Input Manual for ACES II
Release 3.0

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Contents

I. Introduction to The ACES II Program System

ACES II is a series of programs for performing *ab initio* calculations. The package has a high degree of flexibility, and supports many kinds of calculations at a number of levels of theory. The major strengths of the program are in performing calculations using "many-body" methods to treat electron correlation. These approaches, broadly categorized as many-body perturbation theory (MBPT) and the coupled-cluster (CC) approximation, offer a reliable treatment of correlation and have the attractive property of size-extensivity, meaning that energies scale properly with the size of the system. As a result of this property, MBPT and CC methods are ideally suited for the study of chemical reactions.

Two important features of the ACES II program system are its effective use of molecular symmetry, particularly in MBPT and CC calculations, and the sophisticated gradient methods which are included in the program. The implementation of symmetry currently is limited to D_{2h} and its subgroups, and the expected speedup due to symmetry utilization will usually be approximately equal to the square of the order of the point group used in the calculation for all steps except integral and integral derivative generation, and integral sorts, where the speedup can be no greater than the order of the group.

Gradient techniques are implemented for SCF and the following correlated levels of theory : MBPT(2), MBPT(3), MBPT(4), CCD, QCISD, CCSD, QCISD(T), and CCSD(T) for both restricted and unrestricted Hartree-Fock (RHF and UHF, respectively) reference functions. In addition, for the MBPT(2), MBPT(3), CCSD, and CCSD(T) methods, gradients are available for restricted open-shell Hartree-Fock (ROHF) reference functions. They are also available for certain CCSD calculations based on quasi-restricted Hartree-Fock (QRHF) reference functions, namely those for high-spin doublet cases and, more recently, two-determinant CCSD (TD-CCSD) calculations for open-shell singlet states, where the open-shell orbitals have different symmetries.

Efficient algorithms for geometry optimization and transition state location have also been included, and may be used at all levels of theory for which analytical gradients are available. Analytic second derivatives have been implemented for SCF using RHF, UHF and ROHF reference functions. In addition, analytically evaluated NMR chemical shift tensors are available at the SCF and MBPT(2) levels using gauge-including atomic orbitals (GIAOs) to ensure exact gauge-invariance. Other features include the direct calculation of electronic excitation energies using the Tamm-Dancoff (or configuration interaction singles) model, the random-phase approximation and the equation of motion coupled-cluster approach. Transition moments between ground and excited states can be calculated for all of the methods, as well as selected excited state properties.

The programs collectively known as ACES II began development in early 1990, and the first version of the code was written by J.F. Stanton, J. Gauss, J.D. Watts, W.J. Lauderdale and R.J. Bartlett. Program development is continuing, and the capabilities of the package are continually increasing. At present, there are approximately 20 modules, each of which performs a well-defined function and communicates with the rest of ACES II via a small number of files. All of the modules have been written explicitly for Cray supercomputers, but perform efficiently on any vector computer or RISC architecture workstation. For the most time-consuming computational steps, essentially all of the most expensive steps have been coded as matrix multiplications using appropriate BLAS library routines. Hence, the CPU time for ACES II jobs is heavily dependent on the quality of the existing BLAS library.

Since ACES II is the product of academic research group, and not a software company, we are unable to guarantee that all results obtained with it are correct. Although we have made great progress in removing serious errors from the codes, problems may still occur and may be reported by electronic mail to aces2@qtp.ufl.edu. Any suggestions for improving the input or output, "wish-lists" for features, or other comments may also be communicated by electronic mail to aces2@qtp.ufl.edu.

Some of the featured capabilities of ACES II:

- Single point energy calculations.
- Geometry optimizations.
- Vibrational frequency calculations.
- Excitation energy calculations based on equation-of-motion coupled cluster method (EOM-CCSD).
- NMR chemical shift calculations using the gauge-including atomic orbital (GIAO) method (for SCF and MBPT(2) level of theory).
- NMR spin-spin coupling constant calculations using the EOM-CCSD method.
- Hybrid Hartree-Fock Density Functional Theory (HF-DFT) methods.
- Time-dependent Hartree-Fock calculations for determining many properties such as frequency dependent polarizabilities.
- Effective core potentials.

ACES II includes efficient (automatic) finite difference techniques to use energies calculated at any level of theory (regardless of whether or not analytical gradients are available at that level of theory) to determine equilibrium geometries and harmonic frequencies. Automated finite differences of analytic gradients is available to calculate harmonic vibrational frequencies.

The general capabilities of ACES II to determine single point energies, analytical gradients and analytical hessians are as follows:

Single point energies:

- Independent particle models include **RHF**, **UHF** and **ROHF**.

- Corelation methods utilizing RHF and UHF reference determinants include **MBPT(2), MBPT(3), SDQ-MBPT(4), MBPT(4), CCD, CCSD, CCSD(T), CCSD+TQ*(CCSD), CCSD(TQ), CCSDT-1 CCSDT-2, CCSDT-3, QCISD, QCISD(T), QCISD(TQ), UCCS(4), UCCSD(4), CID and CISD.**
- Correlation methods which can utilize ROHF reference determinants include **MBPT(2), CCSD, CCSDT, CCSD(T), CCSDT-1, CCSDT-2 and and CCSDT-3**.
- Correlation methods which can utilize QRHF and Brueckner orbital reference determinants include **CCSD, CCSDT, CCSD(T), CCSDT-1, CCSDT-2 and CCSDT-3**.
- **Two-deteminant CCSD** calculations for open-shell singlet state.
- **HF-DFT** methods combined with a wide selection of density functionals.

Analytical gradients:

- Independent particle models include **RHF, UHF** and **ROHF.**
- Correlation methods utilizing RHF and UHF reference determinats include **MBPT(2), MBPT(3), SDQ-MBPT(4), MBPT(4), CCD, CCSD, CCSD + T(CCSD), CCSD(T), CCSDT-1, CCSDT-2, CCSDT-3, QCISD, QCISD(T), UCC(4), UCCSD(4), CID** and **CISD**.
- Correlation methods which can also utilize ROHF reference determinants include **MBPT(2), CCSD** and **CCSD(T)**.
- Correlation methods which can also utilize **QRHF** reference determinants include **CCSD**.
- **Two-determinant CCSD** calculations for open-shell singlet state based on **QRHF** orbitals.
- **EOM-CCSD** method for excited states.

Analytical Hessians:

- Independent particle models include **RHF, UHF and ROHF.**

For readers who are familiar with the second release of ACES II, we now list the principal new features in the third release (Release 3.0):

- TD-CCSD energies. *Authors : P.G. Szalay and A. Balkova.*
- TD-CCSD analytical derivatives. *Author : P.G. Szalay.*
- Dropped core and/or virtual orbitals in analytical derivative calculations for RHF, UHF, and ROHF references. *Author : K.-K. Baeck.*
- Equation-of-motion CCSD calculation of dynamic polarizabilities (including partitioned scheme). *Authors : J.F. Stanton, S.A. Perera, and M. Nooijen.*
- Equation-of-motion CCSD calculation of NMR spin-spin coupling constants (including partitioned scheme). *Authors : S.A. Perera and M. Nooijen.*
- Partitioned equation-of-motion CCSD calculations of excitation energies.*Authors : S.R. Gwaltney and M. Nooijen.*
- Equation-of-motion CCSD gradient calculations for excited states.*Authors : J. F. Stanton and J. Gauss*

II. ACES II Citation

The users of ACES II must give the following citation:

ACES II is a program product of the Quantum Theory Project, University of Florida. Authors: J.F. Stanton, J. Gauss, J.D. Watts, M. Nooijen, N. Oliphant, S. A. Perera, P. G. Szalay, W.J. Lauderdale, S.R. Gwaltney, S. Beck, A. Balková D. E. Bernholdt, K.-K Baeck, P. Rozyczko, H. Sekino, C. Hober, and R.J. Bartlett. Integral packages included are VMOL (J. Almlöf and P.R. Taylor); VPROPS (P. Taylor) ABACUS; (T. Helgaker, H.J. Aa. Jensen, P. Jørgensen, J. Olsen, and P.R. Taylor).

The basis set distributed with the ACES II release 3.0 is obtained through Pacific Northwest National Laboratory (PNNL) and any calculation which uses basis sets from this catalogue must give the following citation **in addition** to the ACES II citation.

Basis sets were obtained from the Extensible Computational Chemistry Environment Basis Set Database, Version 1.0, as developed and distributed by the Molecular Science Computing Facility, Environmental and Molecular Sciences Laboratory which is part of the Pacific Northwest Laboratory, P.O. Box 999, Richland, Washington 99352, USA, and funded by the U.S. Department of Energy. The Pacific Northwest Laboratory is a multi-program laboratory operated by Battelle Memorial Institue for the U.S. Department Energy under contract DE-AC06-76RLO 1830. Contact David Feller, Karen Schuchardt, or Don Jones for further information.

III. Using this Manual

In principle, all aspects of preparing an ACES II input deck and running a job are covered here, as well as some tips on the construction of Z-matrices and judicious use of certain keywords. All new users of the program are encouraged to *browse* through the entire input manual. Following this, all sections which are of interest should be read in detail. Mandatory reading for new users is the section entitled "Common mistakes and sources of confusion", which begins on page 50. Any errors detected in the manual should be reported to aces2@qtp.ufl.edu.

A useful supplement to this manual is a set of six or so laboratory exercises which have been used in ACES II workshops. Users interested in receiving this material may send email to aces2@qtp.ufl.edu.

IV. Basic Aspects of Input Files for ACES II

A. Overview

Running ACES II calculations is straightforward. In most calculations two files are needed. First, the user must construct an input file, which must be copied in to the user's workspace as ZMAT. Second, the basis set library file GENBAS must also be copied in to the workspace (standard basis set library is provided with the distribution, see under GENBAS file). The program is invoked simply by the command "xaces2 ", and the user must direct output to an output file. For example, a simple script for execution on one of the QTP IBM RS6000 workstations is as follows :

```
#!/bin/ksh
. ./.kshrc
mkdir      /scr_1/tmp/tmp.$$
cd         /scr_1/tmp/tmp.$$
cp         ~rjbprogs/Basis/GENBAS                 GENBAS
cp         /camp/swift_1/qtp/rjb/jw/jobs/c2h5.zmat  ZMAT
xaces2  >  /camp/swift_1/qtp/rjb/jw/jobs/c2h5.out
rm *
cd $HOME
rmdir      /scr_1/tmp/tmp.$$
exit
```

The first two lines reflect our local kornshell environment, and users will have to tailor this to their local environment. In particular, the second line sets the appropriate path to the ACES II executables. The next two lines are also site specific and are to create and change to a temporary directory on a scratch disk. The next three lines are the essentials of running an ACES II job. The basis set file and the input file are copied to the working directory, and the calculation is executed with the xaces2 command. Output is directed to a file on a permanent disk partition. In order for the calculation to run just by invoking xaces2, the path to the ACES II executables must be appropriately included in the user's .kshrc (or .cshrc or other environment setting files). There are a number of variations on this basic theme. For example, the user may on occasion need to copy additional files to the workspace (for example, FCMINT, GUESS, OLDMOS, and OLDAOMOS) prior to execution. Similarly, the user may wish to copy out certain files created by ACES II to permanent storage (for example, AOBASMOS, FCMINT, JOBARC, JAINDX, NEWMOS). The final four lines clear the workspace and remove the temporary directory, thus freeing scratch space for the next job or for other users.

The next section describes the ZMAT file in depth. This file contains the information about the molecule and calculation. This information includes the geometry of the molecule (specified by either a Z-matrix or Cartesian coordinates), the choice of basis set, the type of calculation to run, and several other parameters which are used by the program. The input is keyword-driven, and usually only a few keywords must be specified since intelligent defaults exist for all keywords. Many basis sets are available for immediate use in the GENBAS file. These include the standard Dunning-Huzinaga sets (with various polarization functions), several "Pople" sets (*e.g.* 6-31G*), the correlation-consistent basis sets of Dunning and coworkers (*e.g.* cc-pVTZ), the polarized basis sets of Sadlej, and some atomic natural orbital basis sets from Roos and coworkers. In addition, the user may create his or her own basis set for use by the program by modifying the GENBAS file. Several different calculation types can be performed at different levels. For example, single point, geometry optimization, property evaluation, and vibrational frequency calculations may be performed. Also, many levels of calculation such as SCF, MBPT, CCSD and CI methods are currently available.

A description of the ZMAT file is included in the next section. A second file, the GENBAS file, will be described later. The GENBAS file contains complete specifications of the "standard" basis sets currently available to the user. However, the format of the GENBAS file is very simple, and it is a straightforward matter for the user to add additional basis sets to the library. During the course of the calculation, several additional files are created but on the whole it is not necessary for the user to be familiar with their content. Some exceptions will be discussed in later sections of this manual.

A description of the other parameters that can be adjusted via the ZMAT file is included in the ACES2 namelist section. These parameters can be used to set the type and level of calculation as well as many other options ranging from the SCF occupation to the convergence criterion for geometry optimizations. Although a large number of options are available, only a small subset of them will be needed in most calculations.

A set of test cases, both the ZMAT input files and the corresponding output files, is provided which, along with testing the various modules, provides a sample ZMAT for many different calculation types.

B. The ZMAT File

The ACES II input is via a ZMAT file. Two sample ZMAT files, one with an internal coordinate specification of the geometry and the other with Cartesian coordinate specification are shown below. A detailed description of each section of the ZMAT file follows.

```
CCSD Calculation of C6
X
X 1 RX
C 2 R 1 A
C 2 R 1 A 3 T
C 2 R 1 A 4 T
C 2 R 1 A 5 T
C 2 R 1 A 6 T
C 2 R 1 A 7 T

RX=1.0
R=1.33
A=90.
T=60.

*ACES2(CALC=CCSD,REF=RHF,PROPS=FIRST_ORDER,BASIS=DZP)
```

```
Formaldehyde using cartesian coordinates
O 0.0       0.0          1.22
C 0.0       0.0          0.0
H 0.0       0.873489539  0.545816842
H 0.0      -0.873489539 -0.545816842

*ACES2(CALC=MBPT[2],REF=RHF,PROPS=FIRST_ORDER,BASIS=DZP
COORDINATE=CARTESIAN)
```

The ZMAT file contains up to four sections. The first contains the “non-standard file specification”, which is a way to specify that certain files are to stored in locations other than the job workspace. *This is not used in most calculations, but is sometimes useful (see B..8).* The second contains the title and the initial geometry specification (by Z-matrix or Cartesian coordinates). The third section comprises the ACES2 namelist (ACES2 command line), which specifies the program options such as type of calculation, basis set, etc. The final section is used for nonstandard basis set specification and is omitted if “standard” basis sets are to be used. The individual sections are discussed separately below. We also discuss the conventions used by ACES II for the orientations of the coordinate axes in the different point groups. This information is needed to specify the irreducible representations of orbitals correctly. Finally, some sample ZMAT files are presented and described. It should be stressed that the following is a *complete* description of the various input options and as such may seem unnecessarily complicated to the general user. However, the vast majority of the variables in the namelist need never be specified since they have adequate defaults, and in practice the user will usually need to specify less than ten keywords. This will be illustrated by the sample input files and the various test cases distributed with the program. A general remark pertinent to all sections of the ZMAT file is that all characters should be **upper case**. **Another very important point is that the ZMAT file must terminate with a blank line.**

B..1 Z-Matrix

Provided no nonstandard file declarations are used (see Sec. B..8), the first line of the ZMAT file is reserved for the job title, which is communicated to the rest of ACES II and printed out in a number of places during the execution of the program. Following this is the geometry specification, usually by internal coordinates. The specificaton by internal coordinates is known as the Z-matrix. Centers of the nuclei are expressed relative to previously defined centers by means of distances and angles. The specification includes a length, a bond angle, and a dihedral angle. The number associated with each atom is governed by its position in the Z-matrix. The essentials of Z-matrix construction may be illustrated by considering a Z-matrix for a system of four atoms ABCD, not linked in any particular order.

```
Arbitrary ABCD molecule
A
B 1 RAB
C 1 RAC 2 CAB
D 3 RCD 2 DCB 1 TAU
```

The first line in the Z-matrix contains just the atomic symbol of one of the atoms, say A. The second line specifies the position of a second atom, say B, relative to the first atom (A). Suppose that B is a distance RAB from A. The second line then contains the atomic symbol B, followed by the number 1 (A is atom number 1), and a parameter label, RAB, ("B 1 RAB"). For the specification of the third atom, a distance and an angle are needed. We may use the distance between atoms A and C and the angle CAB or we may use the distance between atoms B and C and the angle CBA. In the first case the third line would have the form "C 1 RAC 2 CAB", while in the second case it would have the form "C 2 RBC 1 CBA". Finally, there is a line specifying the position of D relative to the other atoms. This line must contain a distance, a bond angle, and a dihedral angle, and might have the form "D 3 RCD 2 DCB 1 TAU", TAU being the angle between the BCD and ABC planes. For a system with more than four atoms, the fifth and subsequent lines follow the same pattern as the fourth line of the example given above, i.e. they also contain a length, angle, and dihedral angle and numbers of three previously specified centers. It should be emphasized that this is a somewhat simplified description which would work for a tetraatomic molecule such as hydrogen peroxide, but would not be satisfactory for acetylene. For the latter "dummy" atoms are necessary. These and several other tips for forming Z-matrices are discussed below. Several examples of Z-matrices are given in this manual to assist users who are unfamiliar with the concept.

A more formal description of a line in the Z-matrix input is as follows. Each line may have as many as seven entries. We consider the Ith line. The contents are the Ith element of the ZSYM array, the 3*Ith, (3*I-1)th, and (3*I-2)th elements of the NCON and PARNAM arrays. The ZSYM array is of length N, where N is the number of lines in the Z-matrix (this includes those for any dummy and ghost atoms), and contains the chemical symbols of all the atoms in the Z-matrix. The NCON and PARNAM arrays are of length 3*N. NCON contains the numbers of atoms relative to which each atom is specified. The PARNAM array contains the names of the lengths, angles, and dihedral angles contained in the Z-matrix. Positions 3*I-2 are for lengths, 3*I-1 for angles, and 3*I are for dihedral angles (I=1,2,...,N). It should be clear that elements 1,2,3,5,6, and 9 of NCON and PARNAM are not defined. The Ith line (I=1,2,...,N) then has the general form:

ZSYM The atomic symbol of the atom (dummy atom is 'X').

NCON(3*I-2) The number of the atomic center to which the atom is formally linked. *Note that this need only be a formal link, the two atoms need not be chemically bonded.* (Only for I>1).

PARNAM(3*I-2) A character variable name corresponding to the distance between atom NCON(3*I-2) and atom I.

NCON(3*I-1) The third member of the triangle formed by atoms I and NCON(3*I-2). (Only for I>2).

PARNAM(3*I-1) A character variable corresponding to the associated angle.

NCON(3*I) The fourth member of the dihedral angle formed by atoms I, NCON(3*I-2) and NCON(3*I-1). (Only for I>3).

PARNAM(3*I) A character variable name corresponding to a dihedral angle determined as follows: In the plane perpendicular to the NCON(3*I-2)↔ NCON(3*I-1) axis, the angle is that needed to rotate the projection of the [I← NCON(3*I-2)] vector into the projection of the [NCON(3*I)← NCON(3*I-1)] vector. Clockwise is taken to be positive. Values must be restricted from -180 to 180^o.

All variable names (PARNAM array) are **limited to three characters**. An asterisk (∗) immediately after the variable name specifies that that particular internal coordinate is to be optimized. **One and only one space must separate the different fields on each Z-matrix line.** *No numbers are allowed inside the Z-matrix. All internal coordinates must be given a symbol, even if the value is not going to change.*

B..2 Z-Matrix Parameter Input

After a blank line following the Z-matrix, the values of all *unique* internal coordinates (those which have different names) are specified as follows,

PNM=Value

where PNM is one of the unique members of the PARNAM array (see above), and Value is the value assigned to that coordinate. The parameters may be specified in any order. Angles must be entered in degrees (^{o}), distances must be in Ångströms. Bond angles (as distinct from dihedral angles) of 0 and 180^o are not allowed since these lead to a singularity in the transformation between Cartesian and internal coordinates (and do not allow dihedral angles to be defined). This, of course, does not mean that ACES II is unable to handle linear molecules such as carbon dioxide. Rather, for linear molecules, "dummy atoms" must be used in the ZMAT file to avoid problematic bond angles.

To facilitate construction of Z-matrices for highly symmetric molecules, certain variable names have been reserved for specific values. To use these parameters, which are listed below, the user still must specify a value in the parameter input section, but it need not be correct since it will be converted to the exact value internally.

TDA Specifies the tetrahedral angle, $\mathrm{Cos}^{-1}\left(\frac{-1}{3}\right)$ $(= 109.471\cdots)$.

IHA Specifies the angle $\mathrm{Cos}^{-1}\left(\frac{1}{5^{1/2}}\right)$ (=$63.4349\cdots$), which is useful for icosahedral molecules.

As an example, a Z-matrix and internal coordinate specification is given below for the formaldehyde molecule, in which only the (equivalent) C-H distances are to be optimized.

```
Sample formaldehyde Z-matrix input
O
C 1 R
H 2 R2* 1 A
H 2 R2* 1 A 3 T

R=1.22
R2=1.03
T=180.
A=122.
```

B..3 The Z-matrix Analyzer

A unique feature of ACES II is the Z-matrix analyzer, which is capable of detecting subtle and obvious deficiencies in the definition of internal coordinates. This is particularly important for geometry optimizations, in which the construction of the Z-matrix and the choice of parameters to be optimized are of vital importance. The analyzer inspects the internal coordinates, and carries out a number of checks. These include determination of whether coordinates given the same name are actually equivalent, if coordinates having different names are equivalent, whether a non-zero gradient is possible with respect to modes which are not being optimized, etc. In addition, it determines the number of degrees of freedom within the totally symmetric subspaces of nuclear configurations, and compares this value with the number of independent coordinates which are being optimized. If they are not equal, a warning message is printed out.

For most Z-matrices with poorly defined internal coordinates, the analyzer prints out a number of warning messages, but does not halt the ACES II execution sequence. However, for Z-matrices which are particularly bad, it will terminate your job. All users are encouraged to carefully inspect the output of the analyzer, and also to check that the full molecular point group (printed out below the output from the analyzer) is the one intended. If warning messages are printed out, or the symmetry of the molecule specified by the Z-matrix is not what was intended, reconstruction is necessary.

A rule of thumb for Z-matrix construction is that each internal coordinate included in the Z-matrix must be accompanied by all others which are equivalent to it by the symmetry of the molecule. For example, in water, it is best to specify the molecular geometry by the two O–H distances and the H–O–H bond angle, rather than by the O–H distance, the H–H distance, and the H–H–O angle. Although most users would definitely use the first Z-matrix, the idea of using just chemical bonds as internuclear distances can be dangerous. For example, in a regular hexagonal ring, a little reflection will show that one cannot include *all six* intervertex distances in the Z-matrix. If only five are specified, such as in the Z-matrix below (the 1–6 distance is missing), the internal coordinate gradient cannot have the full symmetry of the molecule, and the first step of a geometry optimization will break the molecular symmetry. This results in extremely slow convergence and significantly increased CPU time due to the reduced molecular symmetry.

```
A poor Z-matrix for hexagonal C6
C
C 1 R
C 2 R 1 A
C 3 R 2 A 1 T
C 4 R 3 A 2 T
C 5 R 4 A 3 T

R=1.33
A=120.
T=0.
```

In these situations, it is always best to use “dummy atoms”, which is simply a way to use a point in space as a reference for the coordinates. A dummy atom is denoted by the symbol “X”, and one or more is needed in essentially all Z-matrices for molecules with high symmetry. As an example of their use, a “good” Z-matrix for the C_6 ring is shown below. Don’t be afraid to use dummy atoms!

```
A better Z-matrix for hexagonal C6
X
X 1 RX
C 2 R 1 A
C 2 R 1 A 3 T
C 2 R 1 A 4 T
C 2 R 1 A 5 T
C 2 R 1 A 6 T
C 2 R 1 A 7 T

RX=1.0
R=1.33
A=90.
T=60.
```

B..4 Cartesian coordinate geometry specification

In addition to Z-matrix geometry specification, a facility exists for geometry specification by Cartesian coordinates. This is of limited value since only single point calculations can be performed with this form of input. The format is straightforward. The first line is a title line, as for Z-matrix input. Following this there is a line for each atom, containing the atomic symbol and the values of the Cartesian coordinates in free format. The coordinates may be given in either atomic or Ångström units. For example, the formaldehyde geometry specified in the Z-matrix on page 5 could be specified with Cartesian coordinates (in Ångströms) as follows.

```
Formaldehyde using cartesian coordinates
O 0.0      0.0          1.22
C 0.0      0.0          0.0
H 0.0      0.873489539  0.545816842
H 0.0     -0.873489539 -0.545816842
```

The ACES2 command line must contain COORDINATE=CARTESIAN for this to work. Otherwise the program will try to process the above coordinates as though they are a Z-matrix. If the cartesian coordinates are specified in atomic units, this can be accomplished by using the keyword UNITS=BOHR in the ACES2 command line which will be described later.

B..5 Ghost atoms

Ghost atoms, which are specified by the symbol GH, have zero nuclear charge. However, while dummy atoms are only used to simplify the Z-matrix input, ghost atoms serve as a center for basis functions. This feature is particularly useful for calculations performed to determine the basis set superposition error (BSSE), and has several other applications, such as describing “lone pair” electrons of a molecule by functions which are not centered at any of the molecular nuclei. Symmetry can be used in such calculations but is in all cases restricted to the symmetry of the “supermolecule” comprised of the real and ghost atoms. The additional basis functions do not necessarily form a complete set of symmetry adapted functions within the point group of the considered molecule. This is different from the use of dummy atoms, which do not affect the symmetry of the calculation.

Note that currently only single point energy calculations are possible with ghost atoms. Also, the basis set has to be supplied in all cases explicitly via the BASIS=SPECIAL feature which is explained in another section.

B..6 The ACES2 Namelist Job Control Parameters

The job control parameters in the ACES2 namelist define the currently available options. These options are set through the use of keywords. In some cases the value for a keyword can be specified by an integer or by a character string. In our opinion the latter is preferable as it makes the input file more readable.

All possible keywords in the ACES2 namelist are discussed below. As there are a lot of keywords (100 or so), we have grouped them according to the type of calculation they affect.

Keywords of **General Relevance** :
The first group of keywords are of general relevance, and include such fundamental parameters as the memory and type of coordinates. Others in this group are rather obscure. They are listed alphabetically. The most commonly used ones are CALCLEVEL, COORDINATES, MEMORY_SIZE, PRINT, and UNITS.

CACHE_RECS The number of records held in the i/o cache used by the post-SCF programs. The maximum number of records which can be held is 100. (Default : 10)

CALCLEVEL Defines the level of calculation to be performed. =0 SCF; =1 MBPT[2]; =2 MBPT[3]; =3 SDQ-MBPT[4]; =4 MBPT[4]; =5 LCCD; =6 LCCSD; =7 UCCSD[4]; =8 CCD; =9 UCC[4]; =10 CCSD; =11 CCSD + T[CCSD]; =12 CCSD + TQ*; =13 CCSDT-1; =14 CCSDT-1b; =15 CCSDT-2; =16 CCSDT-3; =17 CCSDT-4; =18 CCSDT; =19 LCCSDT (NCI); =20 CCD+ST[CCD] (NCI); =21 QCISD[T]; =22 CCSD[T]; =23 QCISD; =24 CID; =25 CISD; =26 QCISD[TQ]; =27 CCSD[TQ]; =28 CCSD+TQ (NCI); =29 CCSDT+Q* (NCI); =30 CCSDT+Q (NCI); =41 HFDFT. Calculation levels with NCI after them are not currently implemented but will be available in future versions of the program. For CALC=HFDFT note that there are several functionals available, which are specified by the FUNCTIONAL keyword. (Default : SCF).

COORDINATES The keyword INTERNAL(=0) means that the geometry is supplied in the usual Z-matrix format, while CARTESIAN(=1) means that the geometry is given in cartesian coordinates. Note that geometry optimizations are only possible with internal coordinates. (Default : INTERNAL)

FILE_RECSIZ This specifies the physical length (in integer words) of the records used in the word-addressable direct access files used by ACES II. This value should always be chosen as a multiple of 512 bytes, as your local system manager certainly understands. (Default : 2048).

HBAR This keyword determines which action is taken by the linear response program. ON (= 1) the full effective Hamiltonian is calculated and written to disk; OFF (= 0) the “lambda” linear response equations are solved. (Default : 0)

INCORE This keyword can be used to significantly reduce disk i/o, and should be implemented very soon. The following options are available: OFF (= 0), no special algorithms are used (the default case); ALL (=1) all quantities except the $\langle ab||cd\rangle$ molecular integral lists are held in core; PARTIAL (= 2), the T2 and T1 vectors are held in core throughout the calculation; (=4) all quantities except the $\langle ab||cd\rangle$ and $\langle ab||ci\rangle$ integrals are held in core; (=5) $\langle ij||kl\rangle$ and $\langle ij||ka\rangle$ and two-index quantities are held in core; (=6) *all direct access files* (MOINTS, GAMLAM, etc.) *are held in core.* **At present, these options have been implemented only in the energy code (xvcc) and the excitation energy code (xvee).** (Default : 0)

INTGRL_TOL Tolerance for storage of two-electron integrals. If this has value N, integrals having absolute value greater than 10^{-N} will be stored on disk. (Default : 14).

JODA_PRINT Controls amount of debug printing performed by xjoda. The higher the number, the more information is printed. Values of 25 or higher generally do not produce anything of interest to the general user. Do not set JODA_PRINT to 999 as this will cause the core vector to be dumped to disk. (Default: 0; Value must be specified as an integer).

MEMORY_SIZE Specifies the total core memory used, in units of *integer* words. (Default : 6 500 000).

PRINT Controls the amount of printing in the energy and energy derivative calculation programs. Using a value of 1 will produce a modest amount of additional output over the default value of 0, which includes some useful information such as SCF eigenvectors. (Default : 0; Value must be specified as an integer).

SAVE_FILES Switch which tells ACES II whether to delete large files (AO integrals and MOINTS file for now) when they are no longer needed. OFF (= 0) They will not be saved, ON (= 1) they will be saved. (Default : 0). *This must currently be set to ON in NMR chemical shift calculations.*

SOLVENT This keyword allows a simple simulation of solvent effects. If SOLVENT is set to an integer N a dielectric constant of N is used to determine the orbitals. A cavity size may also be specified by creating a file “radius” which is read by the SCF code. This contains the cavity radius in Å. If the file is not present, the program uses a value calculated from 0.5 Å+ half the longest internuclear distance. (Default : 0 — i.e. gas phase).

SUBGROUP This keyword allows the user to specify a specific Abelian subgroup to be used in a calculation. Acceptable arguments are DEFAULT (=0); C1 (= 1); C2 (= 2); CS (= 3); CI (= 4); C2V (= 5); C2H (= 6); D2 (= 7) and D2H (= 8). Use of C1 is of course equivalent to setting SYMMETRY=OFF in the input. The DEFAULT option (which is the default) uses the highest order Abelian subgroup (Default : DEFAULT).

SUBGRPAXIS This is a somewhat complicated keyword to use. Allowed values are the integers 1, 2 and 3, which specify the x,y and z axes, respectively. The meaning of the keyword is best described by example : Suppose one is running a calculation on water, and wishes to run it in the C_s point group with the "special" plane being the one which bisects the H–O–H bond angle. Now, what SUBGRPAXIS does is to specify which Cartesian direction in the C_{2v} frame becomes the special direction in the C_s frame. ACES II will orient water in the yz plane, so one wants the y axis in the C_{2v} frame to be the z axis in the C_s frame. Hence, for this case, one would specify SUBGRPAXIS=2. Use of this keyword may be facilitated by studying section D1 of this chapter, entitled "Molecular Orientation". However, when the true Abelian subgroup is either C_{2v} or D_{2h}, the ACES II orientation is not well defined, and it may be necessary to run the XJODA executable directly two times. If SUBGROUP=0 in the first pass, then the reference orientation for the true Abelian subgroup can be determined and the appropriate value of SUBGRPAXIS selected.

SYMMETRY Specifies what subgroup of the full point group is to be used in the energy and/or gradient calculation (The "computational" point group). OFF (=1) forces a no symmetry run (in C_1), ON (=0) runs the calculation in the largest self-adjoint subgroup (D_{2h} and its subgroups), and FULL (=2) uses the full point group. Currently, ACES II does not support groups with degenerate representations, so the FULL option has no value unless Joda is being used to make input decks for another program package. Symmetry is turned off in finite difference v,ibrational frequency calculations which use the FINDIF_OLD algorithm (see keyword VIBRATION). However, the algorithm which determines the number of gradients to be evaluated and performs the resulting construction of the force constant and dipole derivative matrices uses the *full* point group symmetry. (Default: ON unless VIBRATION=FINDIF_OLD, which forces SYMMETRY=OFF). *NOTE: In the vast majority of cases, the general user should not need to use this keyword. Exceptions include error detection (for example, to see if an incorrect result or a program crash occurs with and without symmetry), and some calculations in the presence of finite fields.*

UNITS Specifies the units used for molecular geometries using the Cartesian coordinate format (see entry for COORDINATES). ANGSTROM (= 0) uses Ångström units, BOHR (= 1) specifies atomic units. (Default : ANGSTROM)

Keywords relevant to **Basis Set Specification** :

BASIS Specifies the name of the basis set for all atoms in the system under study. Accepted values are: STO-3G, DZ, 3-21G, 4-31G, 6-31G, 6-311G, DZP, TZP, TZ2P, 6-31G*, 6-31G**, 6-311G*, 6-311G**, PVDZ, PVTZ, PVQZ, PV5Z, PBS and WMR. For hydrogen atoms, the Pople "*" and "**" basis sets default to the corresponding basis with no polarization functions and *p* functions, respectively. In order for this to work, the appropriate basis sets must be in the GENBAS file for all atoms. If you want to use different basis sets on different atoms, to use ghost atoms, or to use a basis which is not in the above list (there are several such families in the standard GENBAS file), the section entitled "Non-Standard Basis Set Specification" should be consulted. Non-standard basis set specification involves setting the BASIS keyword to SPECIAL (equivalently, it may be set to 0 or omitted). A complete list of the basis sets currently in the standard GENBAS file in given in section A of Part IV of this manual. (Default: SPECIAL)

CONTRACTION The contraction scheme used by the integral and integral derivative programs. SEGMENTED (= 0) uses a segmented contraction scheme; GENERAL (= 1) uses a general contraction scheme. *NOTE: Even for truly segmented basis sets, both programs run significantly faster in* GENERAL *mode, and this should be used in practice.* (Default: GENERAL).

ECP This specifies whether effective core potentials (some kind of pseudopotentials) are used (ON = 1) or not (OFF = 0). ECP=ON requires BASIS=SPECIAL and specification of the ECP (see sections E..1 and B..7 for further explanation). (Default : OFF)

GENBAS_1 This keyword applies only to Hydrogen and Helium atoms and specifies the number of contracted Gaussian functions per shell. There is usually no need to use this keyword, but it can be useful for using a subset of the functions in a particular entry in the GENBAS file, particularly for generally contracted basis sets. For example, if entry H:BASIS in the GENBAS file contains 7 contracted *s* functions, 4 *p* functions and a single *d* function, then setting GENBAS_1=730 would eliminate the last *p* function and the *d* function. The default for this keyword is to use the unaltered GENBAS entry.

GENBAS_2 This keyword performs the same function as GENBAS_1 above, but applies only to second-row atoms.

GENBAS_3 This keyword performs the same function as GENBAS_1 and GENBAS_2, but applies only to third-row atoms.

SPHERICAL This keyword specifies whether spherical harmonic (5d, 7f, 9g, etc.) or Cartesian (6d, 10f, 15g, etc.) basis functions are to be used. ON (= 1) uses spherical harmonics, OFF (= 0) uses Cartesians. The latter must be used for correlated gradient calculations at present. (Default : OFF).

Keywords relevant to **Self-Consistent Field Calculations** :

CHARGE The molecular charge. (Default : 0).

DAMPSCF Specifies the static damping factor used in the SCF iterations. =N The static damping factor is N x 0.01. This keyword is only operative when DAMP_TYP=STATIC (Default : 20).

DAMP_TOL Specifies the cutoff for Davidson damping (see DAMP_TYP). If this is N, the cutoff is N x 0.1. Default : 1.

DAMP_TYP Specifies what type of damping is used during the SCF iterations. The choices are NONE (no damping); DAVIDSON (use Davidson's empirical dynamical damping scheme); STATIC (use a fixed damping parameter, the value of which is specified by DAMPSCF). Note that RPP convergence extrapolation is not turned on until after the damp factor has gone below DAMP_TOL and the energy change is below 0.05 a.u. DAMP_TYP=DAVIDSON is recommended. Default : NONE.

FOCK This option is used to control the algorithm used for construction of the Fock matrix in SCF calculations. PK (= 0) uses the PK-supermatrix approach while AO (= 1) constructs the matrix directly from the basis function integrals. In general, PK is faster, but results in *considerable* use of disk space when out-of-core algorithms are required. (Default : PK).

GUESS Where the initial SCF eigenvectors are read from. MOREAD means to read from the disk (the "JOBARC" file) and CORE means to use a core Hamiltonian initial guess. If MOREAD is chosen but no disk file is present, the core Hamiltonian is used. (Default : MOREAD)

LINDEP_TOL The tolerance for basis set linear dependence. =N The basis set is considered linearly dependent and eigenvectors of the overlap matrix are neglected if the associated eigenvalues are less than 10^{-N}. (Default: 5).

LOCK_ORBOCC This keyword is used by the SCF program to determine if the orbital occupancy (by symmetry block) is allowed to change in the course of the calculation. ON (= 1) locks the occupation to that set by the keyword OCCUPATION [or the initial guess if OCCUPATION is omitted]; OFF (= 0) permits the occupation to change. (Default : 1 if the occupation is specified with the OCCUPATION keyword and in second and later steps of optimizations ; 0 if OCCUPATION is omitted.)

LSHF_A1 Sets the doubles-singles level shifting parameter α. If this is set to N, α is N x 0.01. This keyword is currently only meaningful in ROHF calculations. Default : 0.

LSHF_B1 Sets the singles-virtuals level shifting parameter β. If this is set to N, α is N x 0.01. This keyword is currently only meaningful in ROHF calculations. Default : 0.

MULTIPLICTY The spin multiplicity ($2S$+1). (Default : 1)

NEWVRT Specifies if the usual virtual orbitals are to be replaced by a set determined from an $N - 1$ potential. This is an orthogonal transformation within the virtual space and so as long as appropriate f_{ij} and f_{ab} are included, the energies of standard single reference methods are unchanged. However, for TD-CC methods this keyword mixes one of the occupied orbitals with the virtual space, and so the results are changed. It is anticipated that TD-CCSD calculations will be improved by the use of this keyword, but this has not yet been demonstrated. NEWVRT is useful for interpreting results of EOM-EE calculations, as excitations tend to be more easily identified as involving one occupied and one virtual orbital. =OFF (do not rotate the virtual space); =ON (rotate the virtual space). (Default : OFF).

OCCUPATION Specifies the orbital occupancy of the reference function in terms of the occupation numbers of the orbitals and their irreducible representations. The occupancy is specified by either NIRREP or 2*NIRREP integers specifying the number of occupied orbitals of each symmetry type, where NIRREP is the number of irreducible representations in the computational point group. If there are no orbitals of a particular symmetry type a zero must be entered. If the reference function is for an open-shell system, two strings of NIRREP occupation numbers separated by a slash ('/ ') are input for the α and β sets of orbitals. An example of the use of the OCCUPATION keyword for the water molecule would be OCCUPATION=3-1-1-0. For the $^2A_1$ water cation, an open-shell system, the keyword would be specified by OCCUPATION=3-1-1-0/2-1-1-0. It should be noted that the VMOL integral program orders the irreducible representations in a strange way which most users do not perceive to be a logical order. Hence, it is usually advisable initially to run just a single point integral and SCF calculation in order to determine the number and ordering of the irreducible representations. The occupation keyword may be omitted, in which case an initial orbital occupancy is determined by diagonalization of the core Hamiltonian. In many cases, SCF calculations run with the core Hamiltonian guess will converge to the lowest energy SCF solution, but this should not be blindly assumed. (Default : The occupation is given by the core Hamiltonian initial guess).

REFERENCE The type of SCF calculation to be performed. RHF (= 0) restricted Hartree-Fock reference; UHF (= 1) unrestricted Hartree-Fock reference=1; ROHF (= 2) restricted open-shell Hartree- Fock calculation. For the RJB group the following option for REFERENCE is also available : TWODET (=3) two-determinant reference for open-shell singlet CC calculations. *Note : REFERENCE=TWODET is not supported in Release 2.* Note also that when REFERENCE=TWODET the orbitals are obtained for a closed-shell state, and so are *not* optimum open-shell singlet (or low spin triplet) SCF orbitals. The orbital occupancy for subsequent CCSD calculations is specified by the various QRHF keywords. (Default : 0).

RPP Specifies whether or not the reduced partitioning procedure is to be used to accalarate convergence of the SCF equations. =0 Do not use RPP, =1 use RPP. (Default : 1). *Note : This keyword name has been changed to* SCF_EXTRAPO.

RPP_LATEST Sets the latest iteration for initiation of the RPP convergence acceleration procedure in SCF calculations. RPP is switched on when the error falls below a certain threshold, but in difficult cases where the iterations are oscillatory it is necessary to force it on when the error is still large. In such a case, the RPP will begin on the iteration number specified by this parameter. (Default : 15). *Note : This keyword has been changed to* SCF_EXPSTAR.

RPP_ORDER Specifies the number of density matrices to be used in the RPP convergence accelaration procedure. =N N density matrices will be used. (Default : 6). *Note : This keyword has been changed to* SCF_EXPORDE.

SCF_CONV The convergence criterion for the SCF equations. Equations are considered converged when the maximum change in density matrix elements is less than 10^{-N}. (Default : 7).

SCF_MAXCYC Specifies the maximum number of SCF iterations. (Default : 150).

SYM_CHECK This specifies the action taken when the density matrix does not transform as the totally symmetric irreducible representation of the full molecular point group. NORMAL (=0) terminates the run if the molecule is nonlinear, while OVERRIDE (=1) allows the job to continue but prints a warning message. Nonsymmetric density matrices result from calculations on electronically degenerate states or from broken-symmetry SCF solutions. Often, such calculations do not give meaningful results and inexperienced users are encouraged to use SYM_CHECK=NORMAL in their calculations on nonlinear molecules. For Π, Δ, Φ, etc. states of linear molecules, however, meaningful calculations can still be performed even though the density matrix is not symmetric. (Default : OVERRIDE)

Keywords relevant to **Density Functional Theory Calculations** :

- CALC must be set to HFDFT

FUNCTIONAL This keyword only has meaning when CALC=HFDFT and a calculation type other than SINGLE_POINT has been requested. Possible values are : 0 XALPHA; 1 BECKE; 2 LYP; 3 XLYP; 4 BLYP (the default). The ACES II HFDFT program always calculates all of the above energies, but only one functional can be used in, for example, (numerical) geometry optimizations. This keyword specifies which one is to be used.

Keywords relevant to **Hartree-Fock stability analysis** :

HFSTABILITY This is used to control checks of the stability of RHF and UHF wavefunctions, as well as a cursory search for a lower SCF solution. There are three possible options for this keyword. OFF (=0) does nothing, while ON (=1) performs a stability check and returns the number of negative eigenvalues in the orbital rotation Hessian. A third option, FOLLOW (=2) performs the stability check and then proceeds to rotate the SCF orbitals in the direction of a particular negative eigenvalue of the orbital rotation Hessian (see the explanation of keyword ROT_EVEC), after which the SCF is rerun. A more detailed discussion of HF stability testing may be found in the section entitled Hartree-Fock Wavefunction Stability Analysis, below. (Default : OFF)

ROT_EVEC This keyword specifies which eigenvector of the orbital rotation Hessian is to be used to rotate the original SCF orbitals. By default, it will use that associated with the lowest eigenvalue of the totally symmetric part of the block-factored Hessian, as this choice often leads to the lowest energy SCF solution. For RHF stability checks, only those instabilities which correspond to RHF solutions will be considered. It is important to understand that following non-symmetric eigenvectors lowers the symmetry of the wavefunction and that following RHF→UHF stabilities leads to a UHF solution. To converge the SCF roots associated with such instabilities, one must run the calculation in reduced symmetry and as a closed-shell UHF case, respectively. ROT_EVEC=n directs the program to follow the vector associated with the n^{th} lowest eigenvalue having the proper symmetry (totally symmetric) and spin (RHF→RHF or UHF→UHF) properties. (Default : 0 [use the lowest eigenvalue])

Keywords relevant to the execution of the **Integral Transformation** :

DROPMO Specifies which molecular orbitals will be dropped from the post-SCF calculation. The orbitals are numbered in ascending order from the most stable (negative energy) to the most unstable (largest positive energy). Individual orbitals must be separated with a dash, while x>y means orbitals x through y inclusive. For example, the string 1>10-55-58>64, would result in orbitals 1,2,3,4,5,6,7,8,9,10,55,58,59,60,61,62,63 and 64 being dropped. For UHF calculations, the appropriate orbitals are deleted for both spin cases. No dropped MOs are currently allowed for gradient or property calculations. (Default : No dropped MOs)

VTRAN This keyword defines what type of integral transformation is to be performed in the program VTRAN. FULL/PARTIAL (=0) allows the transformation program to choose the appropriate type of transformation, while FULL (=1) requires a full integral transformation and PARTIAL (=2) means an MBPT(2) specific transformation where the (ab | cd) integrals are not formed. (Default : FULL/PARTIAL)

XFORM_TOL The tolerance for storing transformed integrals. Integrals less than 10^{-N} are neglected and not stored on disk. (Default: 11).

Keywords relevant to **Integral Processing** :

ABCDFULL This is a debug aid and is concerned with the storage of four virtual index integrals and effective Hamiltonian elements. It is only of relevance in RHF closed-shell calculations. It should never be necessary for users to set this keyword. Possible values are : UNKNOWN (=0) (the program will choose appropriate value); ON (=1) (full storage); OFF (=2) (reduced storage). Default : UNKNOWN.

ABCDTYPE Specifies the way that the $\langle ab||cd\rangle$ molecular orbital integrals are handled in post-MBPT(2) calculations. STANDARD (= 0) uses a technique which results in a minimum amount of CPU time but a maximum usage of disk space (particularly during execution of program XINTPRC); MULTIPASS (= 1) reduces the amount of disk storage required during XINTPRC, but at the cost of additional CPU time (note that this option requires HF2_FILE=2); AOBASIS (= 2) uses an AO-based algorithm to evaluate all terms involving these integrals. Again, use of this option results in considerably larger CPU times (particularly on vector supercomputers), but reduces the amount of required disk storage significantly. The use of ABCDTYPE=AOBASIS, however, is strongly recommended for single-point CC calculations on work station computers. Implementation within CC gradient calculations is planned, but currently not available.(Default: STANDARD).

HF2_FILE Specifies whether the HF2 (or HF2AA, HF2BB, and HF2AB) files are deleted after the first stage of integral processing. The default is to delete these files. However, when ABCDTYPE=MULTIPASS, these files must not be deleted at this time, and to stop deletion one must put HF2_FILE=2.

Keywords relevant to **Coupled-Cluster and Many-Body Perturbation Theory Calculations** :

- Note : the keywords NEWVRT and REFERENCE in the SCF section should also be consulted.

ABCDTYPE Specifies the way that the $\langle ab||cd\rangle$ molecular orbital integrals are handled in post-MBPT(2) calculations. STANDARD (= 0) uses a technique which results in a minimum amount of CPU time but a maximum usage of disk space (particularly during execution of program XINTPRC); MULTIPASS (= 1) reduces the amount of disk storage required during XINTPRC, but at the cost of additional CPU time (note that this option requires HF2_FILE=2); AOBASIS (= 2) uses an AO-based algorithm to evaluate all terms involving these integrals. Again, use of this option results in considerably larger CPU times (particularly on vector supercomputers), but reduces the amount of required disk storage significantly. The use of ABCDTYPE=AOBASIS, however, is strongly recommended for single-point CC calculations on work station computers. Implementation within CC gradient calculations is planned, but currently not available.(Default: STANDARD).

AO_LADDERS Can be used to control the algorithm used by ACES2 when terms involving $\langle ab||cd\rangle$ molecular orbital integrals are calculated in the atomic orbital basis (see keyword ABCDTYPE above). MULTIPASS (= 0) uses an approach where the AO integral file is read a number of times in order to ensure maximal vectorization and is usually the optimal strategy on supercomputers; SINGLEPASS (= 1) determines the contributions with only a single pass through the AO integrals, but at the cost of significantly reduced vectorization. In general, however, SINGLEPASS is *definitely preferable on workstations with RISC architectures.* (Default : MULTIPASS on all 64-bit machines (e.g., CRAY-YMP) ; SINGLEPASS on all 32-bit machines (e.g., IBM-RS6000, HP-735, SGI-Indigo)).

BRUCK_CONV This option specifies the convergence criterion in Brueckner-based coupled-cluster or configuration interaction calculations. The calculation is considered converged when the large single excitation amplitude falls below 10^{-N}, where N is the value associated with the keyword. (Default : 4)

BRUECKNER Specifies whether Brueckner orbitals are to be determined for the specified CC method. OFF (= 0) Brueckner orbitals are not to be determined, ON (= 1) They are to be determined. (Default : 0).

CC_CONV The convergence criterion for the CC equations. Equations are considered converged when the maximum change in amplitudes is less than 10^{-N}. (Default : N=7).

CC_MAXCYC The maximum number of CC iterations. (Default : 50).

NON-HF This flag tells the correlation energy code if the reference function satisfies the Hartree-Fock equations. Usually there is no need to set this parameter, since standard non-HF reference functions (QRHF and ROHF) set this flag internally. However, if you are inputting a set of orbitals to the correlation energy code directly, it may be necessary to use NON-HF. ON (= 1) signifies that a non-HF reference function is used; OFF (= 0) is used for HF reference functions. (Default : 0).

NTOP_TAMP Specifies how many t amplitudes will be printed for each spin case and excitation level. =N The largest N amplitudes for each spin case and excitation level will be printed. (Default : 15).

ORBITALS This keyword is used in non-HF calculations to specify semicanonical orbitals are used. "Semicanonical" orbitals are obtained by diagonalizing the occupied-occupied and virtual-virtual blocks of the spin-orbital Fock matrix and can be advantageously exploited in certain post-SCF calculations (particularly for ROHF-MBPT and non-iterative triple excitation corrections). There is no specific default value for this parameter, and considerable logic is used internally to choose the orbital type in post-SCF non-HF calculations if the keyword is not included. It is strongly recommended that this keyword not be used by anyone who is not thoroughly familiar with non-HF CC/MBPT methods, since the logic used to set the default value is sound. STANDARD (= 0) uses the orbitals obtained in the reference function calculation without modification; SEMICANONICAL (= 1) forces a transformation to semicanonical orbitals. (Default : See above).

ORDER_RLE Maximum size of the R matrix used in the reduced linear equation method for solving the CC equations. The maximum value allowed is 19. (Default : 5). *Note : This keyword has been changed to* CC_EXPORDER.

QRHF_GENERAL The presence of this keyword specifies that a QRHF-based coupled cluster calculation is to be performed. In this method, an SCF calculation is first performed on a closed-shell state specified by either the OCCUPATION keyword or the CHARGE and MULTIPLICTY keywords. Using the closed-shell state orbitals, a coupled-cluster calculation is then performed on an open-shell state generated from this closed-shell state by removing, adding, or exciting electrons. Any number of electrons may be added to the α spin orbitals, and any number may be removed from the β orbitals. The values associated with this keyword must be separated by slashes "/" and take on either negative (for removal of β electrons) or positive (addition of α electrons) integer values. The absolute values of these parameters specify the symmetry block(s) involved in the addition or removal of electrons. The numerical ordering of the symmetry blocks is consistent with that used in specifying the orbital occupations. By default, the electrons are added to the lowest unoccupied molecular orbital in the symmetry block and removed from the highest occupied molecular orbital. Different orbitals may be specified with the QRHF_ORBITAL keyword (see below). **NOTE:** In Release 2 of ACES

II gradients and property calculations are currently available *only* for cases involving addition or removal of electrons. Mixed cases involving both processes are not available in Release 2. In the RJB group code gradients and properties are available for open-shell singlet CCSD wavefunctions for the case that the open-shell orbitals have different symmetries.

QRHF_ORBITAL By default, in QRHF calculations, electrons are removed from the highest occupied orbital in a symmetry block (symmetry block HOMO), while electrons are added to the lowest unoccupied orbital within a symmetry block (symmetry block LUMO). The purpose of the QRHF_ORBITAL keyword is to allow additional flexibility in choosing which orbitals will have their occupation numbers altered. The value of this keyword gives the offset with respect to the default orbital for the orbital which will be depopulated (or populated) in QRHF-CC calculations. For calculations involving more than one removal or addition of electrons, values are separated by commas and correspond to the QRHF_GENERAL input on a one-to-one basis. For example, specifying QRHF_GENERAL=2/-4,QRHF_ORBITAL=3/2 means that an electron will be added to the third lowest virtual in symmetry block 2 and another will be removed from the second highest occupied orbital in symmetry block 4. Examples given later in this manual further illustrate the QRHF input options and may help to clarify any confusion resulting from this documentation. (Default : 1)

QRHF_SPIN This keyword specifies the spin of the electrons modified by the QRHF_GENERAL and QRHF_ORBITAL keywords, where a value of 1 means α spin, while 2 corresponds to a β electron. By default, electrons that are removed are assigned to β spin, while added electrons are α. Note that this option allows one to construct low-spin determinants, which generally are unsuitable for single-reference coupled-cluster calculations. An important exception is the open-shell singlet coupled-cluster method (see keyword REFERENCE=TWODET below).

RLE Specifies the type of convergence acceleration used to solve the CC equations. STANDARD (= 0), the RLE method of Bartlett and Purvis is used with periodic extrapolation of the solution vector; DIIS (= 1) uses the DIIS approach of Pulay; NOJACOBI (= 2) uses the RLE method with continuous extrapolation; OFF (= 3) no convergence acceleration method is used. In general, STANDARD provides the best performance, but DIIS and particularly NOJACOBI may offer advantages in cases where the reduced subspace becomes singular too rapidly. NOJACOBI requires some additional disk storage which may be disadvantageous for very large calculations. Use of OFF is generally a bad idea for CC calculations, but may be preferable to the other choices for configuration interaction calculations. (Default : 0) *Note : This keyword has been changed to* CC_EXTRAPOL *and the default has been changed to* DIIS.

TAMP_SUM Specifies how often the largest t amplitudes are to be printed. =0 Amplitudes are printed at the beginning and end of the run, =1 Amplitudes are printed every iteration, =2 Amplitudes are printed every other iteration, etc. (Default : 5).

Keywords relevant to **Geometry Optimizations, Transition State Searches and Other Energy Derivative Calculations** :

CONVERGENCE Specifies convergence criterion for geometry optimization. Job terminates when RMS gradient is below 10^{-N} Hartree/bohr, where N is the value specified by CONVERGENCE. (Default: 4; Value must be specified as an integer).

CPHF_CONVER Specifies the convergence criterion for the iterative solution of the CPHF and Z-vector equations. The solutions are considered to be converged when the error falls below 10^{-N}. (Default : 12)

CPHF_MAXCYC The maximum number of cycles allowed for the solution of the CPHF and Z-vector equations. (Default : 64)

CURVILINEAR Specifies whether or not Hessian matrix is transformed (nonlinearly) to curvilinear internal coordinates. A value of 0 (or OFF) turns the transformation off if the analytic force constants are not available, while it is always performed if CURVILINEAR=1 (or ON). Values higher than 1 (or NO) unconditionally turn the transformation off.(Default: ON if analytic Hessian is available, OFF otherwise).

DERIV_LEV Specifies whether or not derivatives of the energy are to be calculated and if so whether first or second. = 0 Derivatives not calculated, =1 First derivatives to be calculated, =2 Second derivatives to be calculated. This need not be set in geometry optimization or vibrational frequency calculations since it is automatically set if the appropriate options in the ACES2 namelist are set. (Default : 0). *NOTE: It is probably dangerous to use this keyword.*

EIGENVECTOR Specifies which eigenvector of the totally symmetric part of the block-factored Hessian is to be followed *uphill* in a transition state search. Eigenvectors are indexed by their eigenvalues – the lowest eigenvalue is 1, the next lowest is 2, etc. The default is 1, which should *always* be used if you are not looking for a specific transition state which you know corresponds to motion along a different mode. Of course, the value of EIGENVECTOR has no meaning if METHOD is not set to TS. (Default: 1; Value must be specified as an integer).

EVAL_HESS Tells ACES II to recompute the Hessian every N cycles, where N is the supplied argument. For correlated calculations, the Hessian is evaluated *only at the SCF level.* (Default: 0 (no recomputation); Value must be specified as an integer).

MAX_STEP Specifies largest step (in millibohr) which is allowed in geometry optimizations. (Default: 300).

METHOD Specifies the geometry optimization strategy. Four values are permitted: 0 (or NR) — Straightforward Newton-Raphson search for minimum; 1 (or RFA) — Rational Function Approximation search for minimum (this method can be used to find minima when the initial structure is in a region where the number of negative Hessian eigenvalues is nonzero); 2 (or TS) Cerjan-Miller eigenvector following search for a transition state (can be started in a region where the Hessian index (the number of negative Hessian eigenvalues) is not equal to one); 3 (or MANR) — Morse-adjusted Newton-Raphson search for minimum (very efficient minimization scheme, particularly if the Hessian is available); 4 is currently unavailable; 5 (or SINGLE_POINT) is a single point calculation. (Default: SINGLE_POINT); 6 — Do a geometry optimization but compute the gradients from energies only.

NEGEVAL Tells the program what to do if negative eigenvalues are encountered in the totally symmetric Hessian during an NR or MANR search. If NEGEVAL=0 (or ABORT), then the job will terminate with an error message; if NEGEVAL=1 (or SWITCH) the program will just switch the eigenvalue to its absolute value and keep plugging away (this is strongly discouraged); and if NEGEVAL=2 (or→RFA), METHOD is switched to RFA internally and the optimization is continued. (Default: ABORT).

OPT_MAXCYC This specifies the maximum allowed number of geometry optimization cycles. (Default : 50)

PERT_ORB The keyword STANDARD means that the gradient formulation assumes that the perturbed orbitals are not those in which the Fock matrix is diagonal. CANONICAL means that the perturbed orbitals are assumed to be canonical. This keyword must be set to CANONICAL in gradient calculations with methods which include triple excitations (MBPT[4], CCSD+T[CCSD], CCSD[T], and QCISD[T]). (Default : STANDARD)

RELAX_DENS Specifies whether the relaxed density matrix is computed for correlated wave functions. OFF (= 0) The relaxed density will not be computed, ON (= 1) it will be computed. This keyword is set by the program and should *not* be set by the user; if the relaxed density is desired, then PROPS=1 should be set. (Default : 0).

SCALE_ON Controls whether step scaling is based on the absolute step length (1-norm) (=0 or MAG(S)) or the largest individual step in the internal coordinate space (=1 or MAX(S)). (Default: MAG(S)).

TRANS_INV This keyword specifies whether or not translational invariance is exploited in derivative calculations. USE(=0) specifies that translational invariance is exploited, while IGNORE (=1) turns it off. (Default : USE)

Keywords relevant to **Vibrational Frequency Calculations** :

FD_CALTYPE In finite difference calculations using the FINDIF option, this keyword controls the algorithm used to compute the harmonic force constants. GRADONLY (= 0) evaluates the force constants and dipole moment derivatives by numerical differentiation of analytic gradients; ENERONLY (= 1) evaluate the force constants by second differences of energies (dipole moment derivatives are not evaluated); while MIXED (= 2) evaluates $1x1$ blocks of the symmetry-blocked force constant matrix by second differences of energies and all other elements by first differences of gradients. The GRADONLY and MIXED approaches may, of course, only be used when using computational methods for which analytic gradients are available.

FD_PROJECT In finite difference calculations using the FINDIF option, this keyword controls whether or not rotational degrees of freedom are projected out of symmetry-adapted coordinates. ON (= 0) uses rotationally projected coordinates, while OFF (= 1) retains the rotational degrees of freedom. At a stationary point on the potential surface, both options will give equivalent harmonic force fields, but OFF should be used at non-stationary points. (Default : ON)

FD_IRREPS This keyword may be used to request that only vibrational frequencies of certain symmetry types be evaluated in a VIBRATION=FINDIF calculation. The numbers of the irreducible representations for which vibrational analysis is to be performed are separated by slashes. For example, FD_IRREP=1/3/4 means compute the frequencies of modes transforming as the first, third, and fourth irreducible representations. If a symmetry is specified for which there are no vibrational modes, the program will terminate. The labels of the irreducible representations for this keyword are not usually the same as those used in the rest of the calculation. Moreover, for some point groups, for example those of linear molecules, the two sets of labels refer to different subgroups. There is as yet no straightforward way to determine what they will be without starting a calculation. If one runs the xjoda and then the xsymcor executables the relevant irreducible representations will be listed. If all vibrational frequencies are desired, this keyword need not be included. (Default : compute vibrational frequencies for all irreducible representations)

FD_STEPSIZE Specifies step length (in 10^{-4} amu$^{1/2}$ bohr) used in generating the force constant matrix by finite difference of Cartesian gradients. (Default: 50 (0.005 amu$^{1/2}$ bohr)).

FD_USEGROUP In finite difference calculations using the FINDIF option, this keyword specifies the point group to be used in generating the symmetry-adapted vibrational coordinates. FULL (= 0) specifies the full molecular point group, COMP (= 1) specifies the Abelian subgroup used in the electronic structure calculation. (Default : FULL)

POINTS Specifies either single (=1, or SINGLE) or double (=2, DOUBLE) sided numerical differentiation in the finite difference evaluation of the Hessian. Two-sided numerical differentiation is considerably more accurate than the single-sided method and its use is *strongly recommended for production work.* (Default: DOUBLE).

VIBRATION For vibrational frequency calculations. A value of 1 (or EXACT) means perform normal mode analysis on an analytic force constant matrix and computes rotationally projected frequencies and infrared intensities. A value of 2 (or FINDIF) signals ACES II to compute the force constant matrix by finite difference of analytically computed gradients or energies using symmetry-adapted mass-weighted Cartesian coordinates (see entries for keywords FD_CALCTYPE, FD_PROJECT and FD_USEGROUP). A value of 3 (or FINDIF_OLD) uses an alternative algorithm based on energy gradients which minimizes the number of gradients which must be evaluated. However, these gradients will be evaluated for nonsymmetric structures, as opposed to the FINDIF method which evaluates more gradients but in general does not require them to run in C_1 symmetry. A choice between FINDIF and FINDIF_OLD requires a great deal of knowhow and experience, and the FINDIF option is recommended for all but the most knowledgable of ACES II gurus. (Default: NO)

Keywords relevant to **Property Calculations** :

- Review also keywords for geometry optimizations. For excited state properties, see also keyords for excited state calculations. Consult also sections of the manual on NMR and TDHF calculations.

EOMPROP Specifies method of calculating EOM-CCSD second-order properties (polarizabilities and spin-spin coupling constants). =CILIKE (use CI-like formula, which is not rigorously size-intensive); =LINEAR (remove unlinked diagrams from CI-like formula); =QUADRATIC (use quadratic formula); =COMBO (compute all approximations). (Default : CILIKE). This keyword only has meaning when PROP=VCCEH, PROP=J_SO, PROP=J_FC, PROP=J_SD, or PROP=JSC_ALL.

PROPS Specifies whether one-electron properties are to be calculated at the end of the run. OFF (=0) Do not compute properties; FIRST_ORDER(=1) compute first-order properties (dipole moment, qudrupole moment, electrical field gradients, spin densities, etc.; SECOND_ORDER(=2) compute second-order properties (static polarizabilities; limited to CALC=SCF and (C_1 symmetry only) CALC=MBPT[2] — for other methods finite field calculations can be used); NMR(=3) compute NMR chemical shifts; J_SO(=8) calculate spin-orbit contribution to spin-spin coupling constant J; J_FC(=9) calculate Fermi contact contribution to spin-spin coupling constant J; J_SD(=10) calculate spin-dipole contribution to spin-spin coupling constant J; CCSDEH(=11) calculate EOM-CCSD dynamic polarizabilities; JSC_ALL(=13) calculate all of J. Note : NMR calculations currently require Cartesian basis functions (*i.e.* SPHERICAL=ON cannot be used). (Default : 0).

TDHF Specifies whether a time-dependent Hartree-Fock calculation of nonlinear optical properties is to be performed. TDHF=0/TDHF=OFF means a TDHF calculation is not to be performed (the default); TDHF=1/TDHF=ON means that a TDHF calculation is to be performed. This keyword can only be used for CALC=SCF and for closed-shell systems, and no orbitals may be dropped. The nonlinear properties which are to be calculated are specified by a namelist which is put at the end of the ZMAT file. A description of this namelist and examples are provided in the section on time-dependent Hartree-Fock calculations.

TREAT_PERT This keyword is used for certain types of correlated second derivative calculations [presently only GIAO NMR shift calculations] and directs ACES II to either treat all perturbations at once or treat them sequentially. The latter approach results in less demand for physical disk space, but at the cost of increased cpu time. Available options are SIMULTANEOUS (=0); and SEQUENTIAL (=1). (Default : SIMULTANEOUS).

XFIELD Specifies the X-component of an external electric field. The value must be specified as an integer and the field used by the program will be the value of the keyword $x10^{-6}$. This allows field strengths $|\mathcal{E}| > 10^{-6}$ to be used. (Default : 0)

YFIELD Specifies the Y-component of an external electric field. See above. (Default : 0)

ZFIELD Specifies the Z-component of an external electric field. See above. (Default : 0)

Keywords relevant to **Equation-of-motion Excitation Energy Calculations** :

EOM_MAXCYC This parameter controls the number of iterations in EOM excited state calculations. If it has the value N and $NROOT$ roots have been requested for a given symmetry, the program will allow up to $N * NROOT$ iterations to find all the requested roots for that symmetry. (Default : 50)

ESTATE_MAXC The maximum number of iterative diagonalization steps for each root in excited state calculations. (Default : 30) [*Note* : this option is not currently used by the EOM excited state code; its role has been taken by EOM_MAXCYC]

ESTATE_PROP This keyword applies only to EOM-CC calculations and specifies whether any excited state one-electron properties are to be calculated. Proper use of this keyword might require some fairly advanced knowledge of quantum chemistry and the available options are discussed here. The options are : OFF (=0) [no properties or transition moments are calculated]; EXPECTATION (=1) [transition moments and dipole strengths are calculated along with selected one-electron properties which are evaluated as expectation values]; UNRELAXED (=2) [selected one-electron properties are calculated in an approximation that neglects relaxation of molecular orbitals]; RESPONSE (=3) [selected one-electron properties are calculated as analytic first derivatives of the energy]. Except for EOMCC calculations on two-electron systems (which are exact), properties obtained by the three approaches will not be equivalent. The default value for this keyword is slightly complicated. For TDA calculations, the default is EXPECTATION since the evaluation of transition moments involves only a negligible amount of additional computation relative to the evaluation of the excitation energies. For EOMCC, the default if OFF since evaluation of any transition moments or properties requires approximately twice the computational time. ESTATE_PROP=RESPONSE is not available for EOMCC calculations. Transition moments and dipole strengths are evaluated by default for all values of ESTATE_PROP other than OFF.

ESTATE_SYM This specifies the number of excited states which are to be determined in each irreducible representation of the computational subgroup. The program attempts to find all of the lowest roots, but this is not guaranteed because the eigenvalue problem is not solved by direct matrix diagonalization, but rather by an iterative (modified Davidson) algorithm. For excited state gradient calculations (TDA only), only one root can be specified, so only one non-zero entry in the string is allowed, and that must be set to one. The format used for this keyword is identical to that used in the OCCUPATION keyword. For example, for a computational subgroup having four symmetry species, the string ESTATE_SYM=3/1/0/2 specifies that 6 total roots should be searched for, three in the first block, one in the second block, and two in the fourth block. (Default : All zeros).

ESTATE_TOL The tolerance used in converging EOM-CC excited state calculations. By default, the iterative diagonalization continues until the RMS residual falls below 10^{-5}, and this value can be changed to 10^{-N} by specifying ESTATE_TOL=N. (Default : 5)

EXCITE This keyword specifies the type of excitation energy calculation which is to be performed. Available options are NONE (=0); TDA (=1) [the Tamm-Dancoff, or configuration interaction singles (CIS) approach]; and EOMEE (=3) [the equation of motion coupled-cluster approach]. At present, the EOMCC method is limited to CCSD reference states. (Default : NONE).

Keywords relevant to **Equation-of-motion Electron Affinity Calculations** :

EA_CALC Specifies whether an equation-of-motion coupled-cluster electron affinity calculation is to be performed or not. =NONE means that an EOM-CC EA calculation will not be performed; =EA_EOMCC means that an EOM-CC EA calculation will be performed. (Default : NONE)

EA_SYM Specifies the symmetry and spin of the added electron in EOM-CC EA calculations. In RHF calculations a string of NIRREP integers, separated by hyphens ('-'), where NIRREP is the order of the computational point group, is given. For example : EA_SYM=3-2-0-2 means that the program is to calculate the energies of 3 electron attached states in which the additional electron occupies an orbital of symmetry 1, 2 electron attached states in which the additional electron occupies an orbital of symmetry 2, and so on. In UHF or ROHF calculations 2*NIRREP integers are specified. The first set denotes α spin and the second β spin, and the two sets are separated by a slash ('/ '). For example : EA_SYM=3-2-0-2/0-1-0-4. If EA_CALC has been set to EA_EOMCC and EA_SYM is not specified, the program will try to find the lowest energy electron attached state. For further information about EOM-CC EA calculations, see the section of this manual entitled "Equation-of-motion coupled-cluster electron attachment calculations".

The job control parameters are entered following a mandatory blank line at the end of the parameter input section (see above). Delimiters separating individual keywords can be commas (","), semicolons (";"), ampersands ("&") or carriage returns.

B..7 Non-standard Basis Set Specification

If the BASIS keyword is set to SPECIAL, or is not included in the keyword list, the basis set specification will be read directly from the ZMAT file after the keyword list. One blank line must separate the last line of the keyword list from the beginning of the basis set input section. Each entry must be placed on an individual line, and the ordering of atoms must follow the Z-matrix ordering *exactly*. The names will then be checked against the GENBAS file in the current directory and the basis, if found, will be extracted and placed in the input file appropriate for the integral program. If the basis is not found, ACES II exits with an error condition. ACES II does not check to make sure that the atom to which the basis set belongs corresponds with the atomic designation in the corresponding row of the Z-matrix. No entries are made for dummy atoms. The format of the basis set names in GENBAS is: XX:BASNAM, where XX is the atomic symbol of the atom (in capital letters), and BASNAM is the name of the basis. For inexperienced users, it is probably best to search the GENBAS file for "XX:", where again XX is the atomic symbol since this will allow you to see all of the available basis sets for that atom. A description of the format of the GENBAS file and its contents are given in Section IV D of this manual.

B..8 Non-standard File Handling and Restart Calculations

Facilities are available in ACES II which allow user control over file locations and permit certain types of restart calculations to be carried out in a straightforward way. By default, all files used by ACES II [IIII, IIJJ, IJIJ, IJKL, JOBARC, JAINDX, MOINTS, GAMLAM, MOABCD, DERGAM, SECDER, OPTARC, *etc.*] are kept in the working area [the directory from which the **xaces2** program is invoked]. In the usual case, this is a scratch directory of some sort and these files are often deleted immediately after the job terminates. However, the location of these files can be respecified in a simple way through lines entered *at the very top* of the ZMAT file. The location of any file (except the input file ZMAT of course) may be respecified as follows :

```
% FILE=/u/usr/safe/FILE
```

where FILE is the name of the particular file. For example, if one wants to calculate isotopic shifts after a vibrational frequency calculation has been performed [see the section which describes how to run these calculations], it is useful to keep the JOBARC and JAINDX files in a safe place. For example, if one wanted to do such a calculation for water, the following ZMAT file might be used :

```
% JOBARC=/u/usr/safe/JOBARC
% JAINDX=/u/usr/safe/JAINDX

Water DZP vibrational frequency calculation
H
O 1 R
```

```
H 2 R 1 A

R=0.957
A=104.51

*ACES2(CALC=SCF,VIB=EXACT,BASIS=DZP)
```

After this job executes, the files JOBARC and JAINDX are located in the directory /u/usr/safe. Then one can simply move to this directory, create the appropriate ISOMASS files (see section on isotopic shift calculations) and run the ACES II executable **XJODA** directly.

The re specification of file locations also can be used to facilitate restarts of geometry optimization and finite difference vibrational frequency calculations. For optimizations, the following files must be saved : JOBARC, JAINDX and OPTARC. For finite difference harmonic frequency calculations (*using* VIB=FINDIF *only*!), one also needs to save JOBARC and JAINDX. If the job exits because a cpu time limit has been exceeded, then re submission will automatically initiate the restart process (no additional keywords are necessary). If however, the maximum number of optimization cycles has been exceeded, then the OPT_MAXCYC keyword needs to be modified. If for example, one wants to run an optimization three cycles at a time, the following ZMAT file might be used for the first stage:

```
% JOBARC=/u/usr/safe/JOBARC
% JAINDX=/u/usr/safe/JAINDX
% OPTARC=/u/usr/safe/OPTARC

Water DZP geometry optimization
H
O 1 R*
H 2 R* 1 A*

R=0.957
A=104.51

*ACES2(CALC=SCF,BASIS=DZP,OPT_MAXCYC=3)
```

After this first phase completes, then OPT_MAXCYC can be reset to 6 and the job resubmitted. The program system only keeps track of the total number of steps completed, and not the incremental values.

While on supercomputers, it is usually recommended to save the restart files in the user's own disk area, the situation is quite different for work station computers. Here, the available scratch space for running a job is often put on several independent disks (in most cases two or three) and it is necessary to redirect several of the large files in order to run the job. This can be done in the same way as described above using the % cards in the ZMAT file.

B..9 Molecular Orientation

The orientation of the molecule in the Cartesian basis is related to its point group. Two orientations are used extensively in the ACES II program system: the "standard" or "computational" orientation (which is a standard orientation for the computational point group) and a "canonical" orientation (which is the standard orientation for the full point group). Note that in some cases, the two orientations are identical. All calculations are performed in the computational orientation, so orbital symmetries should be specified according to this Cartesian axis system. For the most part, the canonical orientation is used internally for tasks such as determining irreducible representations or other properties related to the full point group. The standard orientation for each point group follows

C_n Groups Rotation axis along z.

D_n Groups Rotation axes coincident with Cartesian axes, with the highest order axis along z.

C_s Group Plane of symmetry is xy.

S_n Groups S_n axis along z.

C_{nv} Groups C_n axis along z, xz is σ_v.

C_{nh} Groups C_n axis along z, xy is σ_h.

D_{nh} Groups C_n axis along z, one C_2 axis along x.

D_{nd} Groups S_{2n} axis along z, one C_2 along x.

T Group C_3 axis along (q, q, q).

T_d Group S_4 axis along z.

T_h Group C_3 axis along (q, q, q), symmetry planes are xy, xz and yz.

O Group C_4 axes along x, y and z.

O_h Group C_4 axes along x, y and z.

I Group C_5 axis along z, one C_3 lies in the xz plane.

I_h Group C_5 axis along z, xz is a symmetry plane.

For groups with ambiguities (D_2, D_{2h}, C_{2v}), there is no standard orientation at present, and you may want to run ACES II once to see which orientation is used before assigning orbital symmetries. For example, water belongs to the C_{2v} point group and the symmetry plane containing the hydrogen atoms may be assigned to either the xz or yz planes, leading to an ambiguity between the b_1 and b_2 irreducible representations. Eventually, some criterion may be established which defines a standard orientation for these groups thereby alleviating this annoyance.

B..10 Summary

To summarize, the ZMAT file contains the following information:

Preamble	Nonstandard file declarations (if used).
Line 1	Title for calculation.
Lines 2→i	Z-matrix or Cartesian coordinates.
Line i+1	Blank.
Lines i+2→j	Parameter input (if Z-matrix above).
Line j+1	Blank.
Lines j+2→k	ACES2 Namelist.
Line k+1	Blank.
Lines k+2→l	Basis set input (if BASIS=SPECIAL).
Line l+1	Blank.
Lines l+2→m	ECP input (if ECP=ON).

C. Input Examples

C..1 Example 1 : RHF single-point energy calculation

```
H2O. CCSD(T) energy calculation. DZP basis set.
H
O 1 ROH
H 2 ROH 1 HOH

ROH=0.95
HOH=104.5

*ACES2(CALC=CCSD[T],BASIS=DZP)
```

This illustrates a single-point CCSD(T) energy calculation on the water molecule with the DZP basis set. This input is particularly simple since advantage can be taken of many defaults for this closed-shell neutral molecule. These are CHARGE (default : 0), MULTIPLICITY (default : 1, *i.e.* a singlet), and REFERENCE (default : RHF). The OCCUPATION string is not specified, which means the program will determine this itself. It should be noted that the CCSD(T) method must be specified using square brackets rather than parentheses. By default all electrons are correlated. To exclude some electrons, the DROPMO keyword can be used.

C..2 Example 2 : UHF single-point energy calculation

```
H2O+. UHF-CCSD(T) energy calculation. DZP basis set.
H
O 1 ROH
H 2 ROH 1 HOH

ROH=0.95
HOH=104.5

*ACES2(CALC=CCSD[T],BASIS=DZP,CHARGE=1,MULT=2,REF=UHF
OCCUPATION=3-1-1-0/2-1-1-0)
```

This illustrates a single-point CCSD(T) energy calculation on the $^2A_1$ state of the water cation with the DZP basis set. For this system, one cannot rely on the defaults that were used in the first example. It is necessary to specify the CHARGE, MULTIPLICITY, and REFERENCE. Since we want a particular state, we use the OCCUPATION keyword.

C..3 Example 3 : ROHF single-point energy calculation

```
H2O+. ROHF-CCSD(T) energy calculation. DZP basis set.
H
O 1 ROH
H 2 ROH 1 HOH

ROH=0.95
HOH=104.5

*ACES2(CALC=CCSD[T],BASIS=DZP,CHARGE=1,MULT=2,REF=ROHF
OCCUPATION=3-1-1-0/2-1-1-0)
```

This is essentially identical to the previous example. The difference is that we have requested that a restricted open-shell Hartree-Fock reference is used. The program automatically turns on the NON-HF option so that the appropriate "non-Hartree-Fock" terms are included in the coupled-cluster equations. It also automatically sets ORBITAL=SEMICANONICAL, which is needed to evaluate triple excitations non-iteratively, as in the CCSD(T) method.

C..4 Example 4 : QRHF single-point energy calculation

```
H2O+. QRHF-CCSD(T) energy calculation. DZP basis set.
H
O 1 ROH
H 2 ROH 1 HOH

ROH=0.95
HOH=104.5

*ACES2(CALC=CCSD[T],BASIS=DZP,CHARGE=0,MULT=1,REF=UHF
QRHF_GENERAL=-1
ORBITAL=SEMICANONICAL
OCCUPATION=3-1-1-0/3-1-1-0)
```

This is another way in which one may calculate the energy of an open-shell molecule. Here the energy of the $^2A_1$ state of the water cation is being calculated by the QRHF-CCSD(T) method. The orbitals, however, are not from an SCF calculation on H_2O^+. Rather, they are neutral molecule orbitals. Broadly speaking, QRHF means orbitals are taken from a convenient closed-shell system and are then used in an open-shell system. An important difference between this example and the previous examples is that the CHARGE, MULT, REF, and OCCUPATION keywords *do not* refer to the system being studied (H_2O^+), but instead refer to the system from which the orbitals are obtained (H_2O). QRHF_GENERAL=-1 (along with the default values for QRHF_ORBITAL and QRHF_SPIN) means that the reference function for the correlated calculation is to be formed by removing a β-spin electron from the highest occupied orbital of symmetry 1 (*i.e.* A_1). As in the ROHF example, the program automatically turns on the NON-HF option so that the appropriate "non-Hartree-Fock" terms are included in the coupled-cluster equations. For QRHF-CCSD(T) calculations it is still necessary to set ORBITAL=SEMICANONICAL.

C..5 Example 5 : A simple geometry optimization

```
H2O. CCSD(T) optimization.
H
O 1 ROH*
H 2 ROH* 1 HOH*

ROH=0.95
HOH=104.5

*ACES2(CALC=CCSD[T],BASIS=DZP)
```

This specifies a geometry optimization of the water molecule with the CCSD(T) method and the DZP basis set. The input is exactly the same as in Example 1, except that an asterisk "*" is placed after each variable (both bond lengths and the bond angle) to be optimized. Defaults for all of the optimization keywords (*e.g.* METHOD and CONVERGENCE) are used. The presence of the asterisks turns on all appropriate derivative keywords. Geometry optimizations by default are performed using analytical gradients. If analytical gradients are not available, one can do geometry optimizations from energies using either METHOD=6 or GRAD_CALC=NUMERICAL.

C..6 Example 6 : A more advanced geometry optimization

```
Beryllium borohydride, D3d structure, geometry optimization.
X
BE 1 R1
B 2 R* 1 A
B 2 R* 1 A 3 T
X 2 RX* 1 A 3 T
X 2 RX* 1 A 4 T
H 5 RHX* 2 A 1 T
H 5 RHX* 2 A 1 T60
H 5 RHX* 2 A 1 TM6
H 6 RHX* 2 A 1 T12
H 6 RHX* 2 A 1 TM2
H 6 RHX* 2 A 1 T0
X 3 R1 2 A 1 T0
X 4 R1 2 A 1 T0
H 3 RHT* 13 A 2 T
H 4 RHT* 14 A 2 T

R1=1.207
R=1.05183
RX=0.08546
RHX=1.48313
RHT=0.569
A=90.
T=180.
T60=60.
T12=120.
T0=0.
TM2=-120.
TM6=-60.

*ACES2(METHOD=MANR,EVAL_HESS=3,MAX=750,CONV=5,CALC=1)

BE:6-31G*
B:DZP
B:DZP
H:DZ
H:DZ
H:DZ
H:DZ
H:DZ
```

```
H:DZ
H:DZ
H:DZ
```

This ZMAT file specifies a geometry optimization for the D_{3d} isomer of beryllium borohydride, BeB_2H_8. Compared with the water example above, which uses all default optimization keywords, this optimization input adds some features. The MANR optimization algorithm is used. The (SCF) Hessian will be reevaluated every three cycles, and the maximum step length is set to 750 millibohr. The convergence criterion (CONV) is set to 5, which means the optimization will continue until the root-mean-square force is below 10^{-5}, rather the default of 10^{-4} atomic units. The "non-standard" basis set input format is used, which is automatically selected since the BASIS keyword assumes its default value, SPECIAL. An MBPT(2) calculation is specified by the CALC keyword. This has been specified using the number corresponding to MBPT(2), although our recommendation is to use the name. The default values for CHARGE, MULT, REF, and OCCUPATION are used. The geometry optimization request automatically turns on the necessary gradient options.

C..7 Example 7 : Transition state search.

```
CH2O --> H2 + CO transition state search.  DZP basis.
O
C 1 R*
H 2 R2* 1 A*
H 3 RHH* 2 A* 1 T

R=1.254
R2=1.08
RHH=1.01
A=133.5
T=0.

*ACES2(METHOD=TS,MAX=150,BASIS=DZP
       CALCLEVEL=MBPT[2],OCCUPATION=7-1)
```

As implied by the job title, this ZMAT file specifies an initial geometry and basis set for a transition state search. In the Z-matrix file, the parameters designated R, R2, RHH, and A will be optimized, while parameter T will be fixed at 0 degrees. It is rather easy to see that this constrains the structure to be planar. The ACES2 namelist parameters tell ACES II that 1) this is a transition state search, using the Cerjan-Miller eigenvector following method; 2) the maximum allowed step length is 150 millibohr (this corresponds to the absolute step length (1-norm) since the default value of SCALE_ON has not been overridden); 3) the DZP basis set is to be used; 4) the calculation type is MBPT[2]; and 5) the occupation, appropriate for the C_s point group, is 7-1. It should be noted that the CALCLEVEL keyword uses brackets '[ ]' rather than parentheses '( )'. The keyword "TS" automatically turns on the necessary gradient options. In transition searches it is necessary to provide an initial estimate of the hessian. This is usually done by saving the FCMINT file from a frequency calculation and copying this to the workspace at the beginning of a transition state search. See section V, part D for a further discussion of this point. By default transition states searches use analytical gradients. If these are not available, on can calculate the gradient from energies using the keyword GRAD_CALC=NUMERICAL.

C..8 Example 8 : Finite-difference frequency calculation

```
N4 finite difference frequency calculation
N
X 1 R
N 2 R 1 TDA
N 2 R 1 TDA 3 T
N 2 R 1 TDA 4 T

R=0.945
TDA=110.
T=120.

*ACES2(VIB=FINDIF,BASIS=TZ2P,CALCLEVEL=1)
```

This ZMAT file directs ACES II to perform a harmonic frequency calculation for N_4, and to compute the force constants by numerical differentiation of analytic gradients. The TZ2P basis set is selected. Note that the TDA parameter is used in the Z-matrix. Although the specified value in the parameter input section is not the exact tetrahedral angle, the program will convert TDA to the correct value ($109.4712206\cdots$ degrees) internally. As for example 1, the ACES2 namelist specifies an MBPT(2) calculation, but in a different manner. As the FINDIF option is being used, no symmetry must be specified and so the orbital symmetry specification is omitted. This is because the determination of the force constants requires several gradient calculations at geometries with different symmetries. The FINDIF option automatically turns on the requisite gradient and property options. Note that no asterisks may appear in the Z-matrix in a frequency calculation — this is a common error since frequency calculations are usually preceded by geometry optimizations, which require the asterisks.

C..9 Example 9 : Finite-difference frequencies from energies

```
TEST.011 ROHF-HFDFT NUMERICAL VIBRATION CALCULATION FOR NH2
N
H 1 R
H 1 R 2 A

R=1.031
A=102.9

*ACES2(CALC=HFDFT,REF=ROHF,MULTI=2,BASIS=TZ2P,VIB=FINDIF
FD_CALTYPE=ENERONLY)
```

This ZMAT file specifies a finite difference frequency calculation for NH_2 using energy points only with the HFDFT method. The default Becke-Lee-Yang-Parr (B-LYP) functional value for the energy is used. Another functional could be selected as, for example, FUNCT=LYP (which would use the LYP correlation functional and the Hartree-Fock exchange energy). The FD_CALTYPE=ENERONLY option should be used only for those cases for which analytical gradients are not available (ACES II choses whether to use gradients or energy points in a finite difference calculation in a way which minimizes the number of points which must be determined). This method of calculating frequencies is applicable to all types of calculations, not just HFDFT.

C..10 Example 10 : QRHF-CCSD property calculation

```
NO3 calculation
N
O 1 R
O 1 R 2 A
O 1 R 2 A 3 T

R=1.236
A=120.
T=180.

*ACES2(BASIS=TZ2P,CALC=CCSD,QRHF_G=-2,QRHF_O=2,CHARGE=-1,PROP=1)
```

This ZMAT file specifies a QRHF/CCSD property calculation for the NO_3 radical, using a triple-zeta plus double polarization (TZ2P) basis set. Note that the charge corresponds to the M species (the NO_3 anion) rather than NO_3 itself. The OCCUPATION keyword is left out, therefore the orbital occupations will be estimated by the SCF program. Keep in mind that the SCF calculation *is performed for* NO_3^- *and not* NO_3, so that occupancy specification, charge and multiplicity *must always correspond to the closed-shell species.* The zeroth-order state for the QRHF calculation will be that obtained by removing an electron from the second highest lying molecular orbital in symmetry block 2. With luck, the CCSD will converge to the second lowest doublet state of the this symmetry type. After the CCSD calculation has completed, the first-order properties will be calculated analytically.

C..11 Example 11 : EOM-CCSD excitation energies

```
EOM-CCSD excitation energies and transition moments for water
H
O 1 R
H 2 R 1 A

R=0.957
A=104.5

*ACES2(BASIS=TZ2P,CALC=CCSD,EXCITE=EOMEE,ESTATE_SYM=1/1/1/1
ESTATE_PROP=EXPECTATION)
```

This ZMAT file specifies an equation of motion coupled-cluster excitation energy calculation for the water molecule, using the TZ2P basis set. The program will attempt to find the lowest root in each of the four symmetry species of the C_{2v} point group, and oscillator strengths will be evaluated for all excited states.

C..12 Example 12 : NMR chemical shift calculation

```
GIAO-MBPT(2) NMR chemical shift calculations for the benzonium cation
C           0.000000    0.000000   -1.393615
C           0.000000    0.000000    1.413386
C           0.000000   -1.250334   -0.632255
C           0.000000    1.250334   -0.632255
C           0.000000   -1.237545    0.742530
C           0.000000    1.237545    0.742530
H           0.853412    0.000000   -2.102274
H          -0.853412    0.000000   -2.102274
H           0.000000   -2.189398   -1.180688
H           0.000000    2.189398   -1.180688
H           0.000000   -2.161755    1.310996
H           0.000000    2.161755    1.310996
H           0.000000    0.000000    2.502007

*ACES2(CALC=MBPT[2],BASIS=SPECIAL,PROP=NMR,CHARGE=1
COORD=CARTESIAN,TREAT_PERTURBATION=SEQUENTIAL,MEMORY=24000000)

C:dzp
C:dzp
C:dzp
C:dzp
C:dzp
C:dzp
C:dzp
H:dz
H:dz
H:dz
H:dz
H:dz
H:dz
H:dz
```

This example features a calculation of the NMR chemical shifts at the MBPT(2) level using gauge-including atomic orbitals (GIAOs). NMR shifts are requested by the keyword PROP=NMR. The input of the coordinates in this example is via cartesian coordinates (in Ångströms) and the basis set is specified via the non-standard input which allows the use of different basis sets for different atoms (in this case, dzp for C and dz for H). To reduce disk space requirements, the keyword TREAT_PERTUBATION=SEQUENTIAL is specified which forces the program to treat each magnetic field perturbation separately, thus storing only GIAO integrals of one particular type at one time. The memory requirement in this example is set to 24000000.

D. Common Mistakes and Sources of Confusion

In an ideal world a computer program will trap every input error and tell the user exactly what is wrong and how to fix it. Some might even say that the program should figure out what the user intended and proceed accordingly ! ACES II, traps a number of input errors with explanation. Some errors, however, which will cause the input processor to fail but without a clear explanation. There are other errors that will not become apparent until well into, or even after, execution. The following are some tips which we hope will help users to detect errors. We are, of course, continually trying to improve error detection. At the same time, users should be aware of the need to be careful in their preparation of input decks, and should not expect software to be a substitute for elementary checking. In addition, *small* test calculations are recommended when one is trying a type of calculation for the first time. We welcome suggestions for additions to this list.

- There is no blank line at the end of the ZMAT file.
- The copy of the ZMAT file in the workspace has been changed while the job is running. It is dangerous and in fact should never be necessary to do this if one works in a sensible manner.
- The BASIS=SPECIAL option has been used but the order of the basis sets does not correspond with the order of atoms in the Z-matrix. The code does not check this. For example, one is allowed to put a C basis set on a CL atom, if one so desires. It is quite possible to make this type of error and for the calculation not to abort. It is *usually* clear from the results that something strange has occurred. Note that this "flexibility" is convenient for using ghost atoms, since we often want to put various basis sets on ghost atoms.
- All atomic symbols must be in upper case. For example, "Cl" has to be entered as "CL".
- Problems with *'s in the Z-matrix. They were absent in a geometry optimization, but were needed. They were present in a vibrational frequency calculation but were not needed. *Most likely both of these scenarios are trapped now.*
- Vibrational frequency and geometry optimization keywords are both included in the *ACES2 namelist (*e.g.* both VIBRATION and METHOD are present) and the program is highly confused.
- There is more than one space separating entries in the Z-matrix.
- Lower case characters have been used instead of upper case ones.
- The hierarchy of the OCCUPATION, CHARGE, and MULTIPLICTY keywords and what happens in open-shell SCF calculations can lead to confusion. Several helpful pointers : (*a*) If OCCUPATION has been specified, the CHARGE and MULTIPLICTY

keywords are ignored. It is, however, good practice to make these consistent with OCCUPATION; (*b*) If the REFERENCE keyword is absent from an open-shell calculation or is erroneously set to RHF, unpredictable things happen. ACES II does not have a default for type of open-shell SCF, so basically if the system is an open-shell, a value for REFERENCE needs to be specified; (*c*) the occupation specified in the GUESS file takes precedence over that specified in the ZMAT file. Again, it is sensible to make them the same to avoid confusion; (*d*) There have been cases where one is running an open-shell calculation but the OCCUPATION keyword only specifies an α occupation. What can happen then is that the program thinks that the system has no β electrons, though this was not intended.

- There is a comma at the end of a line of the ACES2 namelist.
- One of the ACES2 namelist lines extends beyond the 80th character.
- There is no title line, and the first line of the Z-matrix has been assumed to be the title.
- There were files from a previous ACES II calculation in the workspace. In general, one should clear the workspace of all previous ACES II files prior to copying in the new files.

V. Some Special Topics and Utilities

A. The GENBAS File

A..1 The format of the GENBAS file

The GENBAS file contains a description of each of the basis sets that are available to the user. Users may easily add additional basis sets to their GENBAS files so a description of the format is given here.

Line #	Fortran format	Description
1	A80	blank line
2	A80	name of the basis set
3	A80	comment line
4	A80	blank line
5	I3	the number of shells in the basis set (NS)
6	NS(I5)	angular momentum for each shell (L)
7	NS(I5)	number of contracted basis functions for each shell (NC)
8	NS(I5)	number of exponents for that shell (NE)
9	A80	blank line
10	NE(F14.7)	exponents for the first shell
11	A80	blank line
12	NC(F10.7,1X)	contraction coefficients for the first shell
13	A80	blank line

It is important that the shells are grouped by angular momentum, with the s shell(s) first, followed by p shell(s), etc. Otherwise, the input file written for the VMOL integral program will be incorrect. Lines 10 through 13 repeat NS number of times. An example of the boron PVTZ basis set entry in the GENBAS file is included below.

```
B:PVTZ
JFS DUNNING CORRELATION CONSISTENT BASIS FROM FTP

  4
    0    1    2    3
    4    3    2    1
   10    5    2    1

  5473.0000000   820.9000000   186.8000000    52.8300000    17.0800000
```

```
     5.9990000     2.2080000     0.5879000     0.2415000     0.0861000

 0.0005550 -0.0001120  0.0000000  0.0000000
 0.0042910 -0.0008680  0.0000000  0.0000000
 0.0219490 -0.0044840  0.0000000  0.0000000
 0.0844410 -0.0176830  0.0000000  0.0000000
 0.2385570 -0.0536390  0.0000000  0.0000000
 0.4350720 -0.1190050  0.0000000  0.0000000
 0.3419550 -0.1658240  0.0000000  0.0000000
 0.0368560  0.1201070  1.0000000  0.0000000
-0.0095450  0.5959810  0.0000000  0.0000000
 0.0023680  0.4110210  0.0000000  1.0000000

    12.0500000     2.6130000     0.7475000     0.2385000     0.0769800

 0.0131180  0.0000000  0.0000000
 0.0798960  0.0000000  0.0000000
 0.2772750  0.0000000  0.0000000
 0.5042700  1.0000000  0.0000000
 0.3536800  0.0000000  1.0000000

     0.6610000     0.1990000

 1.0000000  0.0000000
 0.0000000  1.0000000

     0.4900000

 1.0000000
```

A..2 The contents of the GENBAS file

The following is a listing of the basis sets currently included in the standard GENBAS file. Included are the atoms for which the sets are available and miscellaneous other comments.

STO-3G This is the well known minimal basis set developed by Pople and coworkers in the early 1970s. entries are in the GENBAS file for all atoms from H to Cl. STO-3G basis sets are available in the literature for the third and fourth row main group elements as well as some transition metal elements. The STO-3G basis is now largely obsolete, except for some calculations on large molecules. Its use is not recommended for other than testing and rough preliminary investigations.

3-21G This is a small "split valence" basis set developed by Pople and coworkers. It uses a minimal basis (or single zeta) description for the core orbitals and a double-zeta description for the valence orbitals. Entries are in the GENBAS file for H-Cl. 3-21G sets are available in the literature for heavier elements. This and other sets of this type (such as 4-31G and 6-31G) are often termed "double zeta valence". This is not strictly accurate since the s and p exponents are constrained to be equal, which they are not in a true double zeta set, although the two sets give results of similar quality.

4-31G This is similar to the 3-21G set, but with more primitive gaussian functions. Entries are available for H-Cl.

6-31G This is yet another split valence set, employing still more primitive gaussians. Entries are available for H-Cl.

6-311G This is a split valence set with a triple-zeta description of the valence orbitals and a minimal basis set description of the core orbitals. Entries are available for H-Ne. It has been claimed in the literature that this basis set is not really of triple-zeta valence quality.

6-31G** 6-31G supplemented with d polarization functions (p functions for H and He). It should be used with the SPHERICAL=OFF option (i.e. $6d$ functions) since this is how the set was defined and developed. Entries are available for H-Cl. The 6-31G* basis set excludes p functions from H and He, while retaining d functions on other atoms. Polarization exponents are as follows: H, He (1.1); Li (0.2); Be (0.4); B (0.6); C-Ne (0.8); Na, Mg (0.175); Al (0.325); Si (0.45); P (0.55); S (0.65); Cl (0.75).

6-311G** 6-311G supplemented with polarization functions. This should be used with the SPHERICAL=ON option (i.e. $5d$ functions). Entries are available for H-Ne. Polarization exponents are: H, He (0.75); Li (0.2); Be (0.401); C (0.626); N (0.913); O (1.292); F (1.75); Ne (2.304). This basis set was developed for correlated calculations.

DZ This is the well known Dunning double-zeta contraction of Huzinaga's $9s5p$ primitive gaussian basis set for first row atoms. Entries are available for H, B-F.

DZP This is the DZ set augmented with the polarization functions recommended by Redmon, Purvis, and Bartlett, which were determined from correlated calculations. Entries are available for H, B-F. The polarization exponents are: H (0.7); B (0.386); C (0.654); N (0.902); O (1.211); F (1.580).

D95 This is the same as DZ for H, B-F but also includes $6s4p$ contractions by Dunning and Hay of Huzinaga's $11s7p$ primitive set for Al, Si, P, S, and Cl. The published data for Cl are erroneous, having at least two typographical errors (see W.Craven et al, Chem. Phys. Lett. **116**, 119 (1985)). It is not clear if these are the only errors.

D95* This the D95 set augmented with a set of polarization exponents of uncertain origin. Entries are available for H, B-F, and Al-Cl. The polarization exponents for the first row elements appear to be those recommended by Dunning and Hay, while the source of the second row *d* exponents is uncertain. The exponents are: H (1.0); B (0.7); C (0.75); N (0.8); O (0.85); F (0.9); Al (0.25); Si (0.3247); P (0.37); S (0.532); Cl (0.6).

TZ2P For first row elements this set comprises Dunning's $5s3p$ contraction of Huzinaga's $10s6p$ primitive set augmented with two optimized *d* (*p* for H) functions in a (2,1) contraction of three primitives. Entries are available for H, B-F. The F basis is not optimized. There is also an entry for Cl under this name. This is based on a McLean and Chandler *sp* set.

PVDZ Dunning's polarized valence double-zeta correlation consistent basis set. In terms of contracted functions this set is $3s2p1d$ for second row atoms, with one fewer shell of each angular momentum for H and He, and one extra shell plus an *f* function for Na-Cl. These and the PVTZ and PVQZ sets are hybrids between segmented and generally contracted sets. All of these sets appear to be best used with the SPHERICAL=ON option. Indeed, whether SPHERICAL is ON or OFF has a significant effect on the results. Entries are available for H, He, B-Ne, and Al-Ar. We do not recommend the PVDZ set. For little extra cost one may use the DZP basis set and obtain significantly improved results.

PVTZ Dunning's polarized valence triple-zeta correlation consistent basis ($4s3p2d1f$ for second row atoms). Entries are available for H, He, B-Ne, Al-Ar.

PVQZ Dunning's polarized quadruple-zeta valence correlation consistent basis set ($5s4p3d2f1g$ for second row atoms). Entries are available for H,He, B-Ne, and Al-Ar.

PV5Z Dunning's polarized pentuple-zeta valence correlation consistent basis set ($6s5p4d3f2g1h$ for second-row atoms). Entries are available for H, B-F, Al-Ar.

WMR Generally contracted basis functions developed by Widmark, Malmqvist and Roos for the study of molecular and atomic properties. These are rather large basis sets [$6s4p3d$ for H, $7s4p3d$ for He, $7s6p4d3f$ for second row atoms], and can be reduced to normal size through use of the GENBAS_X keywords. A limited amount of experience with these basis sets suggests that valence double-zeta and valence triple-zeta contractions [$3s2p1d$ and $4s3p2d1f$ for first row atoms, $2s1p$ for H and He] work reasonably well. For a given level of contraction, these basis sets appear to provide superior molecular structures and properties to the correlation consistent sets of Dunning. Entries are available for H-Ne.

PBS These are double-zeta plus diffuse basis sets developed by Sadlej for the calculation of electrical properties. They seem to do a good job of predicting dipole moments and polarizabilities and are also useful in excited state calculations, where the first member of a Rydberg series is usually recovered.

TZP This is a triple-zeta valence plus polarization basis set. Entries are currently available for H,B-Ne,Na, and Mg. For H it comprises Dunning's $3s$ contraction of Huzinaga's $5s$ primitive set augmented with the p exponent of Redmon, Purvis, and Bartlett (0.7). For B-F it comprises Dunning's $5s3p$ contraction of Huzinaga's $10s6p$ primitive set augmented with the polarization exponents of Redmon, Purvis, and Bartlett (see entry DZP above). For Ne the basis set is the Dunning $5s3p$ set augmented with a polarization exponent of 1.9 (an estimate based on the values of Redmon et al). For Na and Mg the basis set is $6s5p1d$, with the sp part coming from McLean and Chandler and d exponents of 0.1 and 0.2 (reasonable estimates).

$5s4p1d$ As TZP but the sp part Dunning's $5s4p$ contraction of Huzinaga's $10s6p$ primitive. Entries are available for B-Ne.

VDZP This is a valence double-zeta plus polarization basis set for all first row atoms except He, taken from Dunning and Hay. It has the advantage that sets for Li and Be exist, in contrast to the DZP set. However, it has not been well tested. The polarization exponents are those of Redmon et al for H,B-F while estimates of 0.2, 0.3, and 1.9 are used for Li, Be, and F.

svp,dzp,tzp,tzplarge,qz2p,... These are the new basis sets from Schäfer, Horn and Ahlrichs which have been optimized for atoms and supplemented by suitable polarization functions. Note that these basis sets are denoted in the GENBAS file by lower case letters They are recommended, in particular, for chemical shift calculations and should in the long run replace the old and not completely optimized Dunning-Huzinaga basis sets (denoted by DZP and TZ2P) in the GENBAS file. Basis sets are, in principle, available for all atoms. If a needed basis set is not included in the GENBAS file, it can be obtained via FTP.

B. The use of effective core potentials

B..1 Specification in the ZMAT file

The use of effective core potentials is specified in the ZMAT file by the keyword ECP=ON. The keyword BASIS must be set to BASIS=SPECIAL. The ecp nicknames are listed below the last basis set (separated by a blank line) using the same format as the non-standard basis set specification, XX:ECPNAM. As for the GENBAS file, the ECPDATA file may be searched for XX, where XX is the atomic symbol, in order to see what ECP's are available for that atom. Atoms included in the ZMAT file without an ecp parameter set are marked by the nickname NONE (see example below). The following ZMAT demonstrates the specifications:

```
CRF6 SINGLE POINT ENERGY CALCULATION USING AN ECP FOR CR
CR
F 1 RMC
F 1 RMC 2 W1
F 1 RMC 3 W1 2 T1
F 1 RMC 4 W1 3 T2
F 1 RMC 5 W1 4 T1
F 1 RMC 6 W1 5 T2

RMC=1.676125
W1=90.
T1=90.
T2=270.

*ACES2(SYMMETRY=ON,BASIS=SPECIAL,ECP=ON,CALCLEVEL=SCF
OCC=10-6-6-2-6-2-2-0,SPHERICAL=ON)

CR:ECP-10 DZP
F:DZP
F:DZP
F:DZP
F:DZP
F:DZP
F:DZP

CR:ECP-10-MDF
F:NONE
F:NONE
F:NONE
F:NONE
F:NONE
```

```
F:NONE
```

B..2 The format of the ECPDATA file

The parameters of the effective core potentials are specified in the file ECPDATA in the same way as the basis set are gathered in GENBAS. As an example, the entry for copper is given below.

```
*
CU:ECP-10-SK
# ECP BY STEVENS/KRAUSS FOR CU - 10 CORE ELECTRONS - LMAX = 2
*
    NCORE = 10    LMAX = 2
d
  -10.00000000    1  511.9951763
  -72.55482820    2   93.2801074
  -12.74502310    2   23.2206669
s-d
    3.00000000    0  173.1180854
   23.83518250    1  185.2419886
  473.89304880    2   73.1517847
  157.63458230    2   14.6884157
p-d
    5.00000000    0  100.7191369
    6.49909360    1  130.8345665
  351.46053950    2   53.8683720
   85.50160360    2   14.0989469
*
CU:ECP-18-SK
# ECP BY STEVENS/KRAUSS FOR CU - 18 CORE ELECTRONS - LMAX = 3
*
    NCORE = 18    LMAX = 3
f
  -18.00000000    1  359.2137111
 -119.92593970    2   67.5347369
  -29.55328670    2   14.7222923
  -10.28924330    2    3.9975558
    -.78363630    2    1.1889410
s-f
    3.00000000    0   19.6202650
   20.15792750    1    5.1604389
```

```
   34.50019060     2     1.2306099
  -18.98120030     2     1.0850105
p-f
    5.00000000     0    31.9385762
   20.60853280     1    14.9202125
   56.00168880     2    15.6835232
   57.21701070     2     4.9311614
    7.71778780     2     1.0622167
d-f
     .25986160     2     5.1159991
    -.46216800     2      .7396784
*
```

The first line contains a single star. The name of the data group starts with the element symbol followed by the ECP nickname. It is useful to give a comment introduced by the #–symbol in the line below in order to indicate the origin of the ECP. The actual ECP data is given in between two lines with a $*$–symbol. The first line specifies the number of core electrons described by the ECP (NCORE) and the maximum angular momentum number of the projector operators (LMAX) in integers i.e. s=0, p=1, d=2 . . . . These are followed by the description of the effective core potential which consists of the angular momentum numbers and by the analytical representation of the operator. The latter includes the coefficient c$_m$, the exponent N$_m$ of r and the exponent α_m of the gaussian:

$$U_l(r) = \sum_m c_m e^{\alpha_m r^2} r^{N_m}.$$

For a detailed description see, for example, L.R. Kahn, P. Baybutt and D.G. Truhlar, *J. Chem. Phys.* **65**, 3826 (1976).

C. Harmonic Vibrational Frequency Calculations with Nonstandard Atomic Masses

ACES II provides a straightforward way to calculate changes in harmonic vibrational frequencies and infrared intensities due to isotopic substitutions. In order to do this, users need to create a file called ISOMASS which contains the desired atomic masses. The file is read free-format; the only restriction is that the atomic masses must appear in the same order as the declaration of the atoms in the ZMAT file, *with dummy centers excluded.* As an example, suppose one wanted to calculate the ^{16}O–^{18}O isotopic shift for the vibrational frequencies of water with the following ZMAT file

```
Water frequency calculation
X
O 1 R
H 2 R1 1 A
H 2 R1 1 A 3 T

R=1.0
R1=0.95
A=130.
T=180.

*ACES2(CALC=SCF,BASIS=DZP,VIB=EXACT)
```

In order to do this, one would use the following ISOMASS file :

```
18.0
1.00797
1.00797
```

where it should be noted that the position of the dummy center has been ignored.

Once an appropriate ISOMASS file has been constructed, the new set of frequencies and intensities can be obtained by *direct* invocation of the ACES II executable **XJODA** (*i.e. not the* **XACES2** *executable*). In addition, it is necessary to have the JOBARC and JAINDX direct access files from the frequency calculation in the same directory. The simplest way to do this sort of calculation is through use of nonstandard file declarations, as described in detail in the Section III C of this manual.

D. Use of Force Constant Matrices in Geometry Optimizations

All of the geometry optimization algorithms incorporated into ACES II are based on the Newton-Raphson method, in which step directions and sizes are related to the first and second derivatives of the molecular potential energy. However, in almost all practical calculations the exact second derivative matrix is not evaluated but rather approximated. As the calculation progresses, well-established numerical methods are used to estimate the elements of the Hessian matrix based on all previous optimization steps. After a large number of steps have been taken, one may safely assume that the totally symmetric Hessian used to form the step is a reasonable approximation to the correct Hessian. However, in the early stages of the optimization there is not a sufficient amount of available information to accurately estimate the Hessian and problems may ensue. By default, ACES II geometry optimizations begin with a very crude estimate of the Hessian in which all force constants for bonded interactions (as specified by the Z-matrix connectivity) are set to 1 hartree/bohr^2, all bending force constants (corresponding to bond angles in the ZMAT file) are set to 0.25 hartree/bohr^2 and all torsional force constants are set to 0.10 hartree/bohr^2. While this initialization and the subsequent numerical updates work satisfactorily for most small molecules, there can be occasional problems. In these cases, one might wish to use an alternative initial force constant matrix, particularly one obtained by ACES II at the same or another level of theory. There are a number of ways in which one might do this. First, the EVAL_HESS keyword can be used. If nonzero, the value associated with this keyword directs ACES II to calculate the *SCF* Hessian matrix prior to the first optimization step and then every N steps thereafter, where N is the value of EVAL_HESS. By setting N to a sufficiently large value (larger than OPT_MAXCYC), then the Hessian will never be recalculated and the optimization will begin with the SCF Hessian.

However, the strategy based on EVAL_HESS is not sufficient for all purposes. For example, one might wish to use a Hessian which is evaluated at the correlated level. This is not possible with EVAL_HESS, since it will direct ACES II to calculate only the SCF Hessian, regardless of the calculation type specified in the ZMAT file. Alternatively, one might adopt the economical strategy of using a Hessian which is evaluated at a low level of theory, such as SCF with the STO-3G basis set. This is the recommended approach for transition state searches and all optimizations for which the default Hessian is inadequate. In any event, it is quite straightforward to use another set of force constants to begin an optimization. First, one simply runs a harmonic frequency calculation at the desired level of theory and saves the FCMINT file. This formatted file contains the full internal coordinate force constant matrix. When the XJODA executable performs a geometry optimization, it checks the active working area for the presence of an FCMINT file. If the file is available, XJODA uses the contents of the file to initialize the Hessian matrix. Hence, one only needs to place the FCMINT file in the same directory as the ZMAT and GENBAS files and the force constants will be read automatically.

While the geometry (and even the point group symmetry) specified by the ZMAT file in the harmonic frequency calculation need not be the same as that used in the first step of the geometry optimization, *the Z-matrix connectivity must be identical.* If one attempts to use an entirely different Z-matrix, then the definitions of internal coordinates are no longer the same and chaos may ensue. While this point may seem to be unimportant, this situation occurs relatively frequently. Suppose you assume that the equilibrium geometry for a transition state is planar and locate a stationary point with METHOD=TS. However, when the harmonic frequencies are calculated, two modes are found to have imaginary frequencies: an a' mode (in-plane) and an a'' mode, with the a' mode corresponding (approximately) to the reaction coordinate of interest. As a result, the true transition state geometry does not contain a plane of symmetry and another search must be performed in a reduced symmetry. To this end, it would certainly be useful to use the FCMINT file obtained in the frequency calculation to start the search, but one must be careful that the ZMAT file used in the reduced symmetry has *exactly* the same connectivity scheme as that used in the search for the planar structure! As a general rule of thumb, you should always save FCMINT files when you do frequency calculations. Keep a library of these files, as they may be of some use in the future.

E. Initial Guessing and SCF Convergence Options.

It is often convenient to be able to use a set of MOs from one calculation as an initial guess for another (with the same basis set). There are some facilities for doing this with the ACES II program system. The first way is to reuse the JOBARC and JAINDX files and the RESET keyword. For example, suppose we wish to run an ROHF calculation but the default ROHF procedure does not converge or converges to the wrong electronic state. We might try to start the ROHF calculation from a converged set of UHF orbitals. We first run a UHF SCF calculation and do not delete any of the files created by ACES II. We then edit the ZMAT file, replacing REF=UHF by REF=ROHF and including the string RESET=ON. Next we run the **xjoda** executable. This resets the option values. We then run the **xvscf** module. This will perform an ROHF SCF calculation, starting with the UHF vectors. This procedure is somewhat limited. In particular, one must keep JOBARC and JAINDX files, and there is no way of doing such things as swapping orbitals to get the right electronic state. Two other procedures are available in ACES II. The first is to use the GUESS file. The second is to use the keyword GUESS=READ_AO_MOS. These methods will now be described.

The use of the GUESS file for initial guesses

The usage of the GUESS file in general terms will be illustrated by considering how we might use a set of UHF orbitals as the initial guess for an ROHF calculation, but without having JOBARC and JAINDX files from the UHF calculation. First, we run a UHF calculation. The SCF writes the UHF orbitals to a small formatted file called NEWMOS. These are expressed in terms of the symmetry adapted basis functions, and are printed by spin and symmetry block (*i.e.* as in the output file). To run an ROHF calculation starting from these UHF orbitals, we first rename or copy NEWMOS to another file. This file must be copied to the work area as OLDMOS when we run the ROHF calculation. We then create a GUESS file, giving the occupation (this overrides the occupation keyword in ZMAT) and instructions to read an initial set of orbitals from OLDMOS (see below for GUESS file options). This file must be copied to the work area as GUESS when we run the ROHF calculation. We then change REF=UHF to REF=ROHF in the ZMAT file. We then are ready to run the ROHF calculation. We copy in GENBAS, ZMAT, OLDMOS, and GUESS and then run the program. Simple scripts for the calculations could be as follows :
First, the UHF job :

```
#
cd /tmp/osu937/jdw
rm *
cp /d/osu937/jdw/craps/tests/h2odzp.zmat       ZMAT
cp /d/osu937/jdw/basis/GENBAS                  GENBAS
xaces2   >   /d/osu937/jdw/craps/tests/h2o.out_uhf
cp NEWMOS    /d/osu937/jdw/craps/tests/h2ouhf.oldmos
```

Then the ROHF job :

```
#
cd /tmp/osu937/jdw
rm *
cp /d/osu937/jdw/craps/tests/h2odzp.zmat      ZMAT
cp /d/osu937/jdw/basis/GENBAS                 GENBAS
cp /d/osu937/jdw/craps/tests/h2odzp.gss       GUESS
cp /d/osu937/jdw/craps/tests/h2ouhf.oldmos    OLDMOS
xaces2   >   /d/osu937/jdw/craps/tests/h2o.out_rohf
cp NEWMOS    /d/osu937/jdw/craps/tests/h2orohf.oldmos
```

Evidently, the OLDMOS file will be much smaller than JOBARC, and it is a formatted file. It is therefore easier to store sets of MOs which may be of use in a future calculation, to move sets of MOs from one computer system to another, and to use MOs from other program systems. Regarding the latter point, one must of course have the appropriate ordering of basis functions and coefficients in terms of symmetry adapted basis functions.

We now consider the format of the GUESS file. The following is an example of the GUESS file for a state of the water cation.

```
H2O. TEST.
  3  1  1  0                  alpha occ
  3  0  1  0                  beta occ
  0  0  0  0                  alpha pairs to be swapped in each irrep
  0  0  0  0
  0  0  0  0
  0  0  0  0
  0  0  0  0                  beta pairs to be swapped in each irrep
  0  0  0  0
  0  0  0  0
  0  0  0  0
  0  0  0  0                  alpha locking within each irrep
  0  0  0  0                  beta  locking within each irrep
  0  0  0  0                  alpha printing of initial guess
  0  0  0  0                  beta printing of initial guess
  0  0                        stopping parameters
  1  0                        reading and writing mos
  1                           nonzero if a uhf wfn is to be got from rhf
  0                           nonzero if GUESS is always to be read
```

The file is a formatted file. The words on the right are not part of the input and are unnecessary, but have been included as a reminder of the options. The input is as follows. NIRREP is the order of the computational point group (4 in the present case).

```
Line 1 : the title, up to 80 characters

Line 2 : alpha occupation, format (NIRREP I3)

Line 3 : beta occupation, format (NIRREP I3) (omitted if
         RHF closed-shell)

Line 4 : pairs of orbitals to be swapped in alpha symmetry
         block 1 (The format is 4I3 regardless of value of NIRREP).
         Two numbers are needed to specify each pair. Therefore
         no more than two interchanges may be made for a given
         symmetry block and spin

Line 5 : as line 4, but the numbers refer to the second symmetry
         block

Line 6 : as line 4, but the numbers refer to the third symmetry
         block


Line 7 : as line 4, but the numbers refer to the fourth symmetry
         block

Lines 8-11 : as Lines 4-7 but for beta spin (omitted if RHF)

Line 12 : (NIRREP I3), specify if any alpha symmetry blocks
          are to be "locked" (i.e. orbital occupation proceeds
          in direction of "minimum change", by monitoring
          C(OLD)T * S * C). Put a zero if no locking and a
          positive integer if you wish a particular block to
          be locked.

Line 13 : as for Line 12, but for beta spin (omitted if
          closed-shell RHF)

Line 14 : (NIRREP I3), determine if alpha initial guess is
          to be printed. Put a 0 if not, put a positive integer
          if you wish a particular symmetry block to be printed.

Line 15 : as previous line, but for beta spin (ommitted if
          closed-shell RHF)
```

```
Line 16 : (2I3) stopping parameters. Set first to a positive
          integer if you wish the SCF to stop after computing
          the initial guess.

Line 17 : (2I3) parameters READMO and WRITMO. If READMO is
          set to a positive integer then initial guess MOS are
          to be read from a file called OLDMOS. If WRITMO is
          set to a positive integer then the final converged
          MOS are to be written to a file called NEWMOS. the
          two files have the same format (and are formatted
          rather than binary). Hence, NEWMOS from one job may
          be used as OLDMOS in a subsequent job. For no reading
          or writing, set both parameters to 0. WRITMO is now
          redundant, NEWMOS is always written.

Line 18 : (I3) a parameter which specifies if a UHF guess is
          to be generated from one or two sets of MOS. This is
          only meaningful if READMO has been set to positive
          integer. this option lets one, for example, start a
          a UHF calculation with an RHF closed-shell set of
          orbitals. set to a positive integer for reading just
          one set of orbitals. set to 0 for reading both sets
          from OLDMOS.

Line 19 : (I3) a parameter which specifies if initial guess
          instructions are to be read from GUESS every time
          an SCF calculation is performed during a job, or
          just the first time. Set to 0 for just the first
          time. otherwise set to positive integer. If it is set
          to 0, GUESS is deleted after it has been read. One would
          usually want to do this in a geometry optimization, for
          example, the second and subsequent points reading the
          MOs on JOBARC from the previous point.
```

It should be noted that one must specify all options in the GUESS file — *i.e.* there are no defaults.

The GUESS=READ_AO_MOS Option.

The main use of this option is in finite-difference vibrational frequency calculations. In these calculations, since the symmetry changes, it is not possible to specify the occupation with the OCCUPATION keyword. Therefore, the SCF program is not always able to converge to the correct electronic state at each geometry, and so sometimes the frequency calculation cannot be completed. The GUESS=READ_AO_MOS option is intended to solve this problem. One begins by performing a single-point SCF calculation at the geometry at which vibrational frequencies are to be calculated. In this calculation one may have the occupation set so as to obtain the correct electronic state. At the end of this calculation, the SCF program creates a formatted file called AOBASMOS. This file must be saved. In the frequency calculation, the OCCUPATION keyword must be removed, the option GUESS=READ_AO_MOS must be set, and the AOBASMOS file must be copied to the workspace and named OLDAOMOS. At each point in frequency calculation, OLDAOMOS is read, the MOs are transformed to the current symmetry and the occupation in the current point group is determined. Since the displacements from the "reference geometry" are small, the initial guess is usually very good. It is also possible to use the final AOBASMOS file from a geometry optimization (or transition state search) as the OLDAOMOS file in a frequency calculation. The following illustrates the general forms of scripts to use this facility :

```
#
# 1st job :
#
# Geometry optimization or single-point, with OCCUPATION, if necessary.
#
cp /camp/swift_1/qtp/rjb/jw/jobs/h2o.zmat_opt ZMAT
cp ~rjbprogs/Basis/GENBAS                     GENBAS
xaces2 > /camp/swift_1/qtp/rjb/jw/jobs/h2o.out.opt
cp AOBASMOS /camp/swift_1/qtp/rjb/jw/jobs/h2o.oldaomos

#
# 2nd job :
#
# Finite-difference vibrational frequency calculation. OCCUPATION
# keyword must be omitted. GUESS=READ_AO_MOS is specified.
#
cp /camp/swift_1/qtp/rjb/jw/jobs/h2o.zmat_vib ZMAT
cp /camp/swift_1/qtp/rjb/jw/jobs/h2o.oldaomos OLDAOMOS
cp ~rjbprogs/Basis/GENBAS                     GENBAS
xaces2 > /camp/swift_1/qtp/rjb/jw/jobs/h2o.out.vib
```

The GUESS=READ_AO_MOS option can be used in other situations, but it may not work well when the geometry changes significantly. The reason for this is that a transformation matrix relating the different geometries must be calculated, and this is only well approximated by a rotation if the geometries are close.

Improving convergence

We turn now to the subject of SCF convergence options. Within ACES II a number of options are available. By default the first few iterations proceed by repeated diagonalization of appropriate Fock matrices. Once either a certain number of iterations (see keyword RPP_LATEST) have been performed or an initial convergence criterion has been met, the DIIS convergence extrapolation procedure of Pulay begins. If convergence difficulties are experienced with the default scheme, one has a number of options. In RHF closed-shell and UHF open-shell calculations, difficult cases will often converge with the use of a dynamical damping algorithm due to E.R. Davidson. This is acheived through the option DAMP_TYP=DAVIDSON. Damping serves to prevent excessively large oscillations in the early iterations. Once the SCF convergence appears to be sufficiently smooth (the damp factor is smaller than DAMP_TOL and the energy difference is sufficiently small), the program reverts to repeated diagonalization and DIIS extrapolation. For ROHF calculations, one can also use the damping algorithm, but in addition the level-shifting technique (M.F. Guest and V.R. Saunders, *Mol. Phys.* **28**, 819 (1974)) is particularly useful. In this scheme one adds a positive number α to all diagonal elements of the singly occupied orbital block of the Fock matrix and a positive number $(\alpha + \beta)$ to the diagonal elements of the virtual orbital block of the MO basis Fock matrix. α and β are set by the LSHF_A1 and LSHF_B1. If one wishes to use a value 0.2 a.u. for the level-shifters, LSHF_A1 and LSHF_B1 should be set to 20. This is a reasonable value for most systems. Larger values of level shifters are sometimes necessary for transition metal systems, especially when the singly occupied orbitals lie below some of the double occupied orbitals. An example is provided by the following $FeCl_4^-$ input deck (excitation energies of this system were recently studied by N. Oliphant and R.J. Bartlett, *J. Am. Chem. Soc.* **116**, 4091 (1994)) :

```
FeCl4 sextet
CL 0.0000 -3.4826 2.2358
FE 0.0000 0.0000 0.0000
CL 0.0000 3.4826 2.2358
CL 3.4826 0.0000 -2.2358
CL -3.4826 0.0000 -2.2358

*ACES2(REF=ROHF,PRINT=1,CALC=SCF,MULT=6,CHARGE=-1
       BASIS=SPECIAL,UNITS=BOHR,COORDINATES=CARTESIAN
       RLE=NOJACOBI,SPHERICAL=ON,ECP=ON
       DAMP_TYP=DAVIDSON,DAMP_TOL=5,LSHF_A1=50
                                    LSHF_B1=50
       OCCUPATION=7-6-6-6/5-5-5-5)

CL:10-MWB3S3P
FE:ECP-10-MDF-F
CL:10-MWB3S3P
```

```
CL:10-MWB3S3P
CL:10-MWB3S3P

CL:ECP-10-MWB
FE:ECP-10-MDF
CL:ECP-10-MWB
CL:ECP-10-MWB
CL:ECP-10-MWB
```

Another tip for ROHF convergence, which we strongly recommend, is to start from orbitals from a closely related closed-shell system.

F. Equation-of-motion coupled-cluster electron attachment calculations.

EOM-CC electron attachment calculations yield energy differences between an N electron reference state and one or more electronic states of the (N+1) electron system obtained by adding an electron. The keywords such as REFERENCE, CHARGE, MULTIPLICITY, and OCCUPATION define the electronic state of the N electron system. If EA_CALC is set to EA_EOMCC, then energies of (N+1) electron states are calculated. The states are specified by the EA_SYM keyword as a string of NIRREP (REFERENCE=RHF) or 2*NIRREP (REFERENCE=UHF or ROHF) integers, where NIRREP is the number of irreducible representations in the computational point group. The string of numbers specifies the numbers of (N+1) electron states of a given symmetry and the spin of the additional electron in each (N+1) electron state. For closed-shell systems only the alpha-roots have to be specified, e.g. EA_SYM=3-2-0-2. For open-shell systems one can either attach an electron of alpha spin or one of beta spin, leading to different states of the (N+1)-electron system. The different spin blocks are separated by a slash ('/'), e.g. EA_SYM=3-2-0-2/0-1-0-4. This keyword does not have to be specified in an EA-EOMCC calculation. If EA_SYM is not specified but EA_CALC=EA_EOMCC, the program tries to find the ground state of the (N+1)-electron system internally.

Basically we can recommend three types of applications of the EA-EOMCC program.

a) The calculation of electron affinities. Only EA_CALC=EA_EOMCC needs to be specified. If it is known what the symmetry of the ground state is for the (N+1)-electron system, specify also EA_SYM.

The following input yields the electron affinity of the sodium atom.

```
NA atom
NA

*ACES2(REFERENCE=UHF,CALC=CCSD,BASIS=DZP
MULTIPLCTY=2,SPHERICAL=ON,EA_CALC=EA_EOMCC)
```

In addition the keyword EA_SYM=0-0-0-0-0-0-0-0/1-0-0-0-0-0-0-0 might have been specified such that only the closed-shell $3s^2$ state of the sodium anion is calculated, and no other possibilities are considered for the symmetry of the anion ground state.

b) The calculation of excitation spectra for systems with an odd number of electrons. Take as a reference a closed-shell configuration of the system with one less electron. Specify EA_SYM to obtain a number of roots of desired symmetry. The excitation spectrum is then calculated.

The following example specifies the input for calculation of the excitation spectrum of MgF. The two core-orbitals are excluded from the correlation treatment (Both CCSD and EA_EOMCC). 5 roots are found in symmetry block 1 ($\sum$ and Δ symmetries), 3 in block 2 (Π symmetry) and one in block 4.

```
MgF Excitation Spectrum
MG
F 1 R

R = 1.752

*ACES2(REFERENCE=RHF,CALC=CCSD,BASIS=TZ2P,CHARGE=1
MULTIPLCTY=1,SPHERICAL=ON,DROPMO=1-2,EA_CALC=EA_EOMCC
EA_SYM=5-3-0-1)
```

c) The calculation of high spin triplet states for systems with a closed-shell ground state. Take as a CC reference the high spin doublet ground state of the positive ion, and add an extra alpha electron by specifying EA_SYM, e.g. EA_SYM=4-3-0-2/0-0-0-0. This yields high spin triplet excited states of the neutral. In addition the closed-shell ground state can be obtained by adding a beta electron to the proper symmetry-block, e.g. EA_SYM=4-3-0-2/1-0-0-0. This has the advantage that the proper excitation energies of the system are tabulated by the program. We note that singlet and low spin triplet excited state energies can also be obtained by adding a beta electron. However such calculations do not yield satisfactory results, due to spin contamination of the resulting EA_EOMCC states.

The following input yields triplet excited states for the beryllium atom. The SCF calculation is on the closed-shell neutral system, while the QRHF option is used to create the positive Be ion.

```
BE Atom Excitation spectrum, QRHF Reference
BE

*ACES2(REFERENCE=RHF,CALC=CCSD,BASIS=SPECIAL
SPHERICAL=ON,QRHF_G=-1,EA_CALC=EA_EOMCC
EA_SYM=8-4-0-4-0-0-0-0/0-0-0-0-0-0-0-0)

BE:WMR
```

WARNING: In all EOMCC calculations it is highly recommended that the reference state transforms according to a one-dimensional representation of the true molecular point group. Otherwhise the likely outcome is inaccurate results, which in addition are very hard to interpret due to a breaking of the symmetry in such a calculation.

G. Calculation of NMR Chemical Shifts

NMR spectroscopy is a very important analytical tool for the identification and characterization of molecules. However, since there is no simple correlation between the measured chemical shifts and structural parameters, the interpretation of experimental NMR spectra is not trivial and can be in many cases quite involved. The ability to calculate NMR chemical shifts *ab initio* is therefore a very important advancement in quantum chemistry. The calculation of chemical shifts can provide in many cases the neccesary information for the correct interpretation of experimental NMR spectra. Therefore, methods for the computation of NMR chemical shifts at SCF and correlated levels (currently limited to MBPT(2)) have been added in the last years to the functionalities of the ACES II program system.

However, before discussing the details of the calculation of NMR chemical shifts, a few general remarks are required. The main problem in all calculations of magnetic properties (i.e., NMR chemical shifts and magnetazibilities) using finite basis sets (as they are usually employed in quantum chemical calculations) is the gauge-invariance problem. This simply means that the results of such a calculation depend on the chosen gauge-origin and are not invariant with respect to gauge transformations as required by exact theory. A trivial solution to the gauge-invariance problem would be the use of very large basis sets in order to minimize the gauge error, but this approach, due to large computational costs, is limited to small molecules. More satisfying solutions are offered by approaches which introduce local gauge-origins to define the vector potential such as the IGLO method of Kutzelnigg and Schindler, the LORG method of Hansen and Bouman and the GIAO-approach of Ditchfield. The latter originates in London's work on molecular diamagnetism in the thirties and was first used by Hameka during the sixties to calculate magnetizabilities and chemical shieldings. ACES II incorporates the GIAO-SCF and GIAO-MBPT(2) method for calculating chemical shifts, since in our opinion, the GIAO approach is the most elegant solution to the gauge-invariance problem and in contrast to the IGLO method, is easily extended to correlated approaches (as for example in the GIAO-MBPT(2) method).

The calculation of NMR chemical shifts are invoked via the keyword PROP=NMR together with the appropriate specification of the quantum chemical method (CALC=SCF gives then GIAO-SCF, CALC=MBPT[2] gives GIAO-MBPT(2)). In principle, no other option is required to run calculations of NMR chemical shifts. However, to ensure the success of GIAO-MBPT(2) calculations and in particular large-scale calculations with the GIAO-MBPT(2) method, the computational requirements of such calculations should be kept in mind. While CPU requirements are of less interest (a GIAO-MBPT(2) calculation is in terms of the CPU usually less expensive than the corresponding MBPT(2) geometry optimization), memory and disk space requirements are of special concern. The memory requirements are for the **xnmr** module approximately $2 * n^2N^2/h^2$ eight byte words with n denoting the number of occupied orbitals, N denoting the number of virtual orbitals, and h specifying the order of the molecular point group. However, the current memory bottleneck is the integral sorting in the module **xintprc** which requires roughly $2 * n^2N^2/h$ eight byte words and which therefore is more demanding. The disk space requirement of a GIAO-MBPT(2) calculation is for most parts determined by the fact that the current version depends on the storage of the GIAO integrals. To summarize the necessary resources, a GIAO-MBPT(2) calculations requires the storage of the AO two-electron integrals (files IIII, IIJJ, IJIJ, and IJKL depending on symmetry and with a total size of approximately $1.5 * N^4_{basis}/(8h)$ eight byte words (note that the CRAY version requires $2 * N^4_{basis}/(8h)$ words), the storage of the MO integrals (file MOINTS, the largest portion is here given by the integrals $\langle ab||ci\rangle$ with a total size nN^3/h eight byte words), the storage of the GIAO integrals (files IIIIX, IIJJX, IJIJX, IJKLX in case of a symmetric perturbation B_x or IIIJX, IJIKX, IJKLX for a non-symmetric perturbation B_x. The files for the perturbations B_y and B_x are named using the same convention with Y or Z instead of X. The total size of these files is for each perturbation approximately given by $1.5 * N^4_{basis}/(4h)$ (CRAY version : $2 * N^4_{basis}/(4h)$)), and the storage of the derivative MO integrals and amplitudes (files DERGAM and DERINT with the largest portion given by the perturbed $\langle ab||ci\rangle$ integrals (size nN^3/h eight byte words)). To keep the disk space requirements at a minimum, it is *strongly recommended* to use the keyword TREAT_PERTURBATION=SEQUENTIAL, as this forces the program to treat each magnetic field component separately and thus requires only the storage of one type of GIAO integrals at one time. TREAT_PERTURBATION=SIMULTANEOUS (which is currently the default) requires the simultaneous storage of all GIAO-integrals and is therefore much more demanding in terms of disk space, though more efficient with respect to CPU timings.

The current limits for GIAO-MBPT(2) calculations depend on the available hardware resources. However, as a rough guide the limits for a IBM RS6000/350 work station with 80 Mbyte memory and 3.5 Gbyte scratch space are given. Within this environment, calculations with about 250 basis functions in D_{2h} symmetry, about 200 basis functions in C_{2v}, C_{2h}, and D_2 symmetry, about 170 basis functions in C_2, C_i, and C_s-symmetry and about 130 basis functions in cases without symmetry are feasible. From these estimates it is seen that the limits strongly depend on the molecular symmetry. Thus, users are urged to use symmetry whenever possible. It should be also noted that the computational requirements depend somewhat on the ratio n/N and that the costs increases with the number of occupied orbitals.

As the final result the corresponding chemical shielding tensors of all nuclei in the molecule are obtained in a GIAO-SCF and/or GIAO-MBPT(2) calculation. The output produced by the module **xjoda** gives the absolute isotropic shielding (one third of the trace of the shielding tensor) as well as the anisotropic shielding which is usually of less interest. In order to compare with experimental results, the absolute shielding σ must be converted to the relative shifts δ. This is easily accomplished via

$$\delta = \sigma_{ref} - \sigma \tag{1}$$

with σ_{ref} as the absolute shielding of the chosen reference compounds. For ^{13}C, tetramethylsilane (TMS) has been chosen as standard and the corresponding σ values are 198.944 (dzp/dz), 193.103 (tzp/dz), 193.419 (tzp/dzp) at GIAO-SCF level and 205.720 (dzp/dz), 198.890 (tzp/dz), and 197.191 (tzp/dzp) at GIAO-MBPT(2) level. The MBPT(2)/6-31G* optimized geometry has been used in all the GIAO calculations for TMS.

With respect to basis sets, the following recommendations can be made. In case of ^{11}B and ^{13}C – nuclei which have been extensively studied – the dzp/dz basis set (dzp for C and dz for H) is in most cases sufficient for relative shifts, though the use of the tzp/dz basis (tzp for C and dz for H) is recommended. Larger basis sets (i.e., tzp, tzp2, or even qz2p) are in most cases not needed for the accurate prediction of chemical shifts. On the other side, ^{15}N, ^{17}O, and ^{19}F NMR chemical shift calculations require larger basis sets of at least triple-zeta plus polarization quality. Though qualitatively good results are obtained in many cases with the tzp basis, even larger basis sets such as tz2p or qz2p are recommended for more reliable calculations. For other nuclei, not very much can be said at the moment and the user is strongly urged to check carefully the basis set dependence to ensure reliable theoretical results. However, limited experience suggests that for second-row elements quite large basis sets are needed for accurate calculations.

Note : NMR chemical shift calculations can currently only be performed with Cartesian basis functions, i.e. SPHERICAL=ON may not be specified.

H. Hartree-Fock Wavefunction Stability Analysis

The Hartree-Fock procedure, at convergence, guarantees the resulting wavefunction is a stationary point in the space of orbital rotations (mixing of occupied and virtual orbitals). Though in the majority of cases this stationary point is also a minimum (all orbital rotations increase the energy), it may not always be so. In some cases, the second derivative of the energy with respect to one or more orbital rotations may be zero or negative, indicating rotations which will leave the energy unchanged or lower it. The ACES II program system has the ability to test RHF and UHF wavefunctions for some of the most common instabilities, controlled by the HFSTABILITY and ROT_EVEC keywords.

Using HFSTABILITY=ON will perform a stability analysis after the two-electron integral transformation and processing. (Use of HFSTABILITY=ON is compatible with continuing on to correlated calculations in the same job.) Stability analysis is accomplished by forming the orbital rotation hessian and diagonalizing it. The eigenvalues of this matrix, and their associated eigenvectors indicate the number and type of instabilities present.

Each negative eigenvalue indicates an instability, and their magnitude indicates the severity. Analysis of the eigenvector corresponding to each instability reveals its nature. The direct product of the symmetry irreps of the orbitals involved in the rotation determines the symmetry of the instability. Only for instabilities whose direct product is the totally symmetric irrep (irrep 1) will the wavefunction maintain the symmetry of the molecular framework. Any other result means the instability leads, at least initially, to a symmetry broken wavefunction. In some cases, symmetry breaking instabilities arise from the presence of lower energy electronic states (different occupations), and the rotation specified by the corresponding eigenvector will correspond to changing the occupation to relieve the instability. For an RHF wavefunction, the UHF orbital rotation hessian is constructed, which allows detection of instabilities in which the wavefunction would prefer to be UHF by comparison of the α and β spin eigenvectors.

Zero eigenvalues will occur for degenerate electronic states and merely indicate the equivalence of occupations within the computational point group. Small numerical inaccuracies frequently result in nominally zero eigenvalues having small non-zero values. The sign of such eigenvalues will determine whether or not they are reported as instabilities. Thus you may not see the number of zero (small) eigenvalues you expect.

Other instabilities, such as the wavefunction becoming complex are not tested since complex wavefunctions are not presently supported in ACES II.

In the program output, stability analysis is headed by the label "@RHFSTAB-I" or "@UHFSTAB-I". The number of instabilities in each irrep is given along with their eigenvalue and classification. For example,

```
@RHFSTAB-I, Performing stability analysis of RHF wavefunction.
Orbital rotation parameters will be evaluated for each symmetry block.
There are   0 instabilities within irrep   1.
There are   1 instabilities within irrep   2.
 Eigenvalue =   -0.1411211526:
```

```
  Instability classification :  RHF ->  UHF with broken symmetry
 There are   1 instabilities within irrep   3.
  Eigenvalue =   -0.1411211526:
  Instability classification :  RHF ->  UHF with broken symmetry
 There are   0 instabilities within irrep   4.
 There are   0 instabilities within irrep   5.
 There are   2 instabilities within irrep   6.
  Eigenvalue =   -0.3586792381:
  Instability classification :  RHF ->  UHF with broken symmetry
  Eigenvalue =   -0.2166464610:
  Instability classification :  RHF ->  RHF with broken symmetry
 There are   2 instabilities within irrep   7.
  Eigenvalue =   -0.3586792381:
  Instability classification :  RHF ->  UHF with broken symmetry
  Eigenvalue =   -0.2166464610:
  Instability classification :  RHF ->  RHF with broken symmetry
 There are   0 instabilities within irrep   8.
```

It is sometimes desirable to obtain solutions corresponding to following instabilities to lower energy stationary points in the orbital rotation space. The keywords HFSTABILITY=FOLLOW and ROT_EVEC are provided to assist with this.

When HFSTABILITY=FOLLOW is set, the stability analysis is performed, as for HFSTABILITY=ON, then the orbital rotation corresponding to the chosen instability is applied to the SCF eigenvectors and the SCF calculation is repeated with these rotated vectors as a starting guess. This is not strictly eigenvector following, nor direct minimization SCF, but in practice, the procedure is quite effective. By default, the lowest eigenvalue of the totally symmetric irrep is followed. Others can be followed by explicitly specifying them with the ROT_EVEC parameter.

Because instabilities in other than the totally symmetric irrep reduce the symmetry of the wavefunction, only those in irrep 1 can be followed. Following other instabilities requires performing the calculation in reduced symmetry. Note that in C_1 symmetry, *all* instabilities will be in the totally symmetric irrep. Likewise, instabilities which take RHF wavefunctions into UHF ones must be followed using a UHF calculation.

Following instabilities often leads to solutions which are lower in energy but lack the symmetry of the molecular framework, are heavily spin contaminated (in the UHF case) or are otherwise non-physical. Instabilities in Hartree-Fock wavefunctions are a very complex problem and must be treated with great care in order to obtain any meaningful information.

Experience has shown that, in general, molecules with instabilities will have more than one and that solutions obtained by following an instability may have further instabilities. It is impossible to predict exactly what will be uncovered by a stability analysis, and the current drivers for ACES II are configured to handle only the simplest cases. Examining a “tree” of instabilities or other specialized procedures will require the user to create an appropriate driver of their own, which is usually specialized to the system under study.

A suprising number of molecules will exhibit instabilities under various conditions. If you encounter one, don't panic. Take a deep breath, go for a walk, get a cup of coffee. Not all instabilities indicate pathological cases or intractable problems.

I. Time-dependent Hartree-Fock Calculations.

In order to provide properties such as frequency dependent polarizabilities, ACES II provides time-depenent Hartree-Fock (TDHF) calculations. The TDHF code can solve the general-order TDHF problem for closed-shell RHF wavefunctions. The TDHF keyword must be set to ON, and additional parameters controlling the TDHF calculation are included in a namelist which is located at the end of the ZMAT file. The variables in the namelist are as follows :
Printing options :

- IOPDA controls density matrix printing (0 means no printing (default) and 1 means print the matrix)
- IOPEV controls MO coefficient printing (0 means no printing (default) and 1 means print the matrix)
- IOPU controls U matrix printing (0 means no printing (default) and 1 means print the matrix)
- IOPFE controls Fock matrix printing (0 means no printing (default) and 1 means print the matrix)
- IOPPR controls property integral printing (0 means no printing (default) and 1 means print the matrix)

For subsequent options, 0 means do not do this type of calculation, otherwise do it. *The default is to do the calculation*, *i.e.* if a parameter is not specified, the program will perform that calculation.
For the polarizability α :

- IDALPH specifies if α is to be calculated

For the first hyperpolarizability β :

- IOR specifies if optical rectification calculation is to be performed
- IEOPE specifies if electro-optical Pockels effects calculation is to be performed
- ISHG specifies if second harmonic generation calculation is to be performed

For the second hyperpolarizability γ :

- IOKE specifies if an optical Kerr effect calculation is to be performed
- IDCOR specifies if a DC electric field induced OR calculation is to be performed
- IIDRI specifies if am intensity dependent refractive index calculation is to be performed

- IDCSHG specifies if DC electric field SHG calculation is to be performed
- ITHG specifies if third harmonic generation calculation is to be performed

The method of solution of the TDHF equations is controlled by the parameter NITER (default value is 20). If NITER is 0 an iterative method of solution is used; if it is 1 a non-iterative method of solution is used; if it is greater than 1 the reduced linear equation method will be used.

When NITER=1 more than one frequency can be solved for. For the other methods of solution, only one frequency can be considered in a single calculation. The number of nonzero frequencies is specified by NFREQ. The NFREQ frequencies are listed one per line following the INPUTP namelist.

Static calculations are also performed along with the dynamic calculations. To obtain only static results, all parameters should be set to 0.

The following is an example of a TDHF calculation on N_2 :

```
N2. TDHF. TEST. Sadlej basis set.
N
N 1 R

R=2.07434

*ACES2(UNITS=BOHR,BASIS=SPECIAL,TDHF=ON)

N:PBS
N:PBS





Hyperpolarizabilities
 $INPUTP IOPU=0,IOPFE=0,IOPEV=0,IOPPR=0,NITER=1,NFREQ=4,IDCSHG=1,IOKE=1,
IDCOR=1,IIDRI=1,ITHG=1,IWRPA=1 $END
 0.072
 0.0886
 0.0934
 0.0995
```

J. Organization of the ACES II program system

The ACES II program system is set up as a library of various modules which exchange information via several files. For running a job, it is not necessary to know the exact function of these modules, since the **XACES2** module usually takes care that the correct modules are called in the appropriate sequence. However, to give the user some familiarity with the program modules currently included in the ACES II program system, a short description of their tasks will be given in the following:

XACES2 determines the order in which the other executables must be invoked and drives the overall calculation.

XJODA reads the geometry of the molecule and the program options specified by the user. Furthermore, it is the driver of the geometry optimization algorithmn implemented in ACES II and performs the update of the geometrical parameters based on analytical gradients and Hessians.

XFINDIF is the driver for a finite difference evaluation of harmonic frequencies and infrared intensities based on analytically evaluated gradients and dipole moments. It is used if VIBRATION=FINDIF_OLD has been specified.

XSYMCOR is the driver for the new finite difference evaluation of harmonic frequencies and infrared intensities based either on single point energy calculations or analytically evaluated gradients and dipole moments. XSYMCOR makes use of symmetry-adapted coordinates and is therefore ideally suited for frequency calculations at correlated levels. It is used if VIBRATION=FINDIF has been specified.

XVMOL evaluates the one- and two-electron integrals over Gaussian basis functions. XVMOL has been written by J. Amlöf and P.R. Taylor and has been interfaced to ACES II. The latest version of XVMOL includes in addition an option for effective core potentials.

XVMOL2JA acts as an interface between XVMOL and the ACES II JOBARC files. Using a knowledge of the internals of XVMOL and information from XJODA, it produces a number of vectors and matrices which relate the "computational" ordering of atoms and basis functions to the order given in the ZMAT file. This data is used by many later ACES II modules during symmetry analysis and other functions.

XVSCF solves the SCF equations for RHF, UHF, and high-spin ROHF wave functions.

XHFDFT calculates the energies for various hybrid HF-DFT methods.

XVTRAN transforms the two-electron integrals from the AO into the MO basis. Both, partial and full transformations are available.

XINTPRC sorts the tranformed two-electron integrals and forms their antisymmetrized combinations, the so-called double-bar integrals.

XVCC solves the CC equations and evaluates the correlation energy for the CCD, QCISD, CCSD, CCSDT-n (n=1-4), CCSDT, QCISD(T), CCSD(T), UCC(4), and several other methods. In the case of finite-order perturbation theory (MBPT(2), MBPT(3), SDQ-MBPT(4), and MBPT(4)) XVCC calculates the corresponding contributions to the correlation energy.

XVCC5T calculates the fifth-order triple excitation energy contributions for methods such as CCSD(TQ).

XVCC5Q calculates the fifth-order quadruple excitation energy contributions for methods such as CCSD(TQ).

XVCCEH calculates EOM-CCSD polarizability and NMR spin-spin coupling constants.

XLAMBDA solves the Λ equations to determine the response of the CC amplitudes to a given perturbation. This module is only called in analytical gradient calculations. For finite-order perturbation theory, several higher-order pieces of the wave function as needed for a gradient calculation are computed by this module.

XDENS calculates the one and two-particle density matrices in the MO basis for MBPT and CC methods.

XANTI sorts the two-particle density matrices prior to the back transformation and de-antisymmetrizes them.

XBCKTRN transforms the two-particle density matrices from the MO basis back to the AO basis.

XVDINT is a heavily modified version of the integral derivative program ABACUS written by T. Helgaker, P. Jørgensen, H. Aa. Jensen, and P.R. Taylor, suitable for CC/MBPT gradient calculations. In addition to integral derivatives with respect to geometrical perturbations it calculates one- and two-electron integrals required for chemical shift calculations within the GIAO scheme.

XCPHF solves the coupled-perturbed HF (CPHF) equations either for geometrical displacements, electric or magnetic field components as perturbation.

XVPROP evaluates one-electron integrals needed for the calculation of various first-order properties such as dipole moment, quadrupole moment, electrical field gradients, or spin densities. It originates from POLYATOM and was interfaced to the VMOL integral program by P.R. Taylor.

XDTRAN transforms the integral derivatives from the AO to the MO basis, calculates the derivatives of the excitation amplitudes, and evaluates various contributions to second derivatives at correlated levels.

XSQUINT calculates various contributions which involve two-electron integrals and CPHF coefficients only to second derivatives at correlated levels.

XVEE calculates excitation energies, transition moments and excited state density matrices for TDA EOM-CC methods.

XVEA calculates electron attachment energies by the EOM-CCSD method.

XNMR calculates the paramagnetic contribution to NMR chemical shifts at correlated levels.

XTDHF performs time-dependent Hartree-Fock calculations.

VI. Bibliography

Of the many methods currently implemented in ACES II some are well established, while others are new and descriptions have not yet been published. It is the purpose of this section to list pertinent literature references which provide more information about the techniques and their implementations and should be cited when results from ACES II calculations are published. Some references to basis sets included in the program are also included.
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