

## Electronic Structure calculations in *MOPAC*

MOPAC has been specially designed to run semiempirical electronic structure calculations. Although archaic in its interface, it offers the great advantage of viewing the molecule during the optimization process. It also appears to perform better than semiempirical calculations run in Gaussian.

### 1. Ground state calculation

The initial structure may be drawn in MOPAC directly or imported as a cartesian coordinate file with the file extension *car*.

With the molecular structure in place, select *Edit* and *Z-matrix*. The pathname and filename are specified under *Name*. Files must be saved to the MOPAC folder or folders within (i.e. *C:\WinMOPACv2\foldername\filename.dat*). All the information about the calculation is specified by so called *Keywords*. These are automatically created by using the dropdown menus and checkboxes. A ground state calculation would look like the following:

EF PM3 PRECISE XYZ GEO-OK

Calculation Type:	EF (Eigenvector Following routine is used for minimum search)
Method:	PM3 (recommended method, parameterized for Li)
Charge:	0 (zero does not explicitly show as a keyword)
Miscellaneous:	Precise (tighter convergence criteria) GEO-OK (highly recommended, overrides geometrical constraints) XYZ (runs calculation in cartesian coordinates. Alternatively, calculation may also be run in Z-Matrix coordinates)

Note that by clicking on the Cartesian checkbox does not automatically create the *XYZ* keyword. It must be typed in addition to the keyword *GEO-OK*.

Click on *Apply* and *OK*. Now select *Start* under the *Calculation* menu. As the molecule is optimized, one can see the progress of the calculation by following the *GNorm* value. It should decrease to the threshold value of 0.04 as the H.O.F (heat of formation) decreases. In case of large systems, the calculation may not finish in 500 cycles which is the maximum allowed cycles. At this point, save the final structure as a cartesian file (*.car*) and restart the calculation. It is recommended to save the final optimized structure as a cartesian file because in this format it can easily be imported to a Gaussian calculation. Due to a bug in the program the *car* extension must be written twice (i.e. *filename.car.car*). At this final stage it may be saved outside the WinMopac folder.

### 1. Transition state calculation

All of the above principles apply except that the keyword *EF* is substituted for *TS* (transition state optimization). For transition states describing deprotonations, it is recommended to use the cartesian coordinate system.

TS PM3 PRECISE XYZ GEO-OK