

(30 December 2008)

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* Section 3 - Input Examples *
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The distribution of GAMESS contains a number of short examples, named EXAM*.INP. You should run all of these tests to be sure you have installed GAMESS correctly. The answers are shown in the comments preceeding each of the short input tests. The "correct" answers were obtained on a IBM computer using the xlf compiler, and other machines may differ in the last energy digit, or the last couple of gradient digits. Please note the existence of a script named

~/gamess/tools/checktst/checktst
to assist in verifying the numerical results.

The examples are listed in the rest of this section, and serve a secondary purpose as a useful tutorial about GAMESS input files.

Example	Description
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1	CH2 RHF geometry optimization
2	CH2 UHF + gradient
3	CH2 ROHF + gradient
4	CH2 GVB + gradient
5	CH2 RHF + CI gradient
6	CH2 MCSCF geometry optimization
7	HPO RHF + gradient
8	H2O RHF + MP2 gradient
9	H2O MCSCF + MCQDPT energy correction
10	H2O RHF + hessian
11	HCN RHF IRC
12	HCCH closed shell DFT geometry opt.
13	H2O RHF properties
14	H2O CI transition moment
15	C2- GVB/ROHF on 2-pi-u state
16	Si GVB/ROHF on 3-P state
17	CH2 GVB/ROHF + hessian
18	P2 RHF + hessian, effective core pot.
19	NH spin-orbit coupling
20	I- exponent TRUDGE optimization
21	CH3 OS-TCSCF hessian
22	H3CN UHF + UMP2 gradient
23	SiH3- PM3 geometry optimization

24	H2O	SCRF test case
25	?	internal coordinate example
26	H3PO	localized orbital test
27	NH3	DRC example
28	H2O-NH3	Morokuma decomposition
29	FNH2OH	surface scan
30	HCONH2(H2O)3	effective fragment solvation
31	CH3OH	PCM test case
32	HNO	coupled cluster test
33	HCN	ORMAS-MCSCF illustration
34	H2CO	CIS optimization
35	As	relativity via Douglas-Kroll
36	C2H4	MCSCF analytic hessian
37	(H2O)3	Fragment Molecular Orbital RHF
38	AsH3	model core potential optimization
39	CH4	Raman and hyper-Raman spectra
40	CH2	minimum energy crossing point search
41	CO	excitation energy/gradient by TD-DFT
42	CN	numerical gradient for open shell CC
43	CH4	heat of formation
44	(HF)6	divide-and-conquer MP2 energy

The following will not run in parallel:

- 05 - CI gradient is not enabled for parallel execution
- 23,25,27 - MOPAC is not enabled for parallel execution
- 32,42 - only RHF-based CCSD and CCSD(T) runs in parallel
- 39 - RUNTYP=TDHFX is not enabled for parallel execution

```
! EXAM01.
!   1-A-1 CH2      RHF geometry optimization using GAMESS.
!
!   Although internal coordinates are used (COORD=ZMAT),
!   the optimization is done in Cartesian space (NZVAR=0).
!   This run uses a criterion (OPTTOL) on the gradient
!   which is tighter than is normally used.
!
!   This job tests the sp integral module, the RHF module,
!   and the geometry optimization module.
!
!   Using the default search METHOD=STANDARD,
!   FINAL E= -37.2322678015, 8 iters, RMS grad= .0264308
!   FINAL E= -37.2308175316, 7 iters, RMS grad= .0320881
!   FINAL E= -37.2375723414, 7 iters, RMS grad= .0056557
!   FINAL E= -37.2379944431, 6 iters, RMS grad= .0017901
!   FINAL E= -37.2380387832, 8 iters, RMS grad= .0003391
!   FINAL E= -37.2380397692, 6 iters, RMS grad= .0000030
!
$CONTRL SCFTYP=RHF RUNTYP=OPTIMIZE COORD=ZMT NZVAR=0 $END
$SYSTEM TIMLIM=2 MEMORY=100000 $END
$STATPT OPTTOL=1.0E-5 $END
$BASIS  GBASIS=STO NGAUSS=2 $END
$GUESS  GUESS=HUCKEL $END
$DATA
Methylene...1-A-1 state...RHF/STO-2G
Cnv  2

C
H  1 rCH
H  1 rCH  2 aHCH

rCH=1.09
aHCH=110.0
$END
```

```
! EXAM02.
!   3-B-1 CH2   UHF calculation on methylene ground
state.
!
!   This test uses the default choice, COORD=UNIQUE, to
!   enter the molecule. Only the symmetry unique atoms
!   are given, and they must be given in the orientation
!   which GAMESS expects.
!
!   This job tests the UHF energy and the UHF gradient.
!   In addition, the orbitals are localized.
!
!   The initial energy is -37.228465066.
!   The FINAL energy is -37.2810867258 after 11
iterations.
!   The unrestricted wavefunction has <S**2> = 2.013.
!   Mulliken, Lowdin charges on C are -0.020584, 0.018720.
!   The spin density at Hydrogen is -0.0167104.
!   The dipole moment is 0.016188.
!   The RMS gradient is 0.027589766.
!   FINAL localization sums are 30.57 and 25.14 Debye**2.
!
$CONTRL SCFTYP=UHF MULT=3 RUNTYP=GRADIENT LOCAL=BOYS $END
$SYSTEM TIMLIM=1 MEMORY=100000 $END
$BASIS  GBASIS=STO NGAUSS=2 $END
$GUESS  GUESS=HUCKEL $END
$DATA
Methylene...3-B-1 state...UHF/STO-2G
Cnv  2

Carbon      6.0
Hydrogen    1.0    0.0    0.82884    0.7079
$END
```

```

! EXAM03.
!   3-B-1 CH2  ROHF calculation on methylene ground state.
!   The wavefunction is a pure triplet state (<S**2> = 2),
!   and so has a higher energy than the second example.
!
!   For COORD=CART, all atoms must be given, and as in the
!   present case, these may be in an unoriented geometry.
!   GAMESS deduces which atoms are unique, and orients
!   the molecule appropriately. The geometry here is thus
!   identical to the second example.
!
!   This job tests the ROHF wavefunction and gradient
code.
!   It also tests the direct SCF procedure.
!
!   The initial energy is -37.228465066.
!   The FINAL energy is -37.2778767089 after 7 iterations.
!   Mulliken, Lowdin charges on C are -0.020346, 0.019470.
!   The Hydrogen atom spin density is 0.0129735.
!   The dipole moment is 0.025099 Debye.
!   The RMS gradient is 0.027505548
!
$CONTRL SCFTYP=ROHF MULT=3 RUNTYP=GRADIENT COORD=CART $END
$SYSTEM TIMLIM=1 MEMORY=100000 $END
$SCF     DIRSCF=.TRUE. $END
$BASIS   GBASIS=STO NGAUSS=2 $END
$GUESS   GUESS=HUCKEL $END
$DATA
Methylene...3-B-1 state...ROHF/STO-2G
Cnv  2

Hydrogen   1.0    0.82884    0.7079    0.0
Carbon     6.0
Hydrogen   1.0   -0.82884    0.7079    0.0
$END

```

```

! EXAM04.
!   1-A-1 CH2   TCSCF calculation on methylene.
!   The wavefunction has two configurations, exciting
!   the carbon sigma lone pair into the out of plane p.
!
!   Note that the Z-matrix used to input the molecule
!   can include identifying integers after the element
!   symbol, and that the connectivity can then be given
!   using these labels rather than integers.
!
!   This job tests the GVB wavefunction and gradient.
!
!   The initial GVB-PP(1) energy is -37.187342653.
!   The FINAL energy is -37.2562020559 after 10 iters.
!   The GVB CI coefs are 0.977505 and -0.210911, giving
!   a pair overlap of 0.64506.
!   Mulliken, Lowdin charges for C are 0.020810, 0.055203.
!   The dipole moment is 1.249835.
!   The RMS gradient = 0.019618475.
!
$CONTRL SCFTYP=GVB  RUNTYP=GRADIENT  COORD=ZMT  $END
$SYSTEM TIMLIM=1  MEMORY=100000  $END
$BASIS  GBASIS=STO  NGAUSS=2  $END
$SCF    NCO=3  NSET0=0  NPAIR=1  $END
$DATA
Methylene...1-A-1 state...GVB...one geminal pair...STO-2G
Cnv  2

C1
H1  C1 rCH
H2  C1 rCH  H1 aHCH

rCH=1.09
aHCH=99.0
$END
! normally a GVB-PP calculation will use GUESS=MOREAD
$GUESS  GUESS=HUCKEL  $END

```

```

! EXAM05
!   CH2   CI calculation.
!   The wavefunction is RHF + CI-SD, within the minimal
!   basis, containing 55 configurations. Two CI roots
!   are found, and the gradient of the higher state is
!   then computed.
!
!   Note that CI gradients have several restrictions,
!   which are further described in the $LAGRAN group.
!
!   FINAL energy of RHF = -38.3704885128 after 10 iters.
!   State 1 EIGENvalue = -38.4270674136, c(1) = 0.970224
!   State 2 EIGENvalue = -38.3130036824, c(29) = 0.990865
!   The upper state dipole moment is 0.708275 Debye.
!   The upper state has RMS gradient 0.032264079
!
$CONTRL SCFTYP=RHF CITYP=GUGA RUNTYP=GRADIENT $END
$SYSTEM TIMLIM=3 MEMORY=300000 $END
$BASIS  GBASIS=STO NGAUSS=3 $END
$GUESS  GUESS=HUCKEL $END
!   look at all state symmetries, by using C1 symmetry
$CIDRT  GROUP=C1 IEXCIT=2 NFZC=1 NDOC=3 NVAL=3 $END
!   ground state is 1-A-1, 1st excited state is 1-B-1
$GUGDIA NSTATE=2 $END
!   compute properties of the 1-B-1 state
$GUGDM  NFLGDM(1)=1,1 IROOT=2 $END
!   compute gradient of the 1-B-1 state
$GUGDM2 WSTATE(1)=0.0,1.0 $END
$DATA
Methylene...CI...STO-3G basis
Cnv    2

Carbon    6.0
Hydrogen  1.0      0.0      0.82884      0.7079
$END

```

```

! EXAM06.
!   1-A-1 CH2      MCSCF methylene geometry optimization.
!   The two configuration ansatz is the same as used in
!   the fourth example.
!
!   The optimization is done in internal coordinates,
!   as NZVAR is non-zero.  Since a explicit $ZMAT is
!   given, these are used for the internal coordinates,
!   rather than those used to enter the molecule in
!   the $DATA.  (Careful examination of this trivial
!   triatomic's input shows that $ZMAT is equivalent
!   to $DATA in this case.  You would normally give
!   $ZMAT only if it is somehow different.)
!   This job tests the MCSCF wavefunction and gradient.
!   At the initial geometry:
!   The initial energy is -37.187342653,
!   the FINAL E= -37.2562020559 after 14 iterations,
!   the RMS gradient is 0.0256396.
!   After 4 steps,
!   FINAL E= -37.2581791686, RMS gradient=0.0000013,
!   r(CH)=1.1243359, ang(HCH)=98.8171674
$CONTRL SCFTYP=MCSCF RUNTYP=OPTIMIZE NZVAR=3 COORD=ZMT $END
$SYSTEM TIMLIM=5 MEMORY=300000 $END
$BASIS  GBASIS=STO NGAUSS=2 $END
$DATA
Methylene...1-A-1 state...MCSCF/STO-2G
Cnv  2

C
H 1 rCH
H 1 rCH 2 aHOH

rCH=1.09
aHOH=99.0
$END
$ZMAT  IZMAT(1)=1,1,2,  1,1,3,  2,2,1,3 $END
! Normally one starts a MCSCF run with converged SCF
! orbitals, as Huckel orbitals normally do not converge.
! Even if they do converge, the extra iterations are
! very expensive, so use MOREAD for your runs!
!
$GUESS  GUESS=HUCKEL $END
!
! two active electrons in two active orbitals.
! must find at least two roots since ground state is 3-B-1
!
$DET    NCORE=3 NACT=2 NELS=2 NSTATE=2 $END

```



```

! EXAM07.
!   1-A' HPO      RHF calculation using GAMESS.
!   This job tests the HONDO integral & gradient packages,
!   due to the d function on phosphorus. The input also
!   illustrates the use of a more flexible basis set than
!   the methylene examples.
!   Although HUCKEL would be better, HCORE is tested.
!
!   The initial energy is -397.591192627,
!   the FINAL E= -414.0945320854 after 18 iterations,
!   The dipole moment is 2.535169.
!   The RMS gradient is 0.023723942.
!
$CONTRL SCFTYP=RHF RUNTYP=GRADIENT $END
$SYSTEM TIMLIM=20 MEMORY=300000 $END
$GUESS GUESS=HCORE $END
$DATA
HP=O ... 3-21G+* RHF calculation at STO-2G* geometry
Cs

Phosphorus 15.0
  N21 3
  L    1
  1    0.039          1.0          1.0
  D    1
  1    0.55          1.0

Oxygen      8.0      1.439
  N21 3

Hydrogen    1.0      -0.3527854      1.36412
  N21 3

$END

```

```
! EXAM08.
!   1-A-1 H2O      RHF + MP2 gradient calculation.
!   This job generates RHF orbitals which should be saved
!   for use with EXAM9.  This run, together with EXAM9,
!   shows a much more typical MCSCF calculation, which
!   should always be started with some sort of SCF MOs.
!   This job also tests the 2nd order Moller-Plesset code.
!
!   The FINAL E is -75.5854099058 after 10 iterations.
!   E(MP2) is -75.7060361996, RMS grad=0.017449524
!   dipole moments are SCF=2.435689, MP2=2.329368
!
$CONTRL SCFTYP=RHF MPLEVL=2 RUNTYP=GRADIENT $END
$SYSTEM TIMLIM=2 MEMORY=100000 memddi=1 parall=.true. $END
$BASIS  GBASIS=N21 NGAUSS=3 $END
$GUESS  GUESS=HUCKEL $END
$DATA
Water...RHF/3-
21G...exp.geom...R(OH)=0.95781,A(HOH)=104.4776
Cnv      2

OXYGEN      8.0
HYDROGEN    1.0    0.0    0.7572157    0.5865358
$END
```

EXAM09.

```

!      1-A-1 H2O      2nd order MC-QDPT calculation
!      This job finds the Full Optimized Reaction Space
!      MCSCF (or CAS-SCF) wavefunction for water.  Its
!      initial RHF orbitals are taken from EXAM08.
!      The MCSCF wavefunction contains 225 determinants,
!      which includes 105 singlet configurations.
!      The second order perturbation theory correction
!      to the MCSCF energy is then obtained, using a
!      determinant code as well.
!
!      MCSCF:
!      On the 1st iteration, the energy is -75.601726236.
!      The FINAL MCSCF E= -75.6386218843 after 13 iters,
!      with c(1) = 0.9884456 and dipole moment = 2.301626
!      MRMP (single state MCQDPT):
!      E(MP2)= -75.7109706213
!
$CONTRL SCFTYP=MCSCF MPEVL=2 $END
$SYSTEM TIMLIM=1 $END
$BASIS  GBASIS=N21 NGAUSS=3 $END
---- EXPERIMENTAL GEOM, R(OH)=0.95781A, HOH=104.4776 DEG.
$DATA
WATER...3-21G BASIS...FORS-MCSCF...EXPERIMENTAL GEOMETRY
Cnv 2

Oxygen      8.0
Hydrogen    1.0    0.0    0.7572157    0.5865358
$END
$GUESS  GUESS=MOREAD  NORB=13 $END
$DET    NCORE=1  NACT=6  NELS=8 $END

---- CONVERGED 3-21G WATER VECTORS, E=-75.585409913 - - -
$VEC
1  1  0.98323195E+00  0.95883436E-01  0.00000000E+00 ...
... vectors deleted to save paper ...
13  3  0.35961579E+00  0.28728587E+00  0.35961579E+00
$END

```

```
! EXAM 10.
!   This run duplicates the first column of table 6 in
!   Y.Yamaguchi, M.Frisch, J.Gaw, H.F.Schaefer, and
!   J.S.Binkley   J.Chem. Phys. 1986, 84, 2262-2278.
!
!   FINAL energy at the VIB 0 geometry is -74.9659012159.
!
!   If run with METHOD=ANALYTIC,
!   the FREQUencies are 2170.05, 4140.00, and 4391.07
!   the INTENSities are 0.17129, 1.04807, and 0.70930
!   the mean POLARIZABILITY is 0.40079
!
!   If run with METHOD=NUMERIC, NVIB=2,
!   the FREQUencies are 2170.14, 4140.18, and 4391.12
!   the INTENSities are 0.17169, 1.04703, and 0.70909
!
$CONTRL SCFTYP=RHF RUNTYP=HESSIAN UNITS=BOHR NZVAR=3 $END
$SYSTEM TIMLIM=4 MEMORY=100000 $END
$FORCE  METHOD=ANALYTIC  $END
$CPHF   POLAR=.TRUE. $END
$BASIS  GBASIS=STO NGAUSS=3 $END
$DATA
Water at the RHF/STO-3G equilibrium geometry
CNV      2

OXYGEN      8.    0.0    0.0                0.0702816679
HYDROGEN    1.    0.0    1.4325665478    -1.1312080153
$END
$ZMAT  IZMAT(1)=1,1,2,    1,1,3,    2,2,1,3  $END
$GUESS  GUESS=HUCKEL  $END
```

```

! EXAM 11.
! 1A' HCN          RHF Intrinsic Reaction Coordinate
! This job tests the reaction path finder. The reaction
! is followed back to the HNC isomer. Four points on the
! IRC (counting the saddle point) are found,
! Pt.   R(N-C)   R(N-H)   A(HNC)   Energy   distance
! T.S.  1.22136  1.43764  52.993  -91.5648510  0.0
! 1     1.22533  1.33296  58.476  -91.5673097  0.29994
! 2     1.22802  1.23827  64.747  -91.5735346  0.59986
! 3     1.22974  1.16350  72.039  -91.5814775  0.89968
!
$CONTRL SCFTYP=RHF RUNTYP=IRC NZVAR=3 $END
$SYSTEM TIMLIM=5 MEMORY=400000 $END
$IRC     PACE=GS2 SADDLE=.TRUE. TSENGY=.TRUE.
        FORWRD=.FALSE. NPOINT=3 $END
$GUESS   GUESS=HUCKEL $END
$ZMAT    IZMAT(1)=1,1,2 1,1,3 2,2,1,3 $END
$BASIS   GBASIS=STO NGAUSS=3 $END
$DATA
HYDROGEN CYANIDE...STO-3G...INTRINSIC REACTION COORDINATE
CS

NITROGEN    7.0    -.0004620071    .0002821165
.0000000000
CARBON      6.0    1.2208931990    -.0003427488
.0000000000
HYDROGEN    1.0    .8654562191    1.1478852258
.0000000000
$END
$HESS
ENERGY IS      -91.5648510307 E(NUC) IS      23.4154954113
1 1 1.10665682E+00 1.58946320E-02 0.00000000E+00...
... 2nd derivatives deleted to save paper ...
9 2-8.04548379E-09 0.00000000E+00 0.00000000E+00-
1.42096449E-08
$END

```

```

! EXAM 12.
!   This job illustrates linear bends, for acetylene, and
!   tests the closed shell LDA density functional program.
!
!   At the input geometry,
!   the FINAL E= -765352334525 after 12 iterations,
!   and the RMS gradient is 0.0944557.
!
!   At the final geometry, 5 steps later,
!   the FINAL E= -76.5841347569, RMS gradient=0.0000007,
!   R(CC)=1.21193 and R(CH)=1.07797.
!
$CONTRL SCFTYP=RHF RUNTYP=OPTIMIZE NZVAR=5 $END
$SYSTEM TIMLIM=2 $END
$DFT     DFTTYP=SVWN $END
$BASIS   GBASIS=N31 NGAUSS=6 NDFUNC=1 $END
$GUESS   GUESS=HUCKEL $END
!   Note, this OPTTOL is smaller than the accuracy of the
!   integration grid actually supports (see REFS.DOC)
$STATPT OPTTOL=0.00001 $END
$DATA
Acetylene geometry optimization in internal coordinates
Dnh          4

CARBON       6.0    0.0  0.0  0.70
HYDROGEN     1.0    0.0  0.0  1.78
$END
$ZMAT  IZMAT(1)=1,1,2,   1,1,3,   1,2,4,
          5,1,2,4,     5,2,1,3 $END
----- XZ is 1st plane for both bends -----
$LIBE  APTS(1)=1.0,0.0,0.0,1.0,0.0,0.0 $END

```

```

! EXAM 13.
! This run duplicates the POLYATOM calculation of
! D.Neumann + J.W.Moskowitz, J.Chem.Phys. 49,2056(1968)
! SCF convergence is a bit better today, so some of the
! results are not precisely the same.
!
! V(NE) = -199.1343264099
! V(EE) = 37.8955167210 T = 75.9557584991
! V(NN) = 9.2390200836 E(TOT)= -76.0440311061
! Mulliken charge(O)=-0.647397 Bond Order=0.905
! Density: O=286.491824 H=0.404989
! Moments: DZ= 2.093290
! QXX=-2.388658 QYY= 2.495388 QZZ=-0.106730
! OXXZ=-0.890362 OYYZ= 2.186853 OZZZ=-1.296490
! Electric field/gradient: H(YZ)=+/-0.365168
! O(Z)=-0.060033 H(Y)=+/-0.006572 H(Z)=0.001233
! O(XX)=1.904867 O(YY)=-1.735891 O(ZZ)=-0.168977
! H(XX)=0.301208 H(YY)=-0.258153 H(ZZ)=-0.043055
! Potential: V(O)=-22.330374 V(H)=-1.006648
!
$CONTRL SCFTYP=RHF RUNTYP=ENERGY UNITS=BOHR ISPHER=1 $END
$SYSTEM TIMLIM=15 MEMORY=300000 $END
$GUESS GUESS=HUCKEL $END
$ELMOM IEMOM=3 $END
$ELFLDG IEFLD=2 $END
$ELPOT IEPOT=1 $END
$ELDENS IEDEN=1 $END
$DATA
Water...properties test...(10,5,2/4,1)/[5,3,2/2,1] basis
Cnv 2

Oxygen 8.0
S 2
  1 31.3166 0.243991
  2 76.232 0.152763
S 3
  1 290.785 0.904785
  2 1424.0643 0.121603
  3 4643.4485 0.029225
S 2
  1 4.6037 0.264438
  2 12.8607 0.458240
S 2
  1 0.9311 1.051534
  2 9.7044 -0.140314
S 1
  1 0.2825 1.0
P 3

```

	1	7.90403	0.124190	
	2	35.1832	0.019580	
	3	2.30512	0.394730	
P	1			
	1	0.21373	1.0	
P	1			
	1	0.71706	1.0	
D	1			
	1	1.5	1.0	
D	1			
	1	0.5	1.0	
Hydrogen	1.0	0.0	1.428036	1.0957706
S	3			
	1	0.65341	0.817238	
	2	2.89915	0.231208	
	3	19.2406	0.032828	
S	1			
	1	0.17758	1.0	
P	1			
	1	1.0	1.0	
\$END				


```

! EXAM 14.
! CI transition moments. Water, using RHF/STO-3G MOs.
! All orbitals are occupied, transition is 1-1A1 to 2-1A1.
!
! E(STATE 1)= -75.0101113548, E(STATE 2)= -74.3945819375
! Dipole LENGTH is <Q>=0.392614
! Dipole VELOCITY is <d/dQ>=0.368205
!
$CONTRL SCFTYP=NONE CITYP=GUGA RUNTYP=TRANSITN UNITS=BOHR
$END
$SYSTEM TIMLIM=1 MEMORY=100000 $END
$BASIS GBASIS=STO NGAUSS=3 $END
!          standard SD-CI calculation
$DRT1 GROUP=C2V IEXCIT=2 NFZC=1 NDOC=4 NVAL=2 $END
$TRANST NFZC=1 IROOTS(1)=2 $END
$DATA
WATER MOLECULE...STO-3G...TRANSITION MOMENT
CNV      2

OXYGEN      8.0    0.0    0.0    0.0
HYDROGEN    1.0    0.0    1.428  -1.096
$END

--- RHF ORBITALS --- GENERATED AT 09:24:04    18-FEB-88
WATER MOLECULE...STO-3G...TRANSITION MOMENT
E(RHF)= -74.9620539825, E(NUC)= 9.2384802989, 8
ITERS
$VEC1
1 1 9.94117078E-01 2.66680164E-02 0.00000000E+00 ...
... vectors deleted to save paper ...
7 2-8.42653177E-01 8.42653177E-01
$END

```

```
! EXAM 15.
!   C2- diatom, in the electronic state doublet-pi-u.
!   This illustrates a open shell SCF calculation, using
!   fed in coupling coefficients, and the GVB/ROHF code.
!
!   The FINAL energy is -75.5579181071 after 8 iterations.
!
$CONTRL SCFTYP=GVB  MULT=2  ICHARG=-1  UNITS=BOHR  $END
$SYSTEM TIMLIM=15 MEMORY=300000 $END
$BASIS  GBASIS=DH NDFUNC=1 POLAR=DUNNING $END
$DATA
C2-...DOUBLET-PI-UNGERADE...OPEN SHELL SCF
DNH      4

CARBON      6.0      0.0  0.0  -1.233
$END
$GUESS  GUESS=MOREAD NORB=30
        NORDER=1  IORDER(5)=7,5,6  $END
$SCF    NCO=5  NSET0=1  NO=2  COUPLE=.TRUE.
        F(1)=1.0, 0.75
        ALPHA(1)=2.0, 1.5, 1.00
        BETA(1)=-1., -.75, -0.5  $END

--- RHF ORBITALS --- GENERATED AT 14:05:16THU MAR 24/88
CC  R(C-C) = 2 * 1.233 BOHR  BAS=831+1D
E(RHF)= -75.3856001855, E(NUC)= 14.5985401460, 18
ITERS
$VEC
1 1-7.06500288E-01-1.39103044E-03-3.57452331E-04 ...
... vectors deleted to save paper ...
$END
```

```

! EXAM 16.
! ROHF/GVB on Si 3-P state, using Gordon's 6-31G basis.
!
! The purpose of this example is two-fold, namely to
! show off the open shell capabilities of the GVB code,
! and to emphasize that the 6-31G basis for Si in GAMESS
! is Mark Gordon's version. The basis stored in GAMESS is
! completely optimized, whereas Pople's uses the core from
! from a 6-21G set, reoptimizing only the -31G part.
! The energy from Pople's basis would be only -288.828405.
!
! Jacobi diagonalization is intrinsically slow, but
! results in pure subspecies in degenerate p irreps.
! In fact, these may be labeled in the highest Abelian
! subgroup of the atomic point group Kh.
!
! The FINAL energy is -288.8285729745 after 7 iterations.
!
$CONTRL SCFTYP=GVB MULT=3 $END
$SYSTEM TIMLIM=2 MEMORY=100000 KDIAG=3 $END
$BASIS GBASIS=N31 NGAUSS=6 $END
$DATA
Si...3-P term...ROHF in full Kh symmetry
Dnh 2

Silicon      14.
$END
$GUESS GUESS=HUCKEL $END
$SCF NCO=6 NSET0=1 NO=3 COUPLE=.TRUE.
      F(1)=1.0, 0.3333333333333333
      ALPHA(1)=2.0, 0.666666666666667, 0.166666666666667
      BETA(1)=-1.0, -0.333333333333333, -0.166666666666667
$END

```

```

! EXAM 17.
! Analytic hessian for an open shell SCF function.
! Methylene's 1-B-1 excited state.
! FINAL energy= -38.3334724780 after 8 iterations.
! The FREQuencies are 1224.19, 3563.44, 3896.23
! The INTENSities are 0.13317, 0.21652, 0.14589
! The mean POLARIZABILITY is 0.53018
!
$CONTRL SCFTYP=GVB MULT=1 RUNTYP=HESSIAN UNITS=BOHR
$END
$SYSTEM TIMLIM=4 MEMORY=100000 $END
$CPHF POLAR=.TRUE. $END
$BASIS GBASIS=STO NGAUSS=3 $END
$SCF NCO=3 NSETO=2 NO(1)=1,1 NPAIR=0 $END
$ZMAT IZMAT(1)=1,1,2, 1,1,3, 2,2,1,3 $END
$GUESS GUESS=HUCKEL $END
$DATA
METHYLENE...1-B-1 STATE...ROHF...STO-3G BASIS
CNV 2

CARBON 6.0 0.0 0.0 0.0041647278
HYDROGEN 1.0 0.0 1.8913952563 0.7563907037
$END

```

```
! EXAM 18.
! effective core potential...diatomic P2...RHF/CEP-31G*
! See Stevens,Basch,Krauss, J.Chem.Phys. 81,6026-33(1984).
! GAMESS FINAL E= -12.6956518702, FREQ=913.17
! A separate run gives E(P)= -6.32635 so De=26.95 kcal/mol
!
$CONTRL SCFTYP=RHF RUNTYP=HESSIAN ECP=SBKJC NZVAR=1 $END
$SYSTEM TIMLIM=15 MEMORY=900000 $END
$GUESS GUESS=HUCKEL $END
$ZMAT IZMAT(1)=1,1,2 $END
$DATA
diatomic phosphorous
Dnh 4

PHOSPHORUS 15.0 0.0000000000 0.0000000000
0.9393077548
SBKJC
D 1
1 0.45 1.0

$END
```

```

! EXAM 19.
! Spin-orbit coupling example.
! This run duplicates the results shown in Table 3 of
! T.R.Furlani, H.F.King, J.Chem.Phys. 82, 5577-83(1985),
! GAMESS 1e-= 114.3851, 2e-= -49.4168, lit=114.38,-49.42
!
! Energies for the singlet CI are
!   State=   1 Energy =  -54.868531216 (1-delta)
!   State=   2 Energy =  -54.868531216 (1-delta)
!   State=   3 Energy =  -54.798836731 (1-sigma-plus)
! Energies for the triplet CI are
!   State=   1 Energy =  -54.938225701 (3-sigma-minus)
! Final energy of all 6 levels in the pi**2 configuration,
! after diagonalization of the spin-orbit Hamiltonian, are
!   BREIT RELATIVE E= -15296.570, -15296.432, -15296.432,
!   BREIT RELATIVE E= 0.0, 0.0, and +15296.570 wavenumbers.
! If run as OPERAT=HS01, with ZEFF taken as true atomic Z,
! then inclusion of only the 1e- operator is 114.3851, and
!   ZEFF RELATIVE E= -15296.859, -15296.432, -15296.432,
!   ZEFF RELATIVE E= 0.0, 0.0, and +15296.859 wavenumbers.
!
! Why are there six levels? The singlet-delta is two roots,
! the singlet-sigma-plus is a third. During the CI, the
! spatial triplet-sigma-minus is one CSF, with alpha/alpha
! spin, hence IROOTS=3,1. The final spin-orbit Hamiltonian
! includes all three triplet spin states, namely adding the
! ab+ba and beta/beta triplets. So, 2+1+3=6 levels. You
! can work out for yourself these have the quantum number
! omega=0,0,1,2. Only the omega=0 states can interact,
! raising the triplet's degeneracy and slightly affecting
! the singlet-sigma-plus state's position.
!
! Note that the lower multiplicity DRT1 is done in C1
! symmetry to generate both components of the delta state.
!
$CONTRL SCFTYP=NONE MULT=3 CITYP=GUGA RUNTYP=TRANSITN
        UNITS=BOHR $END
$SYSTEM TIMLIM=2 MEMORY=900000 $END
$BASIS  GBASIS=N31 NGAUSS=6 $END
$TRANST OPERAT=HS02 NFZC=3 NOCC=5 NUMVEC=1 NUMCI=2
        IROOTS(1)=3,1 $END
$DRT1   GROUP=C1 IEXCIT=2 NFZC=3 NDOC=1 NVAL=1 $END
$DRT2   GROUP=C4V IEXCIT=2 NFZC=3 NALP=2 $END
$DATA
Imidogen radical
Cnv 4

Nitrogen      7.0

```

```
Hydrogen      1.0      0.0    0.0    1.9748
$END
--- ROHF ORBITALS --- GENERATED AT 12:04:18 29 MAR 90 ( 88)
IMIDOGEN RADICAL
E(ROHF)= -54.9382257007, E(NUC)=      3.5446627507,      8
ITERS
$VEC1
...orbitals omitted to save space...
$END
```

```
! EXAM 20.  
! Optimize an orbital exponent.  
! The SBKJC basis for I consists of 5 gaussians, in a -41  
! type split. The exponent of a diffuse L shell for  
! iodide ion is optimized (6th exponent overall). The  
! optimal exponent turns out to be 0.036713, with a  
! corresponding FINAL energy of -11.3010023066  
!  
$CONTRL SCFTYP=RHF RUNTYP=TRUDGE ICHARG=-1 ECP=SBKJC $END  
$SYSTEM TIMLIM=30 MEMORY=300000 $END  
$TRUDGE OPTMIZ=BASIS NPAR=1 IEX(1)=6 $end  
$GUESS GUESS=HUCKEL $END  
$DATA  
I- ion  
Dnh 2  
  
Iodine 53.0  
  SBKJC  
  L 1  
    1 0.02 1.0  
  
$END
```



```

! EXAM 21.
!   Open shell two configuration SCF analytic hessian.
!   M.Duran, Y.Yamaguchi, H.F.Schaefer III
!   J.Phys.Chem. 1988, 92, 3070-3075.
!   Least motion insertion of CH into H2, which leads to
!   a 3rd order hypersaddle point on the 2-B-1 surface.
!
!   Literature values are
!   FINAL E=-39.25104,      C1=0.801,      C2=-0.598
!   FREQ= 4805i, 1793i, 1317i, 989, 2914, 3216
!   mean POLARIZABILITY=2.05
!   GAMESS obtains
!   FINAL E=-39.2510351249, C1=0.801141, C2=-0.598476
!   FREQ= 4805.53i, 1793.00i, 1317.43i,
!   FREQ= 988.81, 2913.52, 3216.42
!   INTENS= 4.54563, 0.09731, 0.00768
!   mean POLARIZABILITY=2.04655
!
$CONTRL SCFTYP=GVB MULT=2 RUNTYP=HESSIAN $END
$SYSTEM TIMLIM=25 MEMORY=100000 $END
$CPHF POLAR=.TRUE. $END
$GUESS GUESS=MOREAD NORB=16 NORDER=1 IORDER(4)=6,4,5 $END
$SCF NCO=3 NSETO=1 NO=1 NPAIR=1 CICOEF(1)=0.7,-0.7 $END
$DATA
Insertion of CH into H2...OS-TCSCF ansatz...DZ basis
CNV 2

```

```

CARBON    6.0    0.0000000000    0.0000000000   -0.0001357549
S    6
  1  4232.61    0.002029
  2   634.882    0.015535
  3   146.097    0.075411
  4    42.4974    0.257121
  5    14.1892    0.596555
  6     1.9666    0.242517
S    1
  1    5.1477    1.0
S    1
  1    0.4962    1.0
S    1
  1    0.1533    1.0
P    4
  1   18.1557    0.018534
  2    3.9864    0.115442
  3    1.1429    0.386206
  4    0.3594    0.640089
P    1
  1    0.1146    1.0

```

```
HYDROGEN  1.0  0.0000000000  0.0000000000  1.0922959062
DH  0  1.2 1.2
```

```
HYDROGEN  1.0  0.0000000000  0.4152229538  -1.4824967459
DH  0  1.2 1.2
```

```
$END
```

```
--- these are 2-A1 ROHF vectors ---
```

```
--- ROHF ORBITALS --- GENERATED AT 08:23:42 27 JUN 90 (178)
```

```
INSERTION OF CH INTO H2...OS-TCSCF ANSATZ...DZ BASIS
```

```
E(ROHF)= -39.2316245004, E(NUC)= 8.0760320442, 12 ITERS
```

```
$VEC
```

```
1 1 6.01223299E-01 4.37813104E-01 ...
```

```
... vectors deleted to save paper ...
```

```
16 4-2.12429766E-02
```

```
$END
```

```
! EXAM22.
!
! 3-A-2 H3CN    UMP2/6-31G*//UHF/6-31G*
!
! The FINAL UHF energy= -94.0039683697 after 14 iters.
! E(MP2)= -94.2315757668, with RMS grad=0.003359454
! Dipoles for HF and MP2 are 2.049391 and 2.098487 D.
!
$CONTRL SCFTYP=UHF MULT=3 RUNTYP=GRADIENT MPLEVL=2
        COORD=ZMT $END
$SYSTEM TIMLIM=5 MWORDS=1 MEMDDI=1 PARALL=.TRUE. $END
$BASIS  GBASIS=N31 NGAUSS=6 NDFUNC=1 NPFUNC=0 $END
$GUESS  GUESS=HUCKEL $END
$DATA
Methylnitrene...UHF/6-31G* structure
Cnv 3

N
C  1  rCN
H  2  rCH  1  aHCN
H  2  rCH  1  aHCN  3  120.0
H  2  rCH  1  aHCN  3 -120.0

rCN=1.4329216
rCH=1.0876477
aHCN=110.21928
$END
```

```

! EXAM23.
!   semiempirical calculation, using the MOPAC/GAMESS combo
!   AM1 gets the geometry disasterously wrong!
!
!   initial geometry,           MNDO           AM1           PM3
!   FINAL HEAT OF FORMATION 105.14088    93.45997    46.89387
!   RMS gradient            0.0818157    0.1008587    0.0366232
!   final geometry (# steps),      8           11           10
!   FINAL HEAT OF FORMATION  46.45649    -1.81716    -2.79647
!   RMS gradient            0.0000246    0.0000294    0.0000015
!   r(SiH)                   1.42117     1.45813     1.52104
!   a(HSiH)                  101.962     120.000     96.280
!
!   At the final PM3 geometry, the charge on Si is -.4681,
!   and the dipole moment is 2.345322 Debye.
!
$CONTRL SCFTYP=RHF RUNTYP=OPTIMIZE COORD=ZMT ICHARG=-1
$END
$SYSTEM TIMLIM=5 MEMORY=200000 $END
$BASIS  GBASIS=PM3 $END
$DATA
Silyl anion...comparison of semiempirical models
Cnv 3

Si
H  1  rSiH
H  1  rSiH  2  aHSiH
H  1  rSiH  2  aHSiH  3  aHSiH  -1

rSiH=1.15
aHSiH=110.0
$END

```

```
! EXAM24.
! Self-consistent reaction field test, of water in water.
! Cavity radius is calculated from the 1.00 g/cm**3
density.
! FINAL energy is -74.9666740755 after 12 iterations
! Induced dipole= -0.03663, RMS gradient= 0.033467686
!
$contrl scftyp=rhf runtyp=gradient coord=zmt $end
$system memory=300000 $end
$basis gbasis=sto ngauss=3 $end
$guess guess=huckel $end
$scrf radius=1.93 dielec=80.0 $end
$data
water in water, arbitrary geometry
Cnv 2

0
H 1 rOH
H 1 rOH 2 aHOH

rOH = 0.95
aHOH = 104.5
$end
```

```

! EXAM25.
! Illustration of coordinate systems for geometry
searches.
! Arbitrary molecule, chosen to illustrate ring, methyl
on
! ring, methine H10, imino in ring, methylene in ring.
!
!
!      H8 H9
!      \ |
!      H7-C6  O1---O5  H13
!           \ /      \ /
!           C2        C4
!          /  \      /  \
!         H10   N3   H12
!              |
!              H11
!
! The initial AM1 energy is -48.6594935
!
!           initial RMS  final E    final RMS
#steps
! Cartesians          0.0200113 -48.7022520  0.0000304    50
! dangling Z-mat      0.0600637 ... 00 bond crashes on 1st
step
! good Z-matrix       0.0232915 -48.7022510  0.0000285    21
! deloc. coords.      0.0176452 -48.7022537  0.0000267    22
! nat. internals      0.0209442 -48.7022570  0.0000183    15
!
! $contrl scftyp=rhf runtyp=optimize coord=zmt $end
! $system memory=300000 $end
! $statpt hess=guess nstep=100 npert=-1 npun=-2 $end
! $basis gbasis=am1 $end
! $guess guess=huckel $end
! $data
Illustration of coordinate systems
C1
O
C 1 rCOa
N 2 rCNa 1 aNCO
C 3 rCNb 2 aCNC 1 wCNCO
O 4 rCOb 3 aOCN 2 wOCNC
C 2 rCC 1 aCCO 5 wCCOO
H 6 rCH1 2 aHCC1 1 wHCCO1
H 6 rCH2 2 aHCC2 1 wHCCO2
H 6 rCH3 2 aHCC3 1 wHCCO3
H 2 rCHa 1 aHCOa 5 wHCOOa
H 3 rNH 2 aHNC 1 wHNCO
H 4 rCHb 5 aHCOb 1 wHCOOb
H 4 rCHc 5 aHCOc 1 wHCOOc

```

```

rCOa=1.43
rCNa=1.47
rCNb=1.47
rCOb=1.43
aNCO=106.0
aCNC=104.0
aOCN=106.0
wCNCO=30.0
wOCNC=-30.0
rCC=1.54
aCCO=110.0
wCCOO=-150.0
rCH1=1.09
rCH2=1.09
rCH3=1.09
aHCC1=109.0
aHCC2=109.0
aHCC3=109.0
wHCCO1=60.0
wHCCO2=-60.0
wHCCO3=180.0
rCHa=1.09
aHCOa=110.0
wHCOOa=100.0
rNH=1.01
aHNC=110.0
wHNCO=170.0
rCHb=1.09
rCHc=1.09
aHCOb=110.0
aHCOc=110.0
wHCOOb=150.0
wHCOOc=-100.0
$end

```

To use Cartesian coordinates:

```

--- $contrl nzvar=0 $end

```

To use conventional Z-matrix, with a dangling O-O bond:

```

--- $contrl nzvar=33 $end

```

To use well chosen internals, with all 5 ring bonds defined:

```

--- $contrl nzvar=33 $end
--- $zmat izmat(1)=1,1,2, 1,2,3, 1,3,4, 1,4,5, 1,5,1,
    2,1,2,3, 2,5,4,3, 3,5,1,2,3, 3,1,5,4,3,
    1,6,2, 2,6,2,1, 3,6,2,1,5,
    1,6,7, 1,6,8, 1,6,9, 2,7,6,2, 2,8,6,2, 2,9,6,2,

```

```

3,7,6,2,1, 3,8,6,2,1, 3,9,6,2,1,
1,10,2, 2,10,2,1, 3,10,2,1,5,
1,11,3, 2,11,3,2, 3,11,3,2,1,
1,12,4, 2,12,4,5, 3,12,4,5,1,
1,13,4, 2,13,4,5, 3,13,4,5,1 $end

```

To use delocalized coordinates:

```

--- $contrl nzvar=33 $end
--- $zmat dlc=.true. auto=.true. $end

```

To use natural internal coordinates:

```

$contrl nzvar=44 $end
$zmat izmat(1)=1,1,2, 1,2,3, 1,3,4, 1,4,5, 1,5,1, ! ring
!
2,5,1,2, 2,1,2,3, 2,2,3,4, 2,3,4,5, 2,4,5,1,
3,5,1,2,3, 3,1,2,3,4, 3,2,3,4,5, 3,3,4,5,1, 3,4,5,1,2,
1,2,6, 2,6,2,1, 2,6,2,3, 4,6,2,1,3, ! methyl C
!
1,6,7, 1,6,8, 1,6,9, ! methyl Hs
!
2,7,6,8, 2,8,6,9, 2,9,6,7, 2,9,6,2, 2,7,6,2,
2,8,6,2, 3,7,6,2,1,
1,10,2, 2,10,2,1, 2,10,2,3, 2,10,2,6, ! methine !
1,11,3, 2,11,3,2, 2,11,3,4, 4,11,3,2,4, ! imino !
1,12,4, 1,13,4, ! methylene !
2,12,4,13, 2,12,4,3, 2,13,4,3, 2,12,4,5, 2,13,4,5

ijS(1)=1,1, 2,2, 3,3, 4,4, 5,5, ! ring !
6,6, 7,6, 8,6, 9,6,10,6,
7,7, 8,7, 9,7,10,7,
11,8,12,8,13,8,14,8,15,8,
11,9,12,9, 14,9,15,9,
16,10, 17,11,18,11, 19,12, ! methyl C
!
20,13, 21,14, 22,15, ! methyl Hs
!
23,16, 24,16, 25,16, 26,16, 27,16, 28,16,
23,17, 24,17, 25,17,
24,18, 25,18,
26,19, 27,19, 28,19,
27,20, 28,20,
29,21,
30,22, 31,23,32,23,33,23, 32,24,33,24, !
methine !
34,25, 35,26,36,26, 37,27, ! imino !
38,28, 39,29, ! methylene !
40,30, 41,30, 42,30, 43,30, 44,30,
41,31, 42,31, 43,31, 44,31,
41,32, 42,32, 43,32, 44,32,

```


41,33, 42,33, 43,33, 44,33

```

Sij(1)=1.0, 1.0, 1.0, 1.0, 1.0,          ! ring !
      1.0, -0.8090, 0.3090, 0.3090, -0.8090,
          -1.1180, 1.8090, -1.8090, 1.1180,
      0.3090, -0.8090, 1.0, -0.8090, 0.3090,
          -1.8090, 1.1180,          -1.1180, 1.8090,
              1.0, 1.0,-1.0, 1.0, ! methyl C !
1.0, 1.0, 1.0,          ! methyl Hs !
1.0, 1.0, 1.0,-1.0,-1.0,-1.0,
2.0,-1.0,-1.0,
      1.0,-1.0,
          2.0,-1.0,-1.0,
              1.0,-1.0,
1.0,
      1.0, 2.0,-1.0,-1.0, 1.0,-1.0, ! methine !
      1.0, 1.0,-1.0, 1.0,          ! imino !
1.0, 1.0,          ! methylene !
4.0, 1.0, 1.0, 1.0, 1.0,
      1.0,-1.0, 1.0,-1.0,
      1.0, 1.0,-1.0,-1.0,
      1.0,-1.0,-1.0, 1.0 $end

```

```

! EXAM26
!   Localized orbital test...Phys.Chem. 1984, 88, 382-389
!
!   FINAL Energy= -415.2660357363 in 11 iters
!
!   If you localize only the valence orbitals, by commenting
!   out the $LOCAL group below, the
!       Boys localization sum is 204.693589
!   Ruedenberg localization sum is   5.081667
!   population localization sum is   4.610528
!
!   The SCF localized charge decomposition forces all MOs
!   to be localized, so the final diagonal sum is 28.389125.
!   The nuclear charge assigned to oxygen "lone pairs" is
!   redistributed so the total nuclear P and O charges are
!   correct. The energies for the PO bond, PH bonds,
!   and O lone pairs are -37.273022, -27.364212, -26.363865.
!   The corresponding dipoles are 2.041, 3.484, and 3.465.
!
!   To analyze MP2 valence contributions, choose MPLEVL=2,
!   and turn EDCOMP and DIPDCM off. The results should be
!   E(MP2)=-415.4952200908, and contributions of PO bond,
!   PH bonds, and O lone pairs to the correlation energy are
!   -0.0442096, -0.0237793, and -0.0378790, respectively.
!
!   $contrl scftype=rhf runtyp=energy local=ruednbrg mplevl=0
!end
!   $system memory=750000 $end
!   $mp2      lmomp2=.true. $end
!   $local    edcomp=.true. moidon=.true. dipdcm=.true.
!             ijmo(1)= 1,11, 2,11, 1,12, 2,12, 1,13, 2,13
!
!   zij(1)=1.666666667,0.333333333,1.666666667,0.333333333,
!           1.666666667,0.333333333
!           moij(1)= 2,1, 2,1, 2,1
!           nnucmo(11)=2,2,2 $end
!   $basis    gbasis=n21 ngauss=3 ndfunc=1 $end
!   $data
!   phosphine oxide...3-21G* basis...localized orbital test
!   Cnv 3
!
!   P 15.0
!   O  8.0  0.0000000000  0.0  1.4701
!   H  1.0  1.2335928631  0.0 -0.6421021244
!   $end

```

```

! EXAM27.
!   NH3   semi-empirical DRC calculation
!
!   The dynamic reaction coordinate is initiated at the
!   planar inversion transition state, with a velocity
!   parallel to the mode with imaginary frequency. The
!   reactive trajectory is given one kcal/mole energy in
!   excess of the amount needed to traverse the barrier.
!   The trajectory is analyzed in terms of the equilibrium
!   geometry's coordinates and normal modes. Because
!   this is a test run, the trajectory is stopped after
!   a much too short time interval.
!
!   The last point on the trajectory has
!   T=0.00163, V=-9.12874, E=-9.12710,
!   q(L6)=-0.153112, p(L6)=-0.014313,
!   velocity(H,z)=0.028857623667
$CONTRL SCFTYP=RHF RUNTYP=DRC $END
$SYSTEM MEMORY=300000 $END
$BASIS  GBASIS=AM1 $END
$DATA
ammonia...DRC starting from the planar transition state
C1
NITROGEN    7.0    0.0000000000    0.0000000000
0.0000000000
HYDROGEN    1.0   -0.4882960784    0.8457536168
0.0000000000
HYDROGEN    1.0   -0.4882960784   -0.8457536168
0.0000000000
HYDROGEN    1.0    0.9765921567    0.0000000000
0.0000000000
$END
$DRC NPRTSM=1 NSTEP=10 DELTAT=0.1 NMANAL=.TRUE. EKin=1.0
      VEL(1)=0.0 0.0 -0.1128,
              0.0 0.0 0.5213,
              0.0 0.0 0.5213,
              0.0 0.0 0.5213
      CO(1)=0.0000000000  0.0000000000  0.0291576578
              -0.4692651161  0.8127910232  -0.3097192193
              -0.4692651161 -0.8127910232  -0.3097192193
              0.9385302321  0.0000000000  -0.3097192193 $END
$HESS
ENERGY IS      -9.1354556210 E(NUC) IS      6.8369847904
 1  1 6.16231432E-01 3.45452916E-11-1.03923982E-05 ...
... 2nd derivatives deleted to save paper ...
12  3 1.38181166E-10 5.72335505E-02
$END

```

```

! EXAM28. Morokuma energy decomposition.
! This run duplicates a result from Table 16 of
! H.Umeyama, K.Morokuma, J.Am.Chem.Soc. 99,1316(1977)
!
!           GAMESS      literature
!      ES=   -14.02      -14.0
!      EX=     8.98       9.0
!      PL=    -1.12      -1.1
!      CT=    -2.37      -2.4
!      MIX=   -0.43      -0.4
!      total -8.96      -9.0
!
$contrl scftyp=rhf runtyp=morokuma coord=zmt $end
$system memory=300000 timlim=5 $end
$basis  gbasis=n31 ngauss=4 $end
$guess  guess=huckel $end
$morokm iatm(1)=3 $end
$data
water-ammonia dimer
Cs

H
O 1 rOH
H 2 rOH 1 aHOH
N 2 R 1 aHOH 3 0.0
H 4 rNH 3 aHNaxis 1 180.0
H 4 rNH 3 aHNaxis 5 +120.0
H 4 rNH 3 aHNaxis 5 -120.0

rOH=0.956
aHOH=105.2
rNH=1.0124
aHNaxis=112.1451 ! makes HNH=106.67
R=2.93
$end

```

```

! EXAM29.  surface scan
! The scan is done over a 3x3 grid centered on the SCF
! transition state for the SN2 type reaction
!      F- + NH2OH -> F-NH2-OH anion -> FNH2 + OH-
!
! Groups 1 and 2 are F and OH, and their distance from
! the N is varied antisymmetrically, which is more or
! less what the IRC should be like. The results seem to
! indicate that the MP2/3-21G saddle point would shift
! further into the product channel, since the higher
! MP2 energies occur at shorter r(NF) and longer r(NO):
!
! FINAL E=   -229.0368324615, E(MP2)=   -229.3873302375
! FINAL E=   -229.0356378402, E(MP2)=   -229.3866642673
! FINAL E=   -229.0309266321, E(MP2)=   -229.3822094777
! FINAL E=   -229.0372146702, E(MP2)=   -229.3923234074
! FINAL E=   -229.0385440296, E(MP2)=   -229.3936486644
! FINAL E=   -229.0367369562, E(MP2)=   -229.3913683073
! FINAL E=   -229.0328601144, E(MP2)=   -229.3918932009
! FINAL E=   -229.0364643934, E(MP2)=   -229.3948325500
! FINAL E=   -229.0372478250, E(MP2)=   -229.3943498144
!
! A more conclusive way to tell this would be to compute
! single point MP2 energies along the SCF IRC, since the
! true reaction path always curves, and thus does not lie
! along rectangular grid points.
!
$contrl  scftyp=rhf runtyp=surface
         icharg=-1 coord=zmt mplevl=2 $end
$system  memory=500000 timlim=30 memddi=2 $end
$surf    ivec1(1)=2,1 igrp1=1
         ivec2(1)=2,5 igrp2(1)=5,6
         disp1= 0.10 ndisp1=3 orig1=-0.10
         disp2=-0.10 ndisp2=3 orig2= 0.10 $end
$basis   gbasis=n21 ngauss=3 $end
$guess   guess=huckel $end
$data
F-NH2-OH exchange (inspired by J.Phys.Chem. 1994,98,7942-4)
Cs

F
N 1 rNF
H 2 rNH   1 aFNH
H 2 rNH   1 aFNH   3 aHNH   +1
O 2 rNO   3 aONH   4 aONH   -1
H 5 rOH   2 aHON   1 180.0

rNF=1.7125469

```

```
rNH=0.9966981  
rNO=1.9359887  
rOH=0.9828978  
aFNH=90.18493  
aONH=79.34339  
aHON=100.78851  
aHNN=108.57000  
$end
```

```

!   EXAM30
!   Test of water EFP ... formamide/three water complex
!   FINAL E= -169.0085352303 after 12 iterations
!   RMS gradient=0.008099469
!   The geometry below combines a computed gas phase
!   structure for formamide, with three waters located
!   in a cyclic fashion whose positions approximate the
!   minimum structure of W.Chen and M.S.Gordon.  This
!   approximate structure lies about 11 mHartree above
!   the actual minimum.
$contrl scftyp=rhf runtyp=gradient coord=zmt $end
$system memory=300000 $end
$basis  gbasis=dh npfunc=1 ndfunc=1 $end
$data
formamide with three effective fragment waters
C1
C
O 1 rCO
N 1 rCN  2 aNCO
H 3 rNHa 1 aCNHa 2 0.0
H 3 rNHb 1 aCNHb 2 180.0
H 1 rCH  2 aHCO  4 180.0

rCO=1.1962565
rCN=1.3534065
rNHa=0.9948420
rNHb=0.9921367
rCH=1.0918368
aNCO=124.93384
aCNHa=119.16000
aCNHb=121.22477
aHCO=122.30822
$end
$efrag
coord=int
fragname=H2ORHF
O1  4 1.926      3 175.0      1 180.0
H2  7 0.9438636  4 117.4      3 -175.0
H3  7 0.9438636  8 106.70327  4 95.0
fragname=H2ORHF
O1  8 1.901      7 175.0      4 0.0
H2 10 0.9438636  8 110.0      4 -5.0
H3 10 0.9438636 11 106.70327  8 -95.0
fragname=H2ORHF
H2  2 1.951      1 150.0      3 0.0
O1 13 0.9438636  2 177.0      3 0.0
H3 14 0.9438636 13 106.70327  3 140.0
$end

```

```

! EXAM31.
!   methanol in PCM water...RHF geometry optimization
!   FINAL E= -115.0425099569, 10 iters, RMS Grad= 0.0019075
!   FINAL E= -115.0425563041,  7 iters, RMS Grad= 0.0006106
!   FINAL E= -115.0425615962,  6 iters, RMS Grad= 0.0001950
!   FINAL E= -115.0425621855,  5 iters, RMS Grad= 0.0000403
!   FINAL E= -115.0425622093,  4 iters, RMS Grad= 0.0000309
!   FINAL E= -115.0425622106,  3 iters, RMS Grad= 0.0000033
!
!   ----- RESULTS OF PCM CALCULATION -----
!   FREE ENERGY IN SOLVENT      = -115.0425622106 A.U.
!   INTERNAL ENERGY IN SOLVENT  = -115.0346408480 A.U.
!   DELTA INTERNAL ENERGY      = .0000000000 A.U.
!   ELECTROSTATIC INTERACTION    = -.0079213626 A.U.
!   PIEROTTI CAVITATION ENERGY  = .0000000000 A.U.
!   DISPERSION FREE ENERGY      = .0000000000 A.U.
!   REPULSION FREE ENERGY       = .0000000000 A.U.
!   TOTAL INTERACTION            = -.0079213626 A.U.
!   TOTAL FREE ENERGY IN SOLVENT = -115.0425622106 A.U.
!
!$contrl scftyp=rhf runtyp=optimize nzvar=12 $end
!$system mwords=2 $end
!$pcm solvnt=water $end
!$basis gbasis=n31 ngauss=6 ndfunc=1 $end
!$guess guess=huckel $end
!$zmat izmat(1)=1,1,2, 1,2,3, 1,3,4, 1,3,5, 1,3,6,
!           2,1,2,3, 2,2,3,4, 2,2,3,5, 2,2,3,6,
!           3,1,2,3,4, 3,1,2,3,5, 3,1,2,3,6 $end
!$statpt opttol=1d-5 $end
!$data
Methanol in PCM water...starting at gas phase geom
Cs
H 1.0 -1.0616171503 0.8036449245 0.0000000000
O 8.0 -0.6870131482 -0.0653470836 0.0000000000
C 6.0 0.7093551399 0.0291827007 0.0000000000
H 1.0 1.0836641283 0.5408321444 0.8835398105
H 1.0 1.0975386849 -0.9797829903 0.0000000000
$end

```



```

! EXAM32.
! Test of Coupled-Cluster energy for HNO
! The basis set used is 6-31G(d,p), with 35 AOs.
! The two chemical core orbitals are not correlated.
!
! RHF FINAL E= -129.7891059393 after 13 iters
! Highest level result is E(CR-CCSD(T))= -130.1486914386
!
! Other results are
! 19 CCSD iterations needed to converge T1 and T2.
! E(MBPT(2)) = -130.1278985212, aka MP2 energy
! E(CCSD)      = -130.1398314376
! E(CCSD(T))   = -130.1508271127
! The T1 diagnostic is 0.01448788, and the largest T2
! amplitude is for the pi->pi* double, namely -0.146352.
! The R-CCSD(T) denominator is 1.126.
!
$contrl scftyp=rhf cctyp=cr-cc runtyp=energy nzvar=3 $end
$system mwords=2 $end
$guess  guess=huckel $end
$basis  gbasis=n31 ngauss=6 ndfunc=1 npfunc=1 $end
$zmat   izmat(1)=1,1,2, 1,2,3, 2,1,2,3 $end
$data
HNO...CR-CCSD(T) computation in small DZP basis
Cs
H 1.0 -0.3153213523 0.9784305023 0.0
N 7.0 0.0188021294 0.0012704060 0.0
O 8.0 1.1940439356 0.0007180427 0.0
$end

```

```

! EXAM 33.
!   This job illustrates occupation restricted multiple
!   active space MCSCF, for HCN.
!
!   The multiple active spaces are sigma, pi-x, and pi-y.
!   The excitation level between these three spaces can be
!   limited to 0, 1, or 2. The number of determinants in
!   each such ORMAS-MCSCF are
!


| excitation | MINE  | MAXE   | # dets | energy     | gradient |
|------------|-------|--------|--------|------------|----------|
| 0          | 6,2,2 | 6,2,2  | 2,610  | -93.014905 | 0.04394  |
| 1          | 5,1,1 | 7,3,3  | 11,290 | -93.014905 | 0.04394  |
| 2          | 4,0,0 | 8,4,4  | 15,410 | -93.022394 | 0.04510  |
| full CI    | 2,0,0 | 10,4,4 | 15,876 | -93.022407 | 0.04511  |


!   Full CI of 10 valence electrons in 9 valence orbitals
!   is well within the capabilities of CISTEP=ALDET, but
!   this example is meant to illustrate using occupational
!   restrictions to limit the number of determinants.
!   Note the singles between spaces don't contribute any
!   energy because in this case the singles determinants
!   all have the wrong total space symmetry.
!
!   FINAL E= -93.0223942017, 11 iters, RMS grad=0.045100935
!
$contrl scftyp=mcscf runtyp=gradient nzvar=3 $end
$system mwords=5 memddi=1 $end
$basis gbasis=n31 ngauss=6 ndfunc=1 npfunc=1 $end
$zmat izmat(1)=1,1,2, 1,2,3, 5,1,2,3 $end
$libe apts(1)=1.0,0.0,0.0 $end
! reordering is sigma before pi-x before pi-y before empty
$guess guess=moread norb=35 norder=1
      iorder(3)=3,4,5,10,14, 6,9, 7,8, 11,12,13 $end
$mcscf soscf=.true. cistep=ormas $end
$det ncore=2 nact=9 nels=10 $end
$ormas nspace=3 mstart(1)=3,8,10 mine(1)=4,0,0
      maxe(1)=8,4,4 $end

!   uncomment the following lines to convert this run
!   from a MCSCF nuclear gradient, into a 2nd order
!   perturbation theory energy correction using GMCQDPT.
!   E(MP2)= -93.1328290859, reference wt= 96.974%
--- $contrl runtyp=energy mplevl=2 $end
--- $system mwords=10 memddi=10 $end
--- $mcscf soscf=.true. cistep=gmcci $end
--- $gmcpt nmofzc=2 nmodoc=0 nmoact=9 reftyp=ormas
---      nspace=3 mstart(1)=3,8,10 mine(1)=4,0,0
---      maxe(1)=8,4,4 $end
--- $mrmp mrpt=gmcpt $end

```

```
$data
HCN...6-31G(d,p) MCSCF using ORMAS...RHF geometry
Cnv 4
```

```
H  1.0  0.0 0.0 -1.0589956
C  6.0  0.0 0.0  0.0
N  7.0  0.0 0.0  1.1327718
```

```
$end
```

```
--- CLOSED SHELL MO's --- GENERATED Mon, Jan 13, 2003
E(RHF)= -92.8771381048, with MVOQ=4 used to make virtuals.
```

```
$VEC
```

```
...orbitals deleted...
```

```
$END
```

```

! EXAM34.
!   CIS treatment of excited states of formaldehyde.
!
!   EXCITED STATE 1's E=-113.7017742428, RMS=0.0290048
!   The S0->S1 transition dipole is (0,0,0.006029),
!   and the S0 -> S1 transition energy is 4.56 eV.
!
!   geometry optimization would lead in 18 steps to
!   -113.7053624528, at r(CO)=1.2553, r(CH)=1.0854,
!   a(HCO)= 117.74, with C's pyramidalization= 24.88.
!   This reproduces the fourth line of Table III in
!   Foresman et al. J.Phys.Chem. 96, 135-149(1992),
!   using no frozen core orbitals in order to do so.
!   Since it is well known that the geometry of this
!   state lies within Cs symmetry, the initial guess
!   geometry below is very slightly bent into Cs.
!
$contrl scftyp=rhf cityp=cis runtyp=gradient nzvar=6 $end
$system timlim=1 $end
$basis  gbasis=n31 ngauss=6 ndfunc=1 diffsp=.t. $end
$guess  guess=huckel $end
$scis    hamtyp=saps mult=1 nacore=0 nstate=1 istate=1 $end
$zmat    izmat(1)=1,1,2,  1,2,3,  1,2,4,
              2,1,2,3,  2,1,2,4,  4,1,2,4,3 $end

$data
Formaldehyde CIS/6-31+G(d) 1(n->pi*) state optimization
Cs

O   8.0   .01  -.8669736159  .0
C   6.0   .0   .3455497481  .0
H   1.0  -0.01  .9295804473  .9376713430
$end

```

```

! EXAM35.
!   As atom...Test of relativistic energy correction,
!   by the Douglas-Kroll transformation to 3rd order.
!
!   the FINAL DK3 energy is -2259.0955118230
!   web page says           -2259.095511826
!
!   convergence of the DK transformation is typical,
!       0th order -2234.2372862734 (non-relativistic)
!       1st order -2264.6131852344
!       2nd order -2258.9450216276
!       3rd order -2259.0955118230
!   in that 1st order way undershoots, 2nd order comes
!   back close, and 3rd order is not insubstantial.
!   Compare with -2259.456841 which is the point
!   nucleus Dirac-Coulomb numerical Hartree-Fock from
!   L.Visscher, K.G.Dyall
!   At.Data Nucl.Data Tables 67, 207-224(1997)
!
!   The uncontracted 20s15p9d basis set below is from
!       T.Tsuchiya, M.Abe, T.Nakajima, K.Hirao
!       J.Chem.Phys. 115, 4463-4472(2001)
!   using exponents downloaded from the web page of
!   this group at the University of Tokyo. A general
!   contraction of this basis can easily be obtained,
!   by manipulating the $VEC coefs produced by this run.
!   The semicolon divides two lines of input that happen
!   to be given on a single physical line of the file.
!
!$contrl scftyp=rohlf mult=4 relwfn=dk ispher=1 $end
!$system mwords=2 $end
!$relwfn norder=3 $end
!$guess guess=huckel $end
!$data
!illustration of 3rd order Douglas-Kroll for As
!Dnh 2

```

Arsenic 33.0

```

S 1 ; 1 7.2421890D+07 1.0
S 1 ; 1 7.7040750D+06 1.0
S 1 ; 1 1.3365730D+06 1.0
S 1 ; 1 3.0394350D+05 1.0
S 1 ; 1 8.3289250D+04 1.0
S 1 ; 1 2.5994450D+04 1.0
S 1 ; 1 8.9795770D+03 1.0
S 1 ; 1 3.3667950D+03 1.0
S 1 ; 1 1.3464700D+03 1.0
S 1 ; 1 5.6774580D+02 1.0

```

```
S 1 ; 1 2.4923080D+02 1.0
S 1 ; 1 1.1199520D+02 1.0
S 1 ; 1 4.6328140D+01 1.0
S 1 ; 1 2.2611220D+01 1.0
S 1 ; 1 1.0910110D+01 1.0
S 1 ; 1 4.5498340D+00 1.0
S 1 ; 1 2.1494630D+00 1.0
S 1 ; 1 1.0337510D+00 1.0
S 1 ; 1 3.0892460D-01 1.0
S 1 ; 1 1.1206710D-01 1.0
P 1 ; 1 4.9515580D+04 1.0
P 1 ; 1 8.4637830D+03 1.0
P 1 ; 1 2.2908560D+03 1.0
P 1 ; 1 7.7965970D+02 1.0
P 1 ; 1 3.0545690D+02 1.0
P 1 ; 1 1.3097990D+02 1.0
P 1 ; 1 5.9698960D+01 1.0
P 1 ; 1 2.8408790D+01 1.0
P 1 ; 1 1.3883000D+01 1.0
P 1 ; 1 6.6102210D+00 1.0
P 1 ; 1 3.0821260D+00 1.0
P 1 ; 1 1.3919830D+00 1.0
P 1 ; 1 4.8254700D-01 1.0
P 1 ; 1 1.9228260D-01 1.0
P 1 ; 1 7.2849660D-02 1.0
D 1 ; 1 7.1896480D+02 1.0
D 1 ; 1 2.0798400D+02 1.0
D 1 ; 1 7.9590850D+01 1.0
D 1 ; 1 3.4514110D+01 1.0
D 1 ; 1 1.5730540D+01 1.0
D 1 ; 1 7.2805600D+00 1.0
D 1 ; 1 3.3000700D+00 1.0
D 1 ; 1 1.4173160D+00 1.0
D 1 ; 1 5.4472730D-01 1.0
```

\$end

```

! EXAM36
!   analytic hessian for determinant MCSCF, at the
!   transition state for C=C rotation in ethylene
!
!   There are 38 AOs and 36 MOs using spherical harmonics.
!   The 4e-, 4 orbital active space (CC sigma, pi, pi*, and
!   sigma* orbitals) generates a total of 36 determinants.
!
!   FINAL E= -77.9753563834 after 14 iterations
!   imaginary FREQ= 1847.32i
!   true FREQ= 319.87(2), 1005.72(2), 1082.80, 1578.13
!   true FREQ= 1605.72, 3311.13, 3315.17, 3405.91(2)
!   the lowest true vibration is the most intense, 1.09748
!
$contrl scftyp=mcscf runtyp=hessian ispher=1 $end
$system mwords=1 memddi=5 timlim=50 $end
$basis  gbasis=n31 ngauss=6 ndfunc=1 $end
$guess  guess=moread norb=36 norder=1
        iorder(3)=4,5,6,7, 3,8,9,10 $end
$det     ncore=6 nact=4 nels=4 $end
$data
C2H4 at rotational saddle point...sigma,pi,pi*,sigma*
active
Dnd 2

C      6.0   0.0000000000   0.0000000000   0.7486926908
H      1.0   0.6500976762   0.6500976762   1.3062796706
$end

```

How to prepare the starting orbitals, also take note of the orbital reordering to select the CC sigma:

```

--- $contrl scftyp=rohff mult=3 runtyp=energy $end
--- $scf     mvoq=2 $end
--- $guess  guess=huckel norder=0 $end

--- OPEN SHELL ORBITALS --- Tue Apr  6 10:00:30 2004
E(ROHF)=      -77.9570103652
$VEC
1  1  7.04639833E-01...
...
36  8  3.55118554E-02-8.89989950E-03-3.55118554E-02
$END

```

```

! EXAM 37.
!   water trimer...illustration of FMO method on clusters
!
!   A total of 21 energies are computed in this run,
!   of which the very first and last are -75.0201194583
!   and -149.9943977172, from various monomer and dimer
!   calculations. Combined together, the results for
!   2-body FMO-RHF are:
!   Euncorr(2)= -224.910612407, RMS GRADIENT = 0.0267805
!
!   Explicit RHF/STO-3G calculation on these coords has
!   E= -224.9112662623,          grad=0.0269349
!
!   See ../gamess/tools/fmo for larger examples based on
!   published data and examples involving bond
fractioning.
!
$contrl scftyp=rhf runtyp=gradient $end
$system timlim=2 $end
$basis  gbasis=sto ngauss=3 $end
$fmo     nfrag=3 icharg(1)=0,0,0
        frgnam(1)=frag01,frag02,frag03
        indat(1)=1,1,1,
                2,2,2,
                3,3,3
$end
$fmoprpr nprint=0 $end
$fmoxxyz
O  O      .000000      .000000      .000000
H  H      .000000      .000000      .957200
H  H      .926627      .000000     -.239987
O  O      2.542027      .893763     -1.001593
H  H      1.991815      1.623962     -1.284979
H  H      2.958433      .581215     -1.804806
O  O      .162059      2.462918     -1.477183
H  H      -.189749      1.755643     -.936605
H  H      -.375542      2.449889     -2.269046
$end
$data
Basis set input, with no atomic coordinates
C1
h-1 1
c-1 6
n-1 7
o-1 8
$end

```



```

! EXAM 38.
! Analytic gradients for Model Core Potentials,
! with a DZP quality basis, for BiCl3. Model Core
! Potentials account for scalar relativity effects,
! and preserve all valence orbital radial nodes.
!
! The latter point stands in contrast to the
! Effective Core Potential (ECP) pseudopotentials.
!
! FINAL RHF E= -116.3966190322, RMS grad= 0.0053955
! FINAL RHF E= -116.3972798590, RMS grad= 0.0036800
! FINAL RHF E= -116.3976422769, RMS grad= 0.0014246
! FINAL RHF E= -116.3976891713, RMS grad= 0.0001135
! FINAL RHF E= -116.3976900830, RMS grad= 0.0000485
! FINAL RHF E= -116.3976902416, RMS grad= 0.0000001
!
$contrl scftyp=rhf runtyp=optimize pp=mcp ispher=1
        coord=zmt nzvar=6 $end
$system timlim=5 mwords=4 $end
$basis  gbasis=mcp-dzp $end
$statpt opttol=1.0d-5 $end
$data
BiCl3
Cnv 3

Bi
Cl  1 rBiCl
Cl  1 rBiCl  2 aClBiCl
Cl  1 rBiCl  2 aClBiCl  3 aClBiCl +1

rBiCl=2.48
aClBiCl=99.0
$end

```

```
! EXAM 39.
! The non-resonant Raman and hyper-Raman spectra of CH4
!
! Please see the actual file, supplied with GAMESS, for
! its very long preamble about the inadequacy of the
! basis set used below, and how to interpret the output.
!
$contrl scftyp=rhf runtyp=tdhfx nosym=1 ispher=0 $end
$system mwords=1 $end
$basis gbasis=n21 ngauss=3 $end
$guess guess=huckel $end
$scf dirscf=.true. conv=1d-6 $end
$force method=analytic $end
$cphf cphf=A0 polar=.false. $end
$tdhfx
  FREQ2
  DADX 0.04
  DADX_NI 0.04
  DBDX 0.04 0.04
  DBDX_NI 0.04 0.04
  RAMAN 0.04
  HRAMAN 0.04
  D2ADX2_NI 0.04
  D2BDX2_NI 0.04 0.04
$end
$data
methane RHF
Td

C      6.0    0.0          0.0          0.0
H      1.0    0.6252197764  0.6252197764  0.6252197764
$END
```

```

! EXAM40.
! CH2 singlet/triplet...minimum energy crossing.
! Ansatz is full valence MCSCF in cc-pVDZ basis,
! 25 AOs and 24 MOs, using spherical harmonics.
!
! It is well known that the ground state of CH2
! (A.Kalemos, T.H.Dunning, A.Mavridis, J.F.Harrison
! Can.J.Chem. 82, 684-693(2004)) is a triplet,
! but that the singlet state becomes the
! lowest surface at small angles. In this basis,
! the states have their minima at
!
!           r(CH)      a(HCH)      Energy
!   3-B-1  1.10155    130.9955   -38.9605726
!   1-A-1  1.13868     99.9417   -38.9415486
! and we know there is a crossing of these states
! somewhere. Starting between the minima, near
! R=1.11 and angle=115, where
!   triplet E= -38.9565003, dE/dZ(C)=+.0259717
!   singlet E= -38.9359506, dE/dZ(C)=-.0411344,
! the seam minimization stops in 13 steps at
!   C   0.0   .0000000000   .0977833873
!   H   0.0   -.8659658151  -.6448916937
!   H   0.0   .8659658151   -.6448916937
! which is R=1.1408, angle=98.77, actually just
! inside the 1-A-1's bond angle. This MEX point
! is the "transition state" for spin-orbit-coupling
! induced inter-system-crossing (ISC) between
! these two surfaces, see N.Matsunaga, S.Koseki,
! M.S.Gordon J.Chem.Phys. 104, 7988-7996(1996).
! Note that the MEX's energy and structure are
! very similar to the singlet state's minimum:
!   Energy of First State = -38.941516
!   Energy of Second State = -38.941513
!   Energy Difference = .000003
!   Max Effective Gradient = .000009
!   RMS Effective Gradient = .000005
!   Max Change of X = .000023
!   RMS change of X = .000011
!   PARALLEL GRADIENT (in seam) has RMS=.026456
!
!$contrl runtyp=mex ispher=1 nzvar=3 $end
!$basis  gbasis=ccd $end
!$guess  guess=moread norb=24 $end
!$zmat   izmat(1)=1,1,2, 1,1,3, 2,2,1,3 $end
!$mex    scf1=mcscf mult1=3 nmos1=24
!         scf2=mcscf mult2=1 nmos2=24 nrdmos=3 $end
!$det1   istsym=3 ncore=1 nact=6 nels=6 $end
!$det2   istsym=1 ncore=1 nact=6 nels=6 $end

```

```
$data
methylene...cc-pVDZ basis set
Cnv 2

Carbon      6.0
Hydrogen    1.0      0.0  0.936  -0.596
$end

3-B-1 state: E(MCSCF)=      -38.9565003122
$VEC1
...snipped...
$END

1-A-1 state: E(MCSCF)=      -38.9359506088
$VEC2
...snipped...
$END
```

```

! EXAM 41.
!   This job illustrates TDDFT/BLYP/6-31+G(d) for
!   the 3 lowest singlet excited states of CO.
!   Note the use of diffuse functions in the basis
!   set, since excited states often have Rydberg
!   character.
!
!   The geometry is optimized at the BLYP level,
!   and is slightly longer than R0(exp)=1.128323.
!   experimental Te is 8.06 to 1-pi,
!   8.17 to 1-sigma-minus
!   Computational results on the log file show you
!   that these two states arise from sigma->pi*,
!   and pi->pi* excitations, respectively.
!
!   ground state FINAL E= -113.3036657017, in 18 iters
!
!   state excitation   transition dipole   oscillator
!   ev               x       y       z       strength
! 0 sig+   .000
! 1 pi    8.107   .6618   .1110   .0000   .089
! 2 pi    8.107   .1110  -.6618   .0000   .089
! 3 sig-   9.407   .0000   .0000   .0000   .000
!
!   RMS gradient of 1st excited state= 0.091670657
!
! $contrl scftyp=rhf dfttyp=blyp tddft=excite
!         runtyp=gradient $end
! $system timlim=10 mwords=7 $end
! $tddft  nstate=3 mult=1 iroot=1 $end
! $guess  guess=huckel $end
! $basis  gbasis=N31 ngauss=6 diffsp=.T. ndfunc=1 $end
! $data
CO...excitation to the three lowest singlet states
Cnv 4
C    6.0    0.0    0.0    0.0
O    8.0    0.0    0.0    1.1497297
$end

```

EXAM 42.

```

! numerical gradient for PH3, using CCTYP=CR-CCL
! there are 40 AOs, 38 MOs, 5 frozen cores, so
! 4 valence orbitals correlated by 29 virtuals.
!
! This tests the numerical gradient driver, and also
! emphasizes that the Dunning correlation consistent
! basis sets should be used in spherical harmonic form.
!
! Since this molecule has two totally symmetric degrees
! of freedom, 1 numerical gradient requires 5 energies:
! at the input geometry, and at a pair of geometries
! displaced along each totally symmetric direction.
!
! See METHOD=FULLNUM in $FORCE for numerical hessians,
! and RUNTYP=FFIELD for numerical polarizabilities.
!
! E(RHF)= -342.4761838200, E(CCSD)= -342.6400065656,
! T1 diag=0.01066308, mu(CCSD)= 0.717048 Debye
! standard E(CCSD(T)) is not generated by this run.
!
! E(CR-CCL)= E(CR-CC(2,3)= -342.6433870011,
! RMS gradient= 0.004511564
!
$contrl scftyp=rhf cctyp=cr-cc1
        runtyp=gradient numgrd=.true.
        ispher=1 coord=zmt nzvar=6 $end
$system timlim=5 mwords=2 $end
$basis gbasis=ccd $end
$data
PH3...RHF/cc-pVDZ geometry
Cnv 3

P
H 1 rPH
H 1 rPH 2 aHPH
H 1 rPH 2 aHPH 3 aHPH +1

rPH=1.412958
aHPH=95.2045121
$end

```

EXAM 42.

```

! numerical gradient for CN, using open shell CC(2,3).
!
! This tests the numerical gradient driver, and also
! emphasizes that the Dunning correlation consistent
! basis sets should be used in spherical harmonic form.
!
! A numerical gradient computation requires the energy
! at the molecule's actual geometry, plus energies at
! a pair of geometries displaced along each of its
! totally symmetric directions.
! A diatomic has 1 totally symmetric degree of freedom,
! so this run requires 3 energies for 1 gradient.
!
! See METHOD=FULLNUM in $FORCE for numerical hessians,
! and RUNTYP=FFIELD for numerical polarizabilities.
!
! There are 30 AOs, 28 MOs, 2 frozen cores, so 5 alpha
! and 4 beta valence electrons are correlated.
!
! E(ROHF)= -92.1960778308, E(CCSD)= -92.4767618032,
! the CR-CCL energy E(CC(2,3)) = -92.4930167395,
! and RMS gradient= 0.029652621 at the CC(2,3) level.
! (will optimize to -92.4941853332 at 1.1966876)
!
$contrl scftyp=rohfcctyp=cr-cc1 mult=2 nzvar=1
        runtyp=gradient numgrd=.true. ispher=1 $end
$system timlim=5 $end
$basis gbasis=ccd $end
$zmat izmat(1)=1,1,2 $end
$ccinp maxcc=50 $end
$data
CN...experimental geometry...X-2-sigma-plus state
Cnv 4

C 6.0 0.0 0.0 0.0
N 7.0 0.0 0.0 1.1718
$end

```

```

! EXAM 43.
!   methane G3(MP2,CCSD(T)) heat of formation
!       6-31G(d) has 23 AOs and 23 MOs,
!       G3Large has 79 AOs and 74 MOs.
! -----
! MP2/6-31G(D)   = -40.332552 CCSD(T)/6-31G(D)= -40.355850
! MP2/G3MP2LARGE = -40.404248 BASIS CONTRIBUT =  -.071696
! ZPE(HF/6-31G(D))=  .042659 ZPE SCALE FACTOR=  .892900
! HLC           =  -.036680 FREE ENERGY      =  .030480
! THERMAL ENERGY =  .050629 THERMAL ENTHALPY=  .051573
!       HEAT OF FORMATION   (0K):      -16.01 KCAL/MOL
!       HEAT OF FORMATION (298K):      -17.83 KCAL/MOL
! -----
! The literature, namely JCP 110,4705(1999), says the
! heat of formation by G3(MP2,QCISD(T)) = -17.8 @ 298
! This run substitutes the standard CCSD(T) energy for
! QCI, as considered by
!   L.A.Curtiss, K.Ragavachari, P.C.Redfern, A.G.Baboul,
!   J.A.Pople Chem.Phys.Lett. 314, 101-107(1999)
! RUNTYP=G3MP2 performs a sequence of computations,
!   First, using the 6-31G(d) Cartesian GTO basis set:
!     HF geometry optimization (much like runtyp=optimize)
!     HF frequencies and ZPE evaluation (runtyp=hessian)
!     MP2 geometry, with no frozen cores (runtyp=optimize)
!     CCSD(T) energy calculation (runtyp=energy)
!   Then, using the G3Large basis, as spherical harmonics:
!     MP2 energy calculation, with frozen cores
! All these intermediate energies are then gathered
! together by the G3 recipe to produce the results.
! Note that there is no particular input. The two basis
! sets that are used, and the switch from Cartesian to
! spherical harmonics is handled internally, so there is
! no $BASIS group. The necessary basis sets are available
! for H-Ca, Ga-Kr. Parallel computation is enabled. The
! reference state must be RHF at present.
! You can assist the run by giving a converged HF/6-31G(d)
! geometry in $DATA, although this is not necessary.
! $contrl scftype=rhf runtyp=g3mp2 $end
! $system timlim=5 mwords=2 memddi=5 $end
! $scf   dirscf=.true. $end
! $data
Methane...G3(MP2,CCSD(T))
Td
C   6.0   0.0000000   0.0000000   0.0000000
H   1.0   0.6375302   0.6375302   0.6375302
! $end

```



```

! EXAM 44.
!   Hydrogen fluoride hexamer...(HF)6
!   using the divide-and-conquer (DC) method
!
!   Divide-and-conquer HF and MP2 energies are:
!       FINAL DC-RHF E= -599.9471636844, 14 iters
!       E(MP2)= -600.7388336079
!   An explicit MP2/6-31G calculation yields:
!       RHF E= -599.9475140963, 12 iters
!       MP2 E= -600.7399209860
!
!   CCSD calculation requires changing one keyword in
!   $CONTRL. The divide-and-conquer CCSD energy is
!       E(CCSD)= -600.7487442686
!   compared to the explicit CCSD/6-31G calculation:
!       CCSD ENERGY= -600.7485966549
!
$CONTRL SCFTYP=RHF RUNTYP=ENERGY MPLEVL=2 COORD=ZMT $END
$SYSTEM MWORDS=1 $END
$BASIS  GBASIS=N31 NGAUSS=6 $END
$GUESS  GUESS=HUCSUB $END
$DCCORR DODCCR=.TRUE. RBUFCR=3.0 $END
$DANDC  DCFLG=.TRUE. BUFRAD=5.0 BUFTYP=RADSUB
NSUBS=6 LBSUBS(1)=1,2,3,4,5,6,1,2,3,4,5,6 $END
$DATA
zigzag hexamer (HF)6
C1
F
F  1 rFF
F  2 rFF  1 aHfH
F  3 rFF  2 aHfH  1 180.0
F  4 rFF  3 aHfH  2 180.0
F  5 rFF  4 aHfH  3 180.0
H  1 rHfL  2 aHfH  3 180.0
H  2 rHF   3 aHfH  4 180.0
H  3 rHF   4 aHfH  5 180.0
H  4 rHF   5 aHfH  6 180.0
H  4 rFH   3 aHfH  2 180.0
H  5 rFH   4 aHfH  3 180.0

rFF=2.5
rHF=0.97
rFH=1.43
aHfH=116.0
rHfL=0.97
$END

```