though their associated energy remains lower than those of the final eigenstates of some of the higher CI states.

The RETAIN directive may be used to establish the criterion whereby the appearance of configurations tagged 'r' will trigger their inclusion as reference functions in the subsequent MRDCI iterations, regardless of their computed weights in any of the current eigenstates. The directive consists of three data fields, read to the variables TEXT, ERETAIN, IRETAIN using format (A,F,I);

- TEXT should be set to the character string RETAIN;
- Those configurations that are tagged 'r' in the selection process will be retained as reference configurations in the next iterative cycle if their associated energy lies within ERETAIN au of the energy of the NROOTS root of the current zero-order eigen problem. i.e.

$$E(\text{configuration}) - EIGVAL(NROOTS) \leq ERETAIN \quad (39)$$

- IRETAIN may be used to delay the onset of this selection criteria. Specifying IRETAIN results in the criteria only coming into effect on iteration IRETAIN of the MRDCI iterative process.

Example

```
RETAIN 0.10
```

The following points should be noted:

- The RETAIN directive may be omitted, when ERETAIN will assume a default value of 0.10 au, and be used in selecting configurations as reference functions from the outset.
- A maximum of 30 configurations may be retained on a given iteration.
- Setting IRETAIN to a high value e.g. 100 provides a potential mechanism for the iterative process to focus on just a sub-set of the final CI eigen states.

29.3 Examples of Excited State Generation

To clarify our discussion of iterative processing using the Semi-direct Table-CI module, we work through a number of example of using the method in calculating the energetics and properties of the lying states of a variety of molecules of increasing complexity.

29.3.1 Calculating the 1A_1 states of Formaldehyde

Data for performing an iterative MRDCI calculation on the ten lowest 1A_1 states of formaldehyde is given below. The calculation is initiated with an SCF calculation on the ground state. The following points should be noted:

1. The C and O 1s inner shell MOs, together with the two highest virtual orbitals are excluded from the calculation under control of the CORE and ACTIVE directives.
2. The SELECT directives requesting the 12 electron singlet CI states of A_1 symmetry are as follows:

```
SYMMETRY 1
SPIN 1
CNTRL 12
```

3. The ITERATE directive

```
ITERATE MAXI 20 MAXROOT 10 SROOT 0.10 DROOT WEIGHT 0.005
```

requests derivation of the lowest 10 roots, allowing a maximum of 20 MRDCI iterations to derive these roots. The initial CI will be based on the lowest 5 roots of the CI Hamiltonian (ROOTS 5) derived from the default set of generated main configurations.

```
CORE 20000000
TITLE
H2CO - TZVP+D(SPD) - MRDCI TREATMENT OF THE 1A1 STATES
HARMONIC
ZMAT ANGSTROM
C
O 1 1.203
H 1 1.099 2 121.8
H 1 1.099 2 121.8 3 180.0
END
BASIS
TZVP O
TZVP C
TZVP H
S 0
1.0 0.02
P 0
1.0 0.02
```

```

D 0
1.0 0.02
END
CORE
1 2 END
ACTIVE
3 TO 57 END
RUNTYPE CI
MRDCI DIRECT
SYMMETRY 1
SPIN 1
CNTRL 12
THRESH 5 5
ROOTS 5
ITERATE MAXI 20 SROOT 0.10 MAXROOT 10 DROOT WEIGHT 0.005
NATORB BYPASS
ENTER

```

29.3.2 Calculating the Excited states of the Formyl Radical

29.3.3 The $^2A'$ States

Data for performing an iterative MRDCI calculation on the eight lowest $2A'$ states of the formyl radical is given below. The calculation is initiated with an SCF calculation on the $2A'$ ground state (under control of the OPEN directive):

```

CORE 20000000
TIME 300
TITLE
HCO DZP + BOND(SP)
HARMONIC
MULT 2
ZMAT
C
BQ 1 RCO2
X 2 1.0 1 90.0
O 2 RCO2 3 90.0 1 180.0
X 1 1.0 2 90.0 3 0.0
H 1 RCH 5 40.0 4 180.0
VARIABLES
RCO2 1.125
RCH 2.076
END
BASIS
DZP H
S BQ
1.0 0.02
P BQ
1.0 0.02
D BQ
1.0 0.02
DZP C
DZP O

```

```

END
OPEN 1 1
CORE
1 2 END
ACTIVE
3 TO 42 END
RUNTYPE CI
MRDCI DIRECT
SYMMETRY 1
SPIN 2
CNTRL 11
THRESH 2 2
ROOTS 5
ITERATE MAXI 20 MAXROOT 8 SROOT 0.30 DROOT
NATORB BYPASS
ENTER

```

The following points should be noted:

1. The C and O 1s inner shell MOs, together with the two highest virtual orbitals are excluded from the calculation under control of the CORE and ACTIVE directives.
2. The SELECT directives requesting the 11 electron doublet CI states of A' symmetry are as follows:

```

SYMMETRY 1
SPIN 2
CNTRL 11

```

3. The ITERATE directive

```

ITERATE MAXI 20 MAXROOT 8 SROOT 0.30 DROOT

```

requests derivation of the lowest 8 roots, allowing a maximum of 20 MRDCI iterations to derive these roots. The initial CI will be based on the lowest 5 roots of the CI Hamiltonian (ROOTS 5) derived from the default set of generated reference configurations.

29.3.4 The $^2A''$ States

Treating the $2A''$ states is somewhat more complex, given the need to perform an additional SCF calculation on the lowest state of that symmetry. We now perform an initial SCF calculation on the ground state, and initiate the CI calculation in the second step by restoring these MOs, interchanging the appropriate orbitals under control of the SWAP directive, and conducting the SCF prior to the CI.

```

TITLE
HCO DZP + BOND(SP) 2AP SCF
HARMONIC

```

```
MULT 2
ZMAT
C
BQ 1 RCO2
X 2 1.0 1 90.0
O 2 RCO2 3 90.0 1 180.0
X 1 1.0 2 90.0 3 0.0
H 1 RCH 5 40.0 4 180.0
VARIABLES
RCO2 1.125
RCH 2.076
END
BASIS
DZP H
S BQ
1.0 0.02
P BQ
1.0 0.02
D BQ
1.0 0.02
DZP C
DZP O
END
OPEN 1 1
ENTER

CORE 20000000
TIME 300
RESTART NEW
TITLE
HCO DZP + BOND(SP) 2APP SCF + CI
HARMONIC
MULT 2
ZMAT
C
BQ 1 RCO2
X 2 1.0 1 90.0
O 2 RCO2 3 90.0 1 180.0
X 1 1.0 2 90.0 3 0.0
H 1 RCH 5 40.0 4 180.0
VARIABLES
RCO2 1.125
RCH 2.076
END
BASIS
DZP H
S BQ
1.0 0.02
P BQ
1.0 0.02
D BQ
1.0 0.02
DZP C
DZP O
END
```

```
OPEN 1 1
CORE
1 2 END
ACTIVE
3 TO 42 END
RUNTYPE CI
MRDCI DIRECT
SYMMETRY 2
SPIN 2
CNTRL 11
THRESH 2 2
ROOTS 5
ITERATE MAXI 20 MAXROOT 8 SROOT 0.30 DROOT
NATORB BYPASS
VECTORS 5
SWAP
8 10
END
ENTER 4 5
```

References

- [1] R.J. Buenker in 'Proc. of the Workshop on Quantum Chemistry and Molecular Physics', Wollongong, Australia (1980); R.J. Buenker in 'Studies in Physical and Theoretical Chemistry', 21 (1982) 17.