

(30 April 2000)

Section 2 - Input Description

This section of the manual describes the input to GAMESS. The section is written in a reference, rather than tutorial fashion. However, there are frequent reminders that more information can be found on a particular input group, or type of calculation, in the 'Further Information' section of this manual. There are also a number of examples shown in the 'Input Examples' section.

The order of this section is chosen to approximate the order in which most people prepare their input (\$CONTRL, \$BASIS/\$DATA, \$GUESS, and so on). After that comes run type related input, then properties input, input for two different solvation models, integral related input, and finally CI/MCSCF input. The next page contains a list of all possible input groups, in the order in which they can be found in this section.

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<u>name</u>	<u>function</u>	<u>module:routine</u> *
Molecule, basis, wavefunction specification:		
\$CONTRL	chemical control data	INPUTA: START
\$SYSTEM	computer related control data	INPUTA: START
\$BASIS	basis set	INPUTB: BASISS
\$DATA	molecule, basis set	INPUTB: MOLE
\$ZMAT	coded z-matrix	ZMATRX: ZMATIN
\$LIBE	linear bend data	ZMATRX: LIBE
\$SCF	HF-SCF wavefunction control	SCFLIB: SCFIN
\$SCFMI	SCF-MI input control data	SCFMI :MIINP
\$DFT	density functional input	DFT :DFTINP
\$MP2	2nd order Moller-Plesset	MP2: MP2INP
\$GUESS	initial orbital selection	GUESS: GUESMO
\$VEC	orbitals (formatted)	GUESS: READMO
\$MOFRZ	freezes MOs during SCF runs	EFPCOV:MFRZIN

Potential energy surface options:

\$STATPT	geometry search control	STATPT: SETSIG
\$TRUDGE	nongradient optimization	TRUDGE: TRUINP
\$TRURST	restart data for TRUDGE	TRUDGE: TRUDGX
\$FORCE	hessian, normal coordinates	HESS: HESSX
\$CPHF	coupled-Hartree-Fock options	CPHF: CPINP
\$HESS	force constant matrix (formatted)	HESS: FCMIN
\$GRAD	gradient vector (formatted)	HESS: EGIN
\$DIPDR	dipole deriv. matrix (formatted)	HESS: DDMIN
\$VIB	HESSIAN restart data (formatted)	HESS: HSSNUM
\$MASS	isotope selection	VIBANL:RAMS
\$IRC	intirinsic reaction path	RXNCRD:IRCX
\$VSCF	vibrational SCF and MP2	VSCF :VSCFIN
\$VIBSCF	VSCF restart data (formatted)	VSCF :VGRID
\$DRC	dynamic reaction path	DRC: DRCDRV
\$GRADEX	gradient extremal path	GRADEX:GRXSET
\$SURF	potential surface scan	SURF :SRFINP

Interpretation, properties:

\$LOCAL	orbital localization control	LOCAL: LMOINP
\$TWOEI	J,K integrals (formatted)	LOCCD: TWEIIN
\$TRUNCN	localized orbital truncations	EFPCOV:TRNCIN
\$ELMOM	electrostatic moments	PRPLIB: INPELM
\$ELPOT	electrostatic potential	PRPLIB: INPELP
\$ELDENS	electron density	PRPLIB: INPELD
\$ELFLDG	electric field/gradient	PRPLIB: INPELF
\$POINTS	property calculation points	PRPLIB: INPPGS
\$GRID	property calculation mesh	PRPLIB: INPPGS
\$PDC	MEP fitting mesh	PRPLIB: INPPDC
\$MOLGRF	orbital plots	PARLEY:PLTMEM
\$STONE	distributed multipole analysis	PRRPOP: STNRD
\$RAMAN	Raman intensity	RAMAN :RAMANX
\$ALPDR	alpha polar. der. (Formatted)	RAMAN :ADMIN
\$MOROKM	Morokuma energy decomposition	MOROKM:MOROIN
\$FFCALC	finite electric field	FFIELD: FFLDX
\$TDHF	time dependent HF NLO properties	TDHF: TDHFX

Solvation models:

\$EFRAG	effective fragment potentials	EFINP:EFINP
\$FRAGNAME	specific named fragment pot.	EFINP:RDSTFR
\$FRGRPL	inter-fragment repulsion	EFINP:RDDFRL
\$PCM	polarizable continuum model	PCM :PCMINP
\$PCMCAV	PCM cavity generation	PCM :MAKCAV
\$NEWCAV	PCM escaped charge cavity	PCM :DISREP
\$DISBS	PCM dispersion basis set	PCMDIS:ENLBS
\$DISREP	PCM dispersion/repulsion	PCMVCH:MORETS
\$COSGMS	conductor-like screening model	COSMO :COSMIN
\$SCRFF	self consistent reaction field	SCRFF:ZRFINP

Integral and integral modification options:

\$ECP	effective core potentials	ECPLIB:ECPPAR
\$RELWFN	relativistic correction	INPUTB:RWFINP
\$FIELD	external electric field	PRPLIB:INPEF
\$INTGRL	format for 2e- integrals	INPUTA:START
\$TRANS	integral transformation	TRFIN :TRANS

MCSCF and CI wavefunctions, and their properties:

\$CIINP	control of CI process	GAMESS:WFNCI
\$DET	determinantal full CI for MCSCF	ALDECI:DETINP
\$CIDET	determinantal full CI	ALDECI:DETINP
\$DRT	distinct row table for MCSCF	GUGDRT:ORDORB
\$CIDRT	distinct row table for CI	GUGDRT:ORDORB
\$MCSCF	parameters for MCSCF	MCSCF :MCSCF
\$MCQDPT	multireference pert. Theory	MCQDPT:MQREAD
\$CISORT	integral sorting	GUGSRT:GUGSRT
\$GUGEM	Hamiltonian matrix formation	GUGEM :GUGAEM
\$GUGDIA	Hamiltonian eigenvalues/vectors	GUGDGA:GUGADG
\$GUGDM	1e- density matrix	GUGDM :GUGADM
\$GUGDM2	2e- density matrix	GUGDM2:GUG2DM
\$LAGRAN	CI lagrangian matrix	LAGRAN:CILGRN
\$TRFDM2	2e- density backtransformation	TRFDM2:TRF2DM
\$TRANST	transition moments, spin-orbit	TRNSTN:TRNSTX

* this column is more useful to programmers than to users.

\$CONTRL group (optional)

This is a free format group specifying global switches.

SCFTYP together with MPLEVL or CITYP specifies the wavefunction. You may choose from:

- = RHF Restricted Hartree Fock calculation (default)
- = UHF Unrestricted Hartree Fock calculation
- = ROHF Restricted open shell Hartree-Fock. (high spin, see GVB for low spin)
- = GVB Generalized valence bond wavefunction or OCBSE type ROHF. (needs \$SCF input)
- = MCSCF Multiconfigurational SCF wavefunction (this requires \$DET or \$DRT input)
- = NONE indicates a single point computation, rereading a converged SCF function. This option requires that you select CITYP=GUGA or ALDET, RUNTYP=ENERGY, or TRANSITN, and GUESS=MOREAD.

MPLEVL = chooses Moller-Plesset perturbation theory level, after the SCF.
See \$MP2 and \$MCQDPT input groups.

- = 0 skips the MP computation (default)
- = 2 performs a second order energy correction. MP2 is implemented only for RHF, UHF, ROHF, and MCSCF wavefunctions. Gradients are available only for RHF, so for the others you may pick from RUNTYP=ENERGY, TRUDGE, SURFACE, or FFIELD only.

CITYP = chooses CI computation after the SCF, for any SCFTYP except UHF.

- = NONE skips the CI. (default)
- = GUGA runs the Unitary Group CI package, which requires \$CIDRT input. Gradients are available only for RHF, so for other SCFTYPs, you may choose only RUNTYP=ENERGY, TRUDGE, SURFACE, FFIELD, or TRANSITN.
- = ALDET runs the Ames Laboratory determinant full CI package, requiring \$CIDET input. RUNTYP=ENERGY only.

Obviously, at most one of MPLEVL or CITYP may be chosen.

RUNTYP specifies the type of computation, for example at a single geometry point:

- = ENERGY Molecular energy. (default)
- = GRADIENT Molecular energy plus gradient.
- = HESSIAN Molecular energy plus gradient plus second derivatives, including harmonic vibrational analysis. See the \$FORCE input group.

multiple geometry options:

- = OPTIMIZE Optimize the molecular geometry using analytic energy gradients. See \$STATPT.

\$CONTRL

- = TRUDGE Non-gradient total energy minimization. See groups \$TRUDGE and \$TRURST.
- = SADPOINT Locate saddle point (transition state). See the \$STATPT group.
- = IRC Follow intrinsic reaction coordinate. See the \$IRC group.
- = VSCF Compute anharmonic vibrational corrections (see \$VSCF)
- = DRC Follow dynamic reaction coordinate. See the \$DRC group.
- = GRADEXTR Trace gradient extremal. See the \$GRADEX group.
- = SURFACE Scan linear cross sections of the potential energy surface. See \$SURF.

single geometry property options:

- = PROP Properties will be calculated. A \$DATA deck and converged \$VEC group should be input. Optionally, orbital localization can be done. See \$ELPOT, etc.
- = MOROKUMA Performs monomer energy decomposition. See the \$MOROKM group.
- = TRANSITN Compute radiative transition moment or spin-orbit coupling. See \$TRANST group.
- = FFIELD applies finite electric fields, most commonly to extract polarizabilities. See the \$FFCALC group.
- = TDHF analytic computation of time dependent polarizabilities. See the \$TDHF group.
- = MAKEFP creates an effective fragment potential.

Note that RUNTYPs involving the energy gradient, which are GRADIENT, HESSIAN, OPTIMIZE, SADPOINT, IRC, GRADEXTR, and DRC, cannot be used for any CI or MP2 computation, except when SCFTYP=RHF.

-
- EXETYP = RUN Actually do the run. (default)
 - = CHECK Wavefunction and energy will not be evaluated. This lets you speedily check input and memory requirements. See the overview section for details.
 - = DEBUG Massive amounts of output are printed, useful only if you hate trees.
 - = routine Maximum output is generated by the routine named. Check the source for the routines this applies to.
-
- MAXIT = Maximum number of SCF iteration cycles. Pertains only to RHF, UHF, ROHF, or GVB runs. See also MAXIT in \$MCSCF. (default = 30)
-
- ICHARG = Molecular charge. (default=0, neutral)
-
- MULT = Multiplicity of the electronic state
 - = 1 singlet (default)
 - = 2,3,... doublet, triplet, and so on.

ICHARG and MULT are used directly for RHF, UHF, ROHF. For GVB, these are implicit in the \$SCF input, while for MCSCF or CI, these are implicit in \$DRT/\$CIDRT or \$DET/\$CIDET input. You must still give them correctly here.

ECP	=	effective core potential control.
	=	NONE all electron calculation (default).
	=	READ read the potentials in \$ECP group.
	=	SBKJC use Stevens, Basch, Krauss, Jasien, Cundari potentials for all heavy atoms (Li-Rn are available).
	=	HW use Hay, Wadt potentials for all the heavy atoms (Na-Xe are available).
RELWFN	=	NONE (default) See also \$RELWFN input group.
	=	NESC normalised elimination of small component, the method of K. Dyall
	=	RESC relativistic elimination of small component, the method of T. Nakajima and K. Hirao.

* * * the next three control molecular geometry * * *

COORD	=	choice for molecular geometry in \$DATA.
	=	UNIQUE only the symmetry unique atoms will be given, in Cartesian coords (default).
	=	HINT only the symmetry unique atoms will be given, in Hilderbrandt style internals.
	=	CART Cartesian coordinates will be input. Please read the warning just below!!!
	=	ZMT GAUSSIAN style internals will be input.
	=	ZMTMPC MOPAC style internals will be input.
	=	FRAGONLY means no part of the system is treated by ab initio means, hence \$DATA is not given. The system is specified by \$EFRAG.

Note that the CART, ZMT, ZMTMPC choices require input of all atoms in the molecule. These three also orient the molecule, and then determine which atoms are unique. The reorientation is very likely to change the order of the atoms from what you input. When the point group contains a 3-fold or higher rotation axis, the degenerate moments of inertia often cause problems choosing correct symmetry unique axes, in which case you must use COORD=UNIQUE rather than Z-matrices.

Warning: The reorientation into principal axes is done only for atomic coordinates, and is not applied to the axis dependent data in the following groups: \$VEC, \$HESS, \$GRAD, \$DIPDR, \$VIB, nor Cartesian coords of effective fragments in \$EFRAG. COORD=UNIQUE avoids reorientation, and thus is the safest way to read these.

Note that the choices CART, ZMT, ZMTMPC require the use of a \$BASIS group to define the basis set. The first two choices might or might not use \$BASIS, as you wish.

\$CONTRL

UNITS = distance units, any angles must be in degrees.
 = ANGS Angstroms (default)
 = BOHR Bohr atomic units

NZVAR = 0 Use Cartesian coordinates (default).
 = M If COORD=ZMT or ZMTMPC and a \$ZMAT is not given: the internal coordinates will be those defining the molecule in \$DATA. In this case, \$DATA must not contain any dummy atoms. M is usually 3N-6, or 3N-5 for linear.
 = M For other COORD choices, or if \$ZMAT is given: the internal coordinates will be those defined in \$ZMAT. This allows the use of more sophisticated internal coordinate choices. M is ordinarily 3N-6 (3N-5), unless \$ZMAT has linear bends.

NZVAR refers mainly to the coordinates used by OPTIMIZE or SADPOINT runs, but may also print the internal's values for other run types. You can use internals to define the molecule, but Cartesians during optimizations!

LOCAL = controls orbital localization.
 = NONE Skip localization (default).
 = BOYS Do Foster-Boys localization.
 = RUEDNBRG Do Edmiston-Ruedenberg localization.
 = POP Do Pipek-Mezey population localization.
 See the \$LOCAL group. Localization does not work for SCFTYP=GVB or CITYP.

ISPHER = Spherical Harmonics option
 = -1 Use Cartesian basis functions to construct symmetry adapted linear combination (SALC) of basis functions. The SALC space is the linear variation space used. (default)
 = 0 Use spherical harmonic functions to create SALC functions, which are then expressed in terms of Cartesian functions. The contaminants are not dropped, hence this option has EXACTLY the same variational space as ISPHER=-1. The only benefit to obtain from this is a population analysis in terms of pure s,p,d,f,g functions.
 = +1 Same as ISPHER=0, but the function space is truncated to eliminate all contaminant Cartesian functions [3S(D), 3P(F), 4S(G), and 3D(G)] before constructing the SALC functions. The computation corresponds to the use of a spherical harmonic basis.

QMTTOL = linear dependence threshold
 Any functions in the SALC variational space whose eigenvalue of the overlap matrix is below this tolerance is considered to be linearly dependent. Such functions are dropped from the variational space. What is dropped is not individual basis functions, but rather some linear combination(s) of the entire basis set that represent the linear dependent part of the function space. The default is a reasonable value for most purposes, 1.0E-6.

When many diffuse functions are used, it is common to see the program drop some combinations. On occasion, in multi-ring molecules, we have raised QMTTOL to 3.0E-6 to obtain SCF convergence, at the cost of some energy.

* * * interfaces to other programs * * *

- MOLPLT = flag that produces an input deck for a molecule drawing program distributed with GAMESS. (default is .FALSE.)
- PLTORB = flag that produces an input deck for an orbital plotting program distributed with GAMESS. (default is .FALSE.)
- AIMPAC = flag to create an input deck for Bader's atoms in molecules properties code. (default=.FALSE.)
For information about this program, contact
Richard F.W. Bader
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McMaster University
Hamilton, Ontario L8S-4M1 Canada
bader@sscvox.cis.mcmaster.ca
- FRIEND = string to prepare input to other quantum programs, choose from
= HONDO for HONDO 8.2
= MELDF for MELDF
= GAMESSUK for GAMESS (UK Daresbury version)
= GAUSSIAN for Gaussian 9x
= ALL for all of the above

PLTORB, MOLPLT, and AIMPAC decks are written to file PUNCH at the end of the job. Thus all of these correspond to the final geometry encountered during jobs such as OPTIMIZE, SAPPOINT, IRC...

In contrast, selecting FRIEND turns the job into a CHECK run only, no matter how you set EXETYP. Thus the geometry is that encountered in \$DATA. The input is added to the PUNCH file, and may require some (usually minimal) massaging.

PLTORB and MOLPLT are written even for EXETYP=CHECK. AIMPAC requires at least RUNTYP=PROP.

The NBO program of Frank Weinhold's group can be attached to GAMESS. The input to control the natural bond order analysis is read by the add in code, so is not described here. The NBO program is available by anonymous FTP to ftp.osc.edu, in the directory /pub/chemistry/software/SOURCES/FORTRAN/nbo

* * * computation control switches * * *

For the most part, the default is the only sensible value, and unless you are sure of what you are doing, these probably should not be touched.

- NPRINT = Print/punch control flag See also EXETYP for debug info. (options -7 to 5 are primarily debug)

\$CONTRL

	= -7	Extra printing from Boys localization.
	= -6	debug for geometry searches
	= -5	minimal output
	= -4	print 2e-contribution to gradient.
	= -3	print 1e-contribution to gradient.
	= -2	normal printing, no punch file
	= 1	extra printing for basis,symmetry,ZMAT
	= 2	extra printing for MO guess routines
	= 3	print out property and 1e- integrals
	= 4	print out 2e- integrals
	= 5	print out SCF data for each cycle. (Fock and density matrices, current MOs
	= 6	same as 7, but wider 132 columns output.
	= 7	normal printing and punching (default)
	= 8	more printout than 7. The extra output is (AO) Mulliken and overlap population analysis, eigenvalues, Lagrangians,
	= 9	everything in 8 plus Lowdin population analysis, final density matrix.
NOSYM	= 0	the symmetry specified in \$DATA is used as much as possible in integrals, SCF, gradients, etc. (this is the default)
	= 1	the symmetry specified in the \$DATA group is used to build the molecule, then symmetry is not used again. Some GVB or MCSCF runs (those without a totally symmetric charge density) require you request no symmetry.
INTTYP	=	POPLE use fast Pople-Hehre routines for sp integral blocks, and HONDO Rys polynomial code for all other integrals. (default)
	=	HONDO use HONDO/Rys integrals for all integrals. This option produces slightly more accurate integrals but is also slower.
		When diffuse functions are used, the inaccuracy in Pople/Hehre sp integrals shows up as inaccurate LCAO coefficients in virtual orbitals. This means the error in SCF (meaning RHF to MCSCF) energies is expected to be about 5d-8 Hartree, but the error in computations that OCCUPY the virtual orbitals may be much larger. We have seen an energy error of 1d-4 in an MP2 energy when diffuse functions were used. We recommend that all MP2 or CI jobs with diffuse functions select INTTYP=HONDO.
NORMF	= 0	normalize the basis functions (default)
	= 1	no normalization
NORMP	= 0	input contraction coefficients refer to normalized Gaussian primitives. (default)
	= 1	the opposite.
ITOL	=	primitive cutoff factor (default=20)
	= n	products of primitives whose exponential factor is less than 10**(-n) are skipped.

ICUT = n integrals less than $10.0^{**(-n)}$ are not saved on disk.
(default = 9)

* * * restart options * * *

IREST = restart control options (for OPTIMIZE run restarts, see \$STATPT) Note that this option is unreliable!

= -1 reuse dictionary file from previous run, useful with
GEOM=DAF and/or GUESS=MOSAVED. Otherwise, this
option is the same as 0.

= 0 normal run (default)

= 1 2e restart (1-e integrals and MOs saved)

= 2 SCF restart (1-,2-e integrals and MOs saved)

= 3 1e gradient restart

= 4 2e gradient restart

GEOM = select where to obtain molecular geometry

= INPUT from \$DATA input (default for IREST=0)

= DAF read from DICTNRY file (default otherwise)

As noted in the first chapter, binary file restart is not a well tested option!

\$SYSTEM

\$SYSTEM group (optional)

This group provides global control information for your computer's operation. This is system related input, and will not seem particularly chemical to you!

TIMLIM = time limit, in minutes. Set to about 95 percent of the time limit given to the batch job so that GAMESS can stop itself gently. (default=600.0)

MWORDS = the maximum replicated memory which your job can use, on every node. This is given in units of 1,000,000 words (as opposed to 1024*1024 words), where a word is always a 64 bit quantity. Most systems allocate this memory at run time, but some more primitive systems may have an upper limit chosen at compile time. (Default=1) In case finer control over the memory is needed, this value can be given in units of words by using the keyword MEMORY instead of MWORDS.

MEMDDI = the grand total memory needed for the distributed data interface (DDI) storage, given in units of 1,000,000 words. See Chapter 5 of this manual for an extended explanation of running with MEMDDI.

note: the memory required on each node for a run using p processors is therefore MWORDS + MEMDDI/p.

PARALL = a flag to cause the distributed data parallel MP2 program to execute the parallel algorithm even if you are running on only one node. The main purpose of this is to allow you to do EXETYP=CHECK runs to learn what the correct value of MEMDDI needs to be.

KDIAG = diagonalization control switch
 = 0 use a vectorized diagonalization routine if one is available on your machine, else use EVVRSP. (default)
 = 1 use EVVRSP diagonalization. This may be more accurate than KDIAG=0.
 = 2 use GIVEIS diagonalization (not as fast or reliable as EVVRSP)
 = 3 use JACOBI diagonalization (this is the slowest method)

COREFL = a flag to indicate whether or not GAMESS should produce a "core" file for debugging when subroutine ABRT is called to kill a job. This variable pertains only to UNIX operating systems. (default=.FALSE.)

* * * the next three refer to parallel GAMESS * * *

The next three apply only to parallel runs, and as they are more or less obsolete, their use is discouraged.

BALTYP = Parallel load balance scheme LOOP turns off dynamic load balancing (DLB) NXTVAL uses dynamic load balancing (default = LOOP)

XDR = a flag to indicate whether or not messages should be converted into a generic format known as external data representation. If true, messages can exchange between machines of different vendors, at the cost of

performing the data type conversions. (default=.FALSE.) --inactive at present--

On machines which do not use TCGMSG (the IBM SP, the Intel Paragon, the CM-5), the BALTP and XDR variables are ignored. LOOP balancing is used exclusively, and there is no possible transfer of data to another vendor so XDR is irrelevant.

PTIME = a logical flag to print extra timing info during parallel runs. This is not currently implemented.

\$BASIS**\$BASIS group (optional)**

This group allows certain standard basis sets to be easily given. If this group is omitted, the basis set must be given instead in the \$DATA group.

GBASIS	=	Name of the Gaussian basis set.
	=	MINI Huzinaga's 3 gaussian minimal basis set. Available H-Rn.
	=	MIDI Huzinaga's 21 split valence basis set. Available H-Rn.
	=	STO Pople's STO-NG minimal basis set. Available H-Xe, for NGAUSS=2,3,4,5,6.
	=	N21 Pople's N-21G split valence basis set. Available H-Xe, for NGAUSS=3. Available H-Ar, for NGAUSS=6.
	=	N31 Pople's N-31G split valence basis set. Available H-Ne,P-Cl for NGAUSS=4. Available H-He,C-F for NGAUSS=5. Available H-Ar, for NGAUSS=6. For Ga-Kr, N31 selects the BC basis.
	=	N311 Pople's "triple split" N-311G basis set. Available H-Ne, for NGAUSS=6. Selecting N311 implies MC for Na-Ar.
	=	DZV "double zeta valence" basis set. a synonym for DH for H,Li,Be-Ne,Al-Cl. (14s,9p,3d)/[5s,3p,1d] for K-Ca. (14s,11p,5d)/[6s,4p,1d] for Ga-Kr.
	=	DH Dunning/Hay "double zeta" basis set. (3s)/[2s] for H. (9s,4p)/[3s,2p] for Li. (9s,5p)/[3s,2p] for Be-Ne. (11s,7p)/[6s,4p] for Al-Cl.
	=	TZV "triple zeta valence" basis set. (5s)/[3s] for H. (10s,3p)/[4s,3p] for Li. (10s,6p)/[5s,3p] for Be-Ne. a synonym for MC for Na-Ar. (14s,9p)/[8s,4p] for K-Ca. (14s,11p,6d)/[10s,8p,3d] for Sc-Zn.
	=	MC McLean/Chandler "triple split" basis. (12s,9p)/[6s,5p] for Na-Ar. Selecting MC implies 6-311G for H-Ne.

* * * the next two are ECP bases only * * *

GBASIS	=	SBKJC Stevens/Basch/Krauss/Jasien/Cundari valence basis set, for Li-Rn. This choice implies an unscaled -31G basis for H-He.
	=	HW Hay/Wadt valence basis. This is a -21 split, available Na- Xe, except for the transition metals. This implies a 3-21G basis for H-Ne.

* * * semiempirical basis sets * * *

The elements for which these exist can be found in the 'further information' section of this manual. If you pick one of these, all other data in this group is ignored. Semi-empirical runs actually use valence-only STO bases, not GTOs.

- GBASIS = MNDO selects MNDO model hamiltonian
 = AM1 selects AM1 model hamiltonian
 = PM3 selects PM3 model hamiltonian
- NGAUSS = the number of Gaussians (N). This parameter pertains only to GBASIS=STO, N21, N31, or N311.
- NDFUNC = number of heavy atom polarization functions to be used. These are usually d functions, except for MINI/MIDI. The term "heavy" means Na on up when GBASIS=STO, HW, or N21, and from Li on up otherwise. The value may not exceed 3. The variable POLAR selects the actual exponents to be used, see also SPLIT2 and SPLIT3. (default=0)
- NFFUNC = number of heavy atom f type polarization functions to be used on Li-Cl. This may only be input as 0 or 1. (default=0)
- NPFUNC = number of light atom, p type polarization functions to be used on H-He. This may not exceed 3, see also POLAR. (default=0)
- DIFFSP = flag to add diffuse sp (L) shell to heavy atoms. Heavy means Li-F, Na-Cl, Ga-Br, In-I, Tl-At. The default is .FALSE.
- DIFFS = flag to add diffuse s shell to hydrogens. The default is .FALSE.

Warning: if you use diffuse functions, please read QMTTOL and INTTYP in the \$CONTRL group for numerical concerns.

- POLAR = exponent of polarization functions
 = POPLE (default for all other cases)
 = POPN311 (default for GBASIS=N311, MC)
 = DUNNING (default for GBASIS=DH, DZV)
 = HUZINAGA (default for GBASIS=MINI, MIDI)
 = HONDO7 (default for GBASIS=TZV)
- SPLIT2 = an array of splitting factors used when NDFUNC or NPFUNC is 2.
 Default=2.0,0.5
- SPLIT3 = an array of splitting factors used when NDFUNC or NPFUNC is 3.
 Default=4.00,1.00,0.25

The splitting factors are from the Pople school, and are probably too far apart. See for example the Binning and Curtiss paper. For example, the SPLIT2 value will usually cause an INCREASE over the 1d energy at the HF level for hydrocarbons.

The actual exponents used for polarization functions, as well as for diffuse sp

or s shells, are described in the 'Further References' section of this manual. This section also describes the sp part of the basis set chosen by GBASIS fully, with all references cited.

Note that GAMESS always punches a full \$DATA group. Thus, if \$BASIS does not quite cover the basis you want, you can obtain this full \$DATA group from EXETYP=CHECK, and then change polarization exponents, add Rydbergs, etc.

\$DATA group (required)
 \$DATAS group (if NESC chosen, gives small component basis)
 \$DATAL group (if NESC chosen, gives large component basis)

This group describes the global molecular data such as point group symmetry, nuclear coordinates, and possibly the basis set. It consists of a series of free format card images. See \$RELWFN for more information on large and small component basis sets. The input structure of \$DATAS and \$DATAL is identical to the COORD=UNIQUE \$DATA input.

-1- TITLE a single descriptive title card.

-2- GROUP, NAXIS

GROUP is the Schoenflies symbol of the symmetry group, you may choose from C1, CS, CI, CN, S2N, CNH, CNV, DN, DNH, DND, T, TH, TD, O, OH.

NAXIS is the order of the highest rotation axis, and must be given when the name of the group contains an N. For example, "CNV 2" is C_{2v} . "S2n 3" means S_6 .

For linear molecules, choose either CNV or DNH, and enter NAXIS as 4. Enter atoms as DNH with NAXIS=2. If the electronic state of either is degenerate, check the note about the effect of symmetry in the electronic state in the SCF section of REFS.DOC.

In order to use GAMESS effectively, you must be able to recognize the point group name for your molecule. This presupposes a knowledge of group theory at about the level of Cotton's "Group Theory", Chapter 3.

Armed with only the name of the group, GAMESS is able to exploit the molecular symmetry throughout almost all of the program, and thus save a great deal of computer time. GAMESS does not require that you know very much else about group theory, although a deeper knowledge (character tables, irreducible representations, term symbols, and so on) is useful when dealing with the more sophisticated wavefunctions.

Cards -3- and -4- are quite complicated, and are rarely given. A *SINGLE* blank card may replace both cards -3- and -4-, to select the 'master frame', which is defined on the next page. If you choose to enter a blank card, skip to the bottom of the next page.

Note ! If the point group is C_1 (no symmetry), skip over cards -3- and -4- (which means no blank card).

-3- X1, Y1, Z1, X2, Y2, Z2

For C1 group, there is no card -3- or -4-.
 For CI group, give one point, the center of inversion.
 For CS group, any two points in the symmetry plane.
 For axial groups, any two points on the principal axis.

For tetrahedral groups, any two points on a two-fold axis.
 For octahedral groups, any two points on a four-fold axis.

-4- X3, Y3, Z3, DIRECT

third point, and a directional parameter.

For CS group, one point of the symmetry plane, noncollinear with points 1 and 2.

For CI group, there is no card -4-.

For other groups, a generator sigma-v plane (if any) is the (x,z) plane of the local frame (CNV point groups).

A generator sigma-h plane (if any) is the (x,y) plane of the local frame (CNH and dihedral groups).

A generator C2 axis (if any) is the x-axis of the local frame (dihedral groups).

The perpendicular to the principal axis passing through the third point defines a direction called D1. If DIRECT='PARALLEL', the x-axis of the local frame coincides with the direction D1. If DIRECT='NORMAL', the x-axis of the local frame is the common perpendicular to D1 and the principal axis, passing through the intersection point of these two lines. Thus D1 coincides in this case with the negative y axis.

The 'master frame' is just a standard orientation for the molecule. By default, the 'master frame' assumes that

1. z is the principal rotation axis (if any),
2. x is a perpendicular two-fold axis (if any),
3. xz is the sigma-v plane (if any), and
4. xy is the sigma-h plane (if any).

Use the lowest number rule that applies to your molecule.

Some examples of these rules:

Ammonia (C3v): the unique H lies in the XZ plane (R1,R3).

Ethane (D3d): the unique H lies in the YZ plane (R1,R2).

Methane (Td): the H lies in the XYZ direction (R2). Since there is more than one 3-fold, R1 does not apply.

HP=O (Cs): the mirror plane is the XY plane (R4).

In general, it is a poor idea to try to reorient the molecule. Certain sections of the program, such as the orbital symmetry assignment, do not know how to deal with cases where the 'master frame' has been changed.

Linear molecules (C4v or D4h) must lie along the z axis, so do not try to reorient linear molecules.

You can use EXETYP=CHECK to quickly find what atoms are generated, and in what order.

This is typically necessary in order to use the general \$ZMAT coordinates.

Depending on your choice for COORD in \$CONTROL,

if COORD=UNIQUE, follow card sequence U

if COORD=HINT, follow card sequence U

if COORD=CART, follow card sequence C

if COORD=ZMT, follow card sequence G

if COORD=ZMTMPC, follow card sequence M

Card sequence U is the only one which allows you to define a completely general basis

here in \$DATA.

Recall that UNIT in \$CONTRL determines the distance units.

-5U- Atom input. Only the symmetry unique atoms are input, GAMESS will generate the symmetry equivalent atoms according to the point group selected above.

if COORD=UNIQUE NAME, ZNUC, X, Y, Z

NAME = 10 character atomic name, used only for printout. Thus you can enter H or Hydrogen, or whatever.
 ZNUC = nuclear charge. It is the nuclear charge which actually defines the atom's identity.
 X,Y,Z = Cartesian coordinates.

if COORD=HINT

NAME,ZNUC,CONX,R,ALPHA,BETA,SIGN,POINT1,POINT2,POINT3

NAME = 10 character atomic name (used only for print out).

ZNUC = nuclear charge.

CONX = connection type, choose from

'LC'	linear conn.	'CCPA'	central conn.
'PCC'	planar central conn.		with polar atom
'NPCC'	non-planar central conn.	'TCT'	terminal conn.
'PTC'	planar terminal conn.		with torsion

R = connection distance.

ALPHA= first connection angle

BETA = second connection angle

SIGN = connection sign, '+' or '-'

POINT1, POINT2, POINT3 =

connection points, a serial number of a previously input atom, or one of 4 standard points: O,I,J,K (origin and unit points on axes of master frame).
 defaults: POINT1='O', POINT2='I', POINT3='J'

ref- R.L. Hilderbrandt, J.Chem.Phys. 51, 1654 (1969).

You cannot understand HINT input without reading this.

Note that if ZNUC is negative, the internally stored basis for ABS(ZNUC) is placed on this center, but the calculation uses ZNUC=0 after this. This is useful for basis set superposition error (BSSE) calculations.

* * * If you gave \$BASIS, continue entering cards -5U- until all the unique atoms have been specified. When you are done, enter a " \$END " card.

* * * If you did not, enter cards -6U-, -7U-, -8U-.

-6U- GBASIS, NGAUSS, (SCALF(i),i=1,4)

\$DATA

GBASIS has exactly the same meaning as in \$BASIS. You may choose from MINI, MIDI, STO, N21, N31, N311, DZV, DH, BC, TZV, MC, SBKJC, or HW. In addition, you may choose S, P, D, F, G, or L to enter an explicit basis set. Here, L means an s and p shell with a common exponent.

NGAUSS is the number of Gaussians (N) in the Pople style basis, or user input general basis. It has meaning only for GBASIS=STO, N21, N31, or N311, and S,P,D,F,G, or L.

Up to four scale factors may be entered. If omitted, standard values are used. They are not documented as every GBASIS treats these differently. Read the source code if you need to know more. They are seldom given.

* * * If GBASIS is not S,P,D,F,G, or L, either add more shells by repeating card -6U-, or go on to -8U-.

* * * If GBASIS=S,P,D,F,G, or L, enter NGAUSS cards -7U-.

-7U- IG, ZETA, C1, C2

IG = a counter, IG takes values 1, 2, ..., NGAUSS.

ZETA = Gaussian exponent of the IG'th primitive.

C1 = Contraction coefficient for S,P,D,F,G shells, and for the s function of L shells.

C2 = Contraction coefficient for the p in L shells.

* * * For more shells on this atom, go back to card -6U-.

* * * If there are no more shells, go on to card -8U-.

-8U- A blank card ends the basis set for this atom.

Continue entering atoms with -5U- through -8U- until all are given, then terminate the group with a " \$END " card.

- - - this is the end of card sequence U - - -

COORD=CART input:

-5C- Atom input.

Cartesian coordinates for all atoms must be entered. They may be arbitrarily rotated or translated, but must possess the actual point group symmetry. GAMESS will reorient the molecule into the 'master frame', and determine which atoms are the unique ones. Thus, the final order of the atoms may be different from what you enter here.

NAME, ZNUC, X, Y, Z

NAME = 10 character atomic name, used only for printout. Thus you can enter H or

Hydrogen, or whatever.
 ZNUC = nuclear charge. It is the nuclear charge which actually defines the atom's identity.
 X,Y,Z = Cartesian coordinates.

Continue entering atoms with card -5C- until all are given, and then terminate the group with a " \$END " card.

- - - this is the end of card sequence C - - -

COORD=ZMT input: (GAUSSIAN style internals)

- 5 G- ATOM

Only the name of the first atom is required.
 See -8G- for a description of this information.

- 6 G- ATOM i1 BLENGTH

Only a name and a bond distance is required for atom 2.
 See -8G- for a description of this information.

- 7 G- ATOM i1 BLENGTH i2 ALPHA

Only a name, distance, and angle are required for atom 3.
 See -8G- for a description of this information.

- 8 G- ATOM i1 BLENGTH i2 ALPHA i3 BETA i4

ATOM is the chemical symbol of this atom. It can be followed by numbers, if desired, for example Si3. The chemical symbol implies the nuclear charge.
 i1 defines the connectivity of the following bond.
 BLENGTH is the bond length "this atom-atom i1".
 i2 defines the connectivity of the following angle.
 ALPHA is the angle "this atom-atom i1-atom i2".
 i3 defines the connectivity of the following angle.
 BETA is either the dihedral angle "this atom-atom i1- atom i2-atom i3", or perhaps a second bond angle "this atom-atom i1-atom i3".
 i4 defines the nature of BETA, If BETA is a dihedral angle, i4=0 (default). If BETA is a second bond angle, i4=+/-1. (sign specifies one of two possible directions).

- Repeat -8G- for atoms 4, 5, ...
- The use of ghost atoms is possible, by using X or BQ for the chemical symbol. Ghost atoms preclude the option of an automatic generation of \$ZMAT.
- The connectivity i1, i2, i3 may be given as integers, 1, 2, 3, 4, 5,... or as strings

\$DATA

which match one of the ATOMs. In this case, numbers must be added to the ATOM strings to ensure uniqueness!

- In -6G- to -8G-, symbolic strings may be given in place of numeric values for BLENGTH, ALPHA, and BETA. The same string may be repeated, which is handy in enforcing symmetry. If the string is preceded by a minus sign, the numeric value which will be used is the opposite, of course. Any mixture of numeric data and symbols may be given. If any strings were given in -6G- to -8G-, you must provide cards -9G- and -10G-, otherwise you may terminate the group now with a " \$END " card.

-9G- A blank line terminates the Z-matrix section.

-10G- STRING VALUE

STRING is a symbolic string used in the Z-matrix.
VALUE is the numeric value to substitute for that string.

Continue entering -10G- until all STRINGS are defined. Note that any blank card encountered while reading -10G- will be ignored. GAMESS regards all STRINGS as variables (constraints are sometimes applied in \$STATPT). It is not necessary to place constraints to preserve point group symmetry, as GAMESS will never lower the symmetry from that given at -2-. When you have given all STRINGS a VALUE, terminate the group with a " \$END " card.

- - - this is the end of card sequence G - - -

The documentation for sequence G above and sequence M below presumes you are reasonably familiar with the input to GAUSSIAN or MOPAC. It is probably too terse to be understood very well if you are unfamiliar with these. A good tutorial on both styles of Z-matrix input can be found in Tim Clark's book "A Handbook of Computational Chemistry", published by John Wiley & Sons, 1985.

Both Z-matrix input styles must generate a molecule which possesses the symmetry you requested at -2-. If not, your job will be terminated automatically.

COORD=ZMTMPC input: (MOPAC style internals)

- 5 M- ATOM

Only the name of the first atom is required.
See -8M- for a description of this information.

- 6 M- ATOM BLENGTH

Only a name and a bond distance is required for atom 2.
See -8M- for a description of this information.

- 7 M- ATOM BLENGTH j1 ALPHA j2

Only a bond distance from atom 2, and an angle with respect to atom 1 is required for atom 3. If you prefer to hook atom 3 to atom 1, you must give connectivity as in -8M-. See -8M- for a description of this information.

- 8 M- ATOM BLENGTH j1 ALPHA j2 BETA j3 i1 i2 i3

ATOM, BLENGTH, ALPHA, BETA, i1, i2 and i3 are as described at -8G-. However, BLENGTH, ALPHA, and BETA must be given as numerical values only. In addition, BETA is always a dihedral angle. i1, i2, i3 must be integers only.

The j1, j2 and j3 integers, used in MOPAC to signal optimization of parameters, must be supplied but are ignored here. You may give them as 0, for example.

Continue entering atoms 3, 4, 5, ... with -8M- cards until all are given, and then terminate the group by giving a " \$END " card.

--- this is the end of card sequence M ---

This is the end of \$DATA!

If you have any doubt about what molecule and basis set you are defining, or what order the atoms will be generated in, simply execute an EXETYP=CHECK job to find out!

\$ZMAT

\$ZMAT group (required if NZVAR is nonzero in \$CONTRL)

This group lets you define the internal coordinates in which the gradient geometry search is carried out. These need not be the same as the internal coordinates used in \$DATA. The coordinates may be simple Z-matrix types, delocalized coordinates, or natural internal coordinates.

You must input a total of $M=3N-6$ internal coordinates ($M=3N-5$ for linear molecules). NZVAR in \$CONTRL can be less than M IF AND ONLY IF you are using linear bends. It is also possible to input more than M coordinates if they are used to form exactly M linear combinations for new internals. These may be symmetry coordinates or natural internal coordinates. If $NZVAR > M$, you must input IJS and SIJ below to form M new coordinates. See DECOMP in \$FORCE for the only circumstance in which you may enter a larger NZVAR without giving SIJ and IJS.

**** IZMAT defines simple internal coordinates ****

IZMAT is an array of integers defining each coordinate.

The general form for each internal coordinate is code number,I,J,K,L,M,N

IZMAT =1 followed by two atom numbers. (I-J bond length)
 =2 followed by three numbers. (I-J-K bond angle)
 =3 followed by four numbers. (dihedral angle) Torsion angle between planes I-J-K and J-K-L.
 =4 followed by four atom numbers. (atom-plane) Out-of-plane angle from bond I-J to plane J-K-L.
 =5 followed by three numbers. (I-J-K linear bend) Counts as 2 coordinates for the degenerate bend, normally J is the center atom. See \$LIBE.
 =6 followed by five atom numbers. (dihedral angle) Dihedral angle between planes I-J-K and K-L-M.
 =7 followed by six atom numbers. (ghost torsion) Let A be the midpoint between atoms I and J, and B be the midpoint between atoms M and N. This coordinate is the dihedral angle A-K-L-B. The atoms I,J and/or M,N may be the same atom number. (If I=J AND M=N, this is a conventional torsion). Examples: N2H4, or, with one common pair, H2POH.

Example - a nonlinear triatomic, atom 2 in the middle:

```
$ZMAT IZMAT(1)=1,1,2, 2,1,2,3, 1,2,3 $END
```

This sets up two bonds and the angle between them. The blanks between each coordinate definition are not necessary, but improve readability mightily.

**** the next define delocalized coordinates ****

DLC is a flag to request delocalized coordinates. (default is .FALSE.)

AUTO is a flag to generate all redundant coordinates, automatically. The DLC space will consist of all non-redundant combinations of these which can be found. The list of redundant coordinates will consist of bonds, angles, and torsions only. (default is .FALSE.)

NONVDW is an array of atom pairs which are to be joined by a bond, but might be skipped by the routine that automatically includes all distances shorter than

the sum of van der Waals radii. Any angles and torsions associated with the new bond(s) are also automatically included.

The format for IXZMAT, IRZMAT, IFZMAT is that of IZMAT:

IXZMAT is an extra array of simple internal coordinates which you want to have added to the list generated by AUTO. Unlike NONVDW, IXZMAT will add only the coordinate(s) you specify.

IRZMAT is an array of simple internal coordinates which you would like to remove from the AUTO list of redundant coordinates. It is sometimes necessary to remove a torsion if other torsions around a bond are being frozen, to obtain a nonsingular G matrix.

IFZMAT is an array of simple internal coordinates which you would like to freeze. See also FVALUE below. Note that IFZMAT/FVALUE work only with DLC, see the IFREEZ option in \$STATPT to freeze coordinates if you wish to freeze simple or natural coordinates.

FVALUE is an array of values to which the internal coordinates should be constrained. It is not necessary to input \$DATA such that the initial values match these desired final values, but it is helpful if the initial values are not too far away.

**** SIJ,IJS define natural internal coordinates ****

SIJ is a transformation matrix of dimension NZVAR x M, used to transform the NZVAR internal coordinates in IZMAT into M new internal coordinates. SIJ is a sparse matrix, so only the non-zero elements are given, by using the IJS array described below. The columns of SIJ will be normalized by GAMESS. (Default: SIJ = I, unit matrix)

IJS is an array of pairs of indices, giving the row and column index of the entries in SIJ.

example - if the above triatomic is water, using

IJS(1) = 1,1, 3,1, 1,2, 3,2, 2,3

SIJ(1) = 1.0, 1.0, 1.0,-1.0, 1.0

gives the matrix S=

1.0	1.0	0.0
0.0	0.0	1.0
1.0	-1.0	0.0

which defines the symmetric stretch, asymmetric stretch, and bend of water.

references for natural internal coordinates:

P.Pulay, G.Fogarasi, F.Pang, J.E.Boggs J.Am.Chem.Soc. 101, 2550-2560(1979)

G.Fogarasi, X.Zhou, P.W.Taylor, P.Pulay J.Am.Chem.Soc. 114, 8191-8201(1992)

reference for delocalized coordinates:

J.Baker, A. Kessi, B.Delley J.Chem.Phys. 105, 192-212(1996)

\$LIBE group (required if linear bends are used in \$ZMAT)

A degenerate linear bend occurs in two orthogonal planes, which are specified with the help of a point A. The first bend occurs in a plane containing the atoms I,J,K and the user input point A. The second bend is in the plane perpendicular to this, and containing I,J,K. One such point must be given for each pair of bends used.

APTS(1)= x1,y1,z1,x2,y2,z2,... for linear bends 1,2,...

Note that each linear bend serves as two coordinates, so that if you enter 2 linear bends (HCCH, for example), the correct value of NZVAR is M-2, where M=3N-6 or 3N-5, as appropriate.

- n=5, except CI or MP2 gradients n=6)
- SOGTOL = second order gradient tolerance. SOSCF will be initiated when the orbital gradient falls below this threshold. (default=0.25 au)
- ETHRSH = energy error threshold for initiating DIIS. The DIIS error is the largest element of $e=FDS-SDF$. Increasing ETHRSH forces DIIS on sooner. (default = 0.5 Hartree)
- MAXDII = Maximum size of the DIIS linear equations, so that at most MAXDII-1 Fock matrices are used in the interpolation. (default=10)
- DEMCUT = Direct energy minimization will not be done once the density matrix change falls below this threshold. (Default=0.5)
- DMPCUT = Damping factor lower bound cutoff. The damping factor will not be allowed to drop below this value. (default=0.0)
 note : The damping factor need not be zero to achieve valid convergence (see Hsu, Davidson, and Pitzer, J.Chem.Phys., 65, 609 (1976), see especially the section on convergence control), but it should not be astronomical either.

For more info on the convergence methods, see the
'Further Information' section.

- Miscellaneous options.

- UHFNOS = flag controlling generation of the natural orbitals of a UHF function. (default=.FALSE.)
- MVOQ = 0 Skip MVO generation (default)
 = n Form modified virtual orbitals, using a cation with n electrons removed. Implemented for RHF, ROHF, and GVB. If necessary to reach a closed shell cation, the program might remove n+1 electrons. Typically, n will be about 6.
- NPUNCH = SCF punch option
 = 0 do not punch out the final orbitals
 = 1 punch out the occupied orbitals
 = 2 punch out occupied and virtual orbitals
 The default is NPUNCH = 2.

- options for virial scaling

- VTSCAL = A flag to request that the virial theorem be satisfied. An analysis of the total energy as an exact sum of orbital kinetic energies is printed. The default is .FALSE.

This option is implemented for RHF, UHF, and ROHF, for RUNTYP=ENERGY, OPTIMIZE, or SADPOINT. Related input is as follows:

- SCALF = initial exponent scale factor when VTSCAL is in use, useful when restarting. The default is 1.0.
- MAXVT = maximum number of iterations (at a single geometry) to satisfy the energy virial theorem. The default is 20.
- VTCONV = convergence criterion for the VT, which is satisfied when $2\langle T \rangle + \langle V \rangle + R \times dE/dR$ is less than VTCONV. The default is 1.0D-6 Hartree.

For more information on this option, which is most economically employed during a geometry search, see

M.Lehd and F.Jensen, J.Comput.Chem. 12, 1089-1096(1991).

- GVB/ROHF options

The next parameters define the GVB wavefunction. Note that ALPHA and BETA also have meaning for ROHF. See also MULT in the \$CONTRL group. The GVB wavefunction assumes orbitals are in the order core, open, pairs.

- NCO = The number of closed shell orbitals. The default almost certainly should be changed! (default=0).
- NSETO = The number of sets of open shells in the function. Maximum of 10. (default=0)
- NO = An array giving the degeneracy of each open shell set. Give NSETO values. (default=0,0,0,...).
- NPAIR = The number of geminal pairs in the -GVB- function. Maximum of 12. The default corresponds to open shell SCF (default=0).
- CICOEF = An array of ordered pairs of CI coefficients for the -GVB- pairs. For example, a two pair case for water, say, might be CICOEF(1)=0.95,-0.05,0.95,-0.05. If not normalized, as in the default, they will be. This parameter is useful in restarting a GVB run, with the current CI coefficients. (default = 0.90,-0.20,0.90,-0.20,...)
- COUPLE = A switch controlling the input of F, ALPHA, and BETA. The default is to use internally stored values for these variables. Note ALPHA and BETA can be given for -ROHF-, as well as -GVB-. (Default=.FALSE.)
- F = An vector of fractional occupations.
- ALPHA = An array of A coupling coefficients given in lower triangular order.
- BETA = An array of B coupling coefficients given in lower triangular order.

Note : The default for F, ALPHA, and BETA depends on the state chosen. Defaults for the most commonly occurring cases are internally stored.

For more discussion of GVB/ROHF input see the 'further information' section

`$SCFMI` group (optional, relevant if SCFTYP=RHF)

The SCF-MI method is a modification of the Roothaan equations that avoids basis set superposition error (BSSE) in intermolecular interaction calculations, by expanding each monomer's orbitals using only its own basis set. Thus, the resulting orbitals are not orthogonal. The presence of a `$SCFMI` group in the input triggers the use of this option.

The implementation is limited to two monomers, treated at the RHF level. The energy, gradient, and therefore numerical hessian are available. The SCF step may be run in direct SCF mode. The first 4 parameters must be given. All atoms of monomer A must be given in `$DATA` before the atoms of monomer B.

- | | | |
|---------------------|---|--|
| <code>NA</code> | = | number of doubly occupied MOs on fragment A. |
| <code>NB</code> | = | number of doubly occupied MOs on fragment B. |
| <code>MA</code> | = | number of basis functions on fragment A. |
| <code>MB</code> | = | number of basis functions on fragment B. |
|
 | | |
| <code>ITER</code> | = | maximum number of SCF-MI cycles, overriding the usual MAXIT value. (default is 50). |
|
 | | |
| <code>DTOL</code> | = | SCF-MI density convergence criteria. (default is 1.0d-10) |
|
 | | |
| <code>ALPHA</code> | = | possible level shift parameter. (default is 0.0, meaning shifting is not used) |
|
 | | |
| <code>IOPT</code> | = | prints additional debug information. |
| | = | 0 standard outout (default) |
| | = | 1 print for each SCF-MI cycle MOs, overlap between the MOs, CPU times. |
| | = | 2 print some extra informations in secular systems solution. |
|
 | | |
| <code>MSHIFT</code> | = | debugging option that permits to shift all the memory pointer of the SCF-MI section of code of the quantity MSHIFT (default is 0). |

"Modification of Roothan Equations to Exclude BSSE from Molecular Interaction Calculations"
E. Gianinetti, M. Raimondi, E. Tornaghi Int. J. Quantum Chem. 60, 157 (1996)

A. Famulari, E. Gianinetti, M. Raimondi, and M. Sironi Int. J. Quantum Chem. (1997),
submitted.

\$DFT group (relevant if SCFTYP=RHF,UHF,ROHF)

This group permits the use of various empirical one- electron operators instead of the correct many electron Hamiltonian. The implementation is based on the use of the resolution of the identity to simplify integrals so that they may be analytically evaluated, instead of the use of grid quadratures. The grid free DFT computations in their present form have various numerical errors.

DFTTYP	= NONE	means ab initio computation (default) exchange functionals:
	= XALPHA	X-Alpha exchange (alpha=0.7)
	= SLATER	Slater exchange (alpha=2/3)
	= LOCAL	a synonym for SLATER
	= LSDA	a synonym for SLATER
	= BECKE	Becke's 1988 exchange
	= DEPRISTO	Depristo/Kress exchange
	= CAMA	Handy et al's mods to Becke exchange
	= HALF	50-50 mix of Becke and HF exchange correlation functionals:
	= VWN	Vosko/Wilke/Nusair correlation, formula 5
	= PWLOC	Perdew/Wang local correlation
	= LYP	Lee/Yang/Parr correlation exchange/correlation functionals:
	= BVWN	Becke exchange + VWN correlation
	= BLYP	Becke exchange + LYP correlation
	= BPWLOC	Becke exchange + Perdew/Wang correlation
	= B3LYP	hybridized HF/Becke/LYP using VWN formula 5
	= CAMB	CAMA exchange + Cambridge correlation
	= XVWN	Xalpha exchange + VWN formula 5 correlation
	= XPWLOC	Xalpha exchange + Perdew/Wang correlation
	= SVWN	Slater exchange + VWN correlation
	= SPWLOC	Slater exchange + PWLOC correlation
	= WIGNER	Wigner exchange + correlation
	= WS	Wigner scaled exchange + correlation
	= WIGEXP	Wigner exponential exchange + correlation
AUXFUN	= AUX0	uses no auxiliary basis set for resolution of the identity, limiting accuracy.
	= AUX3	uses the 3rd generation of RI basis sets, These are available for the elements H to Ar, but have been carefully considered for H-Ne only. (DEFAULT)
THREE	=	a flag to use a resolution of the identity to turn four center overlap integrals into three center integrals. This can be used only if no auxiliary basis is employed. (default=.FALSE.)

Do not use this input group without reading about the numerical limitations of the grid free code in REFS.DOC

\$MP2

\$MP2 group (relevant to SCFTYP=RHF,UHF,ROHF if MPLEVEL=2)

Controls 2nd order Moller-Plesset perturbation runs, if requested by MPLEVEL in \$CONTRL. See also the DIRSCF keyword in \$SCF to select direct MP2. MP2 is implemented for RHF, high spin ROHF, or UHF wavefunctions. Analytic gradients and the first order correction to the wavefunction (i.e. properties) are available only for RHF. The \$MP2 group is usually not given. See also \$MCQDPT.

- NCORE = n Omits the first n occupied orbitals from the calculation.
The default for n is the number of chemical core orbitals.
- MP2PRP = a flag to turn on property computation for RHF MP2 jobs
with RUNTYP=ENERGY. This is appreciably more
expensive than just evaluating the 2nd order energy
correction alone, so the default is .FALSE. Properties are
always computed during gradient runs, when they are an
almost free byproduct. (default=.FALSE.) This parameter
applies only to the serial MP2 program. To see properties
using the parallel DDI code, use RUNTYP=GRADIENT.
- LMOMP2 = a flag to analyze the closed shell MP2 energy in terms of localized
orbitals. Any type of localized orbital may be used. This option is
implemented only for RHF, and its selection forces use of the METHOD=3
transformation. The default is .FALSE.
- OSPT = selects open shell spin-restricted perturbation.
This parameter applies only when SCFTYP=ROHF. Please see the 'further
information' section for more information about this choice.
= ZAPT picks Z-averaged perturbation theory. (default)
= RMP picks RMP (aka ROHF-MBPT) perturbation theory.
- CUTOFF = transformed integral retention threshold, the default is 1.0d-9.

The last 3 input variables apply only UHF+MP2 or ROHF+MP2 using OSPT=RMP, or to runs on one compute node only.

- NWORD = controls memory usage. The default uses all available memory.
(default=0)
- METHOD = n selects transformation method, 2 being the segmented
transformation, and 3 being a more conventional two phase
bin sort implementation. 3 requires more disk, but less
memory. The default is to attempt method 2 first, and
method 3 second.
- AOINTS = defines AO integral storage during conventional integral
transformations, during parallel runs.
DUP stores duplicated AO lists on each node, and is the default
for parallel computers with slow interprocessor
communication, e.g. ethernet.

DIST distributes the AO integral file across all nodes, and is the default for parallel computers with high speed communications.

\$GUESS

\$GUESS group (optional, relevant for all SCFTYP's)

This group controls the selection of initial molecular orbitals.

- GUESS = Selects type of initial orbital guess.
- = HUCKEL Carry out an extended Huckel calculation using a Huzinaga MINI basis set, and project this onto the current basis. This is implemented for atoms up to Rn, and will work for any all electron or ECP basis set. (default for most runs)
 - = HCORE Diagonalize the one electron Hamiltonian to obtain the initial guess orbitals. This method is applicable to any basis set, but does not work as well as the HUCKEL guess.
 - = MOREAD Read in formatted vectors punched by an earlier run. This requires a \$VEC group, and you MUST pay attention to NORB below.
 - = MOSAVED (default for restarts) The initial orbitals are read from the DICTNRY file of the earlier run.
 - = SKIP Bypass initial orbital selection. The initial orbitals and density matrix are assumed to be in the DICTNRY file.

All GUESS types except 'SKIP' permit reordering of the orbitals, carry out an orthonormalization of the orbitals, and generate the correct initial density matrix. The initial density matrix cannot be generated for -CI- and -MCSCF-, so property restarts for these wavefunctions will require 'SKIP' which is an otherwise seldom used option. Note that correct computation of a -GVB- density matrix requires CICOEF in \$SCF. Another possible use for 'SKIP' is to speed up a EXETYP=CHECK job, or a RUNTYP=HESSIAN job where the hessian is supplied.

- PRTMO = a flag to control printing of the initial guess. (default=.FALSE.)
- MIX = rotate the alpha and beta HOMO and LUMO orbitals so as to generate inequivalent alpha and beta orbital spaces. This pertains to UHF singlets only. This may require use of NOSYM=1 in \$CONTRL depending on your situation. (default=.FALSE.)
- NORB = The number of orbitals to be read in the \$VEC group. This applies only to GUESS=MOREAD.

For -RHF-, -UHF-, -ROHF-, and -GVB-, NORB defaults to the number of occupied orbitals. NORB must be given for -CI- and -MCSCF-. For -UHF-, if NORB is not given, only the occupied alpha and beta orbitals should be given, back to back. Otherwise, both alpha and beta orbitals must consist of NORB vectors. NORB may be larger than the number of occupied MOs, if you wish to read in the virtual orbitals. If NORB is less than the number of atomic orbitals, the remaining orbitals are generated as the orthogonal complement to those read.

- NORDER = Orbital reordering switch.
- = 0 No reordering (default)
 - = 1 Reorder according to IORDER and JORDER.
- IORDER = Reordering instructions.
Input to this array gives the new molecular orbital order. For example,

IORDER(3)=4,3 will interchange orbitals 3 and 4, while leaving the other MOs in the original order. This parameter applies to all orbitals (alpha and beta) except for -UHF-, where it only affects the alpha MOs. (default is IORDER(i)=i)

- JORDER = Reordering instructions.
Same as IORDER, but for the beta MOs of -UHF-.
- INSORB = the first INSORB orbitals specified in the \$VEC group will be inserted into the Huckel guess, making the guess a hybrid of HUCKEL/MOREAD. This keyword is meaningful only when GUESS=HUCKEL, and it is useful mainly for QM/MM runs where some orbitals (buffer) are frozen and need to be transferred to the initial guess vector set, see \$MOFRZ. (default=0)
- * * * the next are 3 ways to clean up orbitals * * *
- PURIFY flag to symmetrize starting orbitals. This is the most soundly based of the possible procedures. (default=.FALSE.)
- TOLZ = level below which MO coefficients will be set to zero. (default=1.0E-7)
- TOLE = level at which MO coefficients will be equated. This is a relative level, coefficients are set equal if one agrees in magnitude to TOLE times the other. (default=5.0E-5)
- SYMDEN = project the totally symmetric from the density. Maybe useful if the HUCKEL or HCORE give orbitals of inexact symmetry. Since the density matrix is not idempotent, this can generate a non-variational energy on the first iteration. For the same reason, this should never be used with orbitals of MOREAD quality. (default=.FALSE.)

\$VEC, \$MOFRZ

\$VEC group (optional, relevant for all SCFTYP's)
(required if GUESS=MOREAD)

This group consists of formatted vectors, as written onto file PUNCH in a previous run. It is considered good form to retain the titling comment cards punched before the \$VEC card, as a reminder to yourself of the origin of the orbitals.

For Morokuma decompositions, the names of this group are \$VEC1, \$VEC2, ... for each monomer, computed in the identical orientation as the supermolecule. For transition moment or spin-orbit coupling runs, orbitals for states one and possibly two are \$VEC1 and \$VEC2.

\$MOFRZ group (optional, relevant for RHF, ROHF, GVB)

This group controls freezing the molecular orbitals of your choice during the SCF procedure. If you choose this option, select DIIS in \$SCF since SOSCF will not converge as well. GUESS=MOREAD is required in \$GUESS.

FRZ = flag which triggers MO freezing. (default=.FALSE.)

IFRZ = an array of MOs in the input \$VEC set which are to be frozen. There is no default for this.

\$STATPT group (optional, for RUNTYP=OPTIMIZE or SADPOINT)

This group controls the search for stationary points. Note that NZVAR in \$CONTRL determines if the geometry search is conducted in Cartesian or internal coordinates.

METHOD = optimization algorithm selection. Pick from

NR	Straight Newton-Raphson iterate. This will attempt to locate the nearest stationary point, which may be of any order. There is no steplength control. RUNTYP can be either OPTIMIZE or SADPOINT
RFO	Rational Function Optimization. This is one of the augmented Hessian techniques where the shift parameter(s) is(are) chosen by a rational function approximation to the PES. For SADPOINT searches it involves two shift parameters. If the calculated stepsize is larger than DXMAX the step is simply scaled down to size.
QA	Quadratic Approximation. This is another version of an augmented Hessian technique where the shift parameter is chosen such that the steplength is equal to DXMAX. It is completely equivalent to the TRIM method. (default)
SCHLEGEL	The quasi-NR optimizer by Schlegel.
CONOPT	CONstrained OPTimization. An algorithm which can be used for locating TSs. The starting geometry MUST be a minimum! The algorithm tries to push the geometry uphill along a chosen Hessian mode (IFOLLOW) by a series of optimizations on hyperspheres of increasingly larger radii. Note that there currently are no restart capabilities for this method, not even manually.

OPTTOL = gradient convergence tolerance, in Hartree/Bohr. Convergence of a geometry search requires the largest component of the gradient to be less than OPTTOL, and the root mean square gradient less than 1/3 of OPTTOL. (default=0.0001)

NSTEP = maximum number of steps to take. Restart data is punched if NSTEP is exceeded. (default=20)

- the next four control the step size

DXMAX = initial trust radius of the step, in Bohr.
 For METHOD=RFO, QA, or SCHLEGEL, steps will be scaled down to this value, if necessary. (default=0.3 for OPTIMIZE and 0.2 for SADPOINT)
 For METHOD=NR, DXMAX is inoperative.
 For METHOD=CONOPT, DXMAX is the step along the previous two points to increment the hypersphere radius between constrained optimizations. (default=0.1)

\$STATPT

- the next three apply only to METHOD=RFO or QA:
 - TRUPD = a flag to allow the trust radius to change as the geometry search proceeds. (default=.TRUE.)
 - TRMAX = maximum permissible value of the trust radius. (default=0.5 for OPTIMIZE and 0.3 for SADPOINT)
 - TRMIN = minimum permissible value of the trust radius. (default=0.05)
- the next three control mode following
 - IFOLLOW = Mode selection switch, for RUNTYP=SADPOINT.
For METHOD=RFO or QA, the mode along which the energy is maximized, other modes are minimized. Usually referred to as "eigenvector following". For METHOD=SCHLEGEL, the mode whose eigenvalue is (or will be made) negative. All other curvatures will be made positive. For METHOD=CONOPT, the mode along which the geometry is initially perturbed from the minima. (default is 1)
In Cartesian coordinates, this variable doesn't count the six translation and rotation degrees. Note that the "modes" aren't from mass-weighting.
 - STPT = flag to indicate whether the initial geometry is considered a stationary point. If .true. the initial geometry will be perturbed by a step along the IFOLLOW normal mode with stepsize STSTEP. (default=.false.) The positive direction is taken as the one where the largest component of the Hessian mode is positive. If there are more than one largest component (symmetry), the first is taken as positive.
Note that STPT=.TRUE. has little meaning with HESS=GUESS as there will be many degenerate eigenvalues.
 - STSTEP = Stepsize for jumping off a stationary point. Using values of 0.05 or more may work better. (default=0.01)
 - IFREEZ = array of coordinates to freeze. These may be internal or Cartesian coordinates. For example, IFREEZ(1)=1,3 freezes the two bond lengths in the \$ZMAT example, while optimizing the angle.
- The next two control the hessian matrix quality
 - HESS = selects the initial hessian matrix.
 - = GUESS chooses a positive definite diagonal hessian. (default for RUNTYP=OPTIMIZE)
 - = READ causes the hessian to be read from a \$HESS group. (default for RUNTYP=SADPOINT)
 - = RDAB reads only the ab initio part of the hessian, and approximates the effective fragment blocks.
 - = RDALL reads the full hessian, then converts any fragment blocks to 6x6 T+R shape. (this option is seldom used).
 - = CALC causes the hessian to be computed, see the \$FORCE group.

IHREP = the number of steps before the hessian is recomputed. If given as 0, the hessian will be computed only at the initial geometry if you choose HESS=CALC, and never again. If nonzero, the hessian is recalculated every IHREP steps, with the update formula used on other steps. (default=0)

- the next two control the amount of output

Let 0 mean the initial geometry, L mean the last geometry, and all mean every geometry. Let INTR mean the internuclear distance matrix. Let HESS mean the approximation to the hessian. Note that a directly calculated hessian matrix will always be punched, NPUN refers only to the updated Hessians used by the quasi-Newton step.

NPRT = 1 Print INTR at all, orbitals at all
 0 Print INTR at all, orbitals at O+L (default)
 -1 Print INTR at all, orbitals never
 -2 Print INTR at O+L, orbitals never

NPUN = 3 Punch all orbitals and HESS at all
 2 Punch all orbitals at all
 1 same as 0, plus punch HESS at all
 0 Punch all orbitals at O+L, otherwise only occupied orbitals (default)
 -1 Punch occ orbitals at O+L only
 -2 Never punch orbitals

HSEND = a flag to control automatic hessian evaluation at the end of a successful geometry search. (default=.FALSE.)

---- the following parameters are quite specialized ----

PURIFY = a flag to help eliminate the rotational and translational degrees of freedom from the initial hessian (and possibly initial gradient). This is much like the variable of the same name in \$FORCE, and will be relevant only if internal coordinates are in use. (default=.FALSE.)

PROJECT = a flag to eliminate translation and rotational degrees of freedom from Cartesian optimizations. The default is .TRUE. since this normally will reduce the number of steps, except that this variable is set false when POSITION=FIXED is used during EFP runs.

ITBMAT = number of micro-iterations used to compute the step in Cartesians which corresponds to the desired step in internals. The default is 5.

UPHESS = SKIP do not update Hessian (not recommended)
 BFGS default for OPTIMIZE using RFO or QA
 POWELL default for OPTIMIZE using NR or CONOPT
 POWELL default for SADPOINT
 MSP mixed Murtagh-Sargent/Powell update

NPAR = number of parameters to be optimized.

IEX = defines the parameters to be optimized.

If OPTMIZ=BASIS, IEX declares the serial number of the Gaussian primitives for which the exponents will be optimized.

If OPTMIZ=GEOMETRY, IEX define the pointers to the HINT internal coordinates which will be optimized. (Note that not all internal coordinates have to be optimized.) The pointers to the internal coordinates are defined as: (the number of atom on the input list)*10 + (the number of internal coordinate for that atom). For each atom, the HINT internal coordinates are numbered as 1, 2, and 3 for BOND, ALPHA, and BETA, respectively.

P = Defines the initial values of the parameters to be optimized. You can use this to reset values given in \$DATA. If omitted, the \$DATA values are used. If given here, geometric data must be in Angstroms and degrees.

A complete example is a TCSCF multireference 6-31G geometry optimization for methylene,

```

$CONTRL SCFTYP=GVB CITYP=GUGA RUNTYP=TRUDGE
        COORD=HINT $END
$BASIS  GBASIS=N31 NGAUSS=6 $END
$DATA
Methylene TCSCF+CI SD geometry optimization
Cnv 2

C   6.      LC  0.00  0.0  0.00  -  0  K
H   1.      PCC  1.00  53.  0.00  +  0  K  I
$END
$SCF     NCO=3 NPAIR=1 $END
$TRUDGE OPTMIZ=GEOMETRY  NPAR=2
        IEX(1)=21, 22  P(1)=1.08 $END
$CIDRT  GROUP=C2V SOCI=. TRUE. NFZC=1 NDOC=3 NVAL=1
        NEXT=- 1 $END

```

using GVB-PP(1), or TCSCF orbitals in the CI. The starting bond length is reset to 1.09, while the initial angle will be 106 (twice 53). Result after 17 steps is R=1.1283056, half-angle=51.83377, with a CI energy of -38.9407538472

Note that you may optimize the geometry for an excited CI state, just specify

```
$GUGDIA NSTATE=5 $END
```

```
$GUGDM IROOT=3 $END
```

to find the equilibrium geometry of the third state (of five total states) of the symmetry implied by your \$CIDRT.

\$TRURST, \$FORCE**\$TRURST** group (optional, relevant for RUNTYP=TRUDGE)

This group specifies restart parameters for TRUDGE runs and accuracy thresholds.

KSTART indicates the conjugate gradient direction in which the optimization will proceed. (default = -1)
 -1 indicates that this is a non-restart run.
 0 corresponds to a restart run.

FNOISE accuracy of function values. Variation smaller than FNOISE are not considered to be significant (Def. 0.0005)

TOLF accuracy required of the function (Def. 0.001)

TOLR accuracy required of conjugate directions (Def. 0.05)

For geometry optimization, the values which give better results (closer to the ones obtained with gradient methods) are: TOLF=0.0001, TOLR=0.001, FNOISE=0.00001

\$FORCE group

(optional, relevant for RUNTYP=HESSIAN,OPTIMIZE,SADPOINT)

This group controls the computation of the hessian matrix (the energy second derivative tensor, also known as the force constant matrix), and an optional harmonic vibrational analysis. This can be a very time consuming calculation. However, given the force constant matrix, the vibrational analysis for an isotopically substituted molecule is very cheap. Related input is HESS= in \$STATPT, and the \$MASS, \$HESS, \$GRAD, \$DIPDR, \$VIB groups.

METHOD = chooses the computational method.
 = ANALYTIC is implemented only for SCFTYPs RHF, ROHF, and GVB (when NPAIR is 0 or 1). This is the default for these cases.
 = NUMERIC is the default for all other cases: UHF, MCSCF, and all MP2 or CI runs.

RDHESS = a flag to read the hessian from a \$HESS group, rather than computing it. This variable pertains only to RUNTYP=HESSIAN. See also HESS= in the \$STATPT group. (default is .FALSE.)

PURIFY = controls cleanup
 Given a \$ZMAT, the hessian and dipole derivative tensor can be "purified" by transforming from Cartesians to internals and back to Cartesians. This effectively zeros the frequencies of the translation and rotation "modes", along with their IR intensities. The purified quantities are punched out. Purification does change the Hessian slightly, frequencies at a stationary point can change by a wave number or so. The change is bigger at non-stationary points. (default=.FALSE. if \$ZMAT is given)

PRTIFC = prints the internal coordinate force constants. You MUST have defined a \$ZMAT group to use this. (Default=.FALSE.)

--- the next four apply only to METHOD=NUMERIC ---

NVIB = Number of displacements in each Cartesian direction for force field computation.

= 1 Move one VIBSIZ unit in each positive Cartesian direction. This requires $3N+1$ evaluations of the wavefunction, energy, and gradient, where N is the number of SYMMETRY UNIQUE atoms given in \$DATA. (default)

= 2 Move one VIBSIZ unit in the positive direction and one VIBSIZ unit in the negative direction. This requires $6N+1$ evaluations of the wavefunction and gradient, and gives a small improvement in accuracy. In particular, the frequencies will change from NVIB=1 results by no more than 10-100 wavenumbers, and usually much less. However, the normal modes will be more nearly symmetry adapted, and the residual rotational and translational "frequencies" will be much closer to zero.

VIBSIZ = Displacement size (in Bohrs). Default=0.01

Let O mean the VibO geometry, and D mean all the displaced geometries

NPRT = 1 Print orbitals at O and D
= 0 Print orbitals at O only (default)

NPUN = 2 Punch all orbitals at O and D
= 1 Punch all orbitals at O and occupied orbs at D
= 0 Punch all orbitals at O only (default)

----- the rest control normal coordinate analysis -----

VIBANL = flag to activate vibrational analysis.
(the default is .TRUE. for RUNTYP=HESSIAN, and otherwise is .FALSE.)

SCLFAC = scale factor for vibrational frequencies, used in calculating the zero point vibrational energy. Some workers correct for the usual overestimate in SCF frequencies by a factor 0.89. ZPE or other methods might employ other factors, see A.P.Scott, L.Radom J.Phys.Chem. 100, 16502-16513 (1996). The output always prints unscaled frequencies, so this value is used only during the thermochemical analysis.(Default is 1.0)

TEMP = an array of up to ten temperatures at which the thermochemistry should be printed out. The default is a single temperature, 298.15 K. To use absolute zero, input 0.001 degrees.

FREQ = an array of vibrational frequencies. If the frequencies are given here, the hessian matrix is not computed or read. You enter any imaginary frequencies as negative numbers, omit the zero frequencies corresponding to translation and rotation, and enter all true vibrational frequencies. Thermodynamic properties will be printed, nothing else is done by the run.

\$FORCE

- PRTSCN = flag to print contribution of each vibrational mode to the entropy.
(Default is .FALSE.)
- DECOMP = activates internal coordinate analysis. Vibrational frequencies will be decomposed into "intrinsic frequencies", by the method of J.A.Boatz and M.S.Gordon, J.Phys.Chem., 93, 1819-1826(1989). If set .TRUE., the \$ZMAT group may define more than 3N-6 (3N-5) coordinates.
(default=.FALSE.)
- PROJCT = controls the projection of the hessian matrix.
The projection technique is described by W.H.Miller, N.C.Handy, J.E.Adams in J. Chem. Phys. 1980 , 72, 99-112. At stationary points, the projection simply eliminates rotational and translational contaminants. At points with non-zero gradients, the projection also ensures that one of the vibrational modes will point along the gradient, so that there are a total of 7 zero frequencies. The other 3N-7 modes are constrained to be orthogonal to the gradient. Because the projection has such a large effect on the hessian, the hessian punched is the one BEFORE projection. For the same reason, the default is .FALSE. to skip the projection, which is mainly of interest in dynamical calculations.
-
-

There is a set of programs for the calculation of kinetic or equilibrium isotope effects from the group of Piotr Paneth at the University of Lodz. This ISOEFF package will accept data computed by GAMESS, and can be downloaded at <http://ck-sg.p.lodz.pl/isoeff/isoeff.html>

\$CPHF group (relevant for analytic RUNTYP=HESSIAN)

This group controls the solution of the response equations, also known as coupled Hartree-Fock.

POLAR = a flag to request computation of the static polarizability, alpha. Because this property needs 3 additional response vectors, beyond those needed for the hessian, the default is to skip the property. (default = .FALSE.)

NWORD = controls memory usage for this step. The default uses all available memory. (default=0)

\$HESS group (relevant for RUNTYP=HESSIAN if RDHESS=.TRUE.)
(relevant for RUNTYP=IRC if FREQ,CMODE not given)
(relevant for RUNTYP=OPTIMIZE,SADPOINT if HESS=READ)

Formatted force constant matrix (FCM), i.e. hessian matrix. This data is punched out by a RUNTYP=HESSIAN job, in the correct format for subsequent runs. The first card in the group must be a title card.

A \$HESS group is always punched in Cartesians. It will be transformed into internal coordinate space if a geometry search uses internals. It will be mass weighted (according to \$MASS) for IRC and frequency runs.

The initial FCM is updated during the course of a geometry optimization or saddle point search, and will be punched if a run exhausts its time limit. This allows restarts where the job leaves off. You may want to read this FCM back into the program for your restart, or you may prefer to regenerate a new initial hessian. In any case, this updated hessian is absolutely not suitable for frequency prediction!

\$GRAD, \$DIPDR, \$VIB, \$MASS

\$GRAD group (relevant for RUNTYP=OPTIMIZE or SADPOINT)
(relevant for RUNTYP=HESSIAN when RDHESS=.TRUE.)

Formatted gradient vector at the \$DATA geometry. This data is read in the same format it was punched out.

For RUNTYP=HESSIAN, this information is used to determine if you are at a stationary point, and possibly for projection. If omitted, the program pretends the gradient is zero, and otherwise proceeds normally.

For geometry searches, this information (if known) can be read into the program so that the first step can be taken instantly.

\$DIPDR group (relevant for RUNTYP=HESSIAN if RDHESS=.T.)

Formatted dipole derivative tensor, punched in a previous RUNTYP=HESSIAN job. If this group is omitted, then a vibrational analysis will be unable to predict the IR intensities, but the run can otherwise proceed.

\$VIB group (relevant for RUNTYP=HESSIAN, METHOD=NUMERIC)

Formatted card image -restart- data. This data is read in the format it was punched by a previous HESSIAN job to the file IRCDATA. Just add a "\$END" card, and if the final gradient was punched as zero, delete the last set of data. Normally, IREST in \$CONTRL will NOT be used in conjunction with a HESSIAN restart. The mere presence of this deck triggers the restart from cards. This deck can also be used to turn a single point differencing run into double differencing, as well as recovering from time limits, or other bombouts.

\$MASS group (relevant for RUNTYP=HESSIAN, IRC, or DRC)

This group permits isotopic substitution during the computation of mass weighted Cartesian coordinates. Of course, the masses affect the frequencies and normal modes of vibration.

AMASS = An array giving the atomic masses, in amu. The default is to use the mass of the most abundant isotope. Masses through element 104 are stored.

example - \$MASS AMASS(3)=2.0140 \$END
will make the third atom in the molecule a deuterium.

\$IRC group (relevant for RUNTYP=IRC)

This group governs the location of the intrinsic reaction coordinate, a steepest descent path in mass weighted coordinates, that connects the saddle point to reactants and products.

----- there are five integration methods chosen by PACE.

PACE = GS2 selects the Gonzalez-Schlegel second order method. This is the default method.

Related input is:

GCUT cutoff for the norm of the mass-weighted gradient tangent (the default is chosen in the range from 0.00005 to 0.00020, depending on the value for STRIDE chosen below)

RCUT cutoff for Cartesian RMS displacement vector. (the default is chosen in the range 0.0005 to 0.0020 Bohr, depending on the value for STRIDE)

ACUT maximum angle from end points for linear interpolation (default=5 degrees)

MXOPT maximum number of constrained optimization steps for each IRC point (default=20)

IHUPD is the hessian update formula. 1 means Powell, 2 means BFGS (default=2)

GA is a gradient from the previous IRC point, and is used when restarting.

OPTTOL is a gradient cutoff used to determine if the IRC is approaching a minimum. It has the same meaning as the variable in \$STATPT. (default=0.0001)

PACE = LINEAR selects linear gradient following (Euler's method).

Related input is:

STABLZ switches on Ishida/Morokuma/Komornicki reaction path stabilization. The default is .TRUE.

DELTA initial step size along the unit bisector, if STABLZ is on. Default=0.025 Bohr.

ELBOW is the collinearity threshold above which the stabilization is skipped. If the mass weighted gradients at QB and QC are almost collinear, the reaction path is deemed to be curving very little, and stabilization isn't needed. The default is 175.0 degrees. To always perform stabilization, input 180.0.

READQB,EB,GBNORM,GB are energy and gradient data already known at the current IRC point. If it happens that a run with STABLZ on decides to skip stabilization because of ELBOW, this data will be punched to speed the restart.

\$IRC

PACE = QUAD selects quadratic gradient following.
 Related input is:

SAB distance to previous point on the IRC.
 GA gradient vector at that historical point.

PACE = AMPC4 selects the fourth order Adams-Moulton variable step predictor-corrector.

Related input is:

GA0,GA1,GA2 which are gradients at previous points.

PACE = RK4 selects the 4th order Runge-Kutta variable step method.
 There is no related input.

----- The next two are used by all PACE choices -----

STRIDE = Determines how far apart points on the reaction path will be. STRIDE is used to calculate the step taken, according to the PACE you choose. The default is good for the GS2 method, which is very robust. Other methods should request much smaller step sizes, such as 0.10 or even 0.05. (default = 0.30 sqrt(amu)-Bohr)

NPOINT = The number of IRC points to be located in this run. The default is to find only the next point. (default = 1)

----- The next two let you choose your output volume -----

Let F mean the first IRC point found in this run, and L mean the final IRC point of this run. Let INTR mean the internuclear distance matrix.

NPRT = 1 Print INTR at all, orbitals at all IRC points
 0 Print INTR at all, orbitals at F+L (default)
 -1 Print INTR at all, orbitals never
 -2 Print INTR at F+L, orbitals never

NPUN = 1 Punch all orbitals at all IRC points
 0 Punch all orbitals at F+L, only occupied orbitals at IRC points between (default)
 -1 Punch all orbitals at F+L only
 -2 Never punch orbitals

- The next two tally the reaction path results. The defaults are appropriate for starting from a saddle point, restart values are automatically punched out.

NEXTPT = The number of the next point to be computed.

STOTAL = Total distance along the reaction path to next IRC point, in mass weighted Cartesian space.

- The following controls jumping off the saddle point. If you give a \$HESS group, FREQ and CMODE will be generated automatically.

SADDLE = A logical variable telling if the coordinates given in the \$DATA deck are at

a saddle point (.TRUE.) or some other point lying on the IRC (.FALSE.). If SADDLE is true, either a \$HESS group or else FREQ and CMODE must be given. (default = .FALSE.)

Related input is:

- TSENGY = A logical variable controlling whether the energy and wavefunction are evaluated at the transition state coordinates given in \$DATA. Since you already know the energy from the transition state search and force field runs, the default is .F.
- FORWRD = A logical variable controlling the direction to proceed away from a saddle point. The forward direction is defined as the direction in which the largest magnitude component of the imaginary normal mode is positive. (default = .TRUE.)
- EVIB = Desired decrease in energy when following the imaginary normal mode away from a saddle point. (default=0.0005 Hartree)
- FREQ = The magnitude of the imaginary frequency, given in cm^{-1} .
- CMODE = An array of the components of the normal mode whose frequency is imaginary, in Cartesian coordinates. Be careful with the signs!

You must give FREQ and CMODE if you don't give a \$HESS group, when SADDLE=.TRUE. The option of giving these two variables instead of a \$HESS does not apply to the GS2 method, which must have a hessian input, even for restarts. Note also that EVIB is ignored by GS2 runs.

- For hints about IRC tracking, see the 'further information' section.

\$VSCF**\$VSCF group** (optional, relevant to RUNTYP=VSCF)

This group governs the computation of frequencies including anharmonic effects. Besides the values shown below, the input file must contain a \$HESS group and perhaps a \$DIPDR group, to start with previously obtained harmonic vibrational information. Energies are sampled along the directions of harmonic normal modes, and along pairs of harmonic normal modes, after which vibrational nuclear wavefunctions are obtained at an SCF-like level, termed VSCF, using product nuclear wavefunctions. An MP2-like correction to the vibrational energy, termed correlation corrected (cc-VSCF), is also obtained. By default, the dipole is computed at every grid point to give improved IR intensity values. See also the restart group \$VIBSCF.

NGRID = number of grid points to be computed along each harmonic normal mode, and if NCOUP=2, along each pair of modes. Reasonable values are 8 or 16, with 16 considered significantly more accurate. (default=16)

NCOUP = the order of mode couplings included.
 = 1 computes 1-D grids along each harmonic mode
 = 2 adds additionally, 2-D grids along each pair of normal modes. (default)

The total number of energy and dipole evaluations for NCOUP=2 is $M \cdot \text{NGRID} + M \cdot (M-1)/2 \cdot \text{NGRID}^2$, where M is the number of normal modes: $M = 3N-6$ or $3N-5$.

IEXC = 1 obtain fundamental frequencies (default)
 = 2 instead, obtain first overtones
 = 3 instead, obtain second overtones

IEXC higher than 1 may be speedily obtained using the next parameter to restart with a completed \$VIBSCF group.

READV = flag to indicate restart data \$VIBSCF should be read in to resume an interrupted calculation, or to obtain overtones in follow-on runs. (default is .FALSE.)

The next two relate to simplified intensity computation. These simplifications are aimed at speeding up MP2 runs, if one cares not so much about intensities, and so would like to reduce CPU for computing dipoles. It is pointless to select DMDR for SCF electronic structure, where the dipoles are easily obtainable. DMDR must not be used if overtones are being computed.

DMDR = if true, indicates that the harmonic dipole derivative tensor \$DIPDR is input, rather than computing the dipoles. (default is .FALSE.)

MPDIP = for MP2 electronic structure, a value of .FALSE. uses SCF level dipoles in order to save the time needed to obtain the MP2 density at every grid point. It is more accurate to use the DMDR flag instead of this option, if \$DIPDR is available. Obviously this variable is irrelevant for SCF level electronic structure. (default=.TRUE.)

VCFCT = scaling factor for pair-coupling potential. Sometimes when pair-coupling potential values are larger than the corresponding single mode values, they must be scaled down. (Default=1.0)

Reference:

G.M.Chaban, J.O.Jung, R.B.Gerber J.Chem.Phys. 111, 1823-1829(1999)

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$\$VIBSCF$ group (optional, relevant to RUNTYP=VSCF)

This is restart data, as written to file IRCDATA in a partially completed previous run. Append a " \$END" line, and select READV=.TRUE. to read the data.

=====

\$GRADEX group (optional, for RUNTYP=GRADEXTR)

This group controls the gradient extremal following algorithm. The GEs leave stationary points parallel to each of the normal modes of the hessian. Sometimes a GE leaving a minimum will find a transition state, and thus provides us with a way of finding that saddle point. GEs have many unusual mathematical properties, and you should be aware that they normally differ a great deal from IRCs.

The search will always be performed in cartesian coordinates, but internal coordinates along the way may be printed by the usual specification of NZVAR and \$ZMAT.

- METHOD = algorithm selection.
 SR A predictor-corrector method due to Sun and Ruedenberg (default).
 JJH A method due to Jorgensen, Jensen and Helgaker.
- NSTEP = maximum number of predictor steps to take. (default=50)
- DPRED = the stepsize for the predictor step. (default = 0.10)
- STPT = a flag to indicate whether the initial geometry is considered a stationary point. If .TRUE., the geometry will be perturbed by STSTEP along the IFOLOW normal mode. (default = .TRUE.)
- STSTEP = the stepsize for jumping away from a stationary point. (default = 0.01)
- IFOLOW = Mode selection option. (default is 1)
 If STPT=.TRUE., the initial geometry will be perturbed by STSTEP along the IFOLOW normal mode. Note that IFOLOW can be positive or negative, depending on the direction the normal mode should be followed in. The positive direction is defined as the one where the largest component of the Hessian eigenvector is positive.
 If STPT=.FALSE. the sign of IFOLOW determines which direction the GE is followed in. A positive value will follow the GE in the uphill direction. The value of IFOLOW should be set to the Hessian mode which is parallel to the gradient to avoid miscellaneous warning messages.
- GOFIRST = a flag to indicate whether the algorithm should attempt to locate a stationary point. If .TRUE., a straight NR search is performed once the NR step length drops below SNRMAX. 10 NR step are then allowed, a value which cannot be changed. (default = .TRUE.)
- SNRMAX = upper limit for switching to straight NR search for stationary point location. (default = 0.10 or DPRED, whichever is smallest)
- OPTTOL = gradient convergence tolerance, in Hartree/Bohr. Used for optimizing to a stationary point. Convergence of a geometry search requires the rms gradient to be less than OPTTOL. (default=0.0001)
- HESS = selection of the initial hessian matrix, if STPT=.TRUE.
 = READ causes the hessian to be read from a \$HESS group.

= CALC causes the hessian to be computed. (Default)

- The rest of the parameters apply only to METHOD=SR

DELCOR = the corrector step should be smaller than this value before the next predictor step is taken. (default = 0.001)

MYSTEP = maximum number of micro iteration allowed to bring the corrector step length below DELCOR. (default=20)

SNUMH = stepsize used in the numerical differentiation of the Hessian to produce third derivatives. (default = 0.0001)

HSDFDB = flag to select determination of third derivatives. At the current geometry we need the gradient, the Hessian, and the partial third derivative matrix in the gradient direction.

If .TRUE., the gradient is calculated at the current geometry, and two Hessians are calculated at SNUMH distance to each side in the gradient direction. The Hessian at the geometry is formed as the average of the two displaced Hessians.

If .FALSE., both the gradient and Hessian are calculated at the current geometry, and one additional Hessian is calculated at SNUMH in the gradient direction.

The default double-sided differentiation produces a more accurate third derivative matrix, at the cost of an additional wave function and gradient. (default = .TRUE.)

See the 'further information' section for some help with GRADEXTR runs.

\$DRC group (relevant for RUNTYP=DRC)

This group governs the dynamical reaction coordinate, a classical trajectory method based on quantum chemical potential energy surfaces. In GAMESS these may be either ab initio or semi-empirical. Because the vibrational period of a normal mode with frequency 500 wavenumbers is 67 fs, a DRC needs to run for many steps in order to sample a representative portion of phase space. Almost all DRCs break molecular symmetry, so build your molecule with C1 symmetry in \$DATA, or specify NOSYM=1 in \$CONTRL. Restart data can be found in the job's OUTPUT file, with important results summarized to the IRCDATA file.

- NSTEP = The number of DRC points to be calculated, not including the initial point. (default = 1000)
- DELTAT = is the time step. (default = 0.1 fs)
- TOTIME = total duration of the DRC computed in a previous job, in fs. The default is the correct value when initiating a DRC. (default=0.0 fs)

In general, a DRC can be initiated anywhere, so \$DATA might contain coordinates of the equilibrium geometry, or a nearby transition state, or something else. You must also supply an initial kinetic energy, and the direction of the initial velocity, for which there are a number of options:

- EKIN = The initial kinetic energy (default = 0.0 kcal/mol) See also ENM, NVEL, and VIBLVL regarding alternate ways to specify the initial value.
- VEL = an array of velocity components, in Bohr/fs. When NVEL is false, this is simply the direction of the velocity vector. Its magnitude will be automatically adjusted to match the desired initial kinetic energy, and it will be projected so that the translation of the center of mass is removed. Give in the order vx1, vy1, vz1, vx2, vy2, ...
- NVEL = a flag to compute the initial kinetic energy from the input VEL using the sum of mass*VEL*VEL/2. This flag is usually selected only for restarts. (default=.FALSE.)

The next two allow the kinetic energy to be partitioned over all normal modes. The coordinates in \$DATA are likely to be from a stationary point! You must also supply a \$HESS group.

- VIBLVL = a flag to turn this option on (default=.FALSE.)
- VIBENG = an array of energies (in units of multiples of the hv of each mode) to be imparted along each normal mode. The default is to assign the zero point energy only, VIBENG(1)=0.5, 0.5, ..., 0.5. If given as a negative number, the initial direction of the velocity vector is along the reverse direction of the mode. "Reverse" means the phase of the normal mode is chosen such that the largest magnitude component is a negative value. An example might be VIBENG(4)=2.5 to add two quanta to mode 4, along with zero

point energy in all modes.

The next three pertain to initiating the DRC along a single normal mode of vibration. No kinetic energy is assigned to the other modes. You must also supply a \$HESS group.

- NNM = The number of the normal mode to which the initial kinetic energy is given. The absolute value of NNM must be in the range 1, 2, ..., 3N-6. If NNM is a positive/negative value, the initial velocity will lie in the forward/reverse direction of the mode. "Forward" means the largest component of the normal mode is a positive value. (default=0)
- ENM = the initial kinetic energy given to mode NNM, in units of vibrational quanta $h\nu$, so the amount depends on mode NNM's vibrational frequency, ν . If you prefer to impart an arbitrary initial kinetic energy to mode NNM, specify EKIN instead. (default = 0.0 quanta)
-

To summarize, there are five different ways to specify the DRC trajectory:

1. VEL vector with NVEL=.TRUE. This is difficult to specify at your initial point, and so this option is mainly used when restarting your trajectory. The restart information is always in this format.
 2. VEL vector and EKIN with NVEL=.FALSE. This will give a desired amount of kinetic energy in the direction of the velocity vector.
 3. VIBLVL and VIBENG selected, to give initial kinetic energy to all of the normal modes.
 4. NNM and ENM to give quanta to a single normal mode.
 5. NNM and EKIN to give arbitrary kinetic energy to a single normal mode.
-

The most common use of the next two is to analyze a trajectory with respect to the minimum energy geometry the trajectory is traveling around.

- NMANAL = a flag to select mapping of the mass-weighted Cartesian DRC coordinates and velocity (conjugate momentum) in terms of normal modes step by step. If you choose this option, you must supply both CO and a \$HESS group from the stationary point. (default=.FALSE.)
- CO = an array of the coordinates of the stationary point (the coordinates in \$DATA might well be some other coordinates). Give in the order $x_1, y_1, z_1, x_2, y_2, \dots$
-

The next option applies to all input paths which read a hessian: NMANAL, NNM, or VIBLVL. After the translations and rotations have been dropped, the normal modes are renumbered 1, 2, ..., 3N-6.

- HESSTS = a flag to say if the hessian corresponds to a transition state or a minimum. This parameter controls deletion of the translation and rotation degrees of freedom, i.e. the default is to drop the first six "modes", while setting this flag on drops modes 2 to 7 instead. (default=.FALSE.)

The final variables control the volume of output. Let F mean the first DRC point found in this run, and L mean the last DRC point of this run.

NPRTSM = summarize the DRC results every NPRTSM steps, to the file IRCDATA.
(default = 1)

NPRT = 1 Print orbitals at all DRC points
0 Print orbitals at F+L (default)
-1 Never print orbitals

NPUN = 2 Punch all orbitals at all DRC points
1 Punch all orbitals at F+L, and occupied orbitals at DRC points between
0 Punch all orbitals at F+L only (default)
-1 Never punch orbitals

References:

- J.J.P.Stewart, L.P.Davis, L.W.Burggraf, J.Comput.Chem. 8, 1117-1123 (1987)
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M.S.Gordon, G.Chaban, T.Taketsugu J.Phys.Chem. 100, 11512-11525(1996)

\$SURF group (relevant for RUNTYP=SURFACE)

This group allows you to probe a potential energy surface along a small grid of points. Note that there is no option to vary angles, only distances. The scan can be made for any SCFTYP, or for the MP2 or CI surface.

- IVEC1 = an array of two atoms, defining a coordinate from the first atom given to the second.
- IGRP1 = an array specifying a group of atoms, which must include the second atom given in IVEC1. The entire group will be translated (rigidly) along the vector IVEC1, relative to the first atom given in IVEC1.
- ORIG1 = starting value of the coordinate, which may be positive or negative. Zero corresponds to the distance given in \$DATA.
- DISP1 = step size for the coordinate.
- NDISP1 = number of steps to take for this coordinate.

There are no reasonable defaults for these keywords, so you should input all of them. ORIG1 and DISP1 should be given in Angstrom.

IVEC2, IGRP2, ORIG2, DISP2, NDISP2 = have the identical meaning as their "1" counterparts, and permit you to make a two dimensional map along two displacement coordinates. If the "2" data are not input, the surface map proceeds in only one dimension.

Note that properties are not computed at these points, other than the energy.

\$LOCAL

\$LOCAL group (relevant for LOCAL=RUEDNBRG, BOYS, or POP)

This group allows input of additional data to control the localization methods. If no input is provided, the valence orbitals will be localized as much as possible, while still leaving the wavefunction invariant.

- PRTLOC = a flag to control supplemental printout. The extra output is the rotation matrix to the localized orbitals, and, for the Boys method, the orbital centroids, for the Ruedenberg method, the coulomb and exchange matrices, for the population method, atomic populations. (default=.FALSE.)
- MAXLOC = maximum number of localization cycles. This applies to BOYS or POP methods only. If the localization fails to converge, a different order of 2x2 pairwise rotations will be tried. (default=250)
- CVGLOC = convergence criterion. The default provides LMO coefficients accurate to 6 figures. (default=1.0E-6)
- SYMLOC = a flag to restrict localization so that orbitals of different symmetry types are not mixed. This option is not supported in all possible point groups. The purpose of this option is to give a better choice for the starting orbitals for GVB-PP or MCSCF runs, without destroying the orbital's symmetry. This option is compatible with each of the 3 methods of selecting the orbitals to be included. (default=.FALSE.)

These parameters select the orbitals which are to be included in the localization. You may select from FCORE, NOUTA/NOUTB, or NINA/NINB, but may choose only one of these.

- FCORE = flag to freeze all the chemical core orbitals present. All the valence orbitals will be localized. (default=.TRUE.)
-
- NOUTA = number of alpha orbitals to hold fixed in the localization. (default=0)
- MOOUTA = an array of NOUTA elements giving the numbers of the orbitals to hold fixed. For example, the input NOUTA=2 MOOUTA(1)=8,13 will freeze only orbitals 8 and 13. You must enter all the orbitals you want to freeze, including any cores. This variable has nothing to do with cows.
- NOUTB = number of beta orbitals to hold fixed in -UHF- localizations. (default=0)
- MOOUTB = same as MOOUTA, except that it applies to the beta orbitals, in -UHF- wavefunctions only.
-
- NINA = number of alpha orbitals which are to be included in the localization. (default=0)
- MOINA = an array of NINA elements giving the numbers of the orbitals to be included in the localization. Any orbitals not mentioned will be frozen.

NINB = number of -UHF- beta MOs in the localization. (default=0)

MOINB = same as MOINA, except that it applies to the beta orbitals, in -UHF- wavefunctions only.

N.B. Since Boys localization needs the dipole integrals, do not turn off dipole moment calculation in \$ELMOM.

- The following keywords are used for the localized charge distribution (LCD) energy decomposition.
 - EDCOMP = flag to turn on LCD energy decomposition. Note that this method is currently implemented for SCFTYP=RHF and ROHF and LOCAL=RUEDNBRG only. The SCF LCD forces all orbitals to be localized, overriding input on the previous page. See also LMOMP2 in the \$MP2 group. (default = .FALSE.)
 - MOIDON = flag to turn on LMO identification and subsequent LMO reordering, and assign nuclear LCD automatically. (default = .FALSE.)
 - DIPDCM = flag for LCD molecular dipole decomposition. (default = .FALSE.)
 - QADDCM = flag for LCD molecular quadrupole decomposition. (default = .FALSE.)
 - POLDCM = flag to turn on LCD polarizability decomposition. This method is implemented for SCFTYP=RHF or ROHF and LOCAL=BOYS or RUEDNBRG. (default=.FALSE.)
 - POLNUM = flag to forces numerical rather than analytical calculation of the polarizabilities. This may be useful in larger molecules. The numerical polarizabilities of bonds in or around aromatic rings sometimes are unphysical. (default=.FALSE.) See D.R.Garmer, W.J.Stevens J.Phys.Chem. 93, 8263-8270 (1989).
 - POLANG = flag to choose units of localized polarizability output. The default is Angstroms³, while false will give Bohr³. (default=.TRUE.)
 - ZDO = flag for LCD analysis of a composite wave function, given in a \$VEC group of a van der Waals complex, within the zero differential overlap approximation. The MOs are not orthonormalized and the intermolecular electron exchange energy is neglected. In addition, the molecular overlap matrix is printed out. This is a very specialized option. (default = .FALSE.)
- The remaining keywords can be used to define the nuclear part of an LCD. They are usually used to rectify mistakes in the automatic definition made when MOIDON=.TRUE. The index defining the LMO number then refers to the reordered list of LMOs.
 - NNUCMO = array giving the number of nuclei assigned to a particular LMO.
 - IJMO = is an array of pairs of indices (I,J), giving the row (nucleus I) and

\$LOCAL, \$TWOEI

column (orbital J) index of the entries in ZIJ and MOIJ.

- MOIJ = arrays of integers K, assigning nucleus K as the site of the lth charge of LCD J.
- ZIJ = array of floating point numbers assigning a charge to the lth charge of LCD J.
- IProt = array of integers K, defining nucleus K as a proton.
- DEPRNT = a flag for additional decomposition printing, such as pair contributions to various energy terms, and centroids of the Ruedenberg orbitals. (default = .FALSE.)

For hints about localizations, and the LCD energy decomposition, see the 'further information' section.

\$TWOEI group (relevant for EDCOMP=.TRUE. in \$LOCAL)

Formatted transformed two-electron Coulomb and Exchange integrals as punched during a LOCAL=RUEDNBRG run. If this group is present it will automatically be read in during such a run and the two-electron integrals do not have to be re-transformed. This group is especially useful for EDCOMP=.TRUE. runs when the localization has to be repeated for different definitions of nuclear LCDs.

\$TRUNCN group (optional, relevant for RHF)

This group controls the truncation of some of the localized orbitals to just the AOs on a subset of the atoms. This option is particularly useful to generate localized orbitals to be frozen when the effective fragment potential is used to partition a system across a chemical bond. In other words, this group prepares the frozen buffer zone orbitals. This group should be used in conjunction with RUNTYP=ENERGY (or PROP if the orbitals are available) and either LOCAL=RUEDNBRG or BOYS, with MOIDON set in \$LOCAL.

- DOPROJ = flag to activate MO projection/truncation, the default is to skip this (default=.FALSE.)
- AUTOID = forces identification of MOs (analogous to MOIDON in \$LOCAL). This keyword is provided in case the localized orbitals are already present in \$VEC, in which case this is a faster RUNTYP=PROP with LOCAL=NONE job. Obviously, GUESS=MOREAD. (default=.FALSE.)
- PLAIN = flag to control the MO tail truncation. A value of .FALSE. uses corresponding orbital projections, H.F.King, R.E.Stanton, H.Kim, R.E.Wyatt, R.G.Parr J. Chem. Phys. 47, 1936-1941(1967) and generates orthogonal orbitals. A value of .TRUE. just sets the unwanted AOs to zero, so the resulting Mos need to go through the automatic orthogonalization step when MOREAD in the next job. (default=.FALSE.)
- IMOPR = an array specifying which MOs to be truncated. In most cases involving normal bonding, the options MOIDON or AUTOID will correctly identify all localized MOs belonging to the atoms in the zone being truncated. However, you can inspect the output, and give a list of all MOs which you want to be truncated in this array, in case you feel the automatic assignment is incorrect. Any orbital not in the truncation set, whether this is chosen automatically or by IMOPR, is left completely unaltered.

There are now two ways to specify what orbitals are to be truncated. The most common usage is for preparation of a buffer zone for QM/MM computations, with an Effective Fragment Potential representing the non-quantum part of the system. This input is NATAB, NATBF, ICAPFR, ICAPBF, in which case the \$DATA input must be sorted into three zones. The first group of atoms are meant to be treated in later runs by full quantum mechanics, the second group by frozen localized orbitals as a 'buffer', and the third group is to be substituted later by an effective fragment potential (multipoles, polarizabilities, ...). Note that in the DOPROJ=.TRUE. run, all atoms are still quantum atoms.

- NATAB = number of atoms to be in the 'ab initio' zone.
- NATBF = number of atoms to be in the 'buffer' zone. The program can obtain the number of atoms in the remaining zone by subtraction, so it need not be input.

In case the MOIDON or AUTOID options lead to confused assignments (unlikely in ordinary bonding situations around the buffer zone), there are two fine tuning values.

\$TRUNCN

ICAPFR = array indicating the identity of "capping atoms" which are on the border between the ab initio and buffer zones (in the ab initio zone).

ICAPBK = array indicating the identity of "capping atoms" which are on the border between the buffer and EFP zones (in the effective fragment zone).

See also IXCORL and IXLONE below.

In case truncation seems useful for some other purpose, you can specify the atoms in any order within the \$DATA group, by the IZAT/ILAT approach. You are supposed to give only one of these two lists, probably whichever is shorter:

IZAT = an array containing the atoms which are NOT in the buffer zone.

ILAT = an array containing the atoms which are in the buffer zone.

The AO coefficients of the localized orbitals present in the buffer zone which lie on atoms outside the buffer will be truncated.

See also IXCORL and IXLONE below.

The next two values let you remove additional orbitals within the buffer zone from the truncation process, if that is desirable. These arrays can only include atoms that are already in the buffer zone, whether this was defined by NATBF, or IZAT/ILAT. The default is to include all core and lone pair orbitals, not just bonding orbitals, as the buffer zone orbitals.

IXCORL = an array of atoms whose core and lone pair orbitals are to be considered as not belonging to the buffer zone orbitals.

IXLONE = an array of atoms for which only the lone pair orbitals are to be considered as not belonging to the buffer zone orbitals.

The final option controls output of the truncated orbitals to file PUNCH for use in later runs:

NPUNOP = punch out option for the truncated orbitals
 = 1 the MOs are not reordered.
 = 2 punch the truncated MOs as the first vectors in the \$VEC MO set, with untransformed vectors following immediately after. (default)

\$ELMOM group (not required)

This group controls electrostatic moments calculation.

IEMOM	=	0	skip this property
		1	calculate monopole and dipole (default)
		2	also calculate quadrupole moments
		3	also calculate octupole moments
WHERE	=	COMASS	center of mass (default)
		NUCLEI	at each nucleus
		POINTS	at points given in \$POINTS.
OUTPUT	=	PUNCH, PAPER, or BOTH (default)	
IEMINT	=	0	skip printing of integrals (default)
		1	print dipole integrals
		2	also print quadrupole integrals
		3	also print octupole integrals
		-2	print quadrupole integrals only
		-3	print octupole integrals only

The quadrupole and octupole tensors on the printout are formed according to the definition of Buckingham. Caution: only the first nonvanishing term in the multipole charge expansion is independent of the coordinate origin chosen, which is normally the center of mass.

\$ELPOT group (not required)

This group controls electrostatic potential calculation.

IEPOT	=	0	skip this property (default)
		1	calculate electric potential
WHERE	=	COMASS	center of mass
		NUCLEI	at each nucleus (default)
		POINTS	at points given in \$POINTS
		GRID	at grid given in \$GRID
		PDC	at points controlled by \$PDC.
OUTPUT	=	PUNCH, PAPER, or BOTH (default)	

This property is the electrostatic potential $V(a)$ felt by a test positive charge, due to the molecular charge density. A nucleus at the evaluation point is ignored. If this property is evaluated at the nuclei, it obeys the equation

$$\sum_{\text{on nuclei}(a)} Z(a) \cdot V(a) = 2 \cdot V(\text{nn}) + V(\text{ne}).$$

The electronic portion of this property is called the diamagnetic shielding.

\$ELDENS, \$ELFLDG

\$ELDENS group (not required)

This group controls electron density calculation.

IEDEN	= 0	skip this property (default)
	= 1	compute the electron density.
MORB	=	The molecular orbital whose electron density is to be computed. If zero, the total density is computed. (default=0)
WHERE	= COMASS	center of mass
	NUCLEI	at each nucleus (default)
	POINTS	at points given in \$POINTS
	GRID	at grid given in \$GRID
OUTPUT	=	PUNCH, PAPER, or BOTH (default)
IEDINT	= 0	skip printing of integrals (default)
	1	print the electron density integrals

\$ELFLDG group (not required)

This group controls electrostatic field and electric field gradient calculation.

IEFLD	= 0	skip this property (default)
	1	calculate field
	2	calculate field and gradient
WHERE	= COMASS	center of mass
	NUCLEI	at each nucleus (default)
	POINTS	at points given in \$POINTS
OUTPUT	=	PUNCH, PAPER, or BOTH (default)
IEFINT	= 0	skip printing these integrals (default)
	1	print electric field integrals
	2	also print field gradient integrals
	-2	print field gradient integrals only

The Hellman-Feynman force on a nucleus is the nuclear charge multiplied by the electric field at that nucleus. The electric field is the gradient of the electric potential, and the field gradient is the hessian of the electric potential. The components of the electric field gradient tensor are formed in the conventional way, i.e. see D.Neumann and J.W.Moskowitz.

\$POINTS group (not required)

This group is used to input points at which properties will be computed. This first card in the group must contain the string ANGS or BOHR, followed by an integer NPOINT, the number of points to be used. The next NPOINT cards are read in free format, containing the X, Y, and Z coordinates of each desired point.

\$GRID group (not required)

This group is used to input a grid (plane through the molecule) on which properties will be calculated.

ORIGIN(i) = coordinates of the lower left corner of the plot.
 XVEC(i) = coordinates of the lower right corner of the plot.
 YVEC(i) = coordinates of the upper left corner of the plot.
 SIZE = grid increment, default is 0.25.
 UNITS = units of the above four values, it can be either BOHR or ANGS (the default).

Note that XVEC and YVEC are not necessarily parallel to the X and Y axes, rather they are the axes which you desire to see plotted by the MEPMAP contouring program.

For conversion factors, and references see the 'further information' section.

\$PDC group (relevant if WHERE=PDC in \$ELPOT)

This group determines the points at which to compute the electrostatic potential, for the purpose of fitting atomic charges to this potential. Constraints on the fit which determines these "potential determined charges" can include the conservation of charge, the dipole, and the quadrupole.

PTSEL = determines the points to be used, choose from
 GEODESIC to use a set of points on several fused sphere van der Waals surfaces, with points selected using an algorithm due to Mark Spackman. The results are similar to those from the Kollman/Singh method, but are less rotation dependent. (default)
 CONNOLLY to use a set of points on several fused sphere van der Waals surfaces, with points selected using an algorithm due to Michael Connolly. This is identical to the method used by Kollman & Singh (see below)

	CHELPG	to use a modified version of the CHELPG algorithm, which produces a symmetric grid of points for a symmetric molecule.
CONSTR	= NONE	no fit is performed. The potential at the points is instead output according to OUTPUT in \$ELPOT.
	CHARGE	the sum of fitted atomic charges is constrained to reproduce the total molecular charge. (default)
	DIPOLE	fitted charges are constrained to exactly reproduce the total charge and dipole.
	QUPOLE	fitted charges are constrained to exactly reproduce the charge, dipole, and quadrupole.

Note: the number of constraints cannot exceed the number of parameters, which is the number of nuclei. Planar molecules afford fewer constraint equations, namely two dipole constraints and three quadrupole constraints, instead of three and five, respectively.

* * * the next 5 pertain to PTSEL=GEODESIC or CONNOLLY * * *

VDWSCL	=	scale factor for the first shell of VDW spheres. The default of 1.4 seems to be an empirical best value. Values for VDW radii for most elements up to Z=36 are internally stored.
VDWINC	=	increment for successive shells (default = 0.2). The defaults for VDWSCL and VDWINC will result in points chosen on layers at 1.4, 1.6, 1.8 etc times the VDW radii of the atoms.
LAYER	=	number of layers of points chosen on successive fused sphere VDW surfaces (default = 4)
NFREQ	=	flag for particular geodesic tessellation of points. Only relevant if PTSEL=GEODESIC. Options are: (10*h + k) for {3,5+}h,k tessellations -(10*h + k) for {5+,3}h,k tessellations (of course both nh and nk must be less than 10, so NFREQ must lie within the range -99 to 99) The default value is NFREQ=30 (=03)
PTDENS	=	density of points on the surface of each scaled VDW sphere (in points per square au). Only relevant if PTSEL=CONNOLLY. Default is 0.28 per au squared, which corresponds to 1.0 per square Angstrom, the default recommended by Kollman & Singh.
		* * * <u>the next two pertain to PTSEL=CHELPG</u> * * *
RMAX	=	maximum distance from any point to the closest atom. (default=3.0 Angstroms)
DEL R	=	distance between points on the grid. (default=0.8 Angstroms)

- MAXPDC = an estimate of the total number of points whose electrostatic potential will be included in the fit. (default=10000)
-
- CENTER = an array of coordinates at which the moments were computed.
- DPOLE = the molecular dipole.
- QPOLE = the molecular quadrupole.
- PDUNIT = units for the above values. ANGS (default) will mean that the coordinates are in Angstroms, the dipole in Debye, and quadrupole in Buckingham. BOHR implies atomic units for all 3.

Note: it is easier to compute the moments in the current run, by setting IEMOM to at least 2 in \$ELMOM. However, you could fit experimental data, for example, by reading it in here.

There is no unique way to define fitted atomic charges. Smaller numbers of points at which the electro-static potential is fit, changes in VDW radii, asymmetric point location, etc. all affect the results. A useful bibliography is

- U.C.Singh, P.A.Kollman, J.Comput.Chem. 5, 129-145(1984)
 L.E.Chirlain, M.M.Francl, J.Comput.Chem. 8, 894-905(1987)
 R.J.Woods, M.Khalil, W.Pell, S.H.Moffatt, V.H.Smith, J.Comput.Chem. 11, 297-310(1990)
 C.M.Breneman, K.B.Wiberg, J.Comput.Chem. 11, 361-373(1990)
 K.M.Merz, J.Comput.Chem. 13, 749(1992)
 M.A.Spackman, J.Comput.Chem. 17, 1-18(1996)

\$MOLGRF group (relevant only if you have MOLGRAPH)

This option provides an interface for viewing orbitals through a commercial package named MOLGRAPH, from Daikin Industries. Note that this option uses three disk files which are not defined in the GAMESS execution scripts we provide, since we don't use MOLGRAPH ourselves. You will need to define files 28, 29, 30, as generic names PRGRID, COGRID, MOGRID, of which the latter is passed to MOLGRAPH.

- GRID3D = a flag to generate 3D grid data. (default is .false.).
- TOTAL = a flag to generate a total density grid data. "Total" means the sum of the orbital densities given by NPLT array. (default is .false.).
- MESH = numbers of grids. You can use different numbers for three axes. (default is MESH(1)=21,21,21).
- BOUND = boundary coordinates of a 3D graphical cell. The default is that the cell is larger than the molecular skeleton by 3 bohr in all directions. E.g.,

\$MOLGRF, \$STONE

BOUND(1)=xmin,xmax,ymin,ymax,zmin,zmax

NPLOTS = number of orbitals to be used to generate 3D grid data. (default is NPLOTS=1).

NPLT = orbital IDs. The default is 1 orbital only, the HOMO or SOMO. If the LOCAL option is given in \$CONTRL, localized orbital IDs should be given. For example, NPLT(1)=n1,n2,n3,...

CHECK = debug option, printing some of the grid data.

If you are interested in graphics, look at the WWW page for information about other graphics packages with GAMESS.

\$STONE group (optional)

This group defines the expansion points for Stone's distributed multipole analysis (DMA) of the electrostatic potential.

The DMA takes the multipolar expansion of each overlap charge density defined by two gaussian primitives, and translates it from the center of charge of the overlap density to the nearest expansion point. Some references for the method are

Stone, Chem.Phys.Lett. 83, 233 (1981)
 Price and Stone, Chem.Phys.Lett. 98, 419 (1983)
 Buckingham and Fowler, J.Chem.Phys. 79, 6426 (1983)
 Stone and Alderton, Mol.Phys. 56, 1047 (1985)

The existence of a \$STONE group in the input is what triggers the analysis. Enter as many lines as you wish, in any order, terminated by a \$END record.

ATOM i name, where

ATOM is a keyword indicating that a particular atom is selected as an expansion center.
 i is the number of the atom
 name is an optional name for the atom. If not entered the name will be set to the name used in the \$DATA input.

ATOMS is a keyword selecting all nuclei in the molecule as expansion points. No other input on the line is necessary.

BONDS is a keyword selecting all bond midpoints in the molecule as expansion points. No other input on the line is necessary.

BOND i j name, where

BOND	is a keyword indicating that a bond mid-point is selected as an expansion center.
i,j	are the indices of the atoms defining the bond, corresponding to two atoms in \$DATA.
name	an optional name for the bond midpoint. If omitted, it is set to 'BOND'.

CMASS is a keyword selecting the center of mass as an expansion point. No other input on the line is necessary.

POINT x y z name, where

POINT	is a keyword indicating that an arbitrary point is selected as an expansion point.
x,y,z	are the coordinates of the point, in Bohr.
name	is an optional name for the expansion point. If omitted, it is set to 'POINT'.

While making the EFPs for QM/MM run, a single keyword QMMMBUF is necessary. Adding additional keywords may lead to meaningless results. The program will automatically select atoms and bond midpoints which are outside the buffer zone as the multipole expansion points.

QMMMBUF nmo, where

QMMMBUF	is a keyword specifying the number of QM/MM buffer molecular orbitals, which must be the first NMO orbitals in the MO set. These orbitals must be frozen in the buffer zone, so this is useful only if \$MOFRZ is given.
NMO	is the number of buffer MO-s (if NMO is omitted, it will be set to the number of frozen MOs in \$MOFRZ)

The second and third moments on the printout can be converted to Buckingham's tensors by formula 9 of A.D.Buckingham, Quart.Rev. 13, 183-214 (1959) These can in turn be converted to spherical tensors by the formulae in the appendix of S.L.Price, et al. Mol.Phys. 52, 987-1001 (1984)

\$RAMAN, \$ALPDR

\$RAMAN group

(relevant for all SCFTYPs)

This input controls the computation of Raman intensity by the numerical differentiation procedure of Komornicki and others. It is applicable to any wavefunction for which the analytic gradient is available, including some MP2 and CI cases. The calculation involves the computation of 19 gradients, one without applied electric fields, plus 18 no symmetry runs with electric fields applied in various directions. The numerical second differencing produces intensity information with 2-3 digits of accuracy.

This run must follow an earlier RUNTYP=HESSIAN job, and the \$GRAD and \$HESS groups from that job must be given as input. If the \$DIPDR is computed analytically by this Hessian job, it too may be read in, if not, the numerical Raman job will evaluate \$DIPDR. Once the data from the 19 applied fields is available, the nuclear gradient of the dipole moment and alpha polarizability will be combined with normal coordinate information to produce the IR and Raman intensity of each mode. To study isotopic substitution speedily, simply input the \$GRAD, \$HESS, \$DIPDR, and \$ALPDR information along with the desired atomic masses in \$MASS.

The code does not permit any semi-empirical or solvation models to be used.

EFIELD = applied electric field strength. The literature suggests values in the range 0.001 to 0.005. (default = 0.002 a.u.)

=====

\$ALPDR group

(relevant for RUNTYP=RAMAN)

Formatted alpha derivative tensor, punched by a previous RUNTYP=RAMAN job. If \$DIPDR and this group are found in the input, the applied field computation will be skipped, to immediately evaluate IR and Raman intensities.

\$MOROKM group (relevant for RUNTYP=MOROKUMA)

This group controls how the supermolecule input in the \$DATA group is divided into two or more monomers. Both the supermolecule and its constituent monomers must be well described by RHF wavefunctions.

- MOROKM = a flag to request Morokuma-Kitaura decomposition. (default is .TRUE.)
- RVS = a flag to request "reduced variation space" decomposition. This differs from the Morokuma option, and one or the other or both may be requested in the same run. (default is .FALSE.)
- BSSE = a flag to request basis set superposition error be computed. You must ensure that CTPSPL is selected. This option applies only to MOROKM decompositions, as a basis superposition error is automatically generated by the RVS scheme. This is not the full Boys counterpoise correction, as explained in the reference. (default is .FALSE.)
-
- IATM = An array giving the number of atoms in each of the monomer. Up to ten monomers may be defined. Your input in \$DATA must have all the atoms in the first monomer defined before the atoms in the second monomer, before the third monomer... The number of atoms belonging to the final monomer can be omitted. There is no sensible default for IATM, so don't omit it from your input.
- ICHM = An array giving the charges of the each monomer. The charge of the final monomer may be omitted, as it is fixed by ICH in \$CONTRL, which is the total charge of the supermolecule. The default is neutral monomers, ICHM(1)=0,0,0,...
- EQUM = a flag to indicate all monomers are equivalent by symmetry (in addition to containing identical atoms). If so, which is not often true, then only the unique computations will be done. (default is .FALSE.)
- CTPSPL = a flag to decompose the interaction energy into charge transfer plus polarization terms. This is most appropriate for weakly interacting monomers. (default is .TRUE.)
- CTPLX = a flag to combine the CT and POL terms into a single term. If you select this, you might want to turn CTPSPL off to avoid the extra work that decomposition entails, or you can analyze both ways in the same run (default=.FALSE.)
- RDENG = a flag to enable restarting, by reading the lines containing "FINAL ENERGY" from a previous run. The \$ENERGY group is single lines read under format A16,F20.10 containing the E, and a card \$END to complete. The 16 chars = anything. (default is .FALSE.)
-

The present implementation has some quirks:

1. The initial guess of the monomer orbitals is not controlled by \$GUESS. The program first looks for a \$VEC1, \$VEC2, ... group for each monomer. If they are found, they will be MOREAD. If any of these are missing, the guess for that monomer will be constructed by HCORE. Check your monomer energies carefully! The initial guess orbitals for the supermolecule are formed by a block diagonal matrix of the monomer orbitals.
2. The use of symmetry is turned off internally.
3. There is no direct SCF option. File ORDINT will be a full C1 list of integrals. File APOINTS will contain whatever subset of these is needed for each particular decomposition step. So extra disk space is needed compared to RUNTYP=ENERGY.
4. This kind of run applies only to ab initio cases.
5. This kind of run will work in parallel.

References :

C.Coulson in "Hydrogen Bonding", D.Hadzi, H.W.Thompson, Eds., Pergamon Press, NY, 1957 , pp 339-360.

C.Coulson Research, 10, 149-159 (1957).

K.Morokuma J.Chem.Phys. 55, 1236-44 (1971).

K.Kitaura, K.Morokuma Int.J.Quantum Chem. 10, 325 (1976).

K.Morokuma, K.Kitaura in "Chemical Applications of Electrostatic Potentials", P.Politzer,D.G.Truhlar, Eds. Plenum Press, NY, 1981 , pp 215-242.

The method coded is the newer version described in the latter two papers. Note that the CT term is computed separately for each monomer, as described in the words below equation 16 of the 1981 paper, not simultaneously.

Reduced Variational Space:

W.J.Stevens, W.H.Fink, Chem.Phys.Lett. 139, 15-22(1987).

A comparison of the RVS and Morokuma decompositions can be found in the review article: "Wavefunctions and Chemical Bonding" M.S.Gordon, J.H.Jensen in "Encyclopedia of Computational Chemistry", volume 5, P.V.R.Schleyer, editor, John Wiley and Sons, Chichester, 1998 .

BSSE during Morokuma decomposition:

R.Cammi, R.Bonaccorsi, J.Tomasi Theoret.Chim.Acta 68, 271-283(1985).

The present implementation:

"Energy decomposition analysis for many-body interactions, and application to water complexes" W.Chen, M.S.Gordon J.Phys.Chem. 100, 14316-14328(1996)

\$FFCALC group (relevant for RUNTYP=FFIELD)

This group permits the study of the influence of an applied electric field on the wavefunction. The most common finite field calculation applies a sequence of fields to extract the linear polarizability and first and second order hyperpolarizability. The method is general, and so works for all ab initio wavefunctions in GAMESS.

EFIELD = applied electric field strength (default=0.001 a.u.)

IAXIS and JAXIS specify the orientation of the applied field. 1,2,3 mean x,y,z respectively. The default is IAXIS=3 and JAXIS=0.

If IAXIS=i and JAXIS=0, the program computes alpha(ii), beta(iii), and gamma(iiii) from the energy changes, and a few more components from the dipole changes. Five wavefunction evaluations are performed.

If IAXIS=i and JAXIS=j, the program computes the cross terms beta(ijj), beta(iij), and gamma(iijj) from the energy changes, and a few more components from the dipole changes. This requires nine evaluations of the wavefunction.

AOFF = a flag to permit evaluation of alpha(ij) when the dipole moment is not available. This is necessary only for MP2, and means the off-axial calculation will do 13, not 9 energy evaluations. Default=.FALSE.

SYM = a flag to specify when the fields to be applied along the IAXIS and/or JAXIS (or according to EONE below) do not break the molecular symmetry. Since most fields do break symmetry, the default is .FALSE.

ONEFLD = a flag to specify a single applied field calculation will be performed. Only the energy and dipole moment under this field are computed. If this option is selected, only SYM and EONE input is heeded. The default is .FALSE.

EONE = an array of the three x,y,z components of the single applied field.

Notes on RUNTYP=FFIELD.

Finite field calculations require large basis sets, and extraordinary accuracy in the wavefunction. To converge the SCF to many digits is sometimes problematic, but we suggest you use the input to increase integral accuracy and wavefunction convergence, for example

```
$CONTRL ICUT=20 ITOL=30 INTTYP=HONDO $END
$SCF NCONV=10 FDI FF=. FALSE. $END
```

In many cases, the applied fields will destroy the molecular symmetry. This means the integrals are calculated once with point group symmetry to do the initial field free wavefunction evaluation, and then again with point group symmetry turned off. If the fields applied do not destroy symmetry, you can avoid this second calculation of the integrals by SYM=.TRUE. This option also permits use of symmetry during the applied field wavefunction evaluations.

Examples of fields that do not break symmetry are a Z-axis field for an axial point group which is not centrosymmetric (i.e. C_{2v}). However, a second field in the X or Y direction does break the C_{2v} symmetry. Application of a Z-axis field for benzene breaks D_{6h} symmetry. However, you could enter the group as C_{6v} in \$DATA while using D_{6h} coordinates, and regain the prospect of using SYM=.TRUE. If you wanted to go on to apply a second field for benzene in the X direction, you might want to enter C_s in \$DATA, which will necessitate the input of two more carbon and hydrogen atom, but recovers use of SYM=.TRUE.

Reference: H.A.Kurtz, J.J.P.Stewart, K.M.Dieter J.Comput.Chem. 11, 82-87 (1990).

For analytic computation of static and also frequency dependent NLO properties, for closed shell cases, see the \$TDHF group.

\$TDHF group (relevant for SCFTYP=RHF if RUNTYP=TDHF)

This group permits the analytic calculation of various static and/or frequency dependent polarizabilities, with an emphasis on important NLO properties such as second and third harmonic generation. The method is programmed only for closed shell wavefunctions, at the semi-empirical or ab initio level. Ab initio calculations may be direct SCF, or parallel, if desired.

Because the Fock matrices computed during the time-dependent Hartree-Fock CPHF are not symmetric, you may not use symmetry. You must enter NOSYM=1 in \$CONTRL!

For a more general numerical approach to the static properties, see \$FFCALC.

NFREQ = Number of frequencies to be used. (default=1)

FREQ = An array of energy values in atomic units. For example: if NFREQ=3 then FREQ(1)=0.0,0.1,0.25. By default, only the static polarizabilities are computed. (default is freq(1)=0.0)

The conversion factor from Hartree to wave numbers is 219,474.6, and the wavelength is given (in nm) by 45.56/FREQ.

MAXITA = Maximum number of iterations for an alpha computation. (default=100)

MAXITU = Maximum number of iterations in the second order correction calculation. This applies to iterative beta values and all gammas. (default=100)

ATOL = Tolerance for convergence of first-order results. (default=1.0d-05)

BTOL = Tolerance for convergence of second-order results. (default=1.0d-05)

RETDHF = a flag to choose starting points for iterative calculations from best previous results. (default=.true.)

* * * the following NLO properties are available * * *

- BSHG = Calculate beta for second harmonic generation.
- BEOPE = Calculate beta for electrooptic Pockels effect.
- BOR = Calculate beta for optical rectification.
- GTHG = Calculate gamma for third harmonic generation.
- GEFISH = Calculate gamma for electric-field induced second harmonic generation.
- GIDRI = Calculate gamma for intensity dependent refractive index.
- GOKE = Calculate gamma for optical Kerr effect.

These will be computed only if a nonzero energy is requested. The default for each flag is .TRUE., and they may be turned off individually by setting some .FALSE. Note however that the program determines the best way to calculate them. For example, if you wish to have the SHG results but no gamma results are needed, the SHG beta will be computed in a non-iterative way from $\alpha(\omega)$ and $\alpha(2\omega)$. However if you request the computation of the THG gamma, the second order $U(\omega, \omega)$ results are needed and an iterative SHG calculation will be performed whether you request it or not, as it is a required intermediate.

Reference: S.P.Karna, M.Dupuis J.Comput.Chem. 12, 487-504 (1991).
P.Korambath, H.A.Kurtz, in "Nonlinear Optical Materials", ACS Symposium Series 628,
S.P.Karna and A.T.Yeates, Eds. pp 133-144, Washington DC, 1996 .
Review: D.P.Shelton, J.E.Rice, Chem.Rev. 94, 3-29(1994).

\$EFRAG**\$EFRAG group (optional)**

This group gives the name and position of one or more effective fragment potentials. It consists of a series of free format card images, which may not be combined onto a single line! The position of a fragment is defined by giving any three points within the fragment, relative to the ab initio system defined in \$DATA, since the effective fragments have a frozen internal geometry. All other atoms within the fragment are defined by information in the \$FRAGNAME group.

-1- a line containing one or more of these options:

COORD	=	CART	selects use of Cartesians coords to define the fragment position at line -3-. (default)
	=	INT	selects use of Z-matrix internal coordinates at line -3-.
POLMETHD=	SCF		indicates the induced dipole for each fragment due to the ab initio electric field and other fragment fields is updated only once during each SCF iteration.
	=	FRGSCF	requests microiterations during each SCF iteration to make induced dipoles due to ab initio and other fragment fields self consistent among the fragments. (Default)

Both methods converge to the same dipolar interaction.

POSITION	=	OPTIMIZE	Allows full optimization within the ab initio part, and optimization of the rotational and translational motions of each fragment. (default)
	=	FIXED	Allows full optimization of the ab initio system, but freezes the position of the fragments. This makes sense only with two or more fragments, as what is frozen is the fragments' relative orientation.
	=	EFOPT	the same as OPTIMIZE, but if the fragment gradient is large, up to 5 geometry steps in which only the fragments move may occur, before the geometry of the ab initio piece is relaxed. This may save time by reusing the two electron integrals for the ab initio system.

NBUFFMO	=	n	First n orbitals in the MO matrix are deemed to belong to the QM/MM buffer and will be excluded from the interaction with the EFP region. This makes sense only if these first MOs are frozen via the \$MOFRZ group.
---------	---	---	--

Input a blank line if all the defaults are acceptable.

-2- FRAGNAME=XXX

XXX is the name of the fragment whose coordinates are to be given next. All other information defining the fragment is given in a supplemental \$XXX group, which is referred to below as a \$FRAGNAME group.

A RHF/DZP EFP for water is internally stored in GAMESS. Choose FRAGNAME=H2OEF2 to

look up this numerical data, and then skip the input of \$H2OEF2 and \$FRGRPL groups.

-3- NAME, X, Y, Z (COORD=CART)
NAME, I, DISTANCE, J, BEND, K, TORSION (COORD=INT)

NAME = the name of a fragment point. The name used here must match one of the points in \$FRAGNAME.

X, Y, Z = Cartesian coordinates defining the position of this fragment point RELATIVE TO THE COORDINATE ORIGIN used in \$DATA. The choice of units is controlled by UNITS in \$CONTRL.

I, DISTANCE, J, BEND, K, TORSION = the usual Z-matrix connectivity internal coordinate definition. The atoms I, J, K must be atoms in the ab initio system from in \$DATA, or fragment points already defined in the current fragment or previously defined fragments.

Line -3- must be given a total of three times to define this fragment's position.

Repeat lines -2- and -3- to enter as many fragments as you desire, and then end the group with a \$END line.

Note that it is quite typical to repeat the same fragment name at line -2-, to use the same fragment system at many different positions.

* * * * *

For tips on effective fragment potentials
see the 'further information' section

* * * * *

\$FRAGNAME

\$FRAGNAME group (required for each FRAGNAME given in \$EFRAG)

This group gives all pertinent information for a given effective fragment potential (EFP). This information falls into three categories:
 electrostatic (distributed multipoles, screening)
 distributed polarizabilities
 exchange repulsion

It is input using several different subgroups, which should be given in the order shown below. Each subgroup is specified by a particular name, and is terminated by the word STOP. You may omit any of the subgroups to omit that term from the EFP. All values are given in atomic units.

To input monopoles,	follow input sequence -EM-
To input dipoles,	follow input sequence -ED-
To input quadrupoles,	follow input sequence -EQ-
To input octupoles,	follow input sequence -EO-
To input screening parameters,	follow input sequence -ES-
To input polarizable points,	follow input sequence -P-
To input repulsive points,	follow input sequence -R-

-1- a single descriptive title card

-2- COORDINATES

COORDINATES signals the start of the subgroup containing the multipolar expansion terms (charges, dipoles, ...). Optionally, one can also give the coordinates of the polarizable points, or centers of exchange repulsion.

-3- NAME, X, Y, Z, WEIGHT, ZNUC

NAME is a unique string identifying the point. X, Y, Z are the Cartesian coordinates of the point. WEIGHT and ZNUC are the atomic mass and nuclear charge, and are given only for the points which are nuclei.

Typically the true nuclei will appear twice, once for defining the positive nuclear charge and its screening, and a second time for defining the electronic distributed multipoles.

Repeat line -3- for each expansion point, and terminate the list with a "STOP".

-EM1- MONOPOLES

MONOPOLES signals the start of the subgroup containing the electronic and nuclear monopoles.

-EM2- NAME, CHARGE

NAME must match one given in the COORDINATES subgroup. CHARGE = nuclear or electronic monopole at this point.

Repeat -EM2- to define all desired charges. Terminate this subgroup with a "STOP".

-ED1- DIPOLES

DIPOLES signals the start of the subgroup containing the dipolar part of the multipolar expansion.

-ED2- NAME, MUX, MUY, MUZ

NAME must match one given in the COORDINATES subgroup. MUX, MUY, MUZ are the components of the electronic dipole.

Repeat -ED2- to define all desired dipoles.
Terminate this subgroup with a "STOP".

-EQ1- QUADRUPOLES

QUADRUPOLES signals the start of the subgroup containing the quadrupolar part of the multipolar expansion.

-EQ2- NAME, XX, YY, ZZ, XY, XZ, YZ

NAME must match one given in the COORDINATES subgroup. XX, YY, ZZ, XY, XZ, and YZ are the components of the electronic quadrupole moment.

Repeat -EQ2- to define all desired quadrupoles.
Terminate this subgroup with a "STOP".

-EO1- OCTUPOLES

OCTUPOLES signals the start of the subgroup containing the octupolar part of the multipolar expansion.

-EO2- NAME, XXX, YYY, ZZZ, XXY, XXZ, XYY, YYZ, XZZ, YZZ, XYZ

NAME must match one given in the COORDINATES subgroup. XXX, ... are the components of the electronic octupole.

Repeat -EO2- to define all desired octupoles.
Terminate this subgroup with a "STOP".

-ES1- SCREEN

SCREEN signals the start of the subgroup containing the screening terms ($A \cdot \exp[-B \cdot r^2]$) for the distributed multipoles, which account for charge penetration effects.

-ES2- NAME, A, B

NAME must match one given in the COORDINATES subgroup. A, B are the parameters of the Gaussian screening term.

\$FRAGNAME

Repeat -ES2- to define all desired screening points.
 Terminate this subgroup with a "STOP".

-P1- POLARIZABLE POINTS

POLARIZABLE POINTS signals the start of the subgroup containing the distributed polarizability tensors, and their coordinates.

-P2- NAME, X, Y, Z

NAME gives a unique identifier to the location of this polarizability tensor. It might match one of the points already defined in the COORDINATES subgroup, but often does not. Typically the distributed polarizability tensors are located at the centroids of localized MOs.

X, Y, Z are the coordinates of the polarizability point. They should be omitted if NAME did appear in COORDINATES. The units are controlled by UNITS= in \$CONTRL.

-P3- XX, YY, ZZ, XY, XZ, YZ, YX, ZX, ZY

XX, ... are components of the distributed polarizability, which is not a symmetric tensor. XY means $d\mu_x/dF_y$, where μ_x is a dipole component, and F_y is a component of an applied field.

Repeat -P2- and -P3- to define all desired polarizability tensors, and terminate this subgroup with a "STOP".

-R1- REPULSIVE POTENTIAL

REPULSIVE POTENTIAL signals the start of the subgroup containing the fitted exchange repulsion potential, for the interaction between the fragment and the ab initio part of the system. This term also accounts for charge transfer effects. The term has the form

$$\sum_{i=1}^N C_i \exp[-D_i r_i^2]$$

-R2- NAME, X, Y, Z, N

NAME may match one given in the COORDINATES subgroup, but need not. If NAME does not match one of the known points, you must give its coordinates X, Y, and Z, otherwise omit these three values. N is the total number of terms in the fitted repulsive potential.

-R3- C, D

These two values define the i-th term in the repulsive potential. Repeat line -R3- for all N terms.

Repeat -R2- and -R3- to define all desired repulsive potentials, and terminate this subgroup with a "STOP".

The entire \$FRAGNAME group is terminated by a " \$END".

\$FRGRPL group

This group defines the inter-fragment repulsive potential, which consists primarily of exchange repulsions but also includes charge transfer. Note that the functional form used for the fragment-fragment repulsion differs from that used for the ab initio-fragment repulsion, which is defined in the \$FRAGNAME group. The form of the potential is

$$\sum_i^N A_i \exp[-B_i r]$$

-1- PAIR=FRAG1 FRAG2

specifies which two fragment repulsions are being defined. \$FRAGNAME input for the two names FRAG1 and FRAG2 must have been given.

-2- NAME1 NAME2 A B

* or *

NAME1 NAME2 'EQ' NAME3 NAME4

NAME1 must be one of the "NAME" points defined in the \$FRAG1 group's COORDINATE section. Similarly NAME2 must be a point from the \$FRAG2 group. In addition, NAME1 or NAME2 could be the keyword CENTER, indicating the center of mass of the fragment.

A and B are the parameters of the fitted repulsive potential.

The second form of the input allows equal potential fits to be used. The syntax implies that the potential between the points NAME1 and NAME2 should be taken the same as the potential previously given in this group for the pair of points NAME3 and NAME4.

If there are NPT1 points in FRAG1, and NPT2 points in FRAG2, input line -2- should be repeated NPT1*NPT2 times. Terminate the pairs of potentials with a "STOP" card. Any pairs which you omit will be set to zero interaction.

Typically the number of points on which fitted potentials might be taken to be all the nuclei in a fragment, plus the center of mass.

Repeat lines -1- and -2- for all pairs of fragments, then terminate the group with a \$END line.

\$PCM group (optional)

This group controls solvent effect computations using the Polarizable Continuum Method. If this group is found in the input file, a PCM computation is performed. The default calculation, chosen by selecting only the SOLVNT keyword, is to compute the electrostatic free energy. Appropriate numerical constants are provided for a wide range of solvents. Additional keywords allow for more sophisticated computations, namely cavitation, repulsion, and dispersion free energies. The methodology for these is general, but only numerical constants for water are provided. There is additional information on PCM in the References chapter of this manual.

--- the first set of parameters controls the computation:

ICOMP, ICAV, IDISP, IREP, IDP, and IFIELD.

ICOMP = Renormalization procedure for induced charges.
 Gradient runs require ICOMP be 0 or 2 only.
 = 0 No.
 = 1 Yes, each charge is corrected in proportion to the area of the tessera to which it belongs.
 = 2 Yes, using the same factor for all tesserae. (default)
 = 3 Yes, with explicit consideration of the portion of solute electronic charge outside the cavity, by the method of Mennucci and Tomasi. See the \$NEWCAV group.

ICAV = At the end of the run, calculate the cavitation energy, by the method of Pierotti and Claverie:
 = 0 skip the computation (default)
 = 1 perform the computation.

If ICAV=1, the following parameter is relevant:

TABS = the absolute temperature, in units K. (default=298.0)

There are two procedures for the calculation of the repulsion and dispersion free energy. IDISP is incompatible with IREP and IDP.

IDISP = Calculation of both dispersion and repulsion free energy through the empirical method of Floris and Tomasi.
 = 0 skip the computation (default)
 = 1 perform the computation. See \$DISREP group.

The next two options add repulsive and dispersive terms to the solute hamiltonian, in an ab initio manner, by the method of Amovilli and Mennucci.

IREP = Calculation of repulsion free energy
 = 0 skip the computation (default)
 = 1 perform the computation. See \$NEWCAV group.

IDP = Calculation of dispersion free energy
 = 0 skip the computation (default)
 = 1 perform the computation. See \$DISBS group.

If IDP=1, then three additional parameters must be defined. The two solvent values correspond to water, and therefore these must be input for other solvents.

- WA = solute average transition energy. This is computed from the orbital energies for RHF, but must be input for MCSCF runs. (default=1.10)
- WB = ionization potential of solvent, in Hartrees. (default=0.451)
- ETA2 = square of the zero frequency refractive index of the solvent. (default=1.75)
- IFIELD = At run end, calculate the electric potential and electric field generated by the apparent surface charges.
 = 0 skip the computation (default)
 = 1 on nuclei
 = 2 on a planar grid

If IFIELD=2, the following data must be input:

- AXYZ,BXYZ,CXYZ = each defines three components of the vertices of the plane where the reaction field is to be computed (in Angstroms)
 A ==> higher left corner of the grid
 B ==> lower left corner of the grid
 C ==> higher right corner of the grid
- NAB = vertical subdivision (A--B edge) of the grid
- NAC = horizontal subdivision (A--C edge) of the grid.
- IPRINT = 0 normal printing (default)
 = 1 turns on debugging printout

--- the next group of keywords defines the solvent

- SOLVNT = keyword naming the solvent of choice. The eight numerical constants defining the solvent are internally stored for the following:
- WATER (or H2O)
 - CH3OH
 - C2H5OH
 - CLFORM (or CHCl3)
 - METHYCL (or CH2Cl2)
 - 12DCLET (or C2H4Cl2)
 - CTCL (or CCl4)
 - BENZENE (or C6H6)
 - TOLUENE (or C6H5CH3)
 - CLBENZ (or C6H5Cl)
 - NITMET (or CH3NO2)
 - NEPTANE (or C7H16)
 - CYCHEX (or C6H12)
 - ANILINE (or C6H5NH2)
 - ACETONE (or CH3COCH3)
 - THF
 - DMSO (or DMETSOX)

\$PCM

The default solvent name is

INPUT

which indicates you will specify your solvent by giving the following 8 numerical values:

- RSOLV = the solvent radius, in units Angstrom
 EPS = the dielectric constant
 EPSINF = the dielectric constant at infinite frequency.
 This value must be given only for RUNTYP=TDHF, if the external field frequency is in the optical range and the solvent is polar; in this case the solvent response is described by the electronic part of its polarization. Hence the value of the dielectric constant to be used is that evaluated at infinite frequency, not the static one (EPS). For nonpolar solvents, the difference between the two is almost negligible.
- TCE = the thermal expansion coefficient, in units 1/K
 VMOL = the molar volume, in units ml/mole
 STEN = the surface tension, in units dyne/cm
 DSTEN = the thermal coefficient of log(STEN)
 CMF = the cavity microscopic coefficient

Values for TCE, VMOL, STEN, DSTEN, CMF need to be given only for the case ICAV=1. Input of any or all of these values will override the internally stored value.

--- the next set of keywords defines the molecular cavity

- NESFP = the number of initial spheres. (default = number of atoms in solute molecule)
- ICENT = option for definition of initial spheres.
 = 0 centers spheres on each nucleus. (default)
 = 1 sphere centers XE, YE, ZE and radii RIN will be specified explicitly in \$PCMCAV.

The cavity generation algorithm may use additional spheres to smooth out sharp grooves, etc. The following parameters control how many extra spheres are generated:

- OMEGA and FRO = GEPOL parameters for the creation of the 'added spheres' defining the solvent accessible surface. When an excessive number of spheres is created, which may cause problems of convergence, the value of OMEGA and/or FRO must be increased. For example, OMEGA from 40 to 50 ... up to 90, FRO from 0.2 ... up to 0.7. (defaults are OMEGA=40.0, FRO=0.7)
- RET = minimum radius (in A) of the added spheres. Increasing RET decreases the number of added spheres. A value of 100.0 inhibits the addition of spheres. (default=0.2)

\$PCMCAV group (optional)

This group controls generation of the cavity holding the solute during Polarizable Continuum Method runs. The cavity is a union of spheres, according to ICENT and associated input values given in \$PCM. The data given here must be given in Angstrom units.

XE,YE,ZE = arrays giving the coordinates of the spheres.
 if ICENT=0, the atomic positions will be used.
 if ICENT=1, you must supply NESFP values here.

RIN = an array giving the sphere radii.
 if ICENT=0, the program will look up the internally stored van der Waals radius for: H,He, B,C,N,O,F,Ne, Na,Al,Si,P,S,Cl,Ar, K,As,Se,Br,Kr, Rb,Sb,Te,I, Cs,Bi
 Data for other elements is not tabulated.
 if ICENT=1, give NESFP values.

ALPHA = an array of scaling factors, for the definition of the solvent accessible surface. If only the first value is given, all radii are scaled by the same factor. (default is ALPHA(1)=1.2)

Example: Suppose the 4th atom in your molecule is Fe, but all other atoms have van der Waals radii. You decide a good guess for Fe is twice the covalent radius:
 \$PCMCAV RIN(4)=2.33 \$END

The source for the van der Waals radii is "The Elements", 2nd Ed., John Emsley, Clarendon Press, Oxford, 1991, except that for C,N,O, the U.Pisa's experience with the best radii for PCM treatment of singly bonded C,N,O atoms is used instead. The radii for a few transition metals are given by A.Bondi, J.Phys.Chem. 68, 441-451 (1968).

\$NEWCAV, \$DISBS**\$NEWCAV group**

(optional)

This group controls generation of the "escaped charge" cavity, used when ICOMP=3 or IREP=1 in \$PCM. This cavity is used only to calculate the fraction of the solute electronic charge escapes from the original cavity.

IPTYPE = choice for tessellation of the cavity's spheres.
 = 1 uses a tetrahedron
 = 2 uses a pentakisdodecahedron (default)

ITSNUM = m, the number of tessera to use on each sphere.
 if IPTYPE=1, input $m=30*(n**2)$, with n=1,2,3 or 4
 if IPTYPE=2, input $m=60*(n**2)$, with n=1,2,3 or 4
 (default is 60)

*** the next three parameters pertain to IREP=1 ***

RHOW = density, relative to liquid water (default = 1.0)

PM = molecular weight (default = 18.0)

NEVAL = number of valence electrons on solute (default=8)

The defaults for RHOW, PM, and NEVAL correspond to water, and therefore must be correctly input for other solvents.

\$DISBS group

(optional)

This group defines auxiliary basis functions used to evaluate the dispersion free energy by the method of Amovilli and Mennucci. These functions are used only for the dispersion calculation, and thus have nothing to do with the normal basis given in \$BASIS or \$DATA. If the input group is omitted, only the normal basis is used for the IDP=1 dispersion energy.

NADD = the number of added shells

XYZE = an array giving the x,y,z coordinates (in bohr) of the center, and exponent of the added shell, for each of the NADD shells.

NKTYPE = an array giving the angular momenta of the shells

An example placing 2s,2p,2d,1f on one particular atom,

```

SDISBS  NADD=7  NKTYP(1)= 0 0 1 1 2 2 3
          XYZE(1)=2. 9281086  0.0  .0001726  0.2
          2. 9281086  0.0  .0001726  0.05
          2. 9281086  0.0  .0001726  0.2
          2. 9281086  0.0  .0001726  0.05
          2. 9281086  0.0  .0001726  0.75
          2. 9281086  0.0  .0001726  0.2
          2. 9281086  0.0  .0001726  0.2  SEND

```

\$DISREP group (optional)

This group controls evaluation of the dispersion and repulsion energies by the empirical method of Floris and Tomasi. The group must be given with IDISP=1 in \$PCM. The two options are controlled by ICLAV and ILJ, only one of which should be selected.

- ICLAV = selects Claverie's disp-rep formalism.
 = 0 skip computation.
 = 1 Compute the solute-solvent disp-rep interaction as a sum over atom-atom interactions through a Buckingham-type formula (R^{-6} for dispersion, exp for repulsion). (Default) Ref: Pertsin-Kitaigorodsky "The atom-atom potential method", page 146.
- ILJ = selects a Lennard-Jones formalism.
 = 0 skip computation. (default)
 = 1 solute atom's-solvent molecule interaction is modeled by Lennard-Jones type potentials, R^{-6} for dispersion, R^{-12} for repulsion).

---- the following data must given for ICLAV=1:

- RHO = solvent numeral density
 N = number of atom types in the solvent molecule
 NT = an array of the number of atoms of each type in a solvent molecule
 RDIFF = distances between the first atoms of each type and the cavity
 DK,RW = parameters of atom-atom interactions

The defaults are chosen for water,

RHO=3.348D-02
 N=2
 NT(1)=2,1
 RDIFF(1)=1.20,1.50
 DKT(1)=1.0,1.36
 RWT(1)=1.2,1.5

---- the following data must given for ILJ=1:

- RHO = solvent numeral density
 EPSI = an array of energy constants referred to each atom of the solute molecule.
 SIGMA = an array of typical distances, relative to each solute atom

\$COSGMS group (optional)

The presence of this group in the input turns on the use of the conductor-like screening model with molecular shaped cavity for RHF and closed shell MP2. For RHF, the energy and gradient can be computed, while MP2 is limited to the energy only.

EPSI = the dielectric constant, 80 is often used for H₂O This parameter must be given.

RSOLV = the multiplicative factor for the van der Waals radius used for cavity construction. (default=1.2)

NSPA = the number of surface points on each atomic sphere that form the cavity. (default=92)

Additional information on the COSMO model can be found in the References chapter of this manual.

\$SCRF group (optional)

The presence of this group in the input turns on the use of the Kirkwood-Onsager spherical cavity model for the study of solvent effects. The method is implemented for RHF, UHF, ROHF, GVB and MCSCF wavefunctions and gradients, and so can be used with any RUNTYP involving the gradient. The method is not implemented for MP2, CI, any of the semiempirical models, or for analytic Hessians.

DIELEC = the dielectric constant, 80 is often used for H₂O

RADIUS = the spherical cavity radius, in Angstroms

G = the proportionality constant relating the solute molecule's dipole to the strength of the reaction field. Since G can be calculated from DIELEC and RADIUS, do not give G if they were given.

Additional information on the SCRF model can be found in the References chapter of this manual.

\$ECP group (required if ECP=READ in \$CONTRL)

This group lets you read in effective core potentials, for some or all of the atoms in the molecule. You can use built in potentials for some of the atoms if you like. This is a free format (positional) input group.

*** Give a card set -1-, -2-, and -3- for each atom ***

-card 1- PNAME, PTYPE, IZCORE, LMAX+1

PNAME is a 8 character descriptive tag for this potential. If it is repeated for a subsequent atom, no other information need be given on this card, and cards -2- and -3- may also be skipped. The information will be copied from the first atom by this PNAME. Do not use the option to repeat the previously read ECP for an atom with PTYPE=NONE, instead type "none".

PTYPE = GEN a general potential should be read.
 = SBKJC look up the Stevens/Basch/Krauss/Jasien/ Cundari potential for this type of atom.
 = HW look up the Hay/Wadt built in potential for this type of atom.
 = NONE treat all electrons on this atom.

IZCORE is the number of core electrons to be removed.

LMAX is the maximum angular momentum occupied in the core orbitals being removed (usually). Give IZCORE and LMAX only if PTYPE is GEN.

*** For the first occurrence of PNAME, if PTYPE is GEN, ***
 *** then give cards -2- and -3-. Otherwise go to -1-. ***

*** Card sets -2- and -3- are repeated LMAX+1 times ***

The potential $U(LMAX+1)$ is given first, followed by $U(L)-U(LMAX+1)$, for $L=1,LMAX$.

-card 2- NGPOT

NGPOT is the number of Gaussians in this part of the local effective potential.

-card 3- CLP,NLP,ZLP (repeat this card NGPOT times)

CLP is the coefficient of this Gaussian in the potential.

NLP is the power of r for this Gaussian.

ZLP is the exponent of this Gaussian.

By far the easiest way to use the SBKJC potential for all atoms in the formic acid molecule is to request ECP=SBKJC in \$CONTRL. But the next page shows two alternatives.

The first way is to look up the program's internally stored SBKJC potentials one atom at a time:

```
$ECP
C-ECP SBKJC
H-ECP NONE
O-ECP SBKJC
O-ECP
H-ECP NONE
SEND
```

The second oxygen duplicates the first, no core electrons are removed for hydrogen. The order of the atoms must follow that generated by \$DATA. Note PTYPE allows you to type in one or more atoms explicitly, while using built in data for some other atoms.

The second example reads all SBKJC potentials explicitly:

```
$ECP
C-ECP GEN 2 1
1      ----- CARBON U(P) -----
-0. 89371  1  8. 56468
2      ----- CARBON U(S)-U(P) -----
1. 92926  0  2. 81497
14. 88199  2  8. 11296
H-ECP NONE
O-ECP GEN 2 1
1      ----- OXYGEN U(P) -----
-0. 92550  1 16. 11718
2      ----- OXYGEN U(S)-U(P) -----
1. 96069  0  5. 05348
29. 13442  2 15. 95333
O-ECP
H-ECP NONE
SEND
```

Again, the 2nd oxygen copies from the first. It is handy to use the rest of card - 2- as a descriptive comment.

As a final example, for antimony we have LMAX+1=3 (there are core d's). One must first enter U(f), followed by U(s)-U(f), U(p)-U(f), U(d)-U(f).

Caution:

At the present time, there are some numerical problems in the ECP code, which has been programed to use spdfig basis sets, and core potentials up to g. If one is using a g basis function, or a g potential (bottom row elements beyond the lanthanide series), there are small errors in the ECP integrals. A tight optimization (OPTTOL=1D-05) will usually result in the energy rising slightly during the last few geometry steps. The error seems to be about 0.000002 Hartree, so be cautious about using a g potential or basis function. When both are used in the same run, the error in the energy is about 0.0002, which means the use of both is too inaccurate to be trusted. The use of f functions or f potentials (or lower) seems to be free of any errors.

\$RELWFN group (optional)

This group is relevant if RELWFN in \$CONTRL chose the NESC or RESC option for elimination of small components from relativistic wavefunctions, to produce a corrected single component wavefunction. In case of RESC, only the one electron integral corrections are added, whereas for NESC, corrections to two electron integrals are accounted for by means of a relativistically averaged basis set.

For NESC, you must provide three basis sets, for the large and small components and an averaged one, which are given in \$DATAL, \$DATAS, \$DATA, respectively. The only possible choice for these basis sets is due to Dyal, and these are available from:

<http://www.emsl.pnl.gov:2080/forms/basisform.html>

Their names are similar to cc-pVnZ(pt/sf/lc), pt=point or fi=finite nucleus, sf for spin-free and the final field is lc=large component (\$DATAL), sc=small component (\$DATAS), and wf is a typo for Foldy-Wouthuysen 2e- basis (\$DATA). In GAMESS you can only use point nucleus approximation. The need to input three basis sets means that you cannot use a \$BASIS group, and you must use COORD=UNIQUE style input in the various \$DATA's. The three \$DATA groups must contain identical information except for the primitive expansion coefficients, as the three basis sets must have the same exponents. In case the option to treat only some atoms relativistically is chosen, all non-relativistic atoms must have identical basis input in all three groups.

For RESC, ordinary basis sets are used.

Analytic gradients are programmed for both RESC and NESC computations. For NESC, the one electron part of the spin-orbit operator can be corrected, while for RESC, one can compute spin-orbit coupling with relativistic corrections to both one and two electron SOC integrals.

NESOC = relativistic corrections to SOC integrals. Choose only if RELWFN=RESC or NESC, and if OPERAT=HSO1, HSO2P, or HSO2, for RUNTYP=TRANSITN
 = 0 no corrections
 = 1 one-electron spin-orbit integrals (NESC default)
 = 2 one and two-electron integrals (RESC default)

The remaining parameters pertain only to RELWFN=NESC:

NRATOM the number of different elements to be treated nonrelativistically. For example, in Pb3O4, to treat only lead relativistically, enter NRATOM=1. (default=0)

CHARGE array containing charges of atoms to be treated nonrelativistically. (e.g. CHARGE(1)=8.0, to drop all oxygen atoms)

\$EFIELD group (not required)

This group permits the study of the influence of an external electric field on the molecule. The method is general, and so works for all ab initio SCFTYPs.

EVEC = an array of the three x,y,z components of the applied electric field.

SYM = a flag to specify when the field to be applied breaks the molecular symmetry. Since most fields break symmetry, the default is .FALSE.

Restrictions: analytic Hessians are not available, but numerical Hessians are. Because an external field causes a molecule with a dipole to experience a torque, geometry optimizations must be done in Cartesian coordinates only. Internal coordinates eliminate the rotational degrees of freedom, which are no longer free.

Notes: a Hessian calculation will have two rotational modes with non-zero "frequency", caused by the torque. A gas phase molecule will rotate so that the dipole moment is anti-parallel to the applied field. To carry out this rotation during geometry optimization will take many steps, and you can help save much time by inputting a field opposite the molecular dipole. There is also a stationary point at higher energy with the dipole parallel to the field, which will have two imaginary frequencies in the Hessian. Careful, these will appear as the first two modes in a Hessian run, but will not have the *i* for imaginary included on the printout since they are rotational modes.

\$INTGRL group (optional)

This group controls AO integral formats. It should probably never be given, as the program always picks sensible values.

- SCHWRZ = a flag to activate use of the Schwarz inequality to predetermine small integrals. There is no loss of accuracy when choosing this option, and there are appreciable time savings for bigger molecules. Default=.TRUE. for over 5 atoms, or for direct SCF, and is .FALSE. otherwise.
- NOPK = 0 PK integral option on, which is permissible for RHF, UHF, ROHF, GVB energy/gradient runs.
 = 1 PK option off (default for all jobs). Must be off for anything with a transformation.
- NORDER = 0 (default)
 = 1 Sort integrals into canonical order. There is little point in selecting this option, as no part of GAMESS requires ordered integrals. See also NSQUAR.
- NINTMX = Maximum no. of integrals in a record block.
 (default=15000 for J or P file, =10000 for PK)

The following parameters control the integral sort. (values given are defaults)

- NSQUAR = 0 Sorted integrals will be in triangular canonical order (default)
 = 1 instead sort to square canonical order.
- NDAR = Number of direct access logical records to be used for the integral sort (default=2000)
- LDAR = Length of direct access records (site dependent)
- NBOXMX = 200 Maximum number of bins.
- NWORD = 0 Memory to be used (default=all of it).
- NOMEM = 0 If non-zero, force external sort.

The following parameters control integral restarts (values given are defaults)

IST= 1 JST= 1 KST= 1 LST= 1
 NREC= 1 INTLOC= 1

\$TRANS

\$TRANS group (optional for -CI- or -MCSCF-)
 (relevant to analytic Hessians)
 (relevant to energy localization)

This group controls the integral transformation. MP2 integral transformations are controlled instead by the \$MP2 input group. There is little reason to give any but the first variable.

DIRTRF = a flag to recompute AO integrals rather than storing them on disk. The default is .FALSE. for MCSCF and CI runs. If your job reads \$SCF, and you select DIRSCF=.TRUE. in that group, a direct transformation will be done, no matter how DIRTRF is set.

Note that the transformation may do many passes over the AO integrals for large basis sets, and thus the direct recomputation of AO integrals can be very time consuming.

MPTRAN = method to use for the integral transformation. the default is try 0, then 1, then 2.

0 means use the incore method

1 means use the segmented method. This is the only method that works in parallel.

2 means use the alternate method, which uses less memory than 2, but requires an extra large disk file.

NWORD = Number of words of fast memory to allow. Zero uses all available memory. (default=0)

CUTTRF = Threshold cutoff for keeping transformed two electron integrals. (default= 10**(-9))

AOINTS = defines AO integral storage during conventional integral transformations, during parallel runs.

DUP stores duplicated AO lists on each node, and is the default for parallel computers with slow interprocessor communication, e.g. ethernet.

DIST distributes the AO integral file across all nodes, and it is the default for parallel computers with high speed communications.

The remaining groups apply only to -CI- and -MCSCF- runs.

* * * * *

For hints on how to do -CI- and -MCSCF-
 see the 'further information' section

* * * * *

\$CIINP group (optional, relevant for CITYP=GUGA or ALDET)

This group is the control box for Graphical Unitary Group Approach (GUGA) CI calculations, or Ames Laboratory determinant (ALDET) full CI. Each step which is executed potentially requires a further input group described later.

NRNFG = An array of 10 switches controlling which steps of a CI computation are performed. 1 means execute the module, 0 means don't.

NRNFG(1)= Generate the configurations. See either \$CIDRT or \$CIDET input. (default=1)

NRNFG(2)= Transform the integrals. See \$TRANS. (default=1)

NRNFG(3)= Sort integrals and calculate the Hamiltonian matrix. See \$CISORT and \$GUGEM. (default=1) This does not apply to ALDET.

NRNFG(4)= Diagonalize the Hamiltonian matrix. See \$GUGDIA or \$CIDET. (default=1)

NRNFG(5)= Construct the one electron density matrix, and generate NO's. See \$GUGDM or \$CIDET. (default=1)

NRNFG(6)= Construct the two electron density matrix. See \$GUGDM2 or \$CIDET. (default=0 normally, but 1 for CI gradients)

NRNFG(7)= Construct the Lagrangian of the CI function. Requires DM2 matrix exists. See \$LAGRAN. (default=0 normally, but 1 for CI gradients) This does not apply to ALDET.

NRNFG(8-10) are not used.

Users are not encouraged to change these values, as the defaults are quite reasonable ones.

NPFLG = An array of 10 switches to produce debug printout. There is a one to one correspondence to NRNFG, set to 1 for output. (default = 0,0,0,0,0,0,0,0,0,0) The most interesting is NPFLG(2)=1 to see the transformed 1e- integrals, NPFLG(2)=2 adds the very numerous transformed 2e- integrals to this.

IREST = n Restart the -CI- at stage NRNFG(n).

\$DET/\$CIDET

\$DET group (required for SCFTYP=MCSCF if CISTEP=ALDET)
 \$CIDET group (required if CITYP=ALDET)

This group describes the determinants to be used in a full MCSCF active space, or full CI wavefunction.

Determinants contain several spin states, in contrast to configuration state functions. The Sz quantum number of each determinant is the same, but the Hamiltonian eigenvectors will have various spins $S=S_z, S_z+1, S_z+2, \dots$. In addition, the determinant CI code does not exploit the spatial symmetry of the orbitals, so the CI states will include not only various spin symmetries, but also all space symmetries. You may need to think about NSTATE!

There is no default for NCORE, NACT, and NELS:

NCORE = total number of orbitals doubly occupied in all determinants.

NACT = total number of active orbitals.

NELS = total number of active electrons.

SZ = azimuthal spin quantum number for each of the determinants, two times SZ is therefore the number of excess alpha spins in each determinant. The default is $SZ=S$, extracted from the $MULT=2S+1$ given in \$CONTRL.

* * * the following control the diagonalization * * *

NSTATE = Number of CI states to be found, the default is 1. The maximum number of states is 100.

PRTTOL = Printout tolerance for CI coefficients, the default is to print any larger than 0.05.

ITERMX = Maximum number of Davidson iterations per root. The default is 100.

CVGTOL = Convergence criterion for Davidson eigenvector routine. This value is proportional to the accuracy of the coefficients of the eigenvectors found. The energy accuracy is proportional to its square. The default is 1.0E-5.

NHGSS = dimension of the Hamiltonian submatrix which is diagonalized to obtain the initial guess eigenvectors. The determinants forming the submatrix are chosen on the basis of a low diagonal energy, or if needed to complete a spin eigenfunction. The default is 300.

NSTGSS = Number of eigenvectors from the initial guess Hamiltonian to be included in the Davidson's iterative scheme. It is seldom necessary to include extra states to obtain convergence to the desired states. The default is the value for NSTATE.

MXXPAN = Maximum number of expansion basis vectors in the iterative subspace during the Davidson iterations before the expansion basis is truncated. The default is the larger of 10 or NSTGSS+1. If this value is decreased, convergence is hurt but the memory required is decreased.

* * * the following control the 1st order density * * *

These are ignored during MCSCF, but are used during a CI.

- IROOT = the root whose density is saved on the disk file for subsequent property analysis. Only one root can be saved, and the default value of 1 means the ground state. Be sure to set NFLGDM to form the density of the state you are interested in!
- NFLGDM = Controls each state's density formation.
- 0 do not form density for this state.
 - 1 form density and natural orbitals for this state, print and punch occ.num.s. and NOs.
 - 2 same as 1, plus print density over MOs.
- The default is NFLGDM(1)=1,0,0,...,0 meaning only ground state NOs are generated.

* * * the following control the state averaged

* * * 1st and 2nd order density matrix computation

Usually ignored by CI runs, these are relevant to MCSCF.

- PURES = a flag controlling the spin purity of the state averaging. If true, the WSTATE array pertains to the lowest states of the same S value as is given by the MULT keyword in \$CONTRL. In this case the value of NSTATE will need to be bigger than the total number of weights given by WSTATE if there are other spin states present at low energies. If false, it is possible to state average over more than one S value, which might be of interest in spin-orbit coupling jobs. The default is .TRUE.
- WSTATE = An array of up to 100 weights to be given to the densities of each state in forming the average. The default is to optimize a pure ground state, WSTATE(1)=1.0,0.0,...,0.0 A small amount of the ground state can help the convergence of excited states greatly. Gradient runs are possible only with pure states. Be sure to set NSTATE above appropriately!

\$DRT/\$CIDRT

\$DRT group (required for SCFTYP=MCSCF if CISTEP=GUGA)
 \$CIDRT group (required for CITYP=GUGA)

This group describes the -MCSCF- or -CI- wavefunction. The distinct row table is the means by which the Graphical Unitary Group Approach (GUGA) names the configurations.

The group is spelled DRT for MCSCF runs, and CIDRT for CI runs. The main difference in these is NMCC vs. NFZC.

There is no default for GROUP, and you must choose one of FORS, FOCI, SOCI, or IEXCIT.

GROUP = the name of the point group to be used. This is usually the same as that in \$DATA, except for RUNTYP=HESSIAN, when it must be C1. Choose from the following: C1, C2, CI, CS, C2V, C2H, D2, D2H, C4V, D4, D4H. If your \$DATA group is not listed, choose only C1 here.

FORS = flag specifying the Full Optimized Reaction Space set of configuration should be generated. This is usually set true for MCSCF runs, but if it is not, see FORS in \$MCSCF. Default=.FALSE.

FOCI = flag specifying first order CI. In addition to the FORS configurations, all singly excited CSFs from the FORS reference are included. Default=.FALSE.

SOCI = flag specifying second order CI. In addition to the FORS configurations, all singly and doubly excited configurations from the FORS reference are included. Default=.FALSE.

IEXCIT = electron excitation level, for example 2 will lead to a singles and doubles CI. This variable is computed by the program if FORS, FOCI, or SOCI is chosen, otherwise it must be entered.

* * the next variables define the single reference * *

The single configuration reference is defined by filling in the orbitals by each type, in the order shown. The default for each type is 0.

Core orbitals, which are always doubly occupied:

NMCC = number of MCSCF core MOs (in \$DRT only).

NFZC = number of CI frozen core MOs (in \$CIDRT only).

Internal orbitals, which are partially occupied:

NDOC = number of doubly occupied MOs in the reference.

NAOS = number of alpha occupied MOs in the reference, which are singlet coupled with a corresponding number of NBOS orbitals.

NBOS = number of beta spin singly occupied MOs.

NALP = number of alpha spin singly occupied MOs in the reference, which are coupled high spin.

NVAL = number of empty MOs in the reference.

External orbitals, occupied only in FOCl or SOCl:
 NEXT = number of external MOs. If given as -1, this will be set to all remaining orbitals (apart from any frozen virtual orbitals).
 NFZV = number of frozen virtual MOs, never occupied.

* * the next two help with state symmetry * *
 ISTSYM = irreducible representation for GUGA wavefunction. This option overwrites whatever symmetry is implied by NALP/NAOS/NBOS. Default=0 means the symmetry of the reference configuration is to be used.

ISTSYM=	1	2	3	4	5	6	7	8
C1	A							
Ci	Ag	Au						
Cs	A'	A''						
C2	A	B						
C2v	A1	A2	B1	B2				
C2h	Ag	Bu	Bg	Au	<- differs from \$MCQDPT!			
D2	A	B1	B2	B3				
D2h	Ag	B1g	B2g	B3g	Au	B1u	B2u	B3u

NOIRR = controls labelling of the CI state symmetries.
 = 1 no labelling (default)
 = Ousual labelling. This can be very time consuming if the group is non-Abelian.
 = -1 fast labelling, in which all CSFs with small CI coefficients are ignored. This can produce weights quite different from one, due to ignoring the small coefficients, but overall seems to work OK. Note that it is normal for the weights not to sum to 1 even for NOIRR=0 because for simplicity the weight determination is focused on the relative weights rather than absolute. However weight do not sum to one only for row-mixed MOs.
 = -2,-3... fast labelling and sets SYMTOL=10**NOIRR for runs other than TRANSITN. All irreps with weights greater than SYMTOL are considered.

* * * the final choices are seldom used * * *

INTACT = flag to select the interacting space option. The CI will include only those spin couplings which have a nonvanishing matrix element with the reference configuration.

MXNINT = Buffer size for sorted integrals. (default=20000)

MXNEME = Buffer size for energy matrix. (default=10000)

NPRT = Configuration printout control switch.
 This can consume a HUMUNGUS amount of paper!
 0 no print (default)
 1 print electron occupancies, one per line.
 2 print determinants in each CSF.
 3 print determinants in each CSF (for Ms=S-1).

\$MCSCF group (optional for -MCSCF-)

This group controls the MCSCF orbital optimization step. The difference between the four convergence methods is outlined in Chapter Four of this manual, which you must carefully study before attempting MCSCF computations.

--- the next choose the configuration basis ---

- CISTEP = ALDET chooses the Ames Lab. determinant CI, and requires \$DET input. (default)
 = GUGA chooses the graphical unitary group CSFs, and requires \$DRT input. This is the only value usable with the QUAD converger.

--- the next four choose the orbital optimizer ---

- FOCAS = a flag to select a method with a first order convergence rate. (default=.FALSE.)
 SOSCF = a flag selecting an approximately second order convergence method. (default=.TRUE.)
 FULLNR = a flag selecting a second order method, with an exact orbital hessian. (default=.FALSE.)
 QUAD = a flag to pick a fully quadratic (orbital and CI coefficient) optimization method, which is applicable to FORS or non-FORS wavefunctions. QUAD may not be used with state-averaging. (default = .FALSE.)

Note that FOCAS must be used only with FORS=.TRUE. in \$DRT. The other convergers are usable for either FORS or non-FORS wavefunctions, although convergence is always harder in the latter case, when FORS below must be set .FALSE.

--- the next apply to all convergence methods ---

- FORS = a flag to specify that the MCSCF function is of the Full Optimized Reaction Space type, which is sometimes known as CAS-SCF. .TRUE. means omit act-act rotations from the optimization. Since convergence is usually better for FULLNR with these rotations included, the default is sensible for the case FORS=.TRUE. in \$DRT. (default is .TRUE. for FOCAS/SOSCF, .FALSE. for FULLNR/QUAD)
 ACURCY = the major convergence criterion, the maximum permissible asymmetry in the Lagrangian matrix. (default=1.0E-05)
 ENGTOL = a secondary convergence criterion, the run is considered converged when the energy change is smaller than this value. (default=1.0E-10)
 MAXIT = Maximum number of iterations (default=100 for FOCAS, 60 for SOSCF, 30 for FULLNR or QUAD)
 MICIT = Maximum number of microiterations within a single MCSCF iteration. (default=5 for FOCAS or SOSCF, or 1 for FULLNR or QUAD)

-
- NWORD = The maximum memory to be used, the default is to use all available memory. (default=0)
- CANONC = a flag to cause formation of the closed shell Fock operator, and generation of canonical core orbitals. This will order the MCC core by their orbital energies. (default=.TRUE.)
- EKT = a flag to cause generation of extended Koopmans' theorem orbitals and energies. (Default=.FALSE.)
 For this option, see R.C.Morrison and G.Liu, J.Comput.Chem., 13, 1004-1010 (1992). Note that the process generates non-orthogonal orbitals, as well as physically unrealistic energies for the weakly occupied MCSCF orbitals. The method is meant to produce a good value for the first I.P.
- NPUNCH = MCSCF punch option (analogous to \$SCF NPUNCH)
 = 0 do not punch out the final orbitals
 = 1 punch out the occupied orbitals
 = 2 punch out occupied and virtual orbitals
 The default is NPUNCH = 2.
- NPFLG = an array of debug print control. This is analogous to the same variable in \$CIINP. Elements 1,2,3,4,6,8 make sense, the latter controls debugging the orbital optimization.
- the next refers to SOSCF optimizations ---
- NOFO = set to 1 to skip use of FOCAS for one iteration during SOSCF. This is a testing parameter, at present NOFO defaults to 0 to do one FOCAS iter.
- the next three refer to FOCAS optimizations ---
- CASDII = threshold to start DIIS (default=0.05)
- CASHFT = level shift value (default=1.0)
- NRMCAS = renormalization flag, 1 means do Fock matrix renormalization, 0 skips (default=1)
- the next applies to the QUAD method ---
 (note that FULLNR input is also relevant)
- QUATHR = threshold on the orbital rotation parameter, SQCDF, to switch from the initial FULLNR iterations to the fully quadratic method. (default = 0.05)
- all remaining input applies only to FULLNR ---
- DAMP = damping factor, this is adjusted by the program as necessary. (default=0.0)
- METHOD = DM2 DM2 selects a density driven construction of the Newton-Raphson matrices. (default).
 = TEI selects 2e- integral driven NR construction.

See the 'further information' section for more details concerning these methods. TEI is slow!

LINSER = a flag to activate a method similar to direct minimization of SCF. The method is used if the energy rises between iterations. It may in some circumstances increase the chance of converging excited states. (default=.FALSE.)

FCORE = a flag to freeze optimization of the MCC core orbitals, which is useful in preparation for RUNTYP=TRANSITN jobs. Setting this flag will automatically force CANONC false. This option is incompatible with gradients, so can only be used with RUNTYP=ENERGY. (default=.FALSE.)

--- the next four are seldom used ---

DROPC = a flag to include MCC core orbitals during the CI computation. The default is to drop them during the CI, instead forming Fock operators which are used to build the correct terms in the orbital hessian. (default = .TRUE.)

NORB = the number of orbitals to be included in the optimization, the default is to optimize with respect to the entire basis. This option is incompatible with gradients, so can only be used with RUNTYP=ENERGY. (default=number of AOs given in \$DATA).

MOFRZ = an array of orbitals to be frozen out of the orbital optimization step (default=none frozen).

NOROT = an array of up to 250 pairs of orbital rotations to be omitted from the NR optimization process. The program automatically deletes all core-core rotations, all act-act rotations if FORS=.T., and all core-act and core-virt rotations if FCORE=.T. Additional rotations are input as I1,J1,I2,J2... to exclude rotations between orbital I running from 1 to NORB, and J running up to the smaller of I or NVAL in \$TRANS.

\$MCQDPT group (relevant to SCFTYP=MCSCF if MPLEVEL=2)

Controls 2nd order MCQDPT (multiconfiguration quasi- degenerate perturbation theory) runs, if requested by MPLEVEL=2 in \$CONTRL. MCQDPT2 is implemented only for FORS (aka CASSCF) wavefunctions. The MCQDPT method is a multistate, as well as multireference perturbation theory. The implementation is a separate program, interfaced to GAMESS, with its own procedures for determination of the canonical MOs, CSF generation, integral transformation, CI in the reference CAS, etc. Therefore some of the input in this group repeats data given elsewhere, particularly the \$DET/\$DRT. A more complete discussion may be found in the 'Further Information' chapter. Analytic gradients are not available.

*** MCSCF reference wavefunction ***

NEL = total number of electrons, including core. (default from \$DATA and ICHARG in \$CONTRL)

MULT = spin multiplicity (default from \$CONTRL)

NMOACT = Number of orbitals in FORS active space (default is the active space in \$DET or \$DRT)

NMOFZC = number of frozen core orbitals, NOT correlated in the perturbation calculation. (default is number of chemical cores)

NMODOC = number of orbitals which are doubly occupied in every MCSCF configuration, that is, not active orbitals, which are to be included in the perturbation calculation. (The default is all valence orbitals between the chemical core and the active space)

NMOFZV = number of frozen virtuals, NOT occupied during the perturbation calculation. The default is to use all virtuals in the MP2. (Default=0)

NOSYM = 0 use CSF symmetry (see the ISTSYM keyword). off diagonal perturbations vanish if states are of different symmetry, so the most efficient computation is a separate run for every space symmetry. (default)

1 turn off CSF state symmetry so that all states are treated at once. ISTSYM is ignored.

ISTSYM = the state symmetry of the target state(s).
This is given as an integer, note that only Abelian groups in \$DATA are supported:

ISTSYM=	1	2	3	4	5	6	7	8
C1	A							
Ci	Ag	Au						
Cs	A'	A''						
C2	A	B						
C2v	A1	A2	B1	B2				
C2h	Ag	Bg	Au	Bu	-< differs from \$DRT!			
D2	A	B1	B2	B3				
D2h	Ag	B1g	B2g	B3g	Au	B1u	B2u	B3u

(The default is 1, the totally symmetric state)

*** perturbation specification ***

KSTATE = state is used (1) or not (0) in the MCQDPT2. Maximum of 20 elements, including zeros. For example, if you want the perturbation correction to the second and the fourth roots, KSTATE(1)=0,1,0,1 (default=1,0,0,0,0,0,0,...)

*** MO input and flow control ***

INORB = 0 optimize the MCSCF wavefunction in this run.
 = 1 read the converged orbitals from a \$VEC group, and skip immediately to the MCQDPT computation. A complete \$VEC including virtuals must be given. (default=0)

*** Canonical Fock orbitals ***

IFORB = 1 determine the canonical Fock orbitals
 = 0 omit this step. (default=1)
 AVECOE = weight of each CAS-CI state in computing the closed shell Fock matrix. (default is AVECOE(1)=1.0,1.0,1.0,...)

*** Miscellaneous options ***

REFWGT = a flag to request decomposition of the second order energy into internal, semi-internal, and external contributions, and to obtain the weight of the MCSCF reference in the 1st order wave function. This option significantly increases the run time! (default = .FALSE.)

THRGEN = threshold for one-, two-, and three-body density matrix elements in the perturbation calculation. If you want to obtain energies for instance, to 6 figures after point, choose THRGEN=1.0D-08 or 1.0D-09. (default=1.0D-08)

THRENE = threshold for the energy convergence in the Davidson's method CAS-CI. (default=-1.0D+00)

THRCON = threshold for the vector convergence in the Davidson's method CAS-CI. (default=1.0D-06)

LPOUT = print option, 0 gives normal printout, while <0 gives debug print (e.g. -1,-5,-10,-100) (default=0)

Finally, there are additional very specialized input options, described in the source code routine MQREAD:

IROT, ISELCT, LENGTH, MAXCSF, MAXERI, MAXROW, MDI, MXBASE, MXTRFR, NSOLUT, NSTOP, THRERI, THRWGT, MAINCS, NSTATE.

\$CISORT group (optional, relevant for -CI- and -MCSCF-)

This group provides further control over the sorting of the transformed integrals.

- NDAR = Number of direct access records. (default = 2000)
- LDAR = Length of direct access record (site dependent)
- NBOXMX = Maximum number of boxes in the sort. (default = 200)
- NWORD = Number of words of fast memory to use in this step. A value of 0 results in automatic use of all available memory. (default = 0)
- NOMEM = 0 (set to one to force out of memory algorithm)
-
-

\$GUGEM group (optional, relevant for -CI- or -MCSCF-)

This group provides further control over the calculation of the energy (Hamiltonian) matrix.

- CUTOFF = Cutoff criterion for the energy matrix. (default=1.0E-8)
- NWORD = not used.
-
-

\$GUGDIA group (optional, relevant for -CI- or -MCSCF-)

This group provides control over the Davidson method diagonalization step.

- NSTATE = Number of CI states to be found. (default=1) You can solve for any number of states, but only 100 can be saved for subsequent sections, such as state averaging.
- PRTTOL = Printout tolerance for CI coefficients (default = 0.05)
- MXXPAN = Maximum no. of expansion basis vectors used before the expansion basis is truncated. (default=30)
- ITERMX = Maximum number of iterations (default=50)
- CVGTOL = Convergence criterion for Davidson eigenvector routine. This value is proportional to the accuracy of the coefficients of the eigenvector(s) found. The energy accuracy is proportional to its square. (default = 1.0E-5)
- NWORD = Number of words of fast memory to use in this step. A value of zero results in the use of all available memory. (default = 0)

\$GUGDIA, \$GUGDM

- MAXHAM = specifies dimension of Hamiltonian to try to store in memory. The default is to use all remaining memory to store this matrix in memory, if it fits, to reduce disk I/O to a minimum.
- MAXDIA = maximum dimension of Hamiltonian to send to an incore diagonalization. If the number of CSFs is bigger than MAXDIA, an iterative Davidson procedure is invoked. Default=100
- NIMPRV = Maximum no. of eigenvectors to be improved every iteration. (default = nstate)
- NSELECT = Determines initial guess to eigenvectors.
 = 0 Unit vectors corresponding to the NSTATE lowest diagonal elements and any diagonal elements within SELTHR of them. (default)
 < 0 First abs(NSELECT) unit vectors.
 > 0 use NSELECT unit vectors corresponding to the NSELECT lowest diagonal elements.
- SELTHR = Guess selection threshold when NSELECT=0. (default=0.01)
- NEXTRA = Number of extra expansion basis vectors to be included on the first iteration. NEXTRA is decremented by one each iteration. This may be useful in "capturing" vectors for higher states. (default=5)
- KPRINT = Print flag bit vector used when NPFLG(4)=1 in the \$CIINP group (default=8)
 1 bit 0 print final eigenvalues
 2 bit 1 print final tolerances
 4 bit 2 print eigenvalues and tolerances at each truncation
 8 bit 3 print eigenvalues every iteration
 16 bit 4 print tolerances every iteration

\$GUGDM group (optional, relevant for -CI-)

This group provides further control over formation of the 1-particle density matrix.

- NFLGDM = Controls each state's density formation.
 0 do not form density for this state.
 1 form density and natural orbitals for this state, print and punch occ.num. and NOs.
 2 same as 1, plus print density over MOs. (default=1,99*0, meaning G.S. NOs only) See also NSTATE in \$GUGDIA. Note that forming the 1-particle density for a state is negligible against the diagonalization time for that state.
- IROOT = The -CI- root whose density matrix is saved on the direct access dictionary file for later computation of properties. (default=1)

- IBLOCK = Density blocking switch. If nonzero, the off diagonal block of the density below row IBLOCK will be set to zero before the (approximate) natural orbitals are found. One use for this is to keep the internal and external orbitals in a FOCI or SOCI calculation from mixing. (default=0)
- NWORD = Number of words of fast memory to use in this step. A value of zero uses all available memory (default=0).
-

\$GUGDM2 group (optional, relevant for -CI- or -MCSCF-)

This group provides control over formation of the 2-particle density matrix.

- WSTATE = An array of up to 100 weights to be given to the 2 body density of each state in forming the DM2. The default is to optimize a pure ground state. (Default=1.0,99*0.0) A small amount of the ground state can help the convergence of excited states greatly. Gradient runs are possible only with pure states.

Be sure to set NSTATE in \$GUGDIA appropriately!

- CUTOFF = Cutoff criterion for the 2nd-order density. (default = 1.0E-9)
- NWORD = Number of words of fast memory to use in sorting the DM2. The default uses all available memory. (default=0).
- NOMEM = 0 uses in memory sort, if possible.
= 1 forces out of memory sort.
- NDAR = Number of direct access records. (default=4000)
- LDAR = Length of direct access record (site dependent)
- NBOXMX = Maximum no. of boxes in the sort. (default=200)

\$LAGRAN, \$TRFDM2\$LAGRAN group (optional, relevant for -CI- gradient)

This group provides further control over formation of the CI Lagrangian, a quantity which is necessary for the computation of CI gradients.

NOMEM = 0 form in core, if possible
 = 1 forces out of core formation
 NWORD = 0 (0=use all available memory)
 NDAR = 4000
 LDAR = Length of each direct access record (default is NINTMX from \$INTGRL)

\$TRFDM2 group (optional, relevant for -CI- gradient)

This group provides further control over the back transformation of the 2 body density to the AO basis.

NOMEM = 0 transform and sort in core, if possible
 = 1 transform in core, sort out of core, if poss.
 = 2 transform out of core, sort out of core
 NWORD = 0 (0=use all available memory)
 CUTOFF = 1.0D-9, threshold for saving DM2 values
 NDAR = 2000
 LDAR = Length of each direct access record (default is system dependent)
 NBOXMX = 200

Usually neither of these two groups is given. Since these groups are normally used only for CI gradient runs, we list here some of the restrictions on the CI gradients:

- a) SCFTYP=RHF, only
- b) no FZV orbitals in \$CIDRT, all MOs must be used.
- c) the derivative integrals are computed in the 2nd derivative code, which is limited to spd basis sets.
- d) the code does not run in parallel.
- e) Use WSTATE in \$GUGDM2 to specify the state whose gradient is to be found. Use IROOT in \$GUGDM to specify the state whose other properties will be found. These must be the same state!
- f) excited states often have different symmetry than the ground state, so think about GROUP in \$CIDRT.
- g) the gradient can probably be found for any CI for which you have sufficient disk to do the CI itself. Time is probably about 2/3 additional.

\$TRANST group (relevant for RUNTYP=TRANSITN)
(only for CITYP=GUGA)

This group controls the evaluation of the radiative transition moment, or spin orbit coupling (SOC). The defaults assume that there is one common set of orbitals, all of which are occupied. The program can use two separately optimized MO sets, provided certain conditions are met. If relativistic corrections were included in the underlying spin-free wavefunctions, it is possible to either include or neglect the corrections to SOC, see NESOC in \$RELWFN.

OPERAT selects the type of transition being computed.

- = DM calculates radiative transition moment between states of same spin, using the dipole moment operator. (default)
- = HSO1 one-electron Spin-Orbit Coupling (SOC)
- = HSO2P partial two electron and full 1e- SOC, namely core-active 2e- contributions are computed, but active-active 2e- terms are ignored. This generally captures >90% of the full HSO2 computation, but with spin-orbit matrix element time similar to the HSO1 calculation.
- = HSO2 one and two-electron SOC, this is the full Pauli-Breit operator.
- = HSO2FF one and two-electron SOC, the form factor method gives the same result as HSO2, but is more efficient in the case of small active spaces, small numbers of CI states, and large atomic basis sets.

* * * next define orbitals and wavefunctions * * *

NUMVEC = the number of different MO sets. This can be either 1 or 2, but 2 can be chosen only for FORS/CASSCF or FCI wavefunctions. (Default=1) Note that \$GUESS is not read by this RUNTYP! If you set NUMVEC=2 and you use symmetry in any of the \$DRTx groups, you may have to use ISTSYM in the \$DRT groups since the order of orbitals from the corresponding orbital transformation is unpredictable.

NFZC = When NUMVEC=2, this is the number of identical core orbitals in the two vector sets, and must be equal to NFZC in all \$DRTx groups. When NUMVEC=1, it is the value of NFZC in the \$DRTx. The default is the number of AOs given in \$DATA, again this is not very reasonable.

NOCC = the number of occupied orbitals. The default is the number of AOs given in \$DATA, which is not usually correct.

NUMCI = the number of different CI calculations to do. You may wish to define one \$DRTx group for each irreducible representation within each spin multiplicity. NUMCI may not exceed 64. IVEX, IROOTS, NSTATE, ENGYST below will all have NUMCI values. (Default=1)

\$TRANST

- IVEX = array of indices of \$VECX groups to be used for each CI calculation. The default for NUMVEC=2 is IVEX(1)=1,2,1,1,1,1,1..., and of course for NUMVEC=1, it is IVEX(1)=1,1,1,1,1...
- IROOTS = array containing the number of CI states for which the transition moments are to be found. The default is 1 for each CI, which is probably not a correct choice for OPERAT=DM runs, but is quite reasonable for the HSO operators. See also ETOL.
- ETOL = energy tolerance for CI state elimination. After a CI computation finding up to NSTATE(i) CI roots within each \$DRTx, the number of states kept in the computation is limited to the number given by IROOTS, with a further limitation that the state be within ETOL of the lowest energy state found for any of the \$DRTx. The default is 100.0 Hartree, so that IROOTS is the only limitation. This applies only to OPERAT=HSO1,2,2P.
- NSTATE = array of CI states to be found when diagonalising the CI Hamiltonians. Of these, the first IROOTS(i) states will be used to find transition moments. The default for NSTATE(i) is IROOTS(i).
- ENGYST = energy values to replace the CI spin-free energies. A possible use for this is to use SOCI energies on the diagonal of the Hamiltonian (obtained in previous runs) but to use only FORS wavefunctions to evaluate off diagonal HSO matrix elements. The CI runs are still conducted to obtain CI coefs, needed to evaluate the off diagonal elements. Enter MXRT*NUMCI values as a square array, by the usual FORTRAN convention (that is, MXRT roots of \$DRT1, MXRT roots of \$DRT2 etc), in hartrees, with zeros added to fill each column to MXRT values. MXRT is the maximum value in the IROOTS array.
- * * * some control tolerances * * *
- NOSYM = -1 forces use of symmetry-contaminated orbitals symmetry analysis, otherwise the same as NOSYM=0
 = 0 fully use symmetry
 = 1 do not use point group symmetry, but still use other symmetries (Hermiticity, spin).
 = 2 use no symmetry. Also, include all CSFs for HSO1, 2, 2P.
 = 3 force the code to assume the symmetry specified in \$DATA is the same as in all \$DRT groups, but is otherwise identical to NOSYM=-1. This option saves CPU time and money(memory). Since the \$DRT works by mapping non-Abelian groups into their highest Abelian subgroup, do not use NOSYM=3 for non-Abelian groups.
- SYMTOL = relative error for the matrix elements. This parameter has a great impact upon CPU time, and the default has been chosen to obtain nearly full accuracy while still getting good speedups. (default=1.0E-4)

* * * the next pertain only to spin-orbit runs * * *

ZEFTYP specifies effective nuclear charges to use

- = TRUE uses true nuclear charge of each atom, except protons are removed if an ECP basis is being used (default).
- = 3-21G selects values optimized for the 3-21G basis, but these are probably appropriate for any all electron basis set. Rare gases, transition metals, and $Z > 54$ will use the true nuclear charges.
- = SBKJC selects a set obtained for the SBKJC ECP basis set, specifically. It may not be sensible to use this for other ECP sets. Rare gases, lanthanides, and $Z > 86$ will use the true nuclear charges.

ZEFF =an array of effective nuclear charges, overriding the charges chosen in ZEFTYP.

Note that effective nuclear charges can be used for any HSO type OPERAT, but traditionally these are used mainly for HSO1 as an empirical correction to the omission of the $2e^-$ term, or to compensate for missing core orbitals in ECP runs.

JZ controls the calculation of Jz eigenvalues

- = 0 do not perform the calculation
- = 1 do the calculation

By default, jz is set to 1 for molecules that are recognised as linear (this includes atoms!). The matrix of $J_z = L_z + S_z$ operator is constructed between spin-mixed states (eigenvalues of Hso). Setting Jz to 1 can enforce otherwise avoided (by symmetry) calculations of SOC matrix elements. Interpretation of Jz eigenvalues for systems other than linear molecules aligned along z-axis is left at your discretion. JZ applies only to HSO1,2,2P.

TMOMNT = flag to control computation of the transition dipole moment between spin-mixed wavefunctions (that is, between eigenvectors of the Pauli-Breit Hamiltonian). Applies only to HSO1,2,2P. (default is .FALSE.)

SKIPDM = flag to omit(.TRUE.) or include(.FALSE.) dipole moment matrix elements during spin-orbit coupling. Usually it takes almost no addition effort to calculate $\langle R \rangle$ excluding some cases when the calculation of forbidden by symmetry spin-orbit coupling matrix elements $\langle H_{so} \rangle$ may have to be performed since $\langle R \rangle$ and $\langle H_{so} \rangle$ are computed simultaneously. Applies only to HSO1,2,2P (default is .TRUE.)

IPRHSO = controls output style for matrix elements (HSO*)

- = -1 do not output individual matrix elements otherwise these are accumulative:
- = 0 term-symbol like kind of labelling: labels contain full symmetry info (default)
- = 1 all states are numbered consequently within each spin multiplicity (ye olde style)
- = 2 output only nonzero ($\geq 1e-4$) matrix elements

PRTPRM = flag to provide detailed information about the composition of the

spin-mixed states in terms of adiabatic states. This flag also provides similar information about Jz (if JZ set). (default is .FALSE.)

* * * expert mode HSO control options* * *

MODPAR = parallel options, which are independent bit options, 0=off, 1=on. Bit 1 refers only to HSO2FF, bit 2 to HSO1,2,2P. Enter a decimal value 0, 1, 2, 3 meaning binary 00, 01, 10, 11.

bit 1 = 0/1 (HSO2FF)uses static/dynamic load balancing in parallel if available, otherwise use static load balancing. Dynamic algorithm is usually faster but may utilize memory less efficiently, and I/O can slow it down. Also, dynamical algorithm forces SAVDSK=.F. since its unique distribution of FFs among nodes implies no savings from precalculating form factors.

bit 2 = 0/1 (HSO1,2,2P)duplicate/distribute SOC integrals in parallel. If set, 2e AO integrals and the four-index transformation are divided over nodes (distributed), and SOC MO integrals are then summed over nodes.

The default is 3, meaning both bits are set on (11)

PHYSRC = flag to force the size of the physical record to be equal to the size of the sorting buffers. This option can have a dramatic effect on the efficiency. Usually, setting PHYSRC=.t. is helpful if the code complains that low memory enforces SLOWFF=.TRUE., or you set it yourself. For large active spaces and large memory (more precisely, if reclen is larger than the physical record size) PHYSRC=.TRUE. can slow the code down. Setting PHYSRC to .true. forces SLOWFF to be .false. See MODPAR. (default .FALSE.) (only with HSO2FF)

RECLEN = specifies the size of the record on file 40, where form factors are stored. This parameter significantly affects performance. If not specified, RECLEN have to be guessed, and the guess will usually be either an overestimate or underestimate. If the former you waste disk space, if the latter the program aborts. Note that RECLEN will be different for each pair of multiplicities and you must specify the maximum for all pairs. The meaning of this number is how many non-zero form factors are present given four MO indices. You can decrease RECLEN if you are getting a message "predicted sorting buffer length is greater than needed..." Default depends on active space. (only HSO2FF)

SAVDSK = This avoids wasting disk space as the actually required record size is found during the 1st run. (default=.FALSE.) (only with HSO2FF)

SLOWFF = flag to choose a slower FF write-out method. By default .FALSE., but this is turned on if:

- 1) not enough memory for the fast way is available
- 2) the maximum usable memory is available, as when the buffer is as large as the maximum needed, then the "slow FF" algorithm is faster.

Generally SLOWFF=.true. saves up to 50% or so of disk space. See PHYSRC. (only with HSO2FF)

ACTION controls disk file DAFL30 reuse.
 = NORMAL calculate the form factors in this run.
 = SAVE calculate, and store the form factors on disk for future runs with the same active space characteristics.
 = READ read the form factors from disk from an earlier run which used SAVE.

(default=NORMAL) (only with HSO2FF) Note that currently in order to use ACTION = SAVE or READ you should specify MS= -1, 0, or 1

MS = refers to the difference between ket and bra's Ms It pertains only to HSO2FF.
 = -1 do matrix elements for ms=-1 only
 = 0 do matrix elements for ms=0 only
 = 1 do matrix elements for ms=1 only
 = -2 do matrix elements for all ms (0, 1, and -1), which is the default.
 = -3 calculates form factors so they can be saved.
 (default=-2) (only BREIT)

* * * the remaining parameters are not so important * * *

PRTCMO = flag to control printout of the corresponding orbitals. (default is .FALSE.)

HSOTOL = HSO matrix elements are considered zero if they are smaller than HSOTOL. This parameter is used only for print-out and statistics. (default=1.0E-1 cm-1)

TOLZ = MO coefficient zero tolerance (as for \$GUESS). (default=1.0E-8)

TOLE = MO coefficient equating tolerance (as for \$GUESS). (default=1.0E-5)

For information on RUNTYP=TRANSITN, see the 'further information' section

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