

Visualization: Making INPUT File and Processing of Output Results

Keywords: visualization, input and output structure, molecular orbital, electron density.

In the previous chapters, we have discussed on making INPUT structures for *ab initio* calculations on small molecules only e.g. H₂O system. For large molecules, it is often difficult to prepare 'INPUT' structures correctly. It is often recommended for checking of an INPUT file before actually running an electronic structure calculation by using a visualization program. The program displays the structure of the molecule with the given geometrical input parameters. It is also capable to read the output file generated through *ab initio* electronic structure calculation and display molecular structure. There are many open source programs with academic license for pre- and post- processing of results based on electronic structure calculations. MOLDEN is one such program having a powerful Z-matrix editor which gives full control over the geometry and allows one to build molecules. MOLDEN reads all the required information from the GAMESS output file and capable of displaying molecular orbitals, the electron density etc. MOLDEN can animate reaction paths and molecular vibrations. It can calculate and display the true or multipole Derived Electrostatic Potential and atomic charges can be fitted to the calculated Electrostatic Potential. Both Xwindows and OpenGL versions of MOLDEN are capable of importing and displaying a variety of file formats.

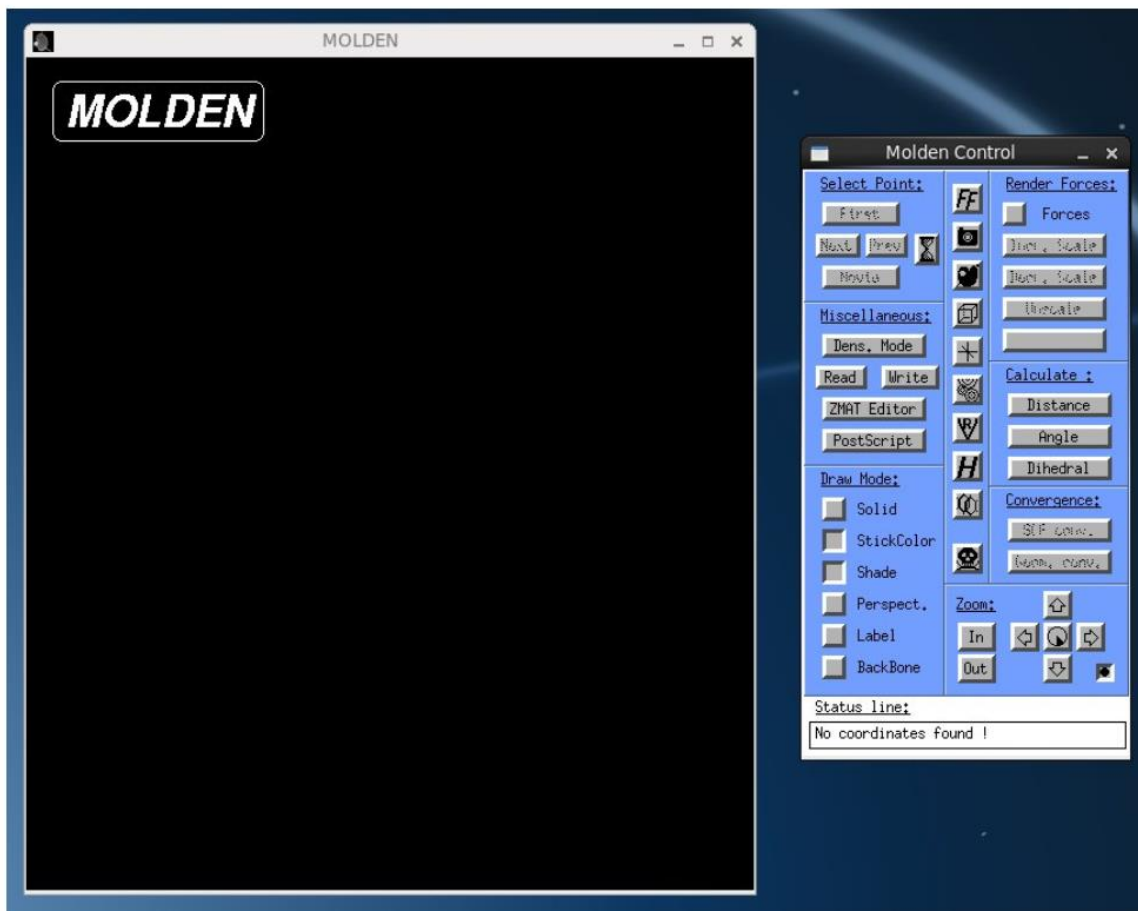
How to get a copy of MOLDEN?

This program is available at <http://www.cmbi.ru.nl/molden/> for academic purpose. One has to register first to download the program for free. This program has hardware and operating system (OS) dependent components. Depending on the availability of type of computational resource, one may like to download precompiled executable file suitable for 32 or 64 bit processor on a LINUX box or the whole source code. MOLDEN is well documented with manual and online support to run on a LINUX based pc quite easily. Whole source code comes as a 'tar file'. When the 'tar file' is extracted, many source files and a 'makefile' to compile the program will be there the directory 'molden'. One has to edit 'makefile' suitably to avail all the required library for compiling to create an executive file on the LINUX box. An easier option is downloading the compiled version of molden suitable for the LINUX box.

How to run MOLDEN?

Suppose, molder program is kept in the directory '~/.program/molder', one may type the following command to run 'molder' from command line.

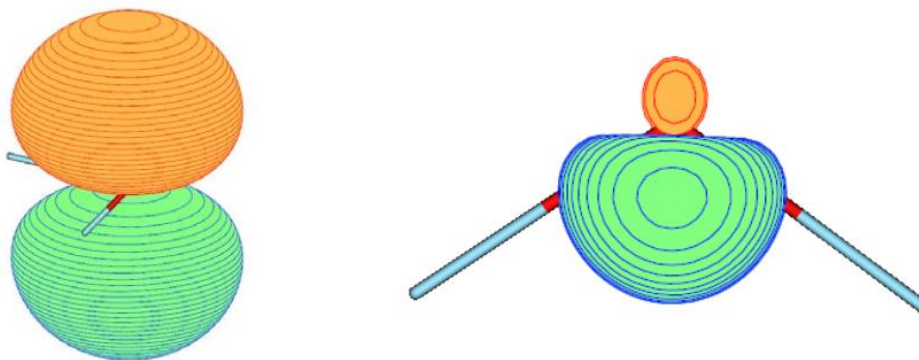
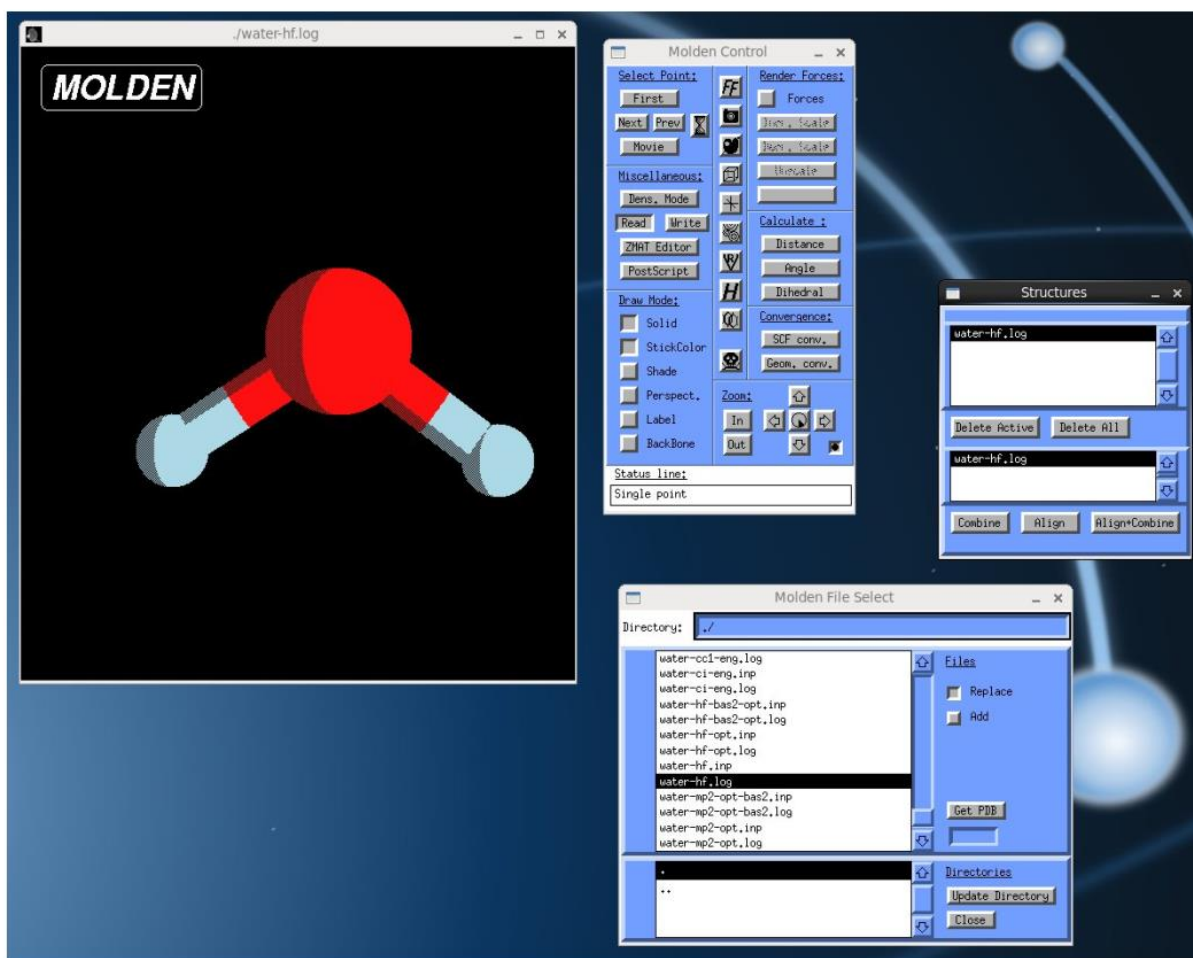
```
/home/user>~/.program/molder/molder &
```



After pressing 'enter' key the following window will appear.

One can browse a working directory by clicking on 'Read' button and read a particular file (input or output) to visualize the molecular geometry. The following snapshot shows the molecular structure of H₂O molecule reading the output file 'water-hf.log'. Molecular structure is shown in 'ball and stick' model. Other formats may be chosen by clicking 'Solid' button in 'Molder Control' window. Bond distance between any two atoms and bond angle between two bonds may be measured by clicking 'Distance' or 'Angle' button. Similarly, angle between two planes (made by three atoms) or dihedral angle may be measured by clicking 'Dihedral' button. One may like to observe how the geometry of the molecule has changed on optimization by clicking 'Movie' button at 'Select Point' leading to the final optimized structure of the molecule. By clicking the button, 'Dens. Mode' one will be able to view all the molecular orbitals of the system by choosing the appropriate orbital. As an example the Highest Occupied Molecular Orbital (HOMO) and

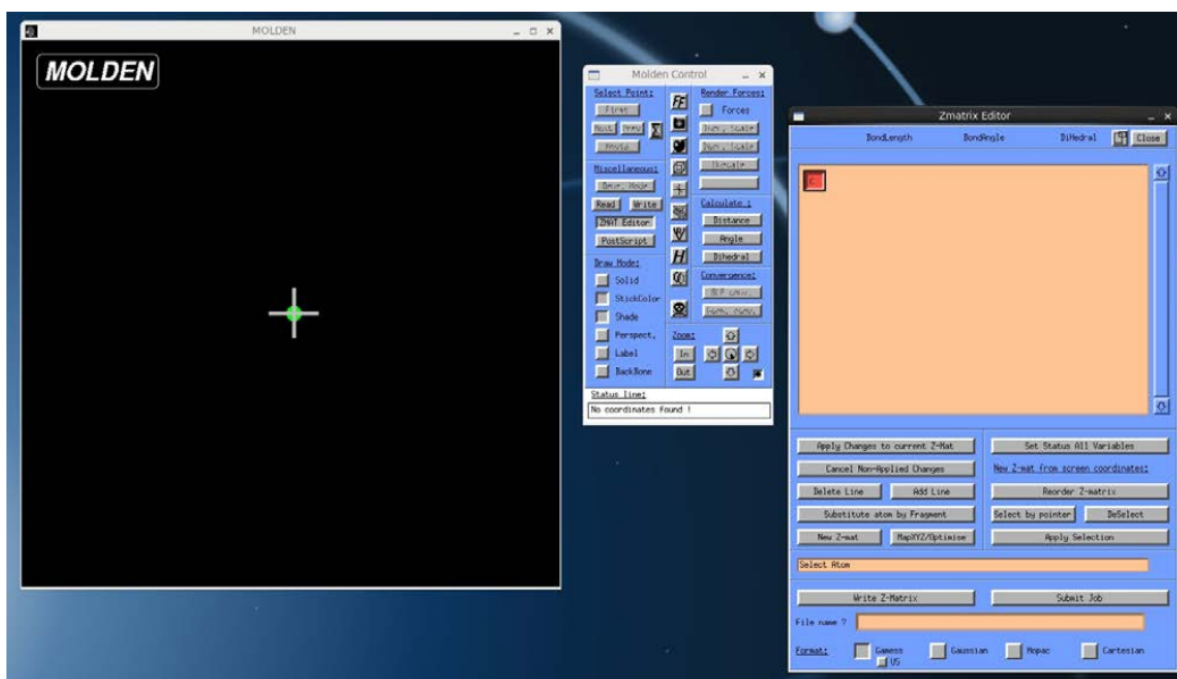
Lowest Unoccupied Molecular Orbital (LUMO) of water molecule are shown below. Note that one has to select an appropriate value of 'cut-off' for contours of MO plot. This is done by supplying a value of 0.15 or so after clicking 'space' button. This button will appear when 'Dens. Mode' button is clicked to view molecular orbital plots. One has to try with different 'cut-off' values for proper view of contour plots for different systems.



HOMO

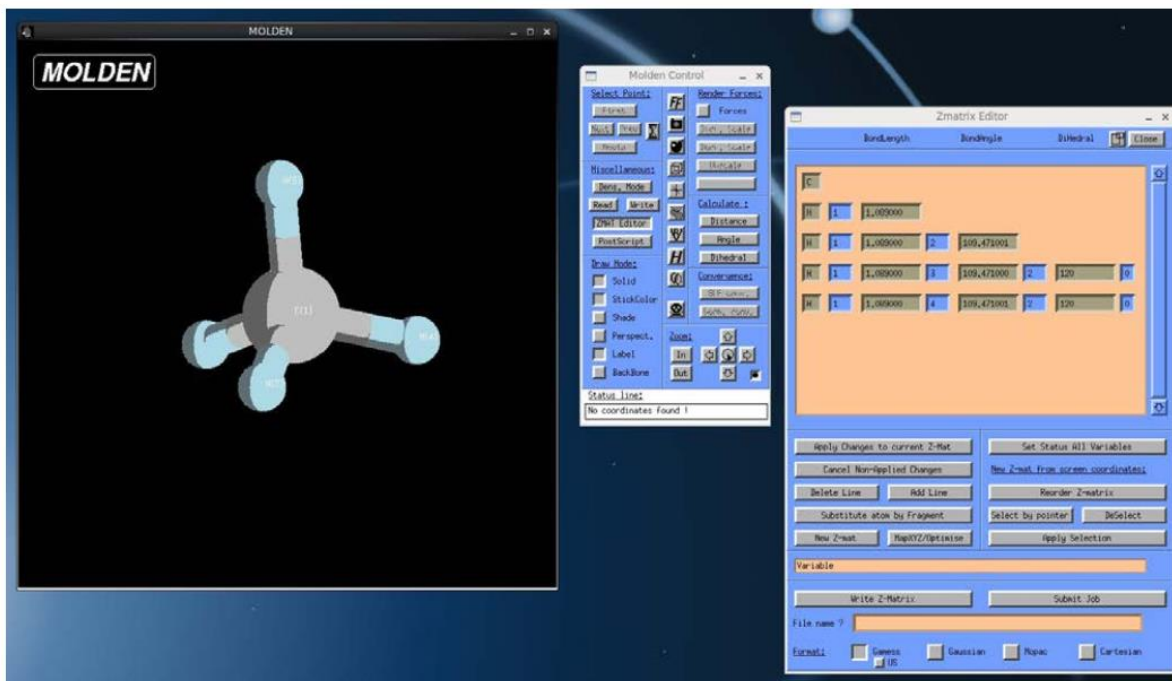
LUMO

As mentioned before, MOL DEN has a powerful Z-Matrix editor. This may be used to prepare an INPUT for a calculation for large size molecule. If one clicks 'ZMAT Editor' the following window appears for giving input data to design a molecule after adding C atom through 'Add Line' button. One may go on adding atoms by



making use of 'Add Line' button of Zmatrix Editor window and defining connectivity of atoms. MOL DEN library has default bond length and bond angle values for different molecules. MOL DEN will choose bond length and bond angle values from its own library. However, user has freedom to define the values on his own. The following window displays CH_4 molecule with bond length, bond angle and dihedral angle values which is designed through Zmatrix Editor of MOL DEN.

As you notice, the bond length, bond angle and dihedral angle values of methane molecule is displayed in the Zmatrix editor. The values may be changed by putting the cursor on a particular value and supplying the value one wishes to give. At present, the supplied geometrical parameters suit a perfect tetrahedral methane molecule. These geometrical parameters may be saved in an input file in either Cartesian Coordinate or Z-matrix format. However, one has to edit the 'INPUT' file in text format to supply appropriate 'header' to run for geometry optimization or any other property calculation using GAMESS. The input parameters may be saved by clicking 'Write' button of 'Molden Control' panel and providing a file name in Cartesian Coordinate format. Alternatively, one may click 'Set Status All Variables' and choosing to either constant or variable value followed by clicking 'Write Z-Matrix' and supplying a name. Suppose, one gives



file name 'methane-geo.inp' after choosing constant value, the file looks as follows in Z-Matrix format.

zmat angstroms

C

```
H 1 1.089
H 1 1.089 2 109.474
H 1 1.089 3 109.474 2 120
H 1 1.089 4 109.474 2 120
```

variables

constant

end

One has to put appropriate 'header' in this input file for a calculation and the edited file looks as follows for DFT calculation applying B3LYP functional.

```
$SYSTEM TIMLIM=6000.0 MWORDS=11 MEMDDI=90 $END
$CONTRL SCFTYP=RHF MLEVEL=0 MAXIT=100 ICHARG=0 MULT=1
COORD=ZMT RUNTYP=OPTIMIZE DFTTYP=B3LYP TDDFT=NONE $END
$DFT METHOD=GRID $END
$SCF DIRSCF=.F. DAMP=.T. SHIFT=.T. $END
$BASIS GBASIS=N31 NGAUSS=6 NDFUNC=1 NPFUNC=1 DIFFSP=.T. DIFFS=.T. $END
$DATA
```

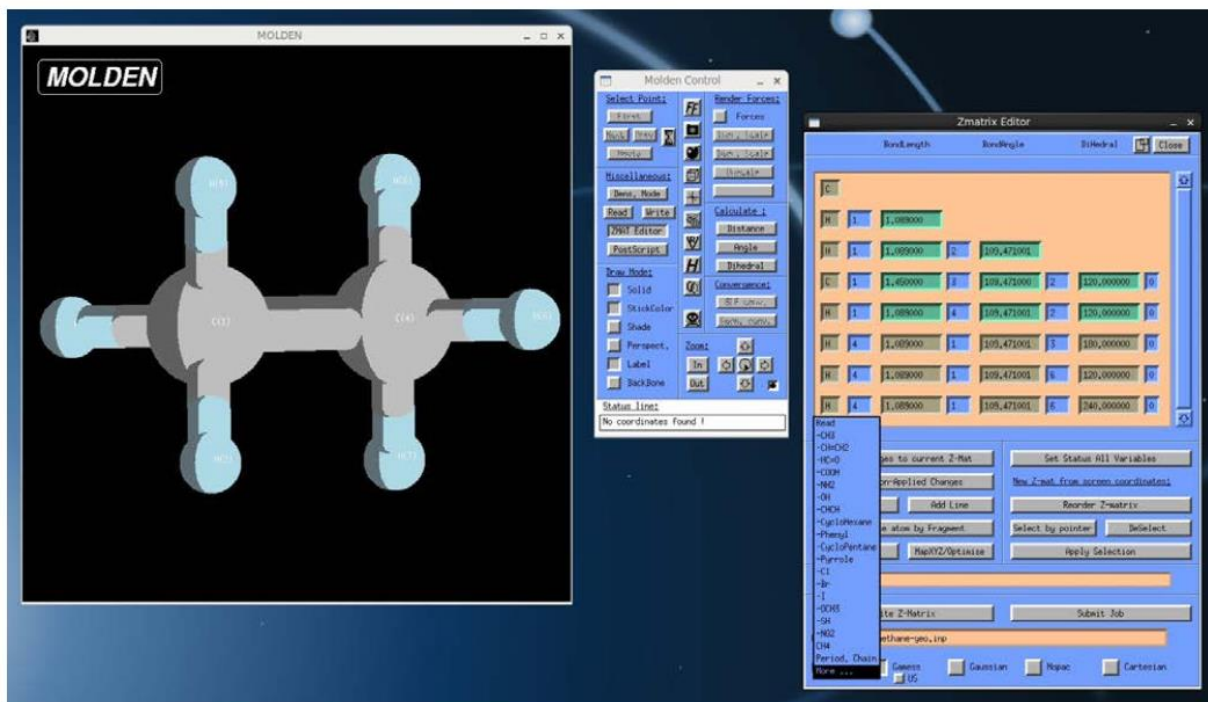
```

Methane:geometry/B3LYP/6-31++G(d,p)
CN 1

C
H 1 1.089
H 1 1.089 2 109.474
H 1 1.089 3 109.474 2 120
H 1 1.089 4 109.474 2 120
$END
*****
    
```

The above input file is now ready for geometry optimization using GAMESS.

From the above input file in MOLDEN, it is quite easy to prepare input for larger molecules. For example, for ethane, one may just substitute one H atom of methane by CH₃ group to get the structure and input geometrical parameters for ethane, CH₃-CH₃. These steps are shown in the following window. Consider the above window showing methane molecule and Zmatrix editor. First one has to click one H atom of Methane to mark it. One will see many options to substitute the marked H atom by clicking the button



‘Substitute atom by Fragment’. If one clicks on –CH₃, the marked H atom will be replaced by CH₃ group. Thus, ethane molecule will be formed and all the geometrical parameters will be shown in Zmatrix editor. It is always suggested to keep the heavy atoms at the beginning of the input file for smooth calculation. So, after the substitution, it is advised to reorder atoms and this is possible by clicking the button ‘Reorder Z-

matrix' followed by clicking the atoms in the molecular structure in order. Once all the atoms in the structure is clicked, the numbering of atoms will change. Now, as in case of methane, this input after reordering the atoms may be saved in a file in Cartesian or Z-Matrix format. The saved file looks as follows in the two formats.

Cartesian Coordinate:

```
*****
8

C  0.000000  0.000000  0.000000
C  0.000000  0.000000  1.450000
H  1.026720  0.000000 -0.362996
H -0.513360 -0.889165 -0.363000
H -0.513360  0.889165 -0.363000
H  0.513360  0.889165  1.813000
H  0.513360 -0.889165  1.813000
H -1.026719  0.000000  1.813000
```

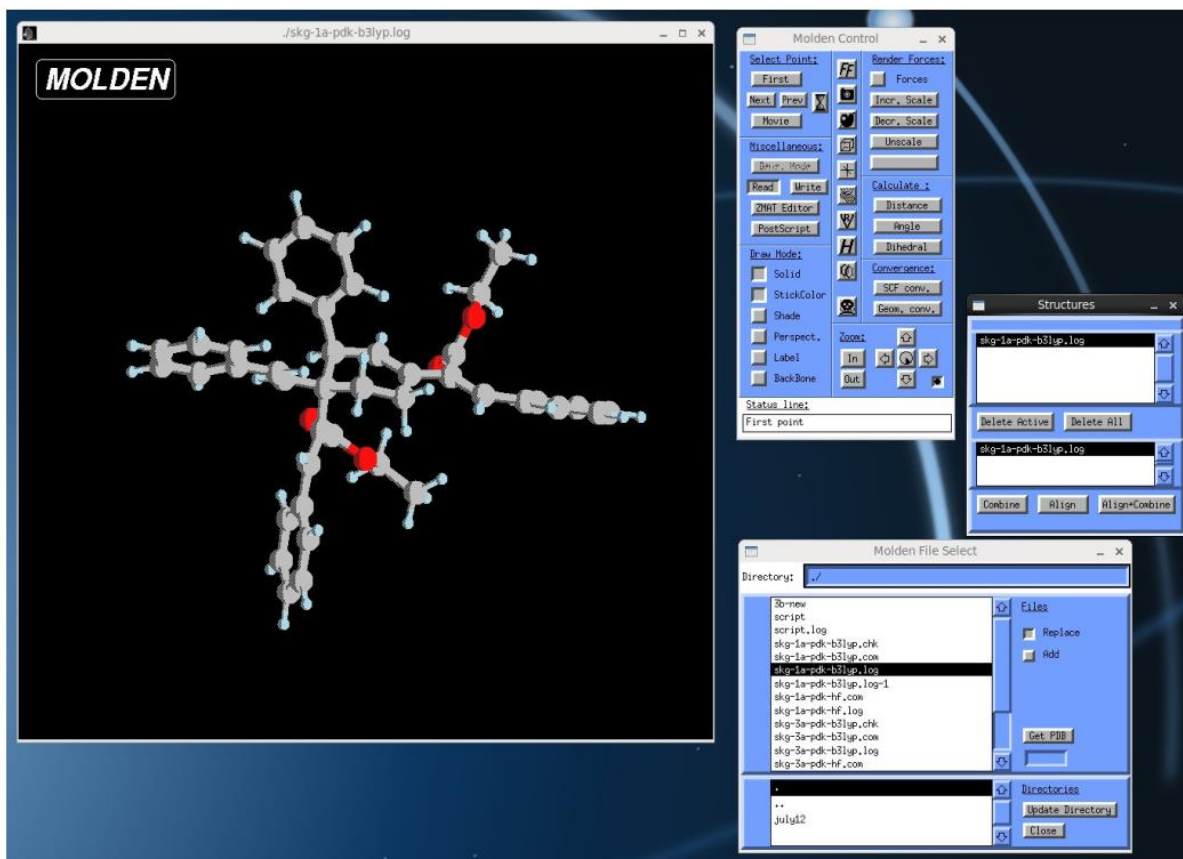
```
*****
```

The number 8 indicates that there are eight atoms in the molecule. After reordering the two C atoms are numbered as atom number 1 and 2 followed by H atoms. The same in Z-Matrix format looks as follows.

```
*****
zmat angstroms
c
c  1 1.45000
h  1 1.08900  2 109.471
h  1 1.08900  2 109.471  3 120.000
h  1 1.08900  2 109.471  4 120.000
h  2 1.08900  1 109.471  3 60.000
h  2 1.08900  1 109.471  3 -60.00
h  2 1.08900  1 109.471  3 180.000
variables
constants
end
```

```
*****
```

In this format connectivity of atoms are also defined for bond length, bond angle and dihedral angle of the molecule. The files need to be edited to run applying GAMESS adding 'header' for keywords for certain calculation and also needs to show the end of the file. For electronic structure calculation, one may consider any of these two formats. Note that one has full freedom to edit any geometrical parameter within Zmatrix editor before saving the data. Thus, Z-Matrix editor of MOLDEN may be used to design any molecule and the geometrical parameters may be saved in a file for electronic structure calculations. The following figure is a snap shot of MOLDEN window aiming to design a large molecule and making an input file for electronic structure calculation applying GAMESS suit of program.



As in the previous cases, one may save the geometrical parameters of this structure in Cartesian Coordinate or in Z-Matrix. In case of Cartesian coordinate, one has to supply atomic number after atomic symbol followed by x,y,z coordinates in free format leaving at least one space between the respective values. For easy identification of atoms in a molecular structure, it is suggested to use colour code for each atom. Colour code may be assigned to any atom of the periodic Table by clicking the 3rd centre button from the top. In the above figure 'red ball' refers to oxygen atoms, grey for carbon atoms and rest are for hydrogen atoms. Suppose one saves the above structure in Cartesian Coordinate format and edits it to run an electronic structure calculation using GAMESS, the input file should be as follows.

```

$SYSTEM TIMLIM=600.0 MWORDS=90 MEMDDI=200 $END
$CONTRL SCFTYP=RHF ICHARG=0 MULT=1 RUNTYP=OPTIMIZE DFTYP=B3LYP COORD=UNIQUE $END
$BASIS GBASIS=N31 NGAUSS=6 NDFUNC=1 NPFUNC=1 $END
$DATA
Test Molecule // B3LYP/6-31G(d,p)
CN 1

```

```

C 6 1.940346 4.318644 -1.228563
C 6 2.107853 3.728405 0.038646
C 6 2.383362 4.574363 1.130296

```

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C 6	2.443113	5.958965	0.975244
C 6	2.251410	6.530894	-0.285537
C 6	2.008284	5.702966	-1.385699
C 6	2.064705	2.274405	0.278211
C 6	1.350640	1.310332	-0.337639
C 6	0.405988	1.650588	-1.457874
O 8	-0.649425	2.365533	-1.035864
C 6	-1.634655	2.731674	-2.040234
C 6	-2.691201	3.575620	-1.354342
C 6	1.530136	-0.181485	0.099759
C 6	0.788684	-1.165726	-0.889071
C 6	-0.709563	-1.082325	-0.730544
C 6	-1.370339	-0.586209	0.339344
C 6	-0.600869	-0.038857	1.524550
C 6	0.896272	-0.372554	1.496830
C 6	-2.845553	-0.513115	0.362522
C 6	-3.558094	-1.009285	-0.871153
O 8	-4.087356	-2.230640	-0.676861
C 6	-4.801286	-2.820632	-1.794119
C 6	-5.286247	-4.188152	-1.353477
C 6	1.270353	-2.620148	-0.813660
C 6	0.740239	-3.543847	0.099301
C 6	1.207087	-4.860677	0.145031
C 6	2.206004	-5.284925	-0.733921
C 6	2.726335	-4.382928	-1.665879
C 6	2.257799	-3.068697	-1.705050
C 6	3.019240	-0.468441	0.076210
C 6	3.792657	-0.850006	1.105178
C 6	5.244619	-1.098646	1.068998
C 6	6.073329	-0.707408	-0.001099
C 6	7.440534	-0.976386	0.015150
C 6	8.021496	-1.638142	1.103016
C 6	7.217203	-2.022906	2.178095
C 6	5.848154	-1.752168	2.159657
C 6	-3.547505	-0.019814	1.413943
C 6	-4.995963	0.158368	1.586049
C 6	-5.904823	0.367025	0.528612
C 6	-7.266856	0.532872	0.779599
C 6	-7.758780	0.503010	2.087955
C 6	-6.869020	0.319627	3.150344
C 6	-5.507073	0.160357	2.900360
O 8	-3.623709	-0.403387	-1.924724
O 8	0.584404	1.325118	-2.619450
H 1	-7.945828	0.701212	-0.052299
H 1	-5.545251	0.438562	-0.492045
H 1	-4.821223	0.022545	3.733260
H 1	-7.234635	0.306582	4.173638
H 1	-2.972159	0.285549	2.283370
H 1	-4.120272	-2.876840	-2.648758
H 1	-5.627948	-2.155703	-2.063186
H 1	-4.446462	-4.836082	-1.082471
H 1	-5.835496	-4.662597	-2.174840
H 1	-5.956026	-4.109346	-0.491203
H 1	-1.268758	-1.456488	-1.584213
H 1	1.020953	-0.829426	-1.904928

```
H 1 -0.059321 -3.240339 0.768696
H 1 0.780871 -5.556727 0.863113
H 1 2.567587 -6.309150 -0.700825
H 1 3.494951 -4.702026 -2.364885
H 1 2.664478 -2.378374 -2.440421
H 1 1.048891 -1.412825 1.805580
H 1 1.409921 0.253529 2.234411
H 1 -1.018005 -0.429352 2.461538
H 1 -0.739972 1.050706 1.560042
H 1 3.472661 -0.323583 -0.903546
H 1 3.332785 -1.026268 2.075913
H 1 5.649615 -0.174776 -0.847491
H 1 8.058273 -0.661087 -0.821782
H 1 9.088223 -1.844312 1.113253
H 1 7.654510 -2.532915 3.032497
H 1 5.229137 -2.057071 3.000658
H 1 2.726293 1.944074 1.078643
H 1 2.541481 4.135907 2.113092
H 1 2.646087 6.590059 1.836375
H 1 1.883328 6.135477 -2.374922
H 1 1.788292 3.692760 -2.101794
H 1 -1.122847 3.277835 -2.838640
H 1 -2.052285 1.811377 -2.457166
H 1 -3.187642 3.011648 -0.558630
H 1 -3.450372 3.870275 -2.088065
H 1 -2.257502 4.483699 -0.922580
H 1 -8.820487 0.633967 2.277782
H 1 2.304762 7.608700 -0.412205
$END
```

```
*****
```

Conclusions

MOLDEN, a visualization program has been introduced and explained how to use this program to prepare input data file and processing of output data files based on GAMESS electronic structure calculation.