



**Computational Chemistry Workshops**  
**West Ridge Research Building-UAF Campus**  
**9:00am-4:00pm, Room 009**

Electronic Structure - July 19-21, 2016  
Molecular Dynamics - July 26-28, 2016

**Hints on Using the Orca Program**

In order to run the Orca program, an input file (e.g. myinp.inp) is created and the executed in the following manner:

```
orca myinp.inp > myinp.log &
```

One of the ways to determine the progress of the job is

```
tail -f myinp.log
```

The general form of the input file for Orca is the following

```
# comment lines (anywhere in input)
! Method BasisSet Additional-Keywords

#Possible input blocks start with '%'
# for example:
%scf maxiter 150
    end

* xyz Charge, Multiplicity
Cartesian coordinates
*
or:
* int Charge, Multiplicity
Z-Matrix
*
```

where Cartesian coordinates ( $xyz$ ), or internal coordinates ( $int$ ) can be used. The multiplicity is defined as  $2S + 1$ , where  $S$  is the total spin of the state of the molecule, and is the the number of unpaired electrons +1.

Here is an example for formaldehyde ( $H_2C=O$ ), where Cartesian coordinates are used:

```
# Check H2CO optimization
! B3LYP SVP Opt TightSCF
* xyz 0 1
  C    0.000000    0.000000    0.000000
  O    1.200000    0.000000    0.000000
  H   -0.550000    0.952628    0.000000
  H   -0.550000   -0.952628   -0.000000
*
```

## Internal Coordinates: The Z-Matrix

If the molecule under investigation is not too large, the most convenient route for building molecules is to manually input bond distances, bond angles and dihedral angles. A definition of the molecular structure in this way is called a Z-Matrix. In order to specify the position of a given atom, one needs six numbers:

- R, A, and D are the bond distance, the bond angle, and dihedral angle.
- NA, NB, NC are the numbers atom numbers to which the new atom is connected.

The integers NA, NB, and NC are used in the following manner:

- NA: the new atom connects to a previously defined atom (NA), and with distance, R in Å.
- NA, NB: the new atom forms an angle with two previously defined atoms (NA and NB), and with angle, A in degrees.
- NA, NB, NC: the new atom forms a dihedral angle with three previously defined atoms (NA, NB, and NC), and with dihedral angle, D in degrees.

This is defined as the angle between the new atom and previously defined atom NC when looking down the NA-NB axis.

1. The first atom is always placed at the origin.
2. The second atom is placed at a distance, R, from the first atom, in Å, along one of the coordinate axes (e.g.  $x$ -axis).
3. The third atom is placed in a plane (e.g the  $xz$ -plane).
4. Any additional atoms require all six parameters (NA, NB, NC, R, A, D) as discussed above.

## Constrained Optimization

In the following input example, a constrained optimization is performed on the formaldehyde molecule ( $\text{H}_2\text{C}=\text{O}$ ), but which also illustrates how to use the Z-Matrix formalism for the use of internal coordinates:

```
! RKS B3LYP/G SV(P) TightSCF Opt
%geom Constraints
    { B 0 1 1.25 C }
    { A 2 0 3 120.0 C }
end
end

* int 0 1
  C  0 0 0 0.0000   0.000   0.00
  O  1 0 0 1.2500   0.000   0.00
  H  1 2 0 1.1075 122.016   0.00
  H  1 2 3 1.1075 122.016 180.00
*
```

Constraining bond distances	:	{ B N1 N2 value C }
Constraining bond angles	:	{ A N1 N2 N1 value C }
Constraining dihedral angles	:	{ D N1 N2 N3 N4 value C }
Constraining cartesian coordinates	:	{ C N1 C }

The following points should be noted with respect to constraining coordinates:

- It is optional to assign a value for the constraint parameter. If a value is not given, the value in the Z-matrix is constrained.

For Cartesian coordinates, the initial position of the atom is constrained.

- It is recommended to use a value close to the initial structure.
- It is possible to constrain whole sets of coordinates.

## Rigid Potential Energy Surface (PES) Scan

A rigid potential energy surface scan can be performed as in the following input example.

```
# Scan the H-O-H angle
! RHF SVP

%paras  R_OH  = 0.950      # O-H distance
        A_HOH = 180,90,19 # H-O-H angle (180 to 90 in 19 steps)
end
* int 0 1
O  0  0  0  0      0.00    0.00    0.00
H  1  0  0  0      {R_OH}   0.00    0.00
H  1  2  0  0      {R_OH}  {A_HOH}  0.00
*
```

In the above example, the H–O–H bond angle will be modified in 18 equidistant  $5^\circ$  steps,  $((180^\circ - 90^\circ)/5 + 1 = 19)$ , and, at each step, a constrained geometry optimization will be carried out to yield a rigid potential energy surface scan of the H–O–H bond angle.

## Relaxed Potential Energy Surface (PES) Scan

A relaxed potential energy surface scan can be performed as in the following Orca input example.

```
! RKS B3LYP/G SV(P) TightSCF Opt
%geom Scan
  B 0 1 = 1.35, 1.10, 12
      # C-O distance that will be scanned
  end
end

* int 0 1
  C  0  0  0  0.0000    0.000    0.00
  O  1  0  0  1.3500    0.000    0.00
  H  1  2  0  1.1075  122.016    0.00
  H  1  2  3  1.1075  122.016  180.00
*
```

In the above example, the C–O bond length will be modified in 12 equidistant steps (1.35 Å - 1.10 Å), and, at each step, a constrained geometry optimization will be carried out to yield a potential energy surface scan of the C–O bond stretch.

## Transition States

In order to find transition states, it is necessary to start with a structure that is reasonably close to the transition state. Structures close to a transition state can be obtained by either a relaxed or rigid potential energy surface scan of the principal reaction coordinate. In addition, chemical intuition can also play an important role. Below is the Orca input for the linear H–H–H molecule, where the coordinates are given in Z-Matrix format:

```
! RHF SVP TightSCF SlowConv Opt PModel NumFreq

%geom TS_search      EF
  Calc_Hess      true # Calculate the exact Hessian initially
                    # Alternatively use InHess read
                    # and InHessName "MyJob.hess" to read
                    # a Hessian calculated at a lower level
                    # of theory

  coordsys redundant
  Recalc_Hess      5 # re-calculate Hessian after 5 steps
  # Additional options:
  #modify_internal
  # { B 1 0 A }      # # add a bond between atoms 0 and 10
  # { B 3 1 A }      # # add a bond between atoms 0 and 10
  # end
  #Update Powell
End

* int 0 2
H 0 0 0 0.0 0 0
H 1 2 0 1.0 0 0
H 2 1 0 1.0 180 0
*
```

## Localized Orbitals (LOCs)

Localized orbitals can be obtained by using the `%loc end` block command, which also creates a file called MyJob.loc.

Analyze the composition of Localized Orbitals (LOCs) by running a second calculation and re-reading them with the `%moinp "Myjob.loc"` keyword so that these MOs are read and `! NoIter` keyword, so that no SCF iterations are performed.

The resulting orbitals can be processed for visualization programs such as VMD, Molden, Gabedit, and others, using the command: `orca_plot MyJob.loc -i`.

## Unrestricted Corresponding Orbitals (UCOs)

An additional analysis tool that can be used here involves unrestricted corresponding orbitals (UCOs). In order to obtain them, use `! UCO` in the input file. This will produce a file called `MyJob.uco` and additional output, which consists of spatial overlaps of spin-up and spin-down orbitals.

Analyze the composition of these orbitals by running a second calculation and re-reading them with the `%moinp "Myjob.uco"` keyword, so that these MOs are read, and `! NoIter` keyword, so that no SCF iterations are performed.

## Quasi Restricted Orbitals (QROs)

A set of Quasi Restricted Orbitals (QROs) can be obtained by employing the `! UNO` keyword, which also creates a file called `MyJob.qro`.

Analyze the composition of Quasi Restricted Orbitals (QROs) by running a second calculation and re-reading them with the `%moinp "Myjob.qro"` keyword so that these MOs are read and `! NoIter` keyword, so that no SCF iterations are performed.

The resulting orbitals can be processed for visualization programs such as VMD, Molden, Gabedit, and others, using the command: `orca_plot MyJob.qro -i`.

## Unrestricted Natural Orbitals (UNOs)

A set of Unrestricted Natural Orbitals (UNOs) can be obtained by employing the `! UNO` keyword, which also creates a file called `MyJob.uno`.

Analyze the composition of Unrestricted Natural Orbitals (UNOs) by running a second calculation and re-reading them with the `%moinp "Myjob.uno"` keyword so that these MOs are read and `! NoIter` keyword, so that no SCF iterations are performed.

The resulting orbitals can be processed for visualization programs such as VMD, Molden, Gabedit, and others, using the command: `orca_plot MyJob.uno -i`.

## Broken Symmetry Calculations

Together with some approximate formalisms, it is possible to extract a value for  $J$  from a high-spin and a broken symmetry calculation. It is possible to specifically ask for such solutions. One of the ways to study antiferromagnetic coupling employs the command `%scf BrokenSym 1,1 end`. In the output can be found the  $J(3)$  value, which is the predicted exchange coupling constant.

## Example Calculation on the $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$ Complex

### Spin-Up Orbitals

In spin-unrestricted calculations, there are separate spin-up and spin-down MOs. In the present case of a  $d^3$  system, one would expect that the three spin-up HOMOs are mainly metal  $t_{2g}$  in character, and the two spin-up LUMOs will have metal  $e_g$  character, which can be verified, by observing the spin-up HOMO/LUMO gap:

39	1.0000	-0.759449	-20.6651
40	1.0000	-0.759446	-20.6651
41	1.0000	-0.759445	-20.6650
42	0.0000	-0.655032	-17.8239
43	0.0000	-0.655029	-17.8238

It can be seen that the three highest occupied and two lowest unoccupied spin-up orbitals are all degenerate, as shown by their composition:

	36	37	38	39	40	41
	-0.82938	-0.82938	-0.82938	-0.75945	-0.75945	-0.75945
	1.00000	1.00000	1.00000	1.00000	1.00000	1.00000
	-----	-----	-----	-----	-----	-----
0 Cr dxz	0.0	0.0	0.0	<b>12.9</b>	<b>56.4</b>	<b>0.2</b>
0 Cr dyz	0.0	0.0	0.0	<b>0.2</b>	<b>0.1</b>	<b>69.2</b>
0 Cr dxy	0.0	0.0	0.0	<b>56.4</b>	<b>13.0</b>	<b>0.1</b>
	-0.65503	-0.65503	-0.49107	-0.29188	-0.29187	-0.29187
	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000
	-----	-----	-----	-----	-----	-----
0 Cr s	<b>0.0</b>	<b>0.0</b>	61.6	0.0	0.0	0.0
0 Cr dz2	<b>5.2</b>	<b>71.0</b>	0.0	0.0	0.0	0.0
0 Cr dx2y2	<b>71.0</b>	<b>5.2</b>	0.0	0.0	0.0	0.0

The result above is the one that is quite reasonable, as can be seen from the compositions of the orbitals. However, they are not pure  $d_{xy}$ ,  $d_{xz}$ , and  $d_{yz}$  orbitals because degenerate orbitals can arbitrarily mix among themselves without changing anything in the physics. These three orbitals simply span the three components of the  $t_{2g}$  representation.



## Spin-Down Orbitals

In addition, the five spin-down LUMOs are expected to represent the spin-down counterparts of the metal  $t_{2g}$  and metal  $e_g$  orbitals which are shown below:

39	0.0000	-0.652195	-17.7467
40	0.0000	-0.652191	-17.7466
41	0.0000	-0.652190	-17.7466
42	0.0000	-0.605269	-16.4698
43	0.0000	-0.605267	-16.4697

The compositions of the LUMOs are given below:

	36	37	38	39	40	41
	-0.82555	-0.82555	-0.82554	-0.65219	-0.65219	-0.65219
	1.00000	1.00000	1.00000	0.00000	0.00000	0.00000
	-----	-----	-----	-----	-----	-----
0 Cr dxz	0.0	0.0	0.0	<b>16.2</b>	<b>62.3</b>	<b>11.6</b>
0 Cr dyz	0.0	0.0	0.0	<b>0.8</b>	<b>11.2</b>	<b>78.1</b>
0 Cr dxy	0.0	0.0	0.0	<b>73.1</b>	<b>16.6</b>	<b>0.4</b>
	42	43	44	45	46	47
	-0.60527	-0.60527	-0.48831	-0.29023	-0.29022	-0.29022
	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000
	-----	-----	-----	-----	-----	-----
0 Cr s	<b>0.0</b>	<b>0.0</b>	62.3	0.0	0.0	0.0
0 Cr dz2	<b>6.9</b>	<b>73.8</b>	0.0	0.0	0.0	0.0
0 Cr dx2y2	<b>73.8</b>	<b>6.9</b>	0.0	0.0	0.0	0.0

Interestingly, the orbital splittings of the spin-up and spin-down levels are quite different. In general DFT without admixture of Hartree-Fock exchange, as is the case with the BP functional used here, orbital energy difference between occupied and virtual orbitals is a 0th order approximation to the excitation energy.

# Excited States

In the present case, a ligand field transition energy is predicted around 2.8 eV ( 23000  $\text{cm}^{-1}$ ). This can be checked by running a TD-DFT calculation for only six excited states, corresponding to the six ways of taking an electron out of a  $t_{2g}$  orbital, and placing it into the  $e_g$  orbital.

----- ABSORPTION SPECTRUM -----							
State	Energy	Wavelength	fosc	T2	TX	TY	TZ
	( $\text{cm}^{-1}$ )	(nm)		( $\text{D}^*2$ )	(D)	(D)	(D)
1	20591.4	485.6	0.000000000	0.00000	0.00000	-0.00002	0.00000
2	20591.5	485.6	0.000000000	0.00000	-0.00000	0.00000	0.00002
3	20591.8	485.6	0.000000000	0.00000	0.00000	-0.00003	0.00001
4	23600.1	423.7	0.000000000	0.00000	0.00001	-0.00000	0.00001
5	23600.7	423.7	0.000000000	0.00000	0.00001	-0.00001	-0.00001
6	23601.3	423.7	0.000000000	0.00000	0.00000	0.00002	0.00001

It can be seen that two excited states that are triply degenerate each and correspond to the singly excited  ${}^4T_{1g}$  and  ${}^4T_{2g}$  terms expected from Table 1. The splitting between the two states is one of the characteristics of electron-electron repulsion leading to different multiplets.

Despite the small basis set, the result compares favorably with experiment, where transitions are observed at 17,400  $\text{cm}^{-1}$  and 24,700  $\text{cm}^{-1}$ . Furthermore, the average of the two transition energies correspond well with the orbital energy difference.

It is possible to determine which state corresponds to each symmetry by using a group theoretical table and working out the allowed transitions for a CD spectrum. The magnetic dipole components  $R_x, R_y, R_z$  transform as the molecular rotations and belong to the  $T_{1g}$  representation for  $O_h$  symmetry. Thus, the  ${}^4A_{2g} \rightarrow {}^4T_{1g}$  is magnetic-dipole allowed because the direct product  $A_{2g} \otimes T_{1g} \otimes T_{1g}$  yields the totally symmetric representation,  $A_{2g}$  which leads to an allowed transition in the CD spectrum for  $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$ .

It is not always the case that TD-DFT calculations agree with experiment, and there is every reason to be critical about the calculational results. Very carefully compare the TD-DFT calculations with experiment. In many cases, artifacts will arise: charge transfer states tend to appear much too low in the spectrum; double excitations are entirely missing; neutral-to-ionic transitions are poorly predicted; and spin-flip transitions cannot be predicted.

## Excited States

The compositions of these transition shows that they indeed correspond to the expected excitations:

```
STATE 1: E= 0.093822 au      2.553 eV      20591.4 cm**-1
 39a -> 43a : 0.040541 (c= -0.20134677)
 40a -> 42a : 0.235055 (c= -0.48482442)
 40a -> 43a : 0.091500 (c= 0.30248889)
 41a -> 42a : 0.033109 (c= 0.18195871)
 41a -> 43a : 0.591178 (c= 0.76888093)

STATE 2: E= 0.093822 au      2.553 eV      20591.5 cm**-1
 39a -> 43a : 0.102372 (c= 0.31995577)
 40a -> 42a : 0.340978 (c= 0.58393339)
 40a -> 43a : 0.178600 (c= -0.42261116)
 41a -> 42a : 0.028003 (c= 0.16734110)
 41a -> 43a : 0.340662 (c= 0.58366233)

STATE 3: E= 0.093823 au      2.553 eV      20591.8 cm**-1
 39a -> 42a : 0.835399 (c= -0.91400145)
 40a -> 42a : 0.010739 (c= -0.10363150)
 40a -> 43a : 0.138077 (c= -0.37158743)

STATE 4: E= 0.107530 au      2.926 eV      23600.1 cm**-1
 41a -> 42a : 0.921691 (c= -0.96004745)
 41a -> 43a : 0.057615 (c= 0.24003050)

STATE 5: E= 0.107533 au      2.926 eV      23600.7 cm**-1
 39a -> 42a : 0.122088 (c= 0.34941155)
 39a -> 43a : 0.011888 (c= 0.10903325)
 40a -> 42a : 0.341659 (c= -0.58451589)
 40a -> 43a : 0.505530 (c= -0.71100658)

STATE 6: E= 0.107536 au      2.926 eV      23601.3 cm**-1
 39a -> 42a : 0.029369 (c= -0.17137471)
 39a -> 43a : 0.828386 (c= 0.91015695)
 40a -> 42a : 0.062645 (c= -0.25029038)
 40a -> 43a : 0.070858 (c= 0.26619100)
```

## Keywords for the Orca Program

Below is a summary for some of the keywords for the Orca program.

ORCA	ACTIONS
RHF	Perform a restricted (closed-shell) Hartree-Fock calculation
UHF	Perform a spin-unrestricted open-shell Hartree-Fock calculation
B3LYP/G	Perform a B3LYP calculation with B3LYP being defined as in the Gaussian series of programs. (Note for spin-unrestricted calculations the keyword is UKS B3LYP/G; the program automatically chooses UHF for open shell systems).
MP2	Perform a MP2 calculation on top of a RHF starting point. This is possible for energy and geometry optimization calculations.
RI-MP2	Perform a RI-MP2 calculation – much faster than standard MP2 but requires the input of an “auxiliary basis set” (here: SV/C if SVP; TZV/C if TZVP and TZVPP/C if TZVPP)
CCSD(T)	Perform a coupled cluster calculation with single- and double excitations together with a perturbative estimate of triple excitations. This is an accurate and expensive level of theory (presently only available for closed shell systems in ORCA).
SVP	Use the SVP basis set. (small double zeta basis set for initial explorations; contains one set of polarization functions: p for H and d for heavier elements. With SV(P) the p functions on the hydrogens are deleted)
TZVP	Use the TZVP basis set. (medium triple-zeta basis set ; already good for geometries and frequencies; contains one set of polarization functions: p for H and d for heavier elements)
TZVPP	Use the TZVPP basis set. (Larger triple-zeta basis set for accurate energies. Contains three sets of polarization functions: 2p1d for H and 2d1f for heavier elements).
QZVP	Large quadruple-zeta basis set with multiple polarization functions. Expensive but accurate for close-to-basis-set-limit results.
Opt	Perform a geometry optimization
NumFreq	Perform a second derivative calculation (ORCA can only do numerical frequency calculations presently). This will also automatically provide a calculated IR spectrum as well as ZPE and thermal corrections to the energy
TightSCF	Request “tight” SCF convergence criteria (Necessary for geometry optimizations and frequency calculations; required input for ORCA).
%cis nroots 10 end	Absorption spectra: Calculate the first 10 excited states using configuration interaction with single excitations (appropriate for RHF or UHF SCF calculations).
%tddft nroots 10 end	Absorption spectra: Calculate the first 10 excited states using the time-dependent density functional theory (appropriate for a DFT SCF calculation)
%epnrmr gtensor true Nuclei = all { also, adip} End	ESR Spectra: Calculate the most important parameters of the ESR spectrum of S=1/2 systems. NMR chemical shifts can also be calculated.
NPA	Perform a natural population analysis