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# **QM Tutorial Documentation**

*Release 0.1*

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## Install required software

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The following instructions describe how to obtain and install GAMESS, Avogadro and wxMacMolPlt on Windows (as of April 2011).

### Install GAMESS

1. Follow the “How to get GAMESS” link from the [GAMESS website](#). When you finally get to the download page, enter your email address and tick the box for “GAMESS version October 1, 2010 R1 for Microsoft Windows”, and click *Submit Request*.
2. After a couple of minutes, you will receive an email containing a link to the WinGAMESS download along with a password. Click on the link and enter the password to download the installer. Run the installer and choose all of the defaults. In particular, you should make sure to install to C:/WinGAMESS.
3. You need to correct an error in C:/WinGAMESS/WG\_DDE.bat. Open the C:/WinGAMESS folder, right-click on C:/WinGAMESS/WG\_DDE.bat and choose *Edit*. Change line 40 of the file to read as follows:

```
set WinGamess_Version=10
```

Naturally, if you are using a different version of GAMESS, you should set this value appropriately.

4. To test your GAMESS installation, save this GAMESS input file ethane.inp on your Desktop, open the folder C:/WinGAMESS, and drag-and-drop ethane.inp onto WG\_DDE.bat. The first time you do this, you may have to say Yes twice to allow it through the Windows firewall (this requires Administrator rights). If GAMESS is working properly, it will create a file ethane.out on your Desktop.

### Install Avogadro

Download **Avogadro** 1.0.1 from <http://avogadro.openmolecules.net>, using the *Get Avogadro* link. Run the installer.

### Install wxMacMolPlt

**wxMacmolPlot** 7.4.2 is available from <http://www.scl.ameslab.gov/MacMolPlt/>. The download link is towards the bottom of the page. Run the installer.



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## Looking at GAMESS output

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When you run GAMESS, an output file (or “log file”) is created. This is a text file that contains all of the results of the calculation.

### 2.1 Example output file

The following output file (available as a 6-page PDF [here](#)) is the result of a single point RHF/STO-3G calculation on a water molecule. A series of questions follows.

```
Distributed Data Interface kickoff program.
Initiating 2 compute processes on 2 nodes to run the following command:
C:\WinGAMESS/gameass.10.exe water_sym
```

```
*****
*           GAMESS VERSION = 1 OCT 2010 (R1)           *
*           FROM IOWA STATE UNIVERSITY                 *
* M.W.SCHMIDT, K.K.BALDRIDGE, J.A.BOATZ, S.T.ELBERT, *
*   M.S.GORDON, J.H.JENSEN, S.KOSEKI, N.MATSUNAGA,   *
*           K.A.NGUYEN, S.J.SU, T.L.WINDUS,           *
*           TOGETHER WITH M.DUPUIS, J.A.MONTGOMERY    *
*           J.COMPUT.CHEM. 14, 1347-1363(1993)        *
***** 32 BIT LINUX VERSION *****
```

SINCE 1993, STUDENTS AND POSTDOCS WORKING AT IOWA STATE UNIVERSITY  
AND ALSO IN THEIR VARIOUS JOBS AFTER LEAVING ISU HAVE MADE IMPORTANT  
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 UNIVERSITY OF ZURICH:  
     ROBERTO PEVERATI, KIM BALDRIDGE  
 N. COPERNICUS UNIVERSITY AND JACKSON STATE UNIVERSITY:  
     MARIA BARYSZ

PARALLEL VERSION RUNNING ON       2 PROCESSORS IN       2 NODES.

EXECUTION OF GAMESS BEGUN Mon Apr 11 13:58:57 2011

ECHO OF THE FIRST FEW INPUT CARDS -  
 INPUT CARD>!   File created by MacMolPlt 7.4  
 INPUT CARD> \$CONTRL SCFTYP=RHF RUNTYP=ENERGY MAXIT=30 MULT=1 \$END  
 INPUT CARD> \$SYSTEM TIMLIM=525600 MEMORY=1000000 \$END  
 INPUT CARD> \$BASIS GBASIS=STO NGAUSS=3 \$END  
 INPUT CARD> \$SCF DIRSCF=.TRUE. \$END  
 INPUT CARD> \$DATA  
 INPUT CARD>Title  
 INPUT CARD>CNV 2  
 INPUT CARD>  
 INPUT CARD>O       8.0       0.00000     0.00000     -0.06673  
 INPUT CARD>H       1.0       0.76334     0.00000     0.52965  
 INPUT CARD> \$END

1000000 WORDS OF MEMORY AVAILABLE

BASIS OPTIONS

-----

GBASIS=STO		IGAUSS=	3	POLAR=NONE	
NDFUNC=	0	NFFUNC=	0	DIFFSP=	F
NPFUNC=	0	DIFFS=	F	BASNAM=	

## RUN TITLE

-----

Title

THE POINT GROUP OF THE MOLECULE IS CNV  
 THE ORDER OF THE PRINCIPAL AXIS IS 2

ATOM	ATOMIC CHARGE	COORDINATES (BOHR)		
		X	Y	Z
O	8.0	0.0000000000	0.0000000000	-0.1261014152
H	1.0	-1.4425034355	0.0000000000	1.0008933694
H	1.0	1.4425034355	0.0000000000	1.0008933694

## INTERNUCLEAR DISTANCES (ANGS.)

-----

	1 O	2 H	3 H
1 O	0.0000000	0.9686883 *	0.9686883 *
2 H	0.9686883 *	0.0000000	1.5266800 *
3 H	0.9686883 *	1.5266800 *	0.0000000

\* ... LESS THAN 3.000

## ATOMIC BASIS SET

-----

THE CONTRACTED PRIMITIVE FUNCTIONS HAVE BEEN UNNORMALIZED  
 THE CONTRACTED BASIS FUNCTIONS ARE NOW NORMALIZED TO UNITY

SHELL TYPE	PRIMITIVE	EXPONENT	CONTRACTION COEFFICIENT (S)		
O					
1	S	1	130.7093214	0.154328967295	
1	S	2	23.8088661	0.535328142282	
1	S	3	6.4436083	0.444634542185	
2	L	4	5.0331513	-0.099967229187	0.155916274999
2	L	5	1.1695961	0.399512826089	0.607683718598
2	L	6	0.3803890	0.700115468880	0.391957393099
H					
4	S	7	3.4252509	0.154328967295	
4	S	8	0.6239137	0.535328142282	
4	S	9	0.1688554	0.444634542185	

TOTAL NUMBER OF BASIS SET SHELLS = 4  
 NUMBER OF CARTESIAN GAUSSIAN BASIS FUNCTIONS = 7  
 NUMBER OF ELECTRONS = 10  
 CHARGE OF MOLECULE = 0  
 SPIN MULTIPLICITY = 1  
 NUMBER OF OCCUPIED ORBITALS (ALPHA) = 5  
 NUMBER OF OCCUPIED ORBITALS (BETA ) = 5  
 TOTAL NUMBER OF ATOMS = 3  
 THE NUCLEAR REPULSION ENERGY IS 9.0871358664

```

$CONTRL OPTIONS
-----
SCFTYP=RHF          RUNTYP=ENERGY      EXETYP=RUN
MPLEVL=            0      CITYP =NONE      CCTYP =NONE      VBTYP =NONE
DFTTYP=NONE        TDDFT =NONE
MULT =             1      ICHARG=          0      NZVAR =          0      COORD =UNIQUE
PP =NONE           RELWFN=NONE          LOCAL =NONE      NUMGRD=          F
ISPHER=            -1      NOSYM =          0      MAXIT =          30      UNITS =ANGS
PLTORB=            F      MOLPLT=          F      AIMPAC=          F      FRIEND=
NPRINT=            7      IREST =          0      GEOM =INPUT
NORMF =            0      NORMP =          0      ITOL =           20      ICUT =           9
INTTYP=BEST        GRDTYP=BEST          QMTTOL= 1.0E-06

$SYSTEM OPTIONS
-----
REPLICATED MEMORY=      1000000 WORDS (ON EVERY NODE).
DISTRIBUTED MEMDDI=      0 MILLION WORDS IN AGGREGATE,
MEMDDI DISTRIBUTED OVER  2 PROCESSORS IS          0 WORDS/PROCESSOR.
TOTAL MEMORY REQUESTED ON EACH PROCESSOR=      1000000 WORDS.
TIMLIM=      525600.00 MINUTES, OR      365.0 DAYS.
PARALL= T  BALTYP= DLB  KDIAG=      0  COREFL= F
MXSEQ2=      300  MXSEQ3=      150

-----
PROPERTIES INPUT
-----

MOMENTS          FIELD          POTENTIAL          DENSITY
IEMOM =          1  IEFLD =          0  IEPOT =          0  IEDEN =          0
WHERE =COMASS    WHERE =NUCLEI    WHERE =NUCLEI    WHERE =NUCLEI
OUTPUT=BOTH      OUTPUT=BOTH      OUTPUT=BOTH      OUTPUT=BOTH
IEMINT=          0  IEFINT=          0                                IEDINT=          0
                                                                MORB =          0

EXTRAPOLATION IN EFFECT
ORBITAL PRINTING OPTION: NPREO=      1      7      2      1

-----
INTEGRAL TRANSFORMATION OPTIONS
-----
NWORD =          0
CUTOFF = 1.0E-09  MPTRAN =          0
DIRTRF =          T  AOINTS =DUP

-----
INTEGRAL INPUT OPTIONS
-----
NOPK =          1  NORDER=          0  SCHWRZ=          T

-----
THE POINT GROUP IS CNV, NAXIS= 2, ORDER= 4
-----

DIMENSIONS OF THE SYMMETRY SUBSPACES ARE
A1 =          4  A2 =          0  B1 =          2  B2 =          1

..... DONE SETTING UP THE RUN .....
CPU      0: STEP CPU TIME=          0.02  TOTAL CPU TIME=          0.0 (          0.0 MIN)
TOTAL WALL CLOCK TIME=          0.0 SECONDS, CPU UTILIZATION IS  93.75%

```

```

*****
1 ELECTRON INTEGRALS
*****
..... END OF ONE-ELECTRON INTEGRALS .....
CPU    0: STEP CPU TIME=      0.00 TOTAL CPU TIME=      0.0 (    0.0 MIN)
TOTAL WALL CLOCK TIME=      0.0 SECONDS, CPU UTILIZATION IS  93.75%

-----
GUESS OPTIONS
-----
GUESS =HUCKEL          NORB =      0          NORDER=      0
MIX   =      F          PRTMO =      F          PUNMO =      F
TOLZ  = 1.0E-08        TOLE  = 1.0E-05
SYMDEN=      F          PURIFY=      F

INITIAL GUESS ORBITALS GENERATED BY HUCKEL  ROUTINE.
HUCKEL GUESS REQUIRES      2569 WORDS.

SYMMETRIES FOR INITIAL GUESS ORBITALS FOLLOW.  BOTH SET(S).
  5 ORBITALS ARE OCCUPIED (    1 CORE ORBITALS).
  2=A1    3=B1    4=A1    5=B2    6=B1    7=A1
..... END OF INITIAL ORBITAL SELECTION .....
CPU    0: STEP CPU TIME=      0.00 TOTAL CPU TIME=      0.0 (    0.0 MIN)
TOTAL WALL CLOCK TIME=      0.0 SECONDS, CPU UTILIZATION IS  93.75%

-----
AO INTEGRAL TECHNOLOGY
-----
S,P,L SHELL ROTATED AXIS INTEGRALS, REPROGRAMMED BY
  KAZUYA ISHIMURA (IMS) AND JOSE SIERRA (SYNSTAR).
S,P,D,L SHELL ROTATED AXIS INTEGRALS PROGRAMMED BY
  KAZUYA ISHIMURA (INSTITUTE FOR MOLECULAR SCIENCE).
S,P,D,F,G SHELL TO TOTAL QUARTET ANGULAR MOMENTUM SUM 5,
  ERIC PROGRAM BY GRAHAM FLETCHER (ELORET AND NASA ADVANCED
  SUPERCOMPUTING DIVISION, AMES RESEARCH CENTER).
S,P,D,F,G,L SHELL GENERAL RYS QUADRATURE PROGRAMMED BY
  MICHEL DUPUIS (PACIFIC NORTHWEST NATIONAL LABORATORY).

-----
2 ELECTRON INTEGRALS
-----

DIRECT SCF METHOD SKIPS INTEGRAL STORAGE ON DISK.
DIRECT TRANSFORMATION SKIPS AO INTEGRAL STORAGE ON DISK.
..... END OF TWO-ELECTRON INTEGRALS .....
CPU    0: STEP CPU TIME=      0.05 TOTAL CPU TIME=      0.1 (    0.0 MIN)
TOTAL WALL CLOCK TIME=      0.1 SECONDS, CPU UTILIZATION IS  79.49%

-----
RHF SCF CALCULATION
-----

NUCLEAR ENERGY =          9.0871358664
MAXIT = 30    NPUNCH= 2
EXTRAP=T DAMP=F SHIFT=F RSTRCT=F DIIS=F DEM=F SOSCF=F
DENSITY MATRIX CONV= 2.00E-05
MEMORY REQUIRED FOR RHF ITERS=      44817 WORDS.

```

DIRECT SCF CALCULATION, SCHWRZ=T FDIFF=T, DIRTHR= 0.00E+00 NITDIR=10  
 SCHWARZ INEQUALITY OVERHEAD: 28 INTEGRALS, T= 0.00

ITER	EX	DEM	TOTAL ENERGY	E CHANGE	DENSITY CHANGE	DIIS ERROR	NONZERO INTEGRALS	BLOCKS SKIPPED
1	0	0	-74.7974092796	-74.7974092796	0.596869468	0.000000000	141	0
2	1	0	-74.9507257506	-0.1533164709	0.181657794	0.000000000	141	0
3	2	0	-74.9629281338	-0.0122023833	0.059598419	0.000000000	141	0
4	3	0	-74.9642035242	-0.0012753904	0.020216252	0.000000000	141	0
5	4	0	-74.9643795359	-0.0001760117	0.007366384	0.000000000	141	0
6	0	0	-74.9644088533	-0.0000293174	0.004742101	0.000000000	141	0
7	1	0	-74.9644154231	-0.0000065699	0.000070104	0.000000000	141	0
8	2	0	-74.9644154252	-0.0000000021	0.000025327	0.000000000	141	0
9	3	0	-74.9644154256	-0.0000000003	0.000009752	0.000000000	141	0

-----  
 DENSITY CONVERGED  
 -----

TIME TO FORM FOCK OPERATORS= 0.0 SECONDS ( 0.0 SEC/ITER)  
 FOCK TIME ON FIRST ITERATION= 0.0, LAST ITERATION= 0.0  
 TIME TO SOLVE SCF EQUATIONS= 0.0 SECONDS ( 0.0 SEC/ITER)

FINAL RHF ENERGY IS -74.9644154256 AFTER 9 ITERATIONS

-----  
 EIGENVECTORS  
 -----

			1	2	3	4	5
			-20.2438	-1.2632	-0.6111	-0.4529	-0.3909
			A1	A1	B1	A1	B2
1	O	1 S	0.994158	-0.233200	-0.000000	0.102889	0.000000
2	O	1 S	0.026315	0.837618	-0.000000	-0.534598	0.000000
3	O	1 X	-0.000000	0.000000	0.606792	-0.000000	0.000000
4	O	1 Y	-0.000000	0.000000	-0.000000	-0.000000	1.000000
5	O	1 Z	0.004251	0.126155	-0.000000	0.772609	0.000000
6	H	2 S	-0.005841	0.157816	-0.446042	0.282964	0.000000
7	H	3 S	-0.005841	0.157816	0.446042	0.282964	0.000000

			6	7
			0.5952	0.7274
			A1	B1
1	O	1 S	-0.130529	0.000000
2	O	1 S	0.863693	0.000000
3	O	1 X	0.000000	0.982566
4	O	1 Y	0.000000	0.000000
5	O	1 Z	0.744429	0.000000
6	H	2 S	-0.788315	0.828700
7	H	3 S	-0.788315	-0.828700

..... END OF RHF CALCULATION .....

CPU 0: STEP CPU TIME= 0.00 TOTAL CPU TIME= 0.1 ( 0.0 MIN)  
 TOTAL WALL CLOCK TIME= 0.1 SECONDS, CPU UTILIZATION IS 79.49%

-----  
 PROPERTY VALUES FOR THE RHF SELF-CONSISTENT FIELD WAVEFUNCTION  
 -----

```

ENERGY COMPONENTS
-----

WAVEFUNCTION NORMALIZATION =      1.0000000000

      ONE ELECTRON ENERGY =     -122.1793235802
      TWO ELECTRON ENERGY =      38.1277722882
      NUCLEAR REPULSION ENERGY =      9.0871358664
      -----
      TOTAL ENERGY =          -74.9644154256

ELECTRON-ELECTRON POTENTIAL ENERGY =      38.1277722882
NUCLEUS-ELECTRON POTENTIAL ENERGY =     -196.7417484352
NUCLEUS-NUCLEUS POTENTIAL ENERGY =      9.0871358664
      -----
      TOTAL POTENTIAL ENERGY =     -149.5268402806
      TOTAL KINETIC ENERGY =      74.5624248550
      VIRIAL RATIO (V/T) =          2.0053913291

..... PI ENERGY ANALYSIS .....

ENERGY ANALYSIS:
  FOCK ENERGY=      -45.9237766278
  BARE H ENERGY=    -122.1793235802
  ELECTRONIC ENERGY =    -84.0515501040
  KINETIC ENERGY=      74.5624248550
  N-N REPULSION=       9.0871358664
  TOTAL ENERGY=     -74.9644142376
  SIGMA PART (1+2)=   -76.2127294486
    (K, V1, 2)=       69.5049624030    -176.7884643168    31.0707724652
  PI PART (1+2)=     -7.8388206554
    (K, V1, 2)=       5.0574624520    -19.9532841185    7.0570010110
  SIGMA SKELETON, ERROR= -67.1255935822    0.0000000000
  MIXED PART= 0.00000E+00 0.00000E+00 0.00000E+00 0.00000E+00
..... END OF PI ENERGY ANALYSIS .....

-----
MULLIKEN AND LOWDIN POPULATION ANALYSES
-----

ATOMIC MULLIKEN POPULATION IN EACH MOLECULAR ORBITAL

          1          2          3          4          5
1         2.000000    2.000000    2.000000    2.000000    2.000000
2         2.001361    1.617307    1.068623    1.667555    2.000000
3        -0.000680    0.191347    0.465688    0.166222    0.000000
4        -0.000680    0.191347    0.465688    0.166222    0.000000

----- POPULATIONS IN EACH AO -----
          MULLIKEN      LOWDIN
1  O  1  S      1.99768    1.99607
2  O  1  S      1.83410    1.68593
3  O  1  X      1.06862    1.09728
4  O  1  Y      2.00000    2.00000
5  O  1  Z      1.45445    1.46728
6  H  2  S      0.82258    0.87672

```

```

7 H 3 S      0.82258      0.87672

----- MULLIKEN ATOMIC OVERLAP POPULATIONS -----
(OFF-DIAGONAL ELEMENTS NEED TO BE MULTIPLIED BY 2)

      1          2          3

1      7.8326767
2      0.2610849      0.6079246
3      0.2610849     -0.0464327      0.6079246

TOTAL MULLIKEN AND LOWDIN ATOMIC POPULATIONS
ATOM      MULL.POP.      CHARGE      LOW.POP.      CHARGE
1 O              8.354846     -0.354846      8.246557     -0.246557
2 H              0.822577      0.177423      0.876722      0.123278
3 H              0.822577      0.177423      0.876722      0.123278

-----
BOND ORDER AND VALENCE ANALYSIS      BOND ORDER THRESHOLD=0.050
-----

ATOM PAIR DIST      BOND      ATOM PAIR DIST      BOND      ATOM PAIR DIST      BOND
1 2 0.969 0.957      1 3 0.969 0.957

ATOM      TOTAL      BONDED      FREE
ATOM      VALENCE      VALENCE      VALENCE
1 O              1.913      1.913      0.000
2 H              0.969      0.969      0.000
3 H              0.969      0.969      0.000

-----
ELECTROSTATIC MOMENTS
-----

POINT 1          X          Y          Z (BOHR)      CHARGE
          0.000000      0.000000      0.000026      0.00 (A.U.)
          DX          DY          DZ          /D/ (DEBYE)
          0.000000      0.000000      1.713972      1.713972
..... END OF PROPERTY EVALUATION .....
CPU      0: STEP CPU TIME=      0.02 TOTAL CPU TIME=      0.1 (      0.0 MIN)
TOTAL WALL CLOCK TIME=      0.1 SECONDS, CPU UTILIZATION IS 81.91%
580000 WORDS OF DYNAMIC MEMORY USED
EXECUTION OF GAMESS TERMINATED NORMALLY Mon Apr 11 13:58:57 2011
DDI: 263224 bytes (0.3 MB / 0 MWords) used by master data server.

-----
CPU timing information for all processes
=====
0: 0.171 + 0.62 = 0.233
1: 0.140 + 0.00 = 0.140
2: 0.00 + 0.15 = 0.15
3: 0.00 + 0.31 = 0.31
-----
ddikick.x: exited gracefully.
----- accounting info -----

```

## 2.2 Questions

### INPUT CARD

The `INPUT CARD` section at the start shows the first few lines of the input file. Here it shows the entire input.

1. Can you figure out from the input file that this is a RHF/STO-3G calculation?
2. The input file appears to only specify the coordinates for two atoms, an oxygen and a hydrogen. How does GAMESS know that there is a second hydrogen? (Hint: see the section after `RUN TITLE`.)

### INTERNUCLEAR DISTANCES

1. In the `INTERNUCELAR DISTANCES` section, what is the point of the asterisks after some of the distance values?

### ATOMIC BASIS SET

1. How many basis functions are there? Can you work out what basis functions they are? (Hint: see the `EIGENVECTORS` section.)
2. How many occupied orbitals are there?
3. Neutral water has 10 electrons, and a spin multiplicity (number of unpaired electrons + 1) of 1. If a molecule had 11 electrons, what values for multiplicity would be possible?

### \$SYSTEM OPTIONS

The amount of memory available to GAMESS can be set using the `MWORDS` command (megawords) in the `$SYSTEM` section. The value of `MWORDS` defaults to 1 (i.e. 1000000 words).

1. If 1 *word* is 8 bytes, how many MB of memory are available to GAMESS by default? Given that modern computers have 2GB or more of RAM, is it safe to increase this value if GAMESS complains about running out of memory?

### RHF SCF CALCULATIONS

Much of the computation time in a typical calculation is spent in the SCF section. This is an iterative procedure that keeps repeating until the difference between the density matrix on successive iterations is less than 0.00002.

1. How many iterations did it take for SCF convergence? What was the final energy?
2. Would you say that the SCF converges nicely in this case? What would you expect to see if there was a problem converging the SCF?
3. Could you make a guess about the meaning of `MAXIT = 30`? Can you think of any circumstance where it might be useful to increase this value?

### EIGENVECTORS

The eigenvectors of a QM calculation are the molecular orbitals. Each molecular orbital is described in terms of the basis functions.

1. How many molecular orbitals are there?
2. Which eigenvector represents the HOMO? What is its energy? Where is the HOMO located?
3. Which eigenvector represents the LUMO? What is its energy?

#### **MULLIKEN AND LOWDIN POPULATION ANALYSES**

1. What are the Mulliken charges on each atom? Do they make sense?

---

## Molecular orbitals of water

---

Let's visualise the molecular orbitals of water at the HF/3-21G level of theory.

### 3.1 Create an initial 3D structure

Using Avogadro, we can create an initial structure of the water molecule. Simply choose the Draw Tool () , change the Element to Oxygen, tick the box for *Adjust Hydrogens*, and click anywhere in the View Window.

This will draw a single oxygen atom, and hydrogens will be added automatically to satisfy the oxygen atom's valency, giving H<sub>2</sub>O.

Now optimise the structure using the MMFF94 forcefield (Extensions/Optimize Geometry).

### 3.2 Generate the GAMESS input file

Under Extensions/GAMESS/Input Generator, choose `Equilibrium Geometry` to find the optimized geometry. Choose `RHF` for the method and `3-21G` for the basis set.

The other options should be left at their default of `Gas phase calculation`, `Singlet multiplicity`, and `Neutral charge`.

Click on *Generate...* to save the GAMESS input file to an appropriate location.

### 3.3 Run GAMESS

Open a Windows folder showing the location of the GAMESS input file. Open another Windows folder showing the location where GAMESS was installed (typically `C:/WinGAMESS`).

Now drag-and-drop the GAMESS input file on top of `C:/WinGAMESS/WG_DDE.BAT`.

This will start the calculation, and the output will be written to a file with the same name and location as the input file, but with the extension `.out`.

### 3.4 Investigate the geometry optimisation

Start wxMacMolPlt, and File/Open the output file from the GAMESS run.

The geometry optimisation probably involved several steps. You can use the slider at the bottom right of the wxMac-MolPlot window to investigate the steps.

If you click on Subwindow/Energy Plot you can see a plot of the energy values and root-mean-squared change in coordinates for the steps.

### 3.5 Look at the electrostatic potential

The molecular electrostatic potential (MEP) is a measure of the force (attractive or repulsive) felt by a point charge at a certain point in space due to the electronic distribution in a molecule. We can colour the molecular surface using the MEP to give some idea of where nucleophiles or electrophiles might attack.

Here we will use an isosurface of the electron density to represent the molecular surface.

Click on Subwindow/Surfaces/"3D Total Electron Density". Click Update to generate a wireframe wire of an isosurface of the electron density.

---

**Note:** What the effect of increasing or decreasing the number of grid points, the grid size, or the contour value?

It is worth remembering that the larger the contour value, the smaller the volume contained by the isosurface.

---

Set the number of grid points to 25, the counter value to 0.04, the Surface Display to Solid, tick the Smooth box and click Update.

To colour the surface using the MEP, tick "Colorize using the surface MEP value" and also "Invert color map". You may want to increase the Transparency to 20%, then click Update.

When finished admiring your work, click *Delete* to remove the surface.

### 3.6 Visualise the orbitals

Now click Add.../"3D Orbital" to bring up the orbital visualiser settings.

Draw the HOMO using a smooth solid surface. Save a copy of the view using File/Export. Choose "Portable Network Graphics (\*.png)", the filename `water_homo.png` and click *Save*. In the Export Options, choose "300dpi (Print)".

Do the same for the LUMO. How do they compare?

---

## Vibrational frequencies of water

---

Vibrational frequency calculations should always be carried out to verify that a geometry optimisation has found a true minimum, and not just a saddle point.

They are also useful in their own right to find and visualise the normal modes of vibration.

### 4.1 Create the GAMESS input file and run GAMESS

The vibrational frequencies are only valid at an optimised geometry so we need to use the geometry obtained in the previous calculation.

To open a GAMESS output file in Avogadro, we need to first rename it from `.out` to `.gamout`. Once this is done, use File/Open in Avogadro to open the file.

Next click Extensions/GAMESS/”Input Generator” and choose “Frequencies” under Calculate. Click on *Generate* and save the GAMESS input file.

Run GAMESS using drag-and-drop as before.

### 4.2 Analyse the frequencies

It is worth opening the GAMESS output file in Wordpad and taking a look at the NORMAL COORDINATE ANALYSIS section (see below). (Hint: In Wordpad, it is useful to “Select All” and change the font size to 8 pt.)

17. Is this molecule at a true geometry minimum?

17. How many frequencies are expected for a 3-atom non-linear molecule? (Hint:  $3N-6$ )

17. How many frequencies are present in the file? How can you account for the difference?

```
-----  
NORMAL COORDINATE ANALYSIS IN THE HARMONIC APPROXIMATION  
-----  
  
ATOMIC WEIGHTS (AMU)  
  
1      O      15.99491  
2      H      1.00782  
3      H      1.00782  
  
MODES 1 TO 6 ARE TAKEN AS ROTATIONS AND TRANSLATIONS.
```

ANALYZING SYMMETRY OF NORMAL MODES...

FREQUENCIES IN CM\*\*-1, IR INTENSITIES IN DEBYE\*\*2/AMU-ANGSTROM\*\*2,  
REDUCED MASSES IN AMU.

		1	2	3	4	5
FREQUENCY:		1.33	0.16	0.00	0.33	6.17
SYMMETRY:		A	A	A	A	A
REDUCED MASS:		1.01401	6.22305	6.00353	12.81051	1.03666
IR INTENSITY:		8.39984	0.00224	0.00000	0.52570	3.14657
1	O	X -0.00000000	-0.04742972	0.23101688	-0.00000000	0.03749320
		Y -0.00000000	0.23166471	0.04641338	-0.00000000	-0.02121402
		Z -0.02017373	0.00000000	0.00000000	0.24794115	-0.00000000
2	H	X -0.00000000	-0.04712588	0.23101681	-0.00000000	0.02610283
		Y 0.00000000	0.21251345	0.04641346	-0.00000000	0.69693540
		Z 0.87470814	0.00000000	0.00000000	0.02267176	-0.00000000
3	H	X -0.00000000	-0.02927595	0.23101629	-0.00000000	-0.64326004
		Y -0.00000000	0.23777094	0.04641325	-0.00000000	-0.25019888
		Z 0.46974713	0.00000000	0.00000000	0.12677581	-0.00000000
TRANS. SAYVETZ	X	-0.00000000	-0.83563375	4.16074267	-0.00000000	-0.02228604
	Y	-0.00000000	4.15926402	0.83593088	-0.00000000	0.11091595
	Z	1.03229856	0.00000000	0.00000000	4.11641335	-0.00000000
	TOTAL	1.03229856	4.24237681	4.24388501	4.11641335	0.11313273
ROT. SAYVETZ	X	0.74353714	-0.00000000	-0.00000000	-0.18361186	-0.00000000
	Y	-1.26256812	0.00000000	0.00000000	0.31924861	0.00000000
	Z	0.00000000	-0.06777613	0.00000119	0.00000000	2.54154460
	TOTAL	1.46523914	0.06777613	0.00000119	0.36828385	2.54154460
		6	7	8	9	
FREQUENCY:		8.88	1799.28	3812.34	3945.80	
SYMMETRY:		A	A	A	A	
REDUCED MASS:		1.01756	1.08983	1.03858	1.08500	
IR INTENSITY:		0.86226	1.89217	0.00115	0.21702	
1	O	X 0.00000000	-0.04089486	-0.02564877	-0.05626299	
		Y -0.00000000	-0.05786491	-0.03630837	0.03975514	
		Z -0.02526058	0.00000000	-0.00000000	-0.00000000	
2	H	X 0.00000000	0.01882370	0.69075509	0.67710255	
		Y 0.00000000	0.67521698	-0.05628041	0.01073177	
		Z -0.47603300	0.00000000	-0.00000000	0.00000000	
3	H	X -0.00000000	0.63020849	-0.28369066	0.21583219	
		Y -0.00000000	0.24314193	0.63252054	-0.64167502	
		Z 0.86919577	-0.00000000	-0.00000000	0.00000000	
TRANS. SAYVETZ	X	-0.00000000	0.00000129	-0.00000014	0.00000052	
	Y	0.00000000	0.00000111	0.00000004	-0.00000057	
	Z	-0.00780139	0.00000000	-0.00000000	0.00000000	
	TOTAL	0.00780139	0.00000170	0.00000015	0.00000077	
ROT. SAYVETZ	X	1.50357589	-0.00000000	0.00000000	0.00000000	
	Y	1.38590886	-0.00000000	0.00000000	-0.00000000	
	Z	0.00000000	-0.00001496	-0.00000000	0.00000153	
	TOTAL	2.04486768	0.00001496	0.00000000	0.00000153	

REFERENCE ON SAYVETZ CONDITIONS - A. SAYVETZ, J.CHEM.PHYS., 7, 383-389(1939).

NOTE - THE MODES J,K ARE ORTHONORMALIZED ACCORDING TO  

$$\text{SUM ON I } M(I) * (X(I,J)*X(I,K) + Y(I,J)*Y(I,K) + Z(I,J)*Z(I,K)) = \text{DELTA}(J,K)$$

-----  
 THERMOCHEMISTRY AT T= 298.15 K  
 -----

USING IDEAL GAS, RIGID ROTOR, HARMONIC NORMAL MODE APPROXIMATIONS.

P= 1.01325E+05 PASCAL.

ALL FREQUENCIES ARE SCALED BY 1.00000

THE MOMENTS OF INERTIA ARE (IN AMU\*BOHR\*\*2)

2.07948 4.38456 6.46404

THE ROTATIONAL SYMMETRY NUMBER IS 1.0

THE ROTATIONAL CONSTANTS ARE (IN GHZ)

867.08597 411.23564 278.94127

THE HARMONIC ZERO POINT ENERGY IS (SCALED BY 1.000)

0.021773 HARTREE/MOLECULE 4778.712676 CM\*\*<sup>-1</sup>/MOLECULE

13.663039 KCAL/MOL 57.166155 KJ/MOL

	Q	LN Q
ELEC.	1.00000E+00	0.000000
TRANS.	3.00431E+06	14.915558
ROT.	8.69029E+01	4.464791
VIB.	1.00017E+00	0.000170
TOT.	2.61127E+08	19.380518

	E	H	G	CV	CP	S
	KJ/MOL	KJ/MOL	KJ/MOL	J/MOL-K	J/MOL-K	J/MOL-K
ELEC.	0.000	0.000	0.000	0.000	0.000	0.000
TRANS.	3.718	6.197	-36.975	12.472	20.786	144.800
ROT.	3.718	3.718	-11.068	12.472	12.472	49.594
VIB.	57.170	57.170	57.166	0.106	0.106	0.014
TOTAL	64.607	67.086	9.123	25.050	33.364	194.407
VIB. THERMAL CORRECTION E(T)-E(0) = H(T)-H(0) =					3.649	J/MOL

	E	H	G	CV	CP	S
	KCAL/MOL	KCAL/MOL	KCAL/MOL	CAL/MOL-K	CAL/MOL-K	CAL/MOL-K
ELEC.	0.000	0.000	0.000	0.000	0.000	0.000
TRANS.	0.889	1.481	-8.837	2.981	4.968	34.608
ROT.	0.889	0.889	-2.645	2.981	2.981	11.853
VIB.	13.664	13.664	13.663	0.025	0.025	0.003
TOTAL	15.441	16.034	2.180	5.987	7.974	46.464
VIB. THERMAL CORRECTION E(T)-E(0) = H(T)-H(0) =					0.872	CAL/MOL

.....END OF NORMAL COORDINATE ANALYSIS.....

## 4.3 Visualise the normal modes

Open the output file in wxMacMolPlt. List the normal modes with Subwindow/Frequencies.

If you click on any mode, the main window will update to show you the displacement vectors associated with it. You can animate the vibration with View/Animate Mode.



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## Effect of basis set

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We are going to compare the effects of the basis set on the energy of a RHF calculation on water.

### 5.1 Running GAMESS

To speed things up, we are going to use the geometry we found for RHF/3-21G and use that for our calculations.

In Avogadro, open the output file from the RHF/3-21G geometry optimisation of water (remember to rename the file to `.gamout`), and create several input files for a single-point RHF calculations with increasing basis set size.

The notation for calculations of this type uses the `//` notation; for example, `RHF/6-31G//RHF/3-21G`.

When they have all been created, run each of them in turn.

(Note to self: Is there time to run an MP2/3-21G calculation?)

### 5.2 Analyse

For each calculation, note the final RHF energy and also the wall clock time (found at the end of the output file).

17. What is the effect of the basis set size on the energy? Based on this, does it make sense to compare the results of calculations with different basis set sizes?
17. What is the effect of the basis set size on the computation speed?



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## Conformations of a cyclohexane

---

The geometry optimisation procedures in QM software involve *local* optimisation of the energy, not *global* optimisation. This allows us to investigate energy differences between different conformations.

We are going to look at the difference in energy between conformations of 1,4-dichloro-cyclohexane.

### 6.1 Create an initial structure

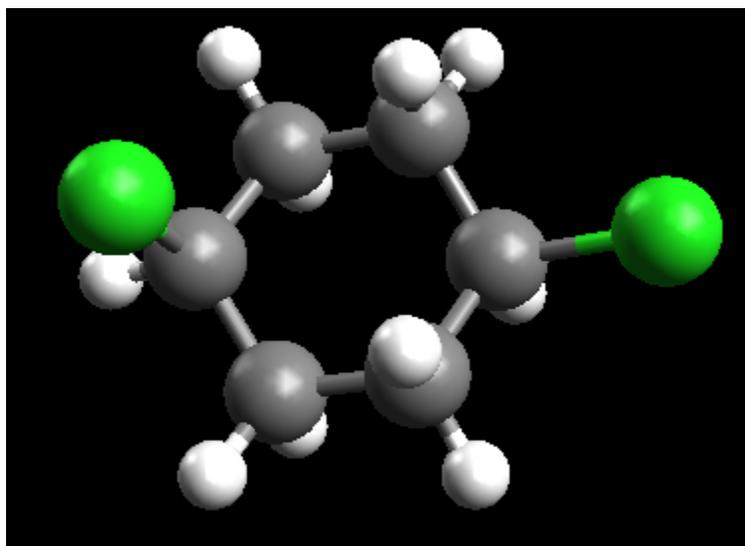
Under Build/Insert/Fragment, choose share/avogadro/fragments/cyclic alkanes/cyclohexane.cml. Click *Insert Fragment*. Choose Edit/Select None to clear the selection.

---

**Note:** Which conformation of cyclohexane is this?

---

Choose the Draw Tool () , and change any hydrogen to a chlorine. Find the hydrogen atom on the opposite carbon that is on the same face of the ring, and change this also to chlorine.



Optimize the geometry using MMFF94.

---

**Note:** What parts of the structure change?

---

## 6.2 Generate conformations interactively

Click on the Auto Optimization Tool () and choose *Start* to turn it on. (Make sure that it is using the MMFF94 forcefield.)

Click on one of the chlorine atoms and drag it to change to another conformation.

---

**Note:** How many conformations of this cyclohexane can you find?

For each conformation:

- use the Measure Tool () to measure the chlorine-chlorine distance
- use Extensions/Molecular Mechanics/Calculate Energy to find the MMFF94 energy
- save each conformation to a CML file

---

Turn off the Auto Optimization by clicking *Stop*.

## 6.3 Calculate accurate energies

Open the saved conformations one-by-one, and generate input files for GAMESS for a geometry optimisation at the HF/3-21G level of theory.

Carry out the calculation for each conformation and note the energy.

---

**Note:** Is the same trend in energies observed for MMFF94 and HF/3-21G?

---