

## MOPAC Molecular Orbital Calculations on Diatomics

To run a molecular orbital calculation for a diatomic on a Windows or Mac system, use a text editor like Word, SimpleText, or Notepad to create the input file. An example input file for LiH at 1.61 Å bond length is given below. The first line contains keywords for the calculation. MNDO specifies the “chemistry” or the Hamiltonian. (AM1 is the most useful Hamiltonian for general organics. PM3 is best for compounds containing P or S. However, MNDO is necessary for compounds containing Be, Li, Na, Mg, and K.) VECTORS is needed to have the program print out the eigenvectors (i.e. the molecular orbital wavefunctions). BONDS has the program print summary calculations on bond orders and valencies. For other keywords and the description of the BONDS calculations, see the keyword list below. The next two lines are for comments. These lines can contain anything you like, but they must be present even if they are blank. The next two lines specify the atoms and the bond length. The atomic symbols should be written in caps. The first atom is specified as lithium. The next line specifies the second atom as hydrogen. The bond length is input as 1.61 in angstrom units. The "0" following the bond length specifies that the bond length is to be kept constant. If a "1" were specified instead, MOPAC would vary the bond length to find the minimum energy. This process is called energy minimization, which corresponds to the same process in molecular mechanics calculations but from a quantum mechanical perspective. A blank line is necessary at the end of the file to signal that no more atoms are to be input.

```
MNDO GEO-OK VECTORS BONDS
LiH MNDO 1.61A
```

```
LI
H 1.61 0
```

The GEO-OK keyword allows input structures with very distorted geometries to run. If you use Word to create the input file, remember to save the file in “text only” or “Plain text” format. The file name should end in “.dat”. You can use the zmatrix application ([www.colby.edu/chemistry/PChem/zmatrix.html](http://www.colby.edu/chemistry/PChem/zmatrix.html)) to create the input files for more complex molecules. Make sure to close the file in Word before trying to run MOPAC.

*Running MOPAC for the PC:* On the Schupf lab systems, MOPAC is installed in the Shared Documents folder: “C:\Documents and Settings\All Users\Shared Documents”. There should be a shortcut to this folder on the desk top. To run MOPAC just drag your input file onto the mopac entry. If this “drag and drop” method doesn’t work, see the section on Alternate Versions of MOPAC below. When the calculation is complete, you use a text editing program to read the results from output files. The main output file has the “.mno” extension.

*Running MOPAC for the OS-X version:* First, you must install a script to run MOPAC in your Documents directory. Instructions for doing this installation are listed below. Note also the section on “Getting the Correct File Formatting on OS-X,” below. After installation, to run MOPAC open a Terminal window (TV-type icon with the ">" symbol), and change to the mopac directory by typing (if you have already not done so):

```
$ cd Documents/mopac
```

Now run MOPAC by typing:

```
$ ./mopac file-name
```

where *file-name* is exactly as you specified when you saved the file but without the ".dat". When the calculation is complete, use Word to read the results from output file (".out"). The easiest way to do this is to right-click on the file name, slide right on "Open with..." and choose "Other.." You can use TextEdit or Word. If TextEdit or Word are not the top listed options, then in the Applications directory scroll down and choose TextEdit or Microsoft Office2011/Word.

*Output Files for the PC version:* The molecular orbital energies and wavefunctions are printed in the file with the ".mno" file extension. You can read this file using Word or the Notepad application. Usually double-clicking on this file automatically opens the file in Note Pad. If you change the ".mno" extension to ".mop" this main output file can also be viewed with your browser using the Chime plugin.

The important parts of the output for LiH are given below.

#### CARTESIAN COORDINATES

NO.	ATOMX	Y	Z
1	Li	0.000	0.000 0.000
2	H	1.610	0.000 0.000

RHF CALCULATION, NO. OF DOUBLY OCCUPIED LEVELS = 1

#### INTERATOMIC DISTANCES

		Li 1	H 2
Li	1	0.000000	
H	2	1.610000	0.000000

FINAL HEAT OF FORMATION = 26.97779 KCAL

TOTAL ENERGY = -19.78933 EV  
ELECTRONIC ENERGY = -27.20810 EV  
CORE-CORE REPULSION = 7.41878 EV

IONIZATION POTENTIAL = 8.38124

NO. OF FILLED LEVELS = 1

MOLECULAR WEIGHT = 7.948

#### EIGENVECTORS

ROOT NO.	1	2	3	4	5
	-8.38124	0.63258	2.45221	2.45221	5.60161
S Li	1 0.41230	0.80110	0.00000	0.00000	-0.43387
PX Li	1 0.34007	-0.57714	0.00000	0.00000	-0.74247
PY Li	1 0.00000	0.00000	-0.92376	0.38298	0.00000
PZ Li	1 0.00000	0.00000	0.38298	0.92376	0.00000
S H	2 0.84520	-0.15858	0.00000	0.00000	0.51039

## NET ATOMIC CHARGES AND DIPOLE CONTRIBUTIONS

ATOM NO.	TYPE	CHARGE	ATOM ELECTRON DENSITY
1	Li	0.4287	0.5713
2	H	-0.4287	1.4287

  

DIPOLE	X	Y	Z	TOTAL
POINT-CHG.	-3.315	0.00	0.00	3.315
HYBRID	-2.929	0.00	0.00	2.929
SUM	-6.244	0.00	0.00	6.244

## ATOMIC ORBITAL ELECTRON POPULATIONS

0.33999      0.23129      0.00000      0.00000      1.42872

## BONDING CONTRIBUTION OF EACH M.O.

1.6324 -0.1437 0.0000 0.0000 -1.4887

## BOND ORDERS AND VALENCIES

Li 1                  H 2  
Li 1 0.816203  
H 2 0.816203 0.816203

### Alternate Versions of MOPAC

For some installations, to run MOPAC just click on MOPAC6 or MOPAC.EXE. The program will ask for the input file name. Type in the name exactly as you specified when you saved the file from Notepad or Word. The program will tell you about the progress of the run in a status window. Still other installations require the input file to be named FOR005. For these versions of MOPAC, you don't specify the file name (you just click on the mopac icon or type mopac in a command line).

### Cleaning Up and Runtime Errors

Some installations produce output files with names such as FOR006. FOR006 contains the results of your calculation. After you are finished with your calculation you must delete all of the FOR files before running MOPAC again. If any of these files exist, MOPAC will stop with an error. On the OS-X version the file names are taken care of for you automatically. MOPAC will also stop with an error if there is no blank line at the end of the input file. There should be one and only one blank line at the end of the input file. If you get such an error, fix the problem with a text editor. Delete any of the FOR files, like FOR006, FOR011, and FOR012, before starting MOPAC again.

Likewise, use a unique file name for every input file. If MOPAC tries to write a new file, when a file of the same name already exists, an error will result.

Another source of errors is forgetting to close the input file in the text editor. Files can't be opened by two applications at once.

### **Installing MOPAC and the Script to run MOPAC on OS-X systems**

First, make a new folder in your “Documents” directory called “mopac”. Then open Safari or Firefox. There are two sources of the executable files, for on-campus or off-campus access.

**On-campus:** Connect to Server.... “smb://files.colby.edu/macfiles” using the directory path “Courses/CH341/mopac7forOS-X”. Copy the data files (.dat files), the mopaclocal.com file, and the mopac7.exe.tar.gz file, which contains the MOPAC program executable file into your local Documents/mopac directory. Double click on the mopac7.exe.tar.gz file to decompress and produce the executable “mopac.exe”.

Open a Terminal window (TV-type icon with the ">" symbol), and change to the mopac directory by typing:

```
$ cd Documents/mopac
```

Type ls at the \$ prompt to see a listing of the files in the directory (ls is short for list). Rename the command file by typing:

```
$ mv mopaclocal.com mopac
```

If “mopaclocal.com.sh” is listed as the file name then include the “.sh” as well (mv is short for move). Next type:

```
$ chmod +x mopac
```

This step allows the file to be run as an executable script; “chmod” is short for “change the file mode”. Check to make sure that the data files are not listed with “.txt” by typing ls again. If they are misnamed, type the following in the Terminal window for example:

```
$ mv O3-180-OSX.dat.txt O3-180-OSX.dat
```

You should now be ready to follow the instruction given above for running MOPAC.

**Off-campus:** Download the OSX executable “mopac7.exe.tar.gz” or just “mopac7.exe.tar” from “[www.webmo.net/support/binaries\\_osx.html](http://www.webmo.net/support/binaries_osx.html)”. Open the Download folder and double click on the “mopac7.exe.tar.gz” entry. The executable “mopac.exe” will be produced. Drag “mopac.exe” to your local Documents/mopac directory. Next, go to the Assignment Tracker and find the link to the runmopac script directory. You can also use the URL:

```
“http://www.colby.edu/chemistry/PChem/software/runmopacforOSX”
```

Right-click on the “mopaclocal” file and “Save link as..” to the “Documents/mopac” directory that you just made.

Do the same “Save link as..” steps with the input data files (.dat files). After saving each data file to your mopac directory, make sure the input files end with the “.dat” extension. Make sure that the input file has one blank line at the end. Note also the section on “Getting the Correct File Formatting on OS-X,” below.

Open a Terminal window (TV-type icon with the ">" symbol), and change to the mopac directory by typing:

```
$ cd Documents/mopac
```

Type `ls` at the `$` prompt to see a listing of the files in the directory (`ls` is short for list). Rename the command file by typing:

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$ mv mopaclocal.com mopac
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If “`mopaclocal.com.sh`” is listed as the file name then include the “.sh” as well (`mv` is short for move). Next type:

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```
$ mv O3-180-OSX.dat.txt O3-180-OSX.dat
```

You should now be ready to follow the instruction given above for running MOPAC.

### **Getting the Correct File Formatting on OS-X**

The easiest way to get the proper input file formatting is to use the TextEdit application. The first time that you edit a “.dat” or “.out” file, you will be asked what application you want to use. From the Applications list choose TextEdit. All subsequent times that you click on a file with that extension should again open the file with the TextEdit application. When saving a file in TextEdit, from “File/Save As...” enter the file name with the “.dat” extension. Then click on Save. A dialog window will open that reads ‘You have used the extension “.dat” at the end of the name. The standard extension is “.txt”’. Click on the “Use .dat” button. In the Finder file listing, check that the file has the .dat extension and not “.dat.txt”.

## MOPAC Keywords

MOPAC calculations are controlled by keywords that appear on the first line of the input file. The following list gives the descriptions of just a few. Please see the MOPAC documentation for a complete listing. The book by Tim Clark also gives an excellent introduction to doing MOPAC calculations: Tim Clark, *A Handbook of Computational Chemistry: A Practical Guide to Chemical Structure and Energy Calculations*, Wiley, New York, NY, 1985.

\*\*\*\*\***Caution:** You need to know the spin multiplicity of your molecule. Most ground state molecules are singlets. The default calculation method of Restricted Hartree-Fock theory (RHF) is fine for these molecules. However, if you have an odd-electron molecule or ion, the ground state is almost certainly a doublet. If you are working with excited states or transition states the spin multiplicity can vary. When working with molecules that are not ground state singlets, UHF calculations are the best method to use. However, you can use the DOUBLET, TRIPLET, and EXCITED keywords to stay within the RHF method. These RHF calculations are not as accurate, but they may be sufficient for back-of-the-envelope calculations and they are certainly much faster. Please see the MOPAC documentation for more information on UHF calculations.

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### AM1

The AM1 method is to be used. By default MNDO is run. In AM1 the Hamiltonian is calculated slightly differently.

### BONDS

The bond order between all pairs of atoms is printed. In this context a bond is defined as the sum of the squares of the density matrix elements connecting any two atoms. For ethane, ethylene, and acetylene the carbon-carbon orders are roughly 1.00, 2.00, and 3.00, respectively. The diagonal terms are the valencies calculated from the atomic terms only and are defined as the sum of the bonds the atom makes with other atoms.

The bonding contributions of all M.O.'s in the system are printed immediately before the bonds matrix. Just as an atomic orbital has a valency, so has a molecular orbital. This leads to the following relations: The sum of the bonding contributions of all occupied M.O.'s is the same as the sum of all valencies which, in turn is equal to two times the sum of all the bonds. The sum of the bonding contributions of all M.O.'s is zero.

### CHARGE=n

When the system being studied is an ion, the charge, n, on the ion must be supplied. For cations n can be 1 or 2 or 3, etc., for anions -1 or -2 or -3 etc. For example for  $\text{NH}_4^+$  CHARGE=1, and for  $\text{PO}_4^{3-}$  CHARGE=-3.

### DENSITY

At the end of the job, when the results are being printed, the density matrix is also printed. If the density is not requested, then the diagonal of the density matrix, i.e., the electron density on the atomic orbitals, will be printed.

## DOUBLET

When a configuration interaction calculation is done, all spin states are calculated simultaneously. When only doublet states are of interest, the DOUBLET can be specified, and all other spin states, while calculated, are ignored in the choice of root to be used. DOUBLET has no meaning in a UHF calculation.

## EXCITED

The state to be calculated is the first excited open-shell singlet state. This state would normally be the state resulting from a one-electron excitation from the HOMO to the LUMO. MOPAC automatically uses a configuration interaction, CI, calculation for excited states. See the MOPAC manual if your molecule is not a ground state singlet.

## FORCE

The vibrational frequencies of the normal modes in a molecule are calculated. These frequencies can then be used to predict the infrared spectrum of the molecule. The force constants are first calculated from the second derivatives of the energy with respect to displacements of all pairs of atoms. The force constants and the isotopic masses are then used to calculate the vibrational frequencies.

## PI

The normal density matrix is composed of atomic orbitals, that is s, px, py, and pz. PI allows the user to see how each atom-atom interaction is split into sigma and pi bonds. The resulting "density matrix" is composed of the following basis-functions: s-sigma, p-sigma, p-pi, d-sigma, d-pi, d-dell. The on-diagonal terms give the hybridization state, so that an sp<sup>2</sup> hybridized system would be represented as s-sigma 1.0, p-sigma 2.0, p-pi 1.0.

## POLAR

The polarizability is calculated. The polarizability allows you to calculate the strength of London dispersion forces between molecules.

## SINGLET

Do a configuration interaction calculation for the ground state singlet of the molecule.

## TRIPLET

The triplet state is defined and a configuration interaction (CI) calculation is performed. The occupancy of the M.O.'s in the SCF calculation is defined as (...2,1,1,0,...), that is, one electron is put in each of the two highest occupied M.O.'s. ( TRIPLET has an alternate effect in a UHF calculation.)

## UHF

The unrestricted Hartree-Fock Hamiltonian is to be used. UHF calculations are the best method to use for open shell system, i.e. ground state doublets, triplets, etc., and excited states.

## VECTORS

The eigenvectors are to be printed.