Gaussview/Gaussian Guide and Exercise Manual

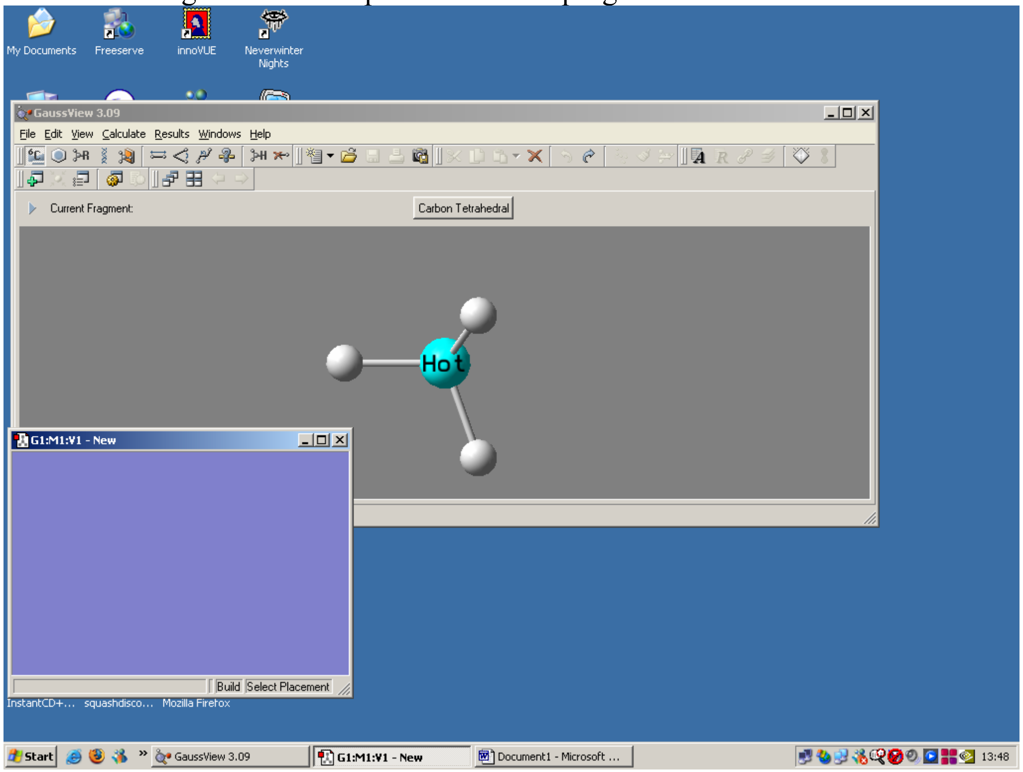
Introduction
In this manual some of the principal features of the Gaussview and Gaussian programs are highlighted to enable the student to start working productively with both programs. The examples/descriptions are inevitably brief and do not aim to be a comprehensive guide. Experience in using the programs and consulting the manuals supplied with them is the only means of achieving proficiency. It is hoped that this training manual plus the accompanying exercises will help ease the initial learning curve.

Each workshop, with exercises, should take approximately 3-4 hours to complete.

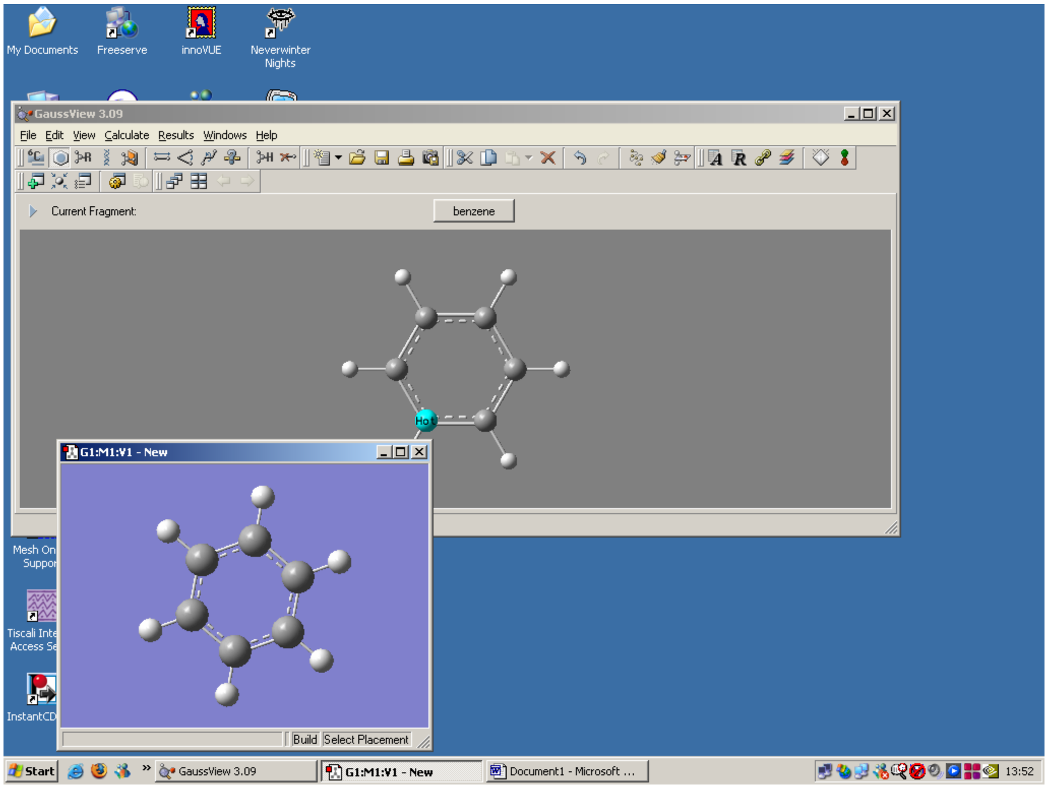
Workshop 1. Gaussview/Gaussian principal features and a sample building exercise and calculation

Gaussian calculations are best prepared using the Gaussview interface. Gaussview allow you to build the required molecule on your screen and using menu pull-dowms you can load the file into the Gaussian program for execution. After the Gaussian run has completed you can view the completed .log file written by Gaussian and also you can use the binary. chk file to generate various graphical surfaces.

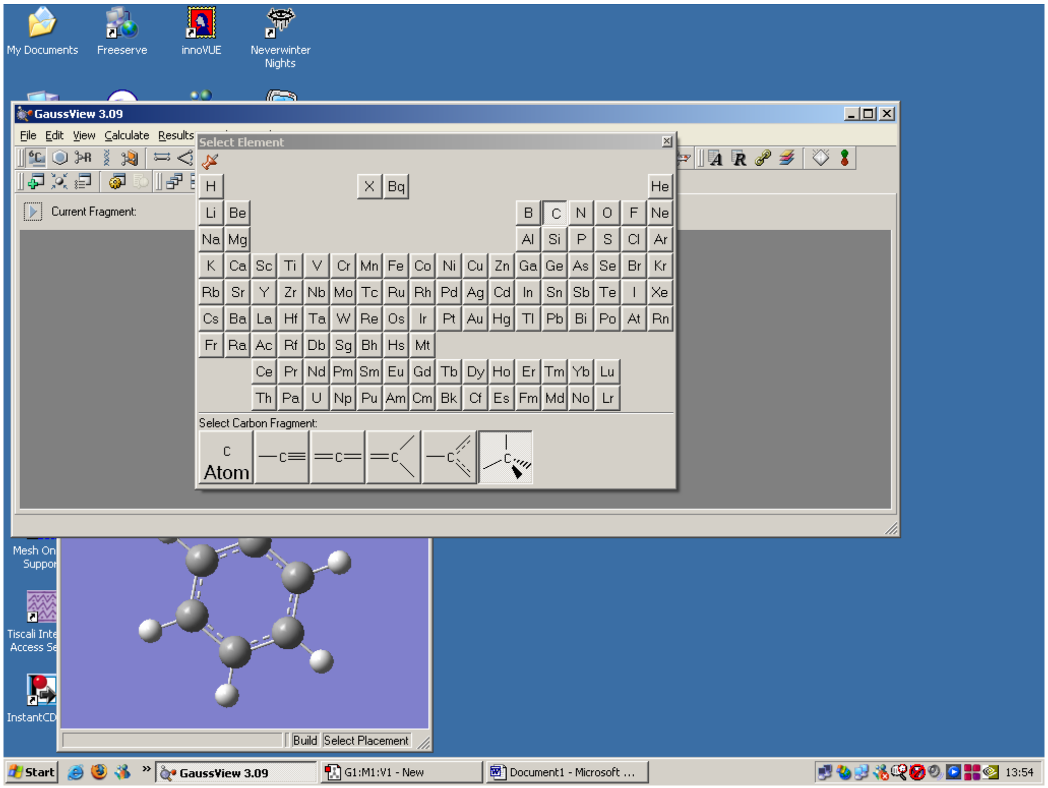
After loading Gaussian and Gaussview on to your computer create a desktop icon for the Gaussview program. If you are running the program over a network you will need to find the location of the program from your network manager.
Double clicking on the desktop icon starts the program as shown below.



The blue empty window NEW is the builder window where the required molecule is built. To build toluene, for example, click on the benzene ring icon on the main window. Place the cursor in the builder window and click. A benzene ring will appear as shown below.

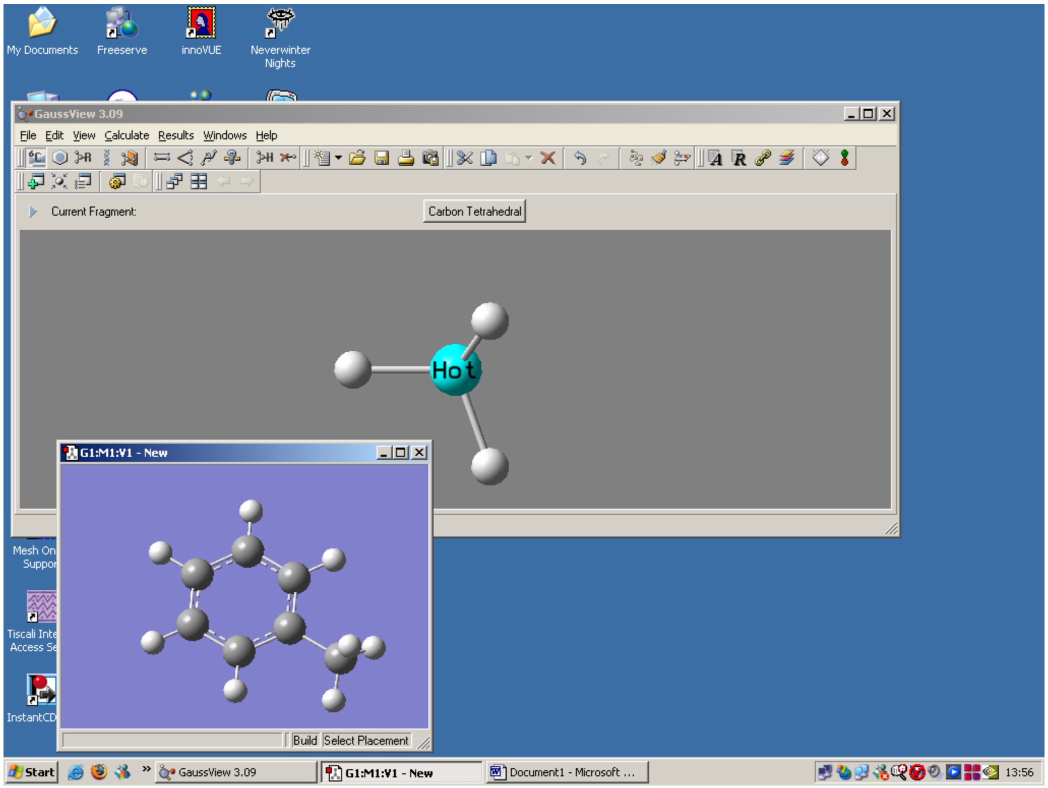


Then click on the atom type icon in the main window ^{6}C. A periodic table will appear

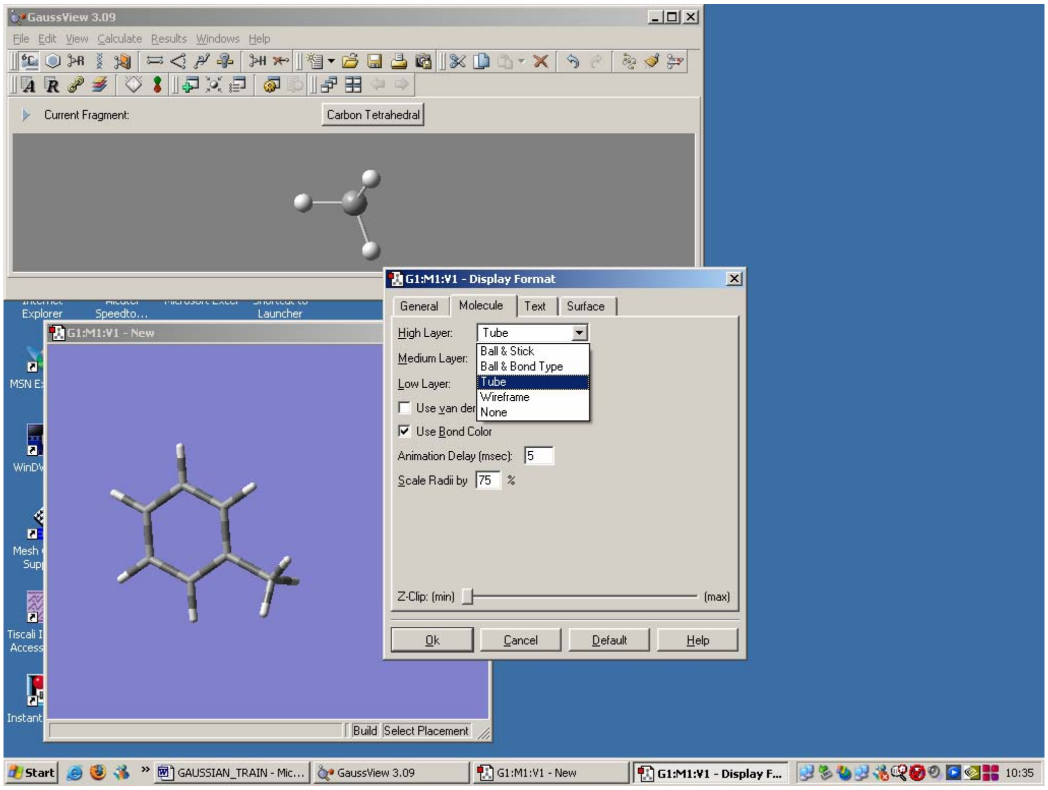


Click on **C** and select the tetrahedral atom type.

Now click on a H atom of the benzene ring in the builder menu and the Toluene molecule should be built.



You now can change the molecule display properties by going to the **VIEW** menu and selecting **DISPLAY FORMAT**. A variety of formats Ball and Bond, Wireframe

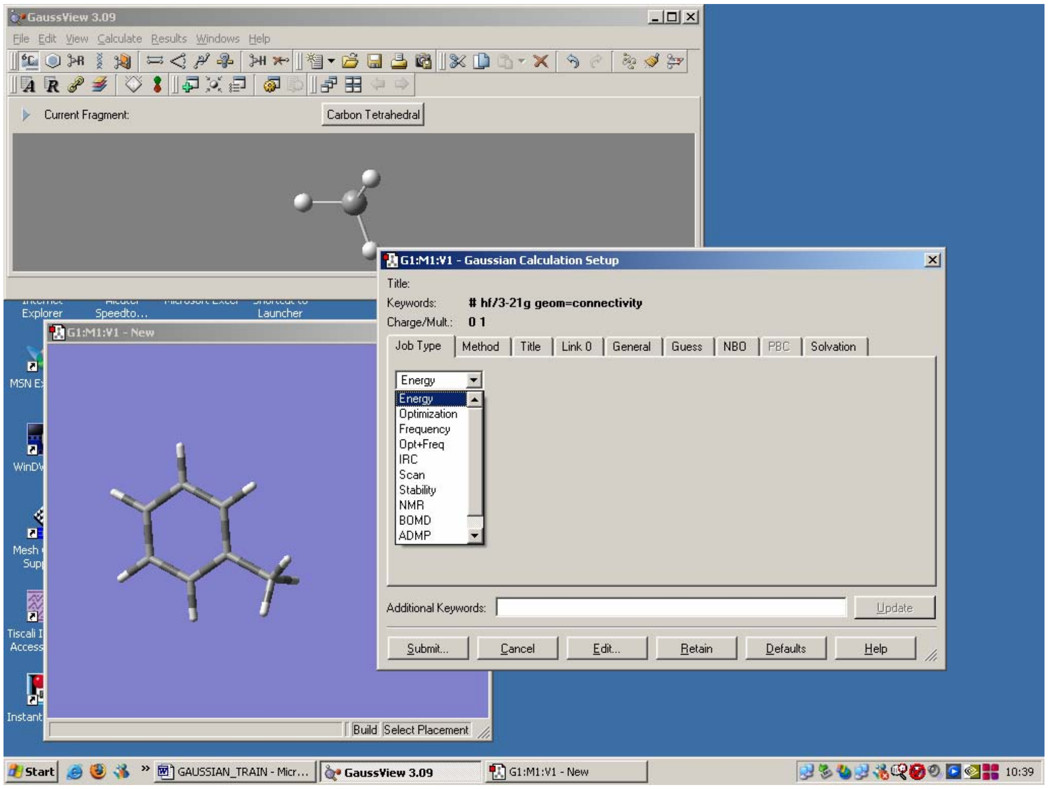


High Layer: Tube
Medium Layer:
Low Layer:
☐ Use van der
☑ Use Bond Color
Animation Delay (msec): 5
Scale Radii by 75 %

and Tube are available. Choose **TUBE** and note change in display window. Click **OK** to save this display change.

Calculations using the Gaussian program are set-up and run using the **CALCULATE** menu.

Upon opening the following is displayed



Current Fragment: Carbon Tetrahedral

G1:M1:V1 - Gaussian Calculation Setup

Title:

Keywords: # hf/3-21g geom=connectivity

Charge/Mult.: 0 1

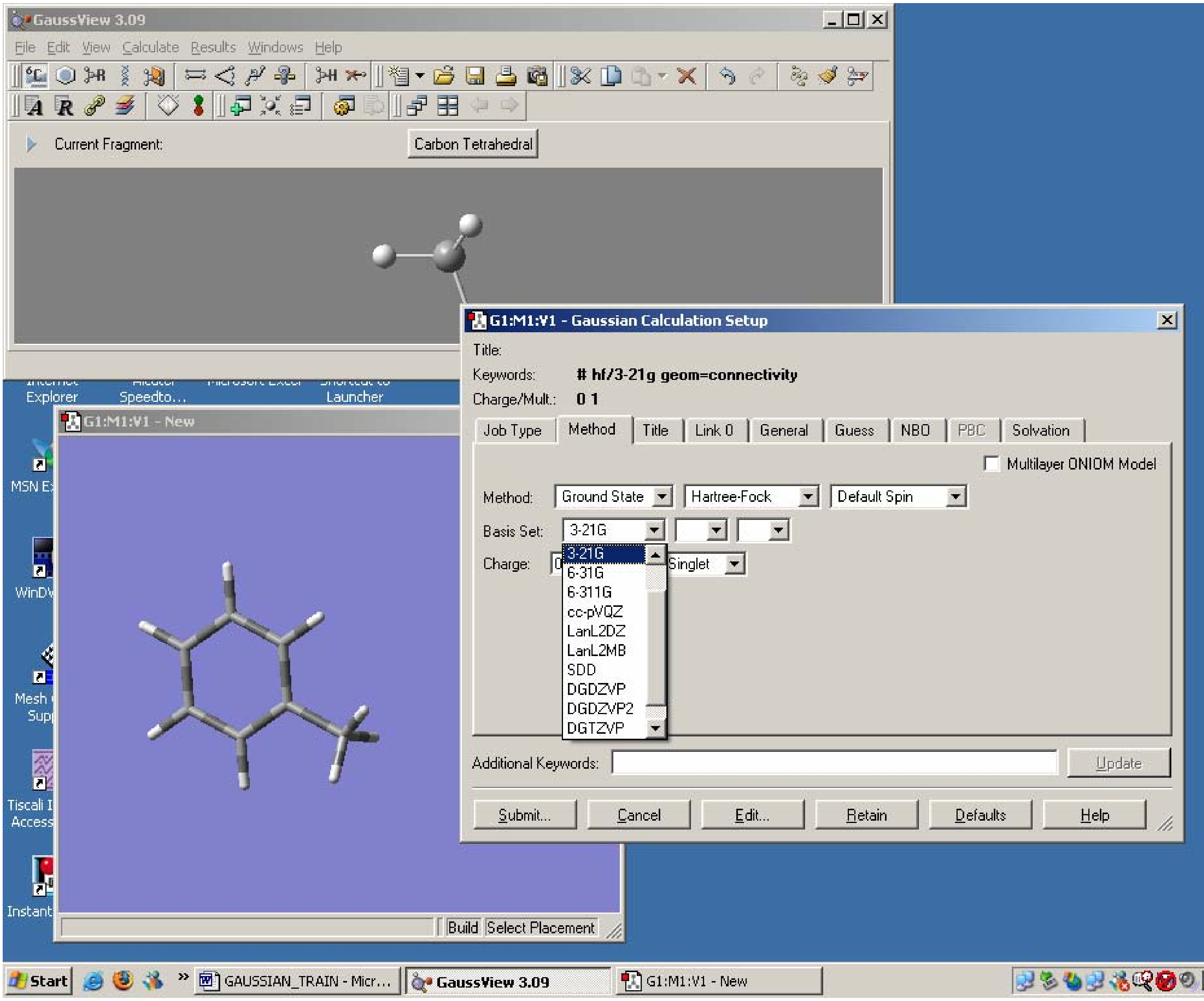
Job Type: Energy

Additional Keywords:

This allows various types of electronic structure calculations to be performed using Gaussian. For an example choose **Energy** under the **JOB TYPE** sub-menu. Note one can also choose a variety of other jobs such as geometry optimisation or vibrational frequency analysis.

Under the **METHOD** sub-menu we can choose the type of calculation we wish to perform. This can be Hartree-Fock (HF) with or without some form of electron correlation treatment, Semiempirical, e.g PM3 or AM1 or a Density Functional Theory (DFT) Calculations using an appropriate density functional either local, gradient corrected or hybrid type.

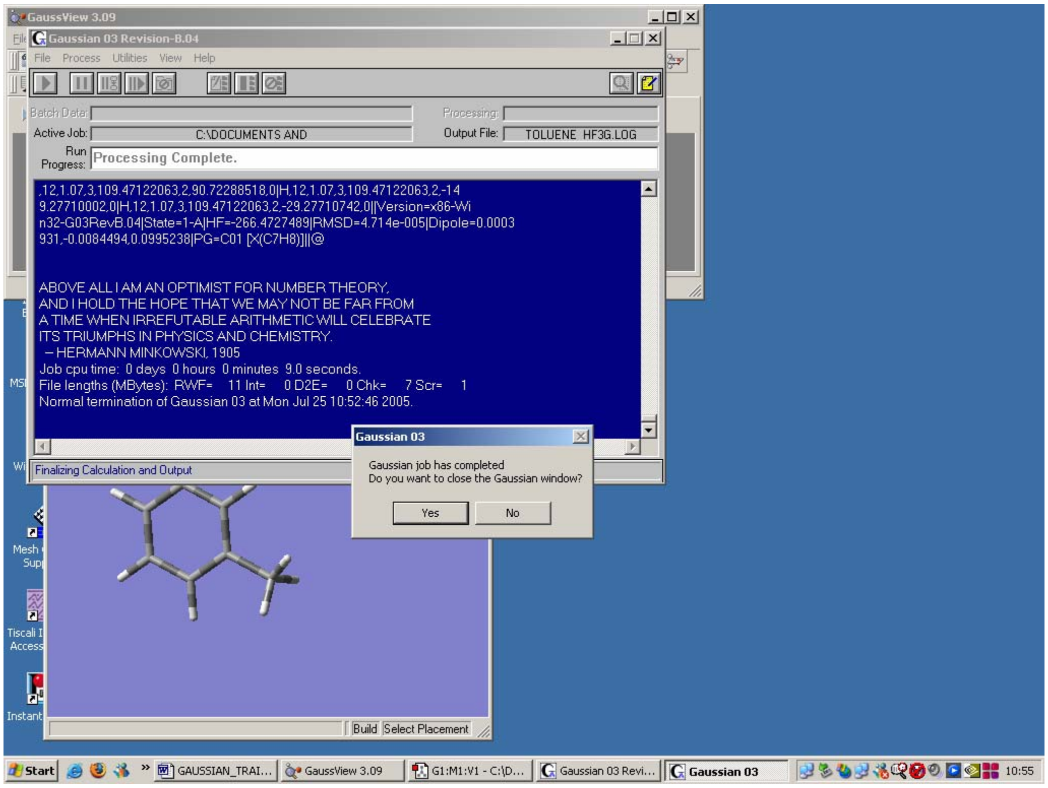
For HF or DFT calculations we also have the opportunity of choosing an appropriate basis set from a sub-menu.
For our example calculation we will choose the HF method with the STO-3G basis set. Not it is also necessary to choose the charge and multiplicity of the molecule or complex under investigation. Here we use a multiplicity of 1 and charge of zero. If for example we needed a calculation for the toluene cation radical we would use a charge of +1 and a multiplicity of 2.



G1:M1:V1 - Gaussian Calculation Setup

Title:
Keywords: # hf/3-21g geom=connectivity
Charge/Mult.: 0 1
Method: Ground State | Hartree-Fock | Default Spin
Basis Set: 3-21G
Charge: 0
Singlet

We submit our calculation using the **Submit** button. You are asked for a file name to save the job. Choose an appropriate/instructive name e.g. toluene_hf3g. Save the file and continue with the submission. A new window will open where the progress of the run can be monitored. After completion you are notified



Batch Data:

Processing:

Active Job: C:\DOCUMENTS AND

Output File: TOLUENE HF3G.LOG

Run Progress: Processing Complete.

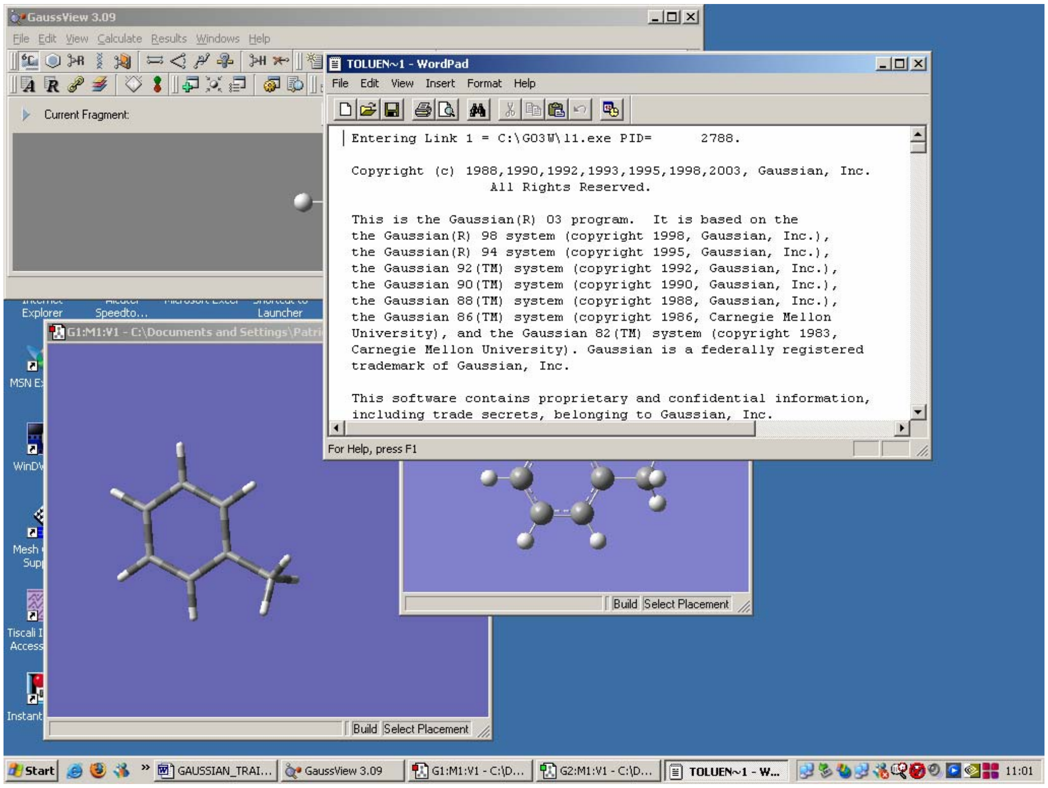
```
,12,1.07,3,109.47122063,2,90.72288518,0|H,12,1.07,3,109.47122063,2,-14
9.27710002,0|H,12,1.07,3,109.47122063,2,-29.27710742,0||Version=x86-Wi
n32-G03RevB.04|State=1-A|HF=-266.4727489|RMSD=4.714e-005|Dipole=0.0003
931,-0.0084494,0.0995238|PG=C01 [X(C7H8)]||@


ABOVE ALL I AM AN OPTIMIST FOR NUMBER THEORY,
AND I HOLD THE HOPE THAT WE MAY NOT BE FAR FROM
A TIME WHEN IRREFUTABLE ARITHMETIC WILL CELEBRATE
ITS TRIUMPHS IN PHYSICS AND CHEMISTRY.
 -- HERMANN MINKOWSKI, 1905
Job cpu time:  0 days  0 hours  0 minutes  9.0 seconds.
File lengths (MBytes):  RWF=     11 Int=      0 D2E=      0 Chk=      7 Scr=      1
Normal termination of Gaussian 03 at Mon Jul 25 10:52:46 2005.
```

Finalizing Calculation and Output

Gaussian 03

Gaussian job has completed
Do you want to close the Gaussian window?

You can then choose to examine the output file in the window if you wish . Alternatively you can close the window and you will be asked next if you wish to view a results file. The output data is written to 2 types of results file a .log file which is a text listing of the program steps and a .chk file which is a binary file that can be used to generate various surface representations. Choose the .log file first and the toluene molecule will appear in a new window. To view the .log file go to the **RESULTS** menu and choose **VIEW FILE**. A window containing the file listing should appear



```
Entering Link 1 = C:\G03W\l1.exe PID=      2788.

 Copyright (c) 1988,1990,1992,1993,1995,1998,2003, Gaussian, Inc.
                  All Rights Reserved.

 This is the Gaussian(R) 03 program.  It is based on the
 the Gaussian(R) 98 system (copyright 1998, Gaussian, Inc.),
 the Gaussian(R) 94 system (copyright 1995, Gaussian, Inc.),
 the Gaussian 92(TM) system (copyright 1992, Gaussian, Inc.),
 the Gaussian 90(TM) system (copyright 1990, Gaussian, Inc.),
 the Gaussian 88(TM) system (copyright 1988, Gaussian, Inc.),
 the Gaussian 86(TM) system (copyright 1986, Carnegie Mellon
 University), and the Gaussian 82(TM) system (copyright 1983,
 Carnegie Mellon University). Gaussian is a federally registered
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 This software contains proprietary and confidential information,
 including trade secrets, belonging to Gaussian, Inc.
```

as a Wordpad text file. Scroll down through the file to see the information contained.

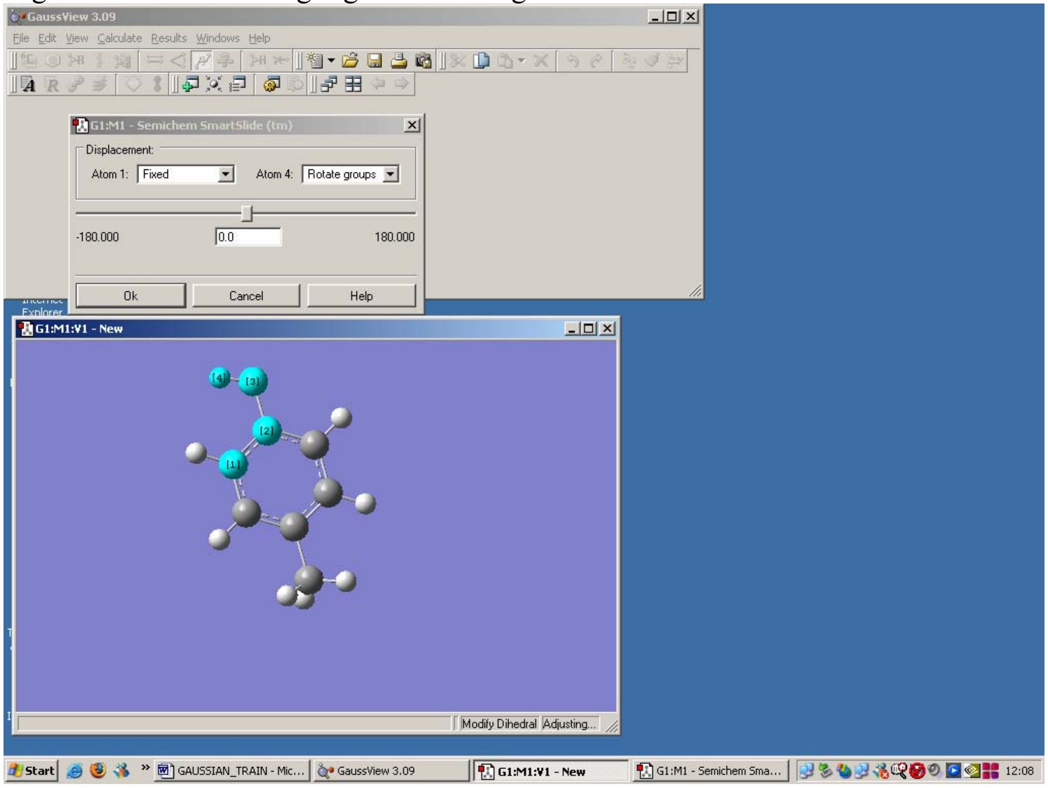
Exercises:

1. Perform the calculation above on toluene using the semiempirical AM1 method and also perform a HF/6-31G and a B3LYP/6-31G calculation. Compare the time for completion of each job and comment on any trend observed.
2. Construct the phenol, C_6H_5OH, molecule and perform similar calculations to the Toluene molecule above.
3. Build each of the following molecules and perform a single-point B3LYP/STO-3G calculation:

   Aniline, anthracene, p-benzoquinone, p-methylphenol, $Mn(H_2O)_6$

Workshop 2. Displaying Molecular Orbitals, Electron Density and Electrostatic Potentials

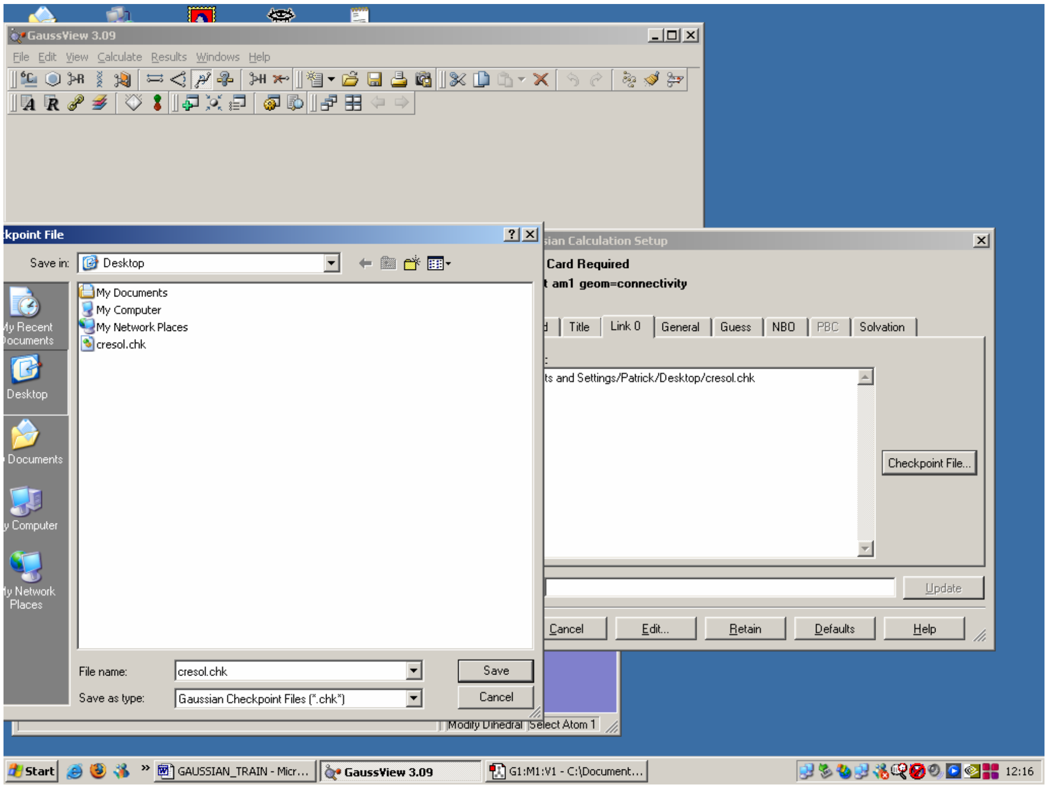
Build the p-methylphenol molecule as described in Workshop 1. Modify the molecule such that the OH group lies in the ring plane. This can be done using the dihedral angle modifier shown highlighted in the figure below:



Displacement:
Atom 1: Fixed
Atom 4: Rotate groups
-180.000 0.0 180.000
Modify Dihedral Adjusting...

Note one can keep some atoms fixed, in this case the ring atom and the OH group can be interactively rotated into the ring plane. Alternatively the dihedral angle value required can be entered in the text box provided.

Set up an AM1 single point calculation using the **CALCULATE** menu. In this case we will be looking at graphical surfaces so we need to save a copy of the .chk or checkpoint file in our working directory. We do this by opening the **LINK 0** menu in the set-up box and clicking the **checkpoint file** box.



File name: cresol.chk

Save as type: Gaussian Checkpoint Files (*.chk)

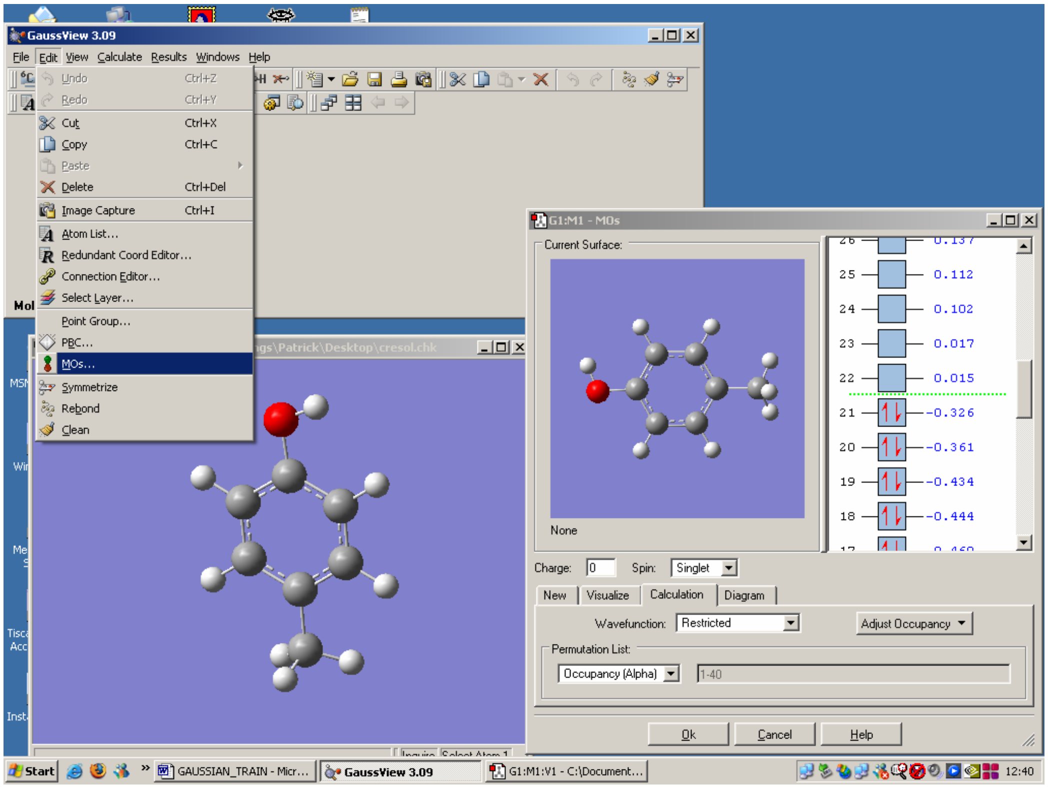
Card Required

t am1 geom=connectivity

ts and Settings/Patrick/Desktop/cresol.chk

By giving the .chk file an appropriate name we can retain it in our working directory after job runs for analysis.

For graphical representations of orbital and electron densities the checkpoint, .chk, file is required.
Use the **FILE/OPEN** combination to obtain this using the .chk filter.
Open the cresol.chk file saved in your working directory.
The molecule appears in a separate window. To examine the orbital energy levels and the orbital electron densities use **EDIT/MOs**

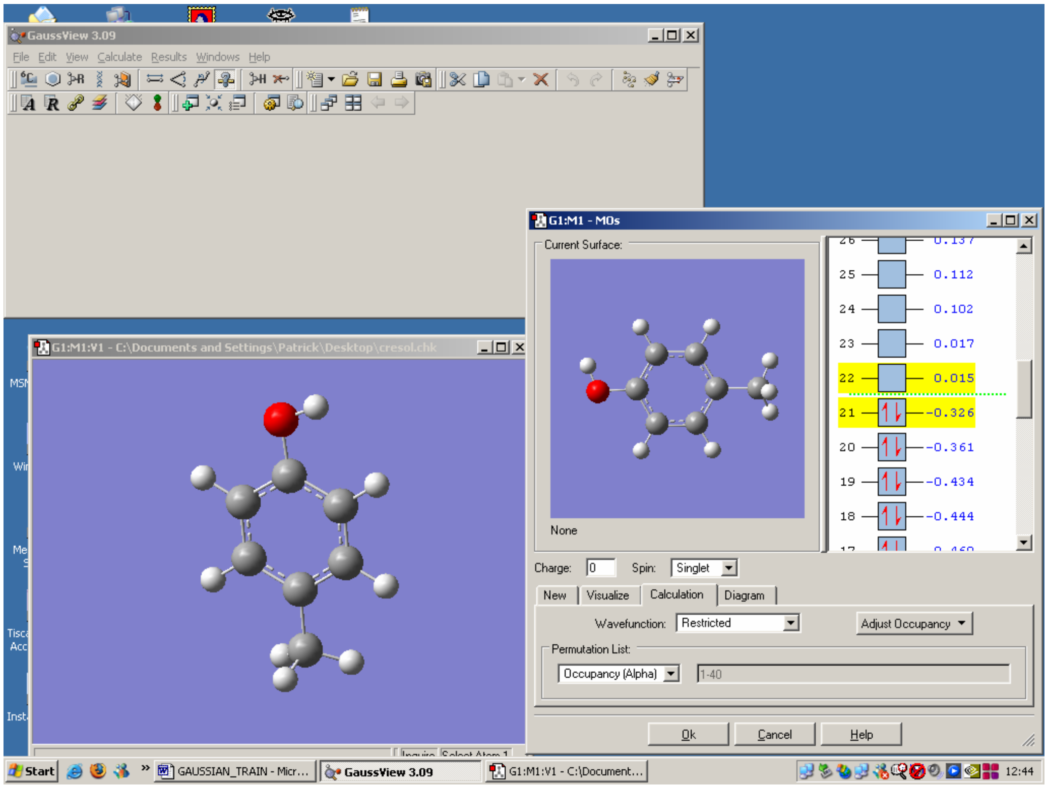


26 — 0.137
25 — 0.112
24 — 0.102
23 — 0.017
22 — 0.015
21 ↑↓ −0.326
20 ↑↓ −0.361
19 ↑↓ −0.434
18 ↑↓ −0.444

Charge: 0
Spin: Singlet
Wavefunction: Restricted
Occupancy (Alpha) 1-40

An orbital energy level diagram is produced and the occupied 1-21 in this case and unoccupied orbitals are presented. The HOMO is molecular orbital 21 and the LUMO is molecular orbital 22.

To get an electron density surface for any orbital simply click on the orbital or combination of orbitals and highlight them. This is shown for the HOMO and LUMO below.



Current Surface:

None

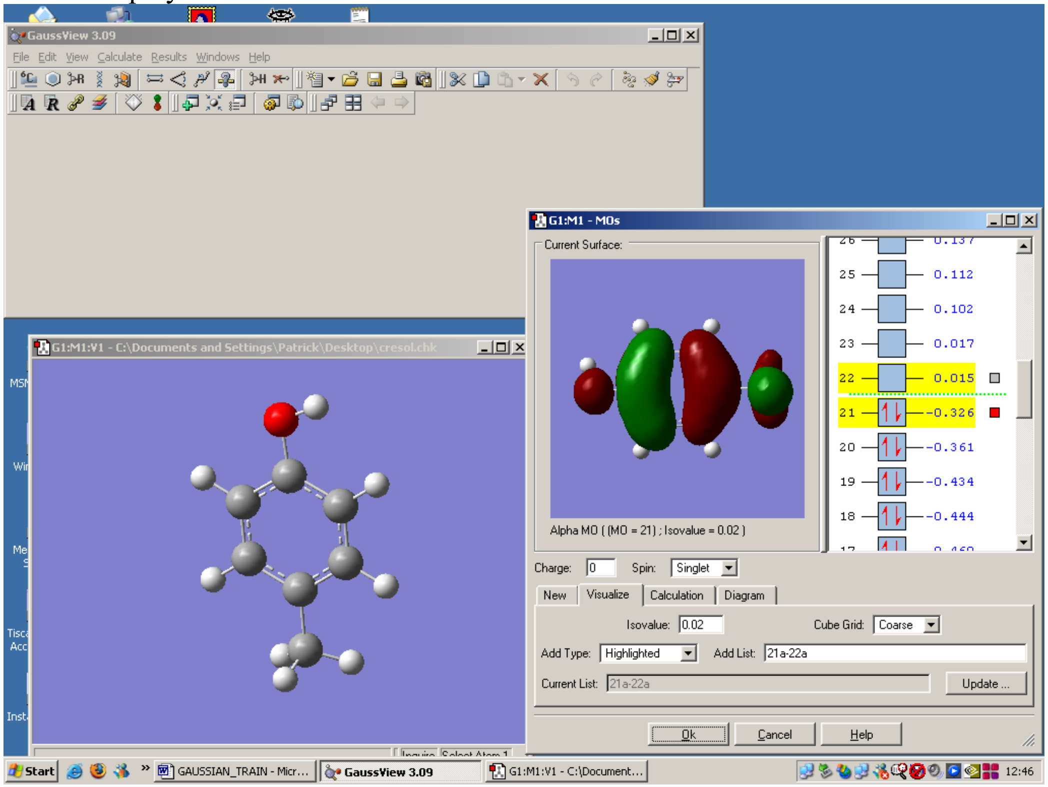
25	0.112
24	0.102
23	0.017
22	0.015
21	-0.326
20	-0.361
19	-0.434
18	-0.444

Charge: 0 Spin: Singlet

Wavefunction: Restricted

Permutation List: Occupancy (Alpha) 1-40

Select **VISUALISE** followed by **UPDATE** from the Surface window display and after a few seconds an electron density contour of the HOMO and LUMO orbitals will be displayed.



Current Surface:

Alpha MO ((MO = 21) ; Isovalue = 0.02)

25	0.112	
24	0.102	
23	0.017	
22	0.015	☐
21	-0.326	🟥
20	-0.361	
19	-0.434	
18	-0.444	

Charge: 0 Spin: Singlet

Isovalue: 0.02 Cube Grid: Coarse

Add Type: Highlighted Add List: 21a-22a

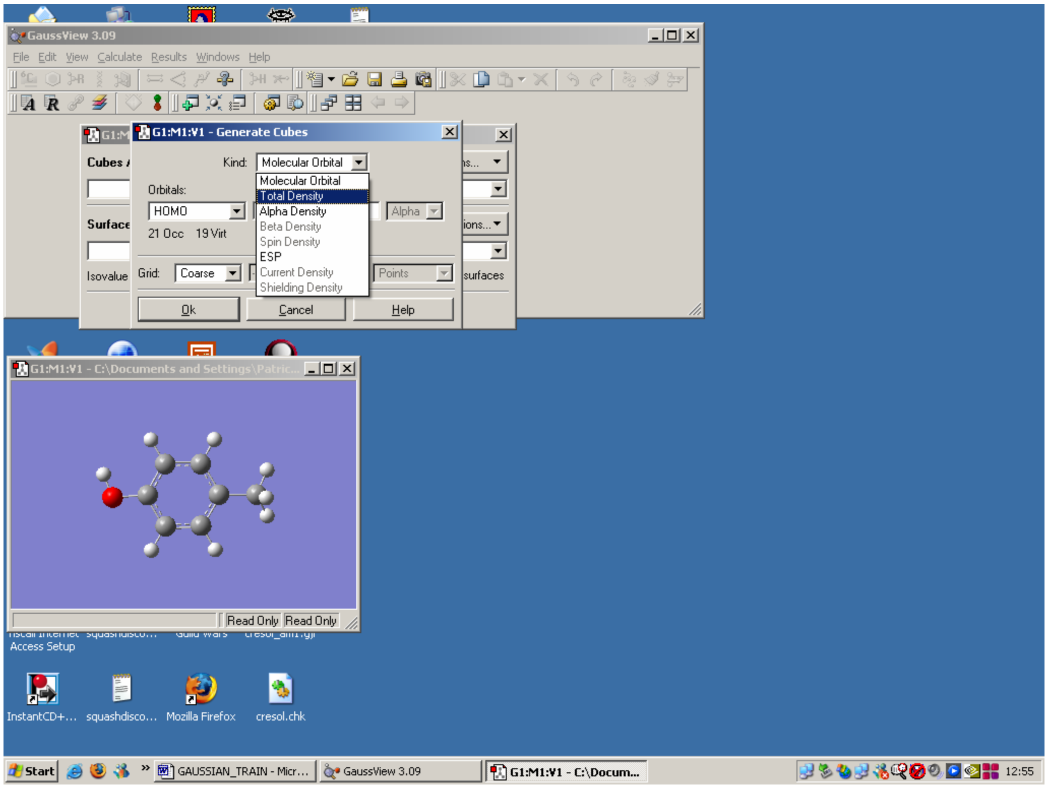
Current List: 21a-22a

The orbital display can be alternated between the HOMO or LUMO by highlighting the desired display. Notice a red box handle appears next to the displayed orbital.

The Surface window also contains a number of refinements, e.g orbital electron density contour value can be changed, and can be experimented with.

Only molecular orbitals can be generated using this procedure. To display other graphical surfaces the **RESULTS/SURFACES** menus must be chosen from the main Gaussview window.

An electron density contour plot can be obtained as shown below.



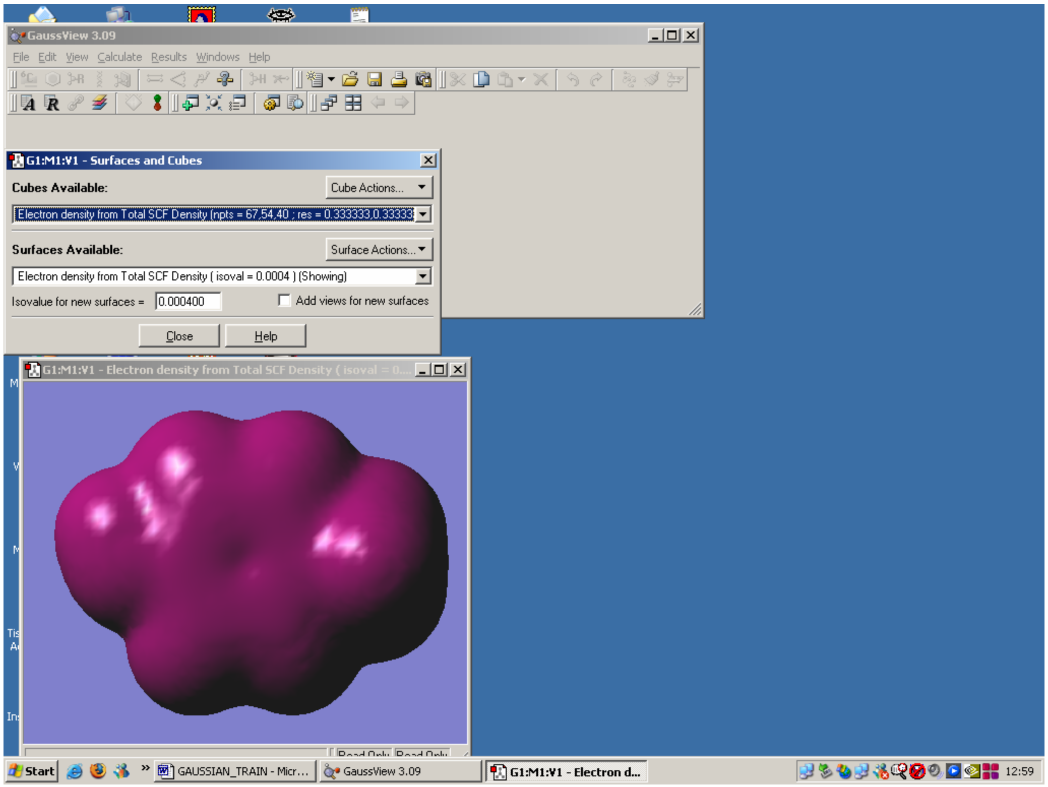
Kind: Molecular Orbital

Orbitals: HOMO

21 Occ 19 Virt

Grid: Coarse

Note that other plots of alpha or beta electron density can be accessed. After submission the electron density plot is available in the “**cubes available**”. Under **Surface Actions** choose new surface and the electron density plot will be displayed in a few seconds.



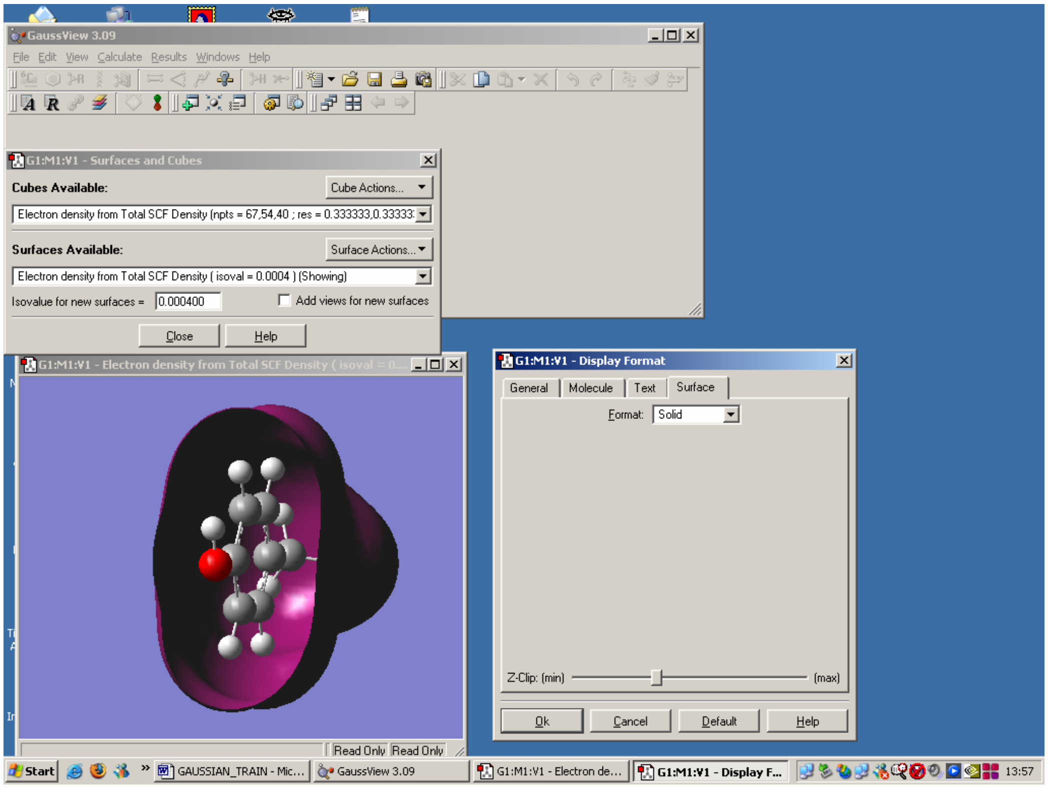
Cubes Available: Electron density from Total SCF Density (npts = 67,54,40 ; res = 0.333333,0.33333

Surfaces Available: Electron density from Total SCF Density (isoval = 0.0004) (Showing)

Isovalue for new surfaces = 0.000400

☐ Add views for new surfaces

The display is a contour of electron density at a chosen value . This can be changed to any desired value by typing the value in the "isovalue for new surfaces" text box. The "skin-like" nature of the representation is demonstrated by introducing z-clipping. This is performed by right-button clicking in the display window, selecting **DISPLAY FORMAT** and then in the resulting new window selecting **SURFACES**. Moving the z-clip slider enables the interior of the display to be shown as demonstrated below.



Cubes Available: Electron density from Total SCF Density (npts = 67,54,40 ; res = 0.333333,0.33333

Surfaces Available: Electron density from Total SCF Density (isoval = 0.0004) (Showing)

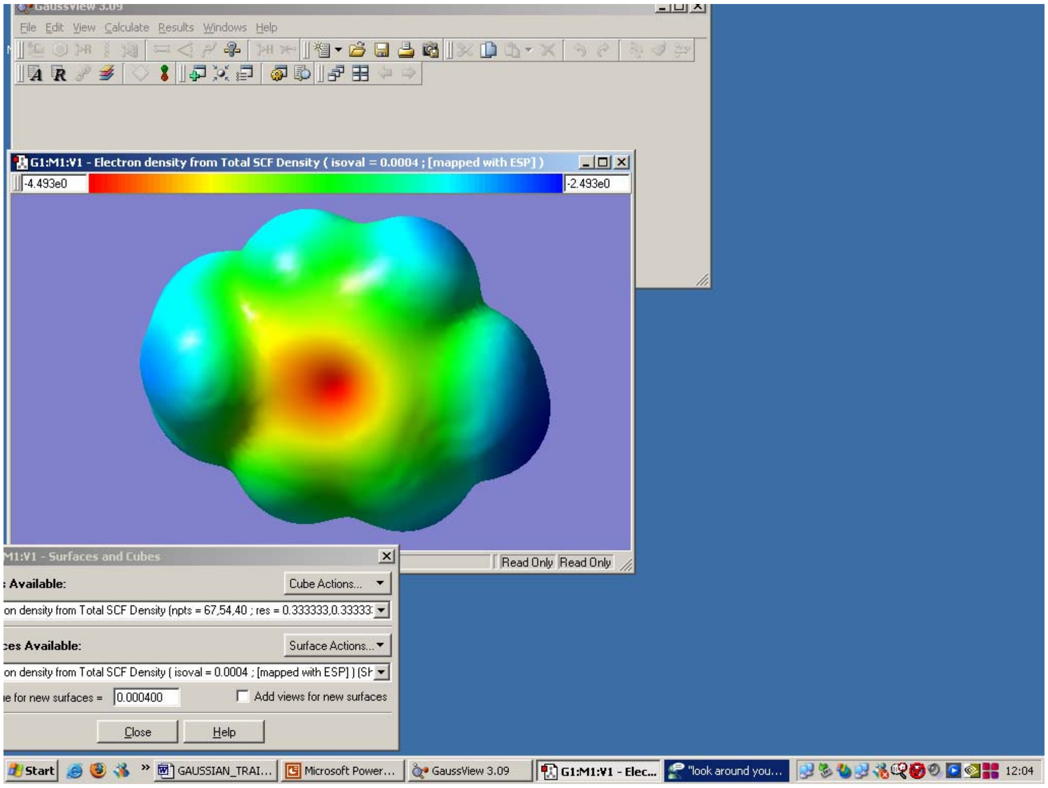
Isovalue for new surfaces = 0.000400

☐ Add views for new surfaces

Format: Solid

Another useful graphical display is a *mapped surface*. Here two properties can be displayed at the same time providing additional information. A good example is the display of the electrostatic potential on a total electron density surface. While the total electron density surface represent the steric requirements of the molecule, by mapping with the electrostatic potential , the electrostatic properties can be displayed at the same time.

In our example here we first calculate the total electron density default contour and map the electrostatic potential onto this surface. The result is demonstrated below. You will need to adjust the default values used by Gaussview to those shown below to get the required display.



G1:M1:V1 - Electron density from Total SCF Density (isoval = 0.0004 ; [mapped with ESP])

-4.493e0 … 2.493e0

M1:V1 - Surfaces and Cubes

s Available: on density from Total SCF Density (npts = 67,54,40 ; res = 0.333333,0.33333

ces Available: on density from Total SCF Density (isoval = 0.0004 ; [mapped with ESP]) (Sh

e for new surfaces = 0.000400

☐ Add views for new surfaces

Exercises

1. For the Phenol molecule above, obtain the electron density contours of the four highest energy occupied orbitals at values of 0.09 and 0.05 e/au^3 respectively.
2. Again for the Phenol molecule get contours of the total electron density at values of 0.002 and 0.05 e/au^3. Explain the differences between the two representations. Which representation could be used to demonstrate bonding regions of the molecule.
3. Plot the mapped surface of electostatic potential on the 0.09 e/au^3 electron density surface and compare with the above.
4. Compare the electron density/electrostatic potential mapped surfaces of benzene and pyridine. From you surface representations predict where you would expect electrophilic attack to occur for each.
5. Build the water molecule. Perform a HF/STO-3G and AM1 geometry optimisation. Examine the occupied molecular orbital energy levels (find out what units the energy levels are given in) and obtain electron density contours for each. The experimental Photoelectron Spectrum for water has four major bands at 12.6, 14.8 18.6, 32.1 eV. Do you find any correspondence between the molecular orbital energy levels you have calculated and these experimental spectral values. The calculated energy levels are not usually reported in eV so you will have to convert to eV for comparison with the experimentally reported values. Explain any correspondence.
6. Build ethanol (a weak acid), ethanoic acid (a moderately strong acid), nitric acid (a strong aid) and sulphuric acid (a strong acid). Optimise their geometries at the HF/3-21G level. Map the electrostatic potential for each

model on to a total electron density surface. Display each map side by side using the same scale for each. The relative acidity of each should be reflected in the value of the electrostatic potential near the acidic H of the OH group. Do the maps correctly predict the relative acidities of these molecules. Explain your conclusions.

Workshop 3. Geometry Optimisation and Vibrational Frequencies.

Build the p-methylphenol molecule as described in Workshop 2. Select **geometry optimisation** under the **Method Type**.
Submit the job and open the .log file as described in Workshop 1.
Scroll down through the file and examine the criteria the program uses to test for geometry optimisation.

```
   D22       -1.58146  -0.00016   0.00000   0.01132   0.01128  -
1.57018
   D23       -0.53471  -0.00004   0.00000   0.01549   0.01560  -
0.51911
         Item               Value     Threshold  Converged?
 Maximum Force            0.053007     0.000450     NO
 RMS     Force            0.011552     0.000300     NO
 Maximum Displacement     0.224657     0.001800     NO
 RMS     Displacement     0.052400     0.001200     NO
 Predicted change in Energy=-1.272322D-02
```

Geometry optimization is complete when all four tests have a YES in the Converged column.

For our molecule this happens after 15 steps.

```
                                                                 D23
-0.40254   0.00000   0.00249  -0.00163   0.00086  -0.40168
         Item               Value     Threshold  Converged?
 Maximum Force            0.000030     0.000450     YES
 RMS     Force            0.000008     0.000300     YES
 Maximum Displacement     0.001618     0.001800     YES
 RMS     Displacement     0.000392     0.001200     YES
 Predicted change in Energy=-1.452436D-08
 Optimization completed.
    -- Stationary point found.
                           ----------------------------
                           !   Optimized Parameters   !
                           ! (Angstroms and Degrees)  !
 --------------------------                            --------------
------------
 ! Name  Definition              Value          Derivative Info.
!
 --------------------------------------------------------------------
------------
 ! R1    R(1,2)                  1.3897         -DE/DX =    0.0
!
 ! R2    R(1,6)                  1.4018         -DE/DX =    0.0
!
 ! R3    R(1,7)                  1.1007         -DE/DX =    0.0
!
 ! R4    R(2,3)                  1.405          -DE/DX =    0.0
!
 ! R5    R(2,8)                  1.0987         -DE/DX =    0.0
!
```

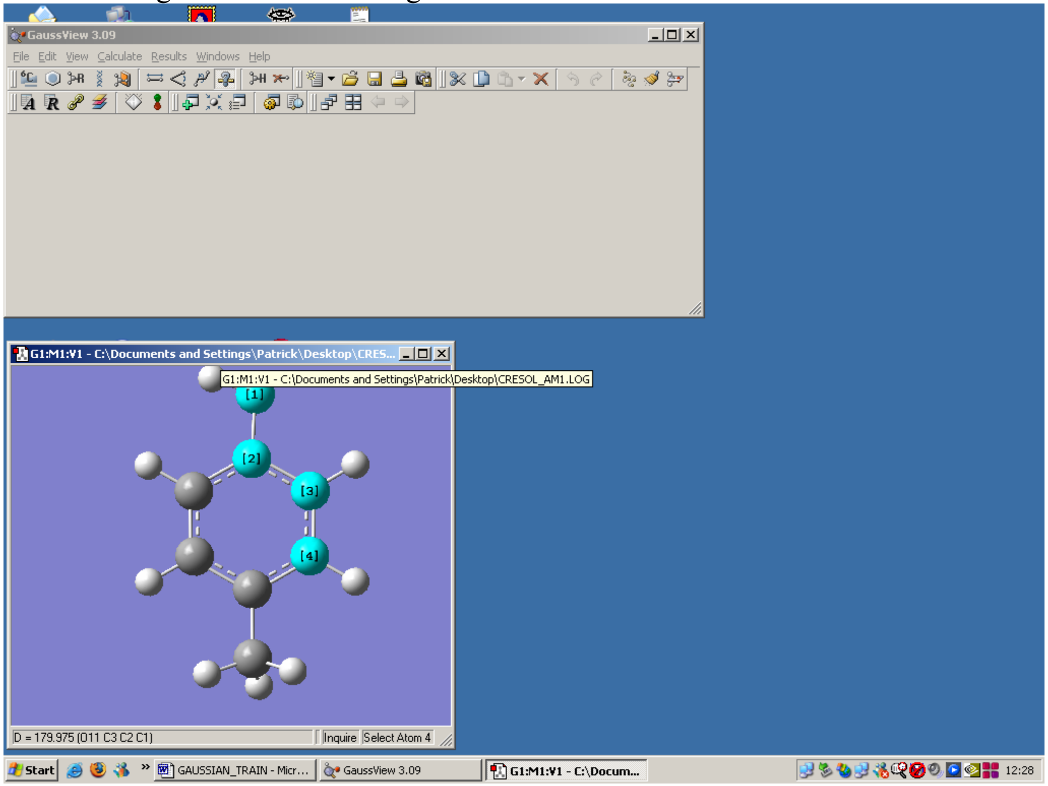
```
 ! R6    R(3,4)                  1.4013         -DE/DX =    0.0
!
 ! R7    R(3,11)                 1.3769         -DE/DX =    0.0
!
 ! R8    R(4,5)                  1.3926         -DE/DX =    0.0
!
 ! R9    R(4,9)                  1.0987         -DE/DX =    0.0
!
 ! R10   R(5,6)                  1.3986         -DE/DX =    0.0
!
 ! R11   R(5,10)                 1.1006         -DE/DX =    0.0
!
 ! R12   R(6,13)                 1.4806         -DE/DX =    0.0
!
 ! R13   R(11,12)                0.968          -DE/DX =    0.0
!
 ! R14   R(13,14)                1.1177         -DE/DX =    0.0
!
 ! R15   R(13,15)                1.1194         -DE/DX =    0.0
!
 ! R16   R(13,16)                1.1181         -DE/DX =    0.0
!
 ! A1    A(2,1,6)              120.9488         -DE/DX =    0.0
!
 ! A2    A(2,1,7)              119.5222         -DE/DX =    0.0
!
 ! A3    A(6,1,7)              119.5289         -DE/DX =    0.0
!
 ! A4    A(1,2,3)              119.0123         -DE/DX =    0.0
!
 ! A5    A(1,2,8)              121.3901         -DE/DX =    0.0
!
 ! A6    A(3,2,8)              119.5977         -DE/DX =    0.0
!
 ! A7    A(2,3,4)              120.7751         -DE/DX =    0.0
!
 ! A8    A(2,3,11)             116.5031         -DE/DX =    0.0
!
 ! A9    A(4,3,11)             122.7217         -DE/DX =    0.0
!
 ! A10   A(3,4,5)              119.2523         -DE/DX =    0.0
!
 ! A11   A(3,4,9)              120.333          -DE/DX =    0.0
!
 ! A12   A(5,4,9)              120.4147         -DE/DX =    0.0
!
 ! A13   A(4,5,6)              120.7281         -DE/DX =    0.0
!
 ! A14   A(4,5,10)             119.5038         -DE/DX =    0.0
!
 ! A15   A(6,5,10)             119.7681         -DE/DX =    0.0
!
 ! A16   A(1,6,5)              119.2833         -DE/DX =    0.0
!
 ! A17   A(1,6,13)             120.1441         -DE/DX =    0.0
!
 ! A18   A(5,6,13)             120.5699         -DE/DX =    0.0
!
 ! A19   A(3,11,12)            107.8666         -DE/DX =    0.0
!
```

```
 ! A20   A(6,13,14)            111.1472         -DE/DX =    0.0
!
 ! A21   A(6,13,15)            110.0152         -DE/DX =    0.0
!
 ! A22   A(6,13,16)            110.8296         -DE/DX =    0.0
!
 ! A23   A(14,13,15)           108.21           -DE/DX =    0.0
!
 ! A24   A(14,13,16)           108.3947         -DE/DX =    0.0
!
 ! A25   A(15,13,16)           108.1485         -DE/DX =    0.0
!
 ! D1    D(6,1,2,3)              0.0252         -DE/DX =    0.0
!
 ! D2    D(6,1,2,8)            179.9932         -DE/DX =    0.0
!
 ! D3    D(7,1,2,3)           -179.9299         -DE/DX =    0.0
!
 ! D4    D(2,1,6,5)             -0.0855         -DE/DX =    0.0
!
 ! D5    D(2,1,6,13)           179.3292         -DE/DX =    0.0
!
 ! D6    D(7,1,6,5)            179.8695         -DE/DX =    0.0
!
 ! D7    D(1,2,3,4)              0.0383         -DE/DX =    0.0
!
 ! D8    D(1,2,3,11)           179.9754         -DE/DX =    0.0
!
 ! D9    D(8,2,3,4)           -179.9303         -DE/DX =    0.0
!
 ! D10   D(2,3,4,5)             -0.0402         -DE/DX =    0.0
!
 ! D11   D(2,3,4,9)            179.9253         -DE/DX =    0.0
!
 ! D12   D(11,3,4,5)          -179.9733         -DE/DX =    0.0
!
 ! D13   D(2,3,11,12)         -180.0123         -DE/DX =    0.0
!
 ! D14   D(4,3,11,12)           -0.0765         -DE/DX =    0.0
!
 ! D15   D(3,4,5,6)             -0.0215         -DE/DX =    0.0
!
 ! D16   D(3,4,5,10)           179.941          -DE/DX =    0.0
!
 ! D17   D(9,4,5,6)           -179.9869         -DE/DX =    0.0
!
 ! D18   D(4,5,6,1)              0.0835         -DE/DX =    0.0
!
 ! D19   D(4,5,6,13)          -179.3287         -DE/DX =    0.0
!
 ! D20   D(10,5,6,1)          -179.8789         -DE/DX =    0.0
!
 ! D21   D(1,6,13,14)          157.5292         -DE/DX =    0.0
!
 ! D22   D(1,6,13,15)          -82.6354         -DE/DX =    0.0
!
 ! D23   D(5,6,13,14)          -23.0636         -DE/DX =    0.0
!
 --------------------------------------------------------------------
------------
```

```
GradGradGradGradGradGradGradGradGradGradGradGradGradGradGradGradGradG
rad
```

The output shows that the derivative of the energy with respect to atom coordinates is zero denoting a stationary point on the potential energy surface.

The optimised geometry can be examined interactively as well. This is done by highlighting the **?** icon on the main Gaussview window. Clicking on any 2 atoms then gives the distance between these atoms in angstroms in the window pane underneath. Clicking 3 atoms consecutively gives the value for the angle in degrees and 4 atoms gives the dihedral angle value.



D = 179.975 (O11 C3 C2 C1)

Harmonic vibrational frequency calculations are also set up via the **CALCULATE** menu. It is essential to perform the vibrational analysis using the exact same method that you have used to perform a prior geometry optimisation. Hence for the p-methylphenol molecule above, which has been already optimised, we could perform the vibrational analysis directly so long as we use the same calculation method i.e AM1. Performing a vibrational analysis using a different method e.g PM3 or a HF or DFT method would give meaningless results. Often it is best to perform the geometry optimisation and vibrational analysis in the same run and this can be done most conveniently using the **OPT+FREQ** job-type in the **CALCULATE** box.

For our example we will use the water molecule. Build the water molecule and in the **CALCULATE** box choose **OPT+FREQ** as job-type, **HF** method and **STO-3G** basis. set. Multiplicity is 1 and charge is zero.

Open the .log file on completion and scroll down the text file. Note that the geometry optimisation is performed initially and, after completion, the resulting optimised geometry is submitted automatically for a vibrational analysis

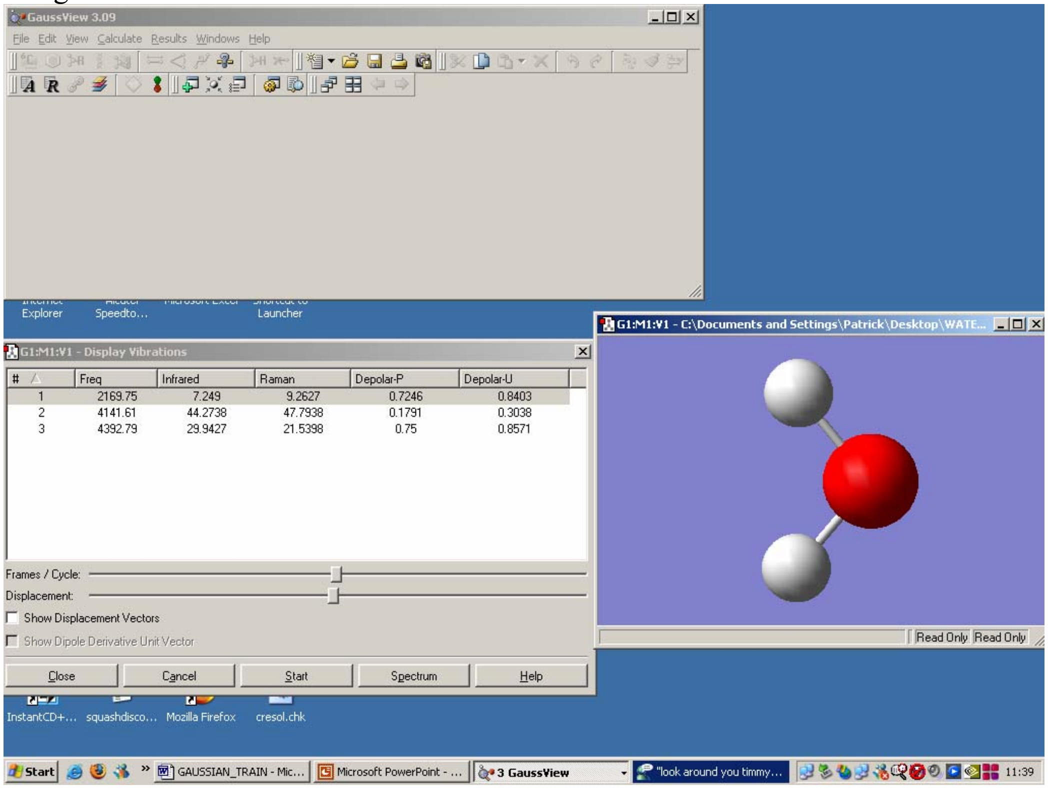
```
1|1|UNPC-UNK|FOpt|RHF|STO-3G|H2O1|PCUSER|26-Jul-2005|0||# OPT FREQ
HF/
 STO-3G GEOM=CONNECTIVITY||Title Card Required||0,1|O,-
0.1038205153,0.,
 -0.0733730859|H,-0.0222031588,0.,0.9125196127|H,0.8527672814,0.,-
0.325
 5349255||Version=x86-Win32-G03RevB.04|State=1-A1|HF=-
74.9659012|RMSD=7
 .765e-012|RMSF=1.090e-004|Dipole=0.5492043,0.,0.3881392|PG=C02V
[C2(O1
 ),SGV(H2)]||@


 KINETICS       FACT
 ---------  =  -------
 MECHANISM     FICTION
 Job cpu time:  0 days  0 hours  0 minutes 19.0 seconds.
 File lengths (MBytes):  RWF=     12 Int=      0 D2E=      0 Chk=
7 Scr=      1
 Normal termination of Gaussian 03 at Tue Jul 26 11:21:39 2005.
 Link1:  Proceeding to internal job step number  2.
 -------------------------------------------------------------
 #N Geom=AllCheck Guess=Read SCRF=Check GenChk RHF/STO-3G Freq
 -------------------------------------------------------------
 1/10=4,29=7,30=1,38=1,40=1,46=1/1,3;
 2/40=1/2;
 3/6=3,11=1,16=1,25=1,30=1,70=2,71=2/1,2,3;
 4/5=1,7=1/1;
 5/5=2,38=6/2;
 8/6=4,10=90,11=11,27=262144000/1;
 10/13=10/2;
 11/6=2,8=1,9=11,15=111,16=1/1,2,10;
 10/6=1/2;
 6/7=2,8=2,9=2,10=2,18=1,28=1/1;
 7/8=1,10=1,25=1/1,2,3,16;
 1/10=4,30=1,46=1/3;
 99//99;
 -------------------
```

The vibrational frequencies, intensities and the mode forms are given after the analysis is complete

```
Harmonic frequencies (cm**-1), IR intensities (KM/Mole), Raman scattering
 activities (A**4/AMU), depolarization ratios for plane and unpolarized
 incident light, reduced masses (AMU), force constants (mDyne/A),
 and normal coordinates:
                      1                    2                    3
                     A1                   A1                   B2
 Frequencies --  2169.7549            4141.6088            4392.7894
```

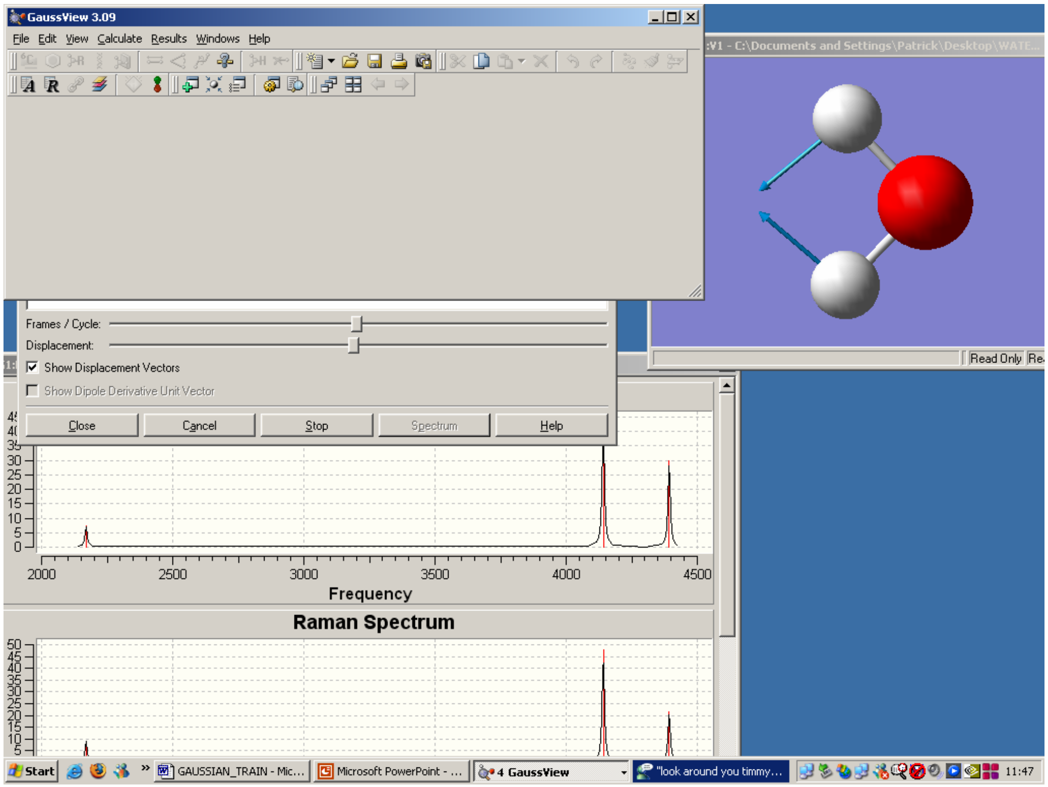
```
Red. masses --     1.0785            1.0491            1.0774
Frc consts  --     2.9915           10.6023           12.2489
IR Inten    --     7.2490           44.2738           29.9427
Raman Activ --     9.2627           47.7938           21.5398
Depolar (P) --     0.7246            0.1791            0.7500
Depolar (U) --     0.8403            0.3038            0.8571
Atom AN      X      Y      Z        X      Y      Z        X      Y      Z
  1   8     0.00   0.00   0.07     0.00   0.00   0.05     0.00   0.07   0.00
  2   1     0.00  -0.45  -0.54     0.00   0.57  -0.42     0.00  -0.54   0.45
  3   1     0.00   0.45  -0.54     0.00  -0.57  -0.42     0.00  -0.54  -0.45
```

Alternatively the vibrational data can be displayed from the main Gaussview window using the **RESULTS/Vibrations** menu combination



#	Freq	Infrared	Raman	Depolar-P	Depolar-U
1	2169.75	7.249	9.2627	0.7246	0.8403
2	4141.61	44.2738	47.7938	0.1791	0.3038
3	4392.79	29.9427	21.5398	0.75	0.8571

The vibrational frequency of all three modes and the Infa Red and Raman intensities are given. Each vibrational mode can be animated by highlighting the mode and clicking the **START** button. This provides an easy and convenient way of analysing the atom displacements in the mode form.
In addition the calculated Infra Red and Raman spectra can be calculated and displayed by clicking on the **SPECTRUM** button.



☑ Show Displacement Vectors

In addition DISPLACEMENT vectors can be displayed by highlighting the **show displacement vectors** button as shown above.

Exercises

1. Perform a HF/3-31G optimisation and vibrational analysis on the formaldehyde H_2CO molecule using C_{2v} symmetry. The experimental frequency results are given below. Compare experimental with predicted values by completing the Table below. Experimental values represent the anharmonic frequencies and hence are usually lower in value than the calculated harmonic modes. Give a reason for this.

Symmetry of Mode	**Description of Mode**	**Experimental infrared frequency (cm^{-1}) and intensity**	**Calculated frequency (cm^{-1})**
A1	CH_2 symm. stretch	2783 strong	
	CO stretch	1746 very strong	
	CH_2 scissors	1500 strong	
B1	CH_2 anti. stretch	2843 very strong	
	CH_2 rock	1249 strong	
B2	CH_2 wag	1167 strong	

2. Perform a geometry optimisation and vibrational frequency analysis on the Phenol molecule at the B3LYP/3-31G level of theory. The experimental gas phase values are given in the Table overleaf. In general the anharmoicity

values can be scaled by 0.96 to allow for anharmonicity corrections. Scale the calculated values by this amount and assign the experimentally observed bands to a mode form. Include a brief description of the mode form.

Mode	Mode Form	B3LYP/6-31G	Exp	Scaled EXP
1			225	
2			309	
3			403	
4			408	
5			503	
6			527	
7			619	
8			686	
9			751	
10			817	
11			823	
12			881	
13			958	
14			973	
15			999	
16			1026	
17			1072	
18			1151	
19			1169	
20			1177	
21			1262	
22			-	
23			1343	
24			1472	
25			1501	
26			1603	
27			1610	
28			3027	
29			NO	
30			3049	
31			3063	
32			3074	
33			3656	

Workshop 4. Energy calculations and inclusion of solvation.

Up to now we have concentrated on essentially isolated molecules, which are in essence models of the gas phase. Arguably the most interesting chemistry occurs in the solution phase and it is therefore important to be able to be able to predict the influence of the solvent on the calculated property.

The Gaussview/Gaussian program allows most molecules to be modelled in the solution phase by use of polarisable continuum models (PCM).

Here we use an example calculation on the relative base strength of ammonia and pyridine to provide an example of the calculation of the energetics of a reaction and also the inclusion of solvation effects.

We begin by posing the problem of which is the stronger base, ammonia or pyridine? Experimentally pyridine is the stronger base in the gas phase but ammonia is the stronger in the aqueous phase. This question like many others regarding chemical reactivity, can be better understood if it is expressed in terms of a chemical equilibrium. In this case the equilibrium involves the transfer of a proton between ammonia and pyridine i.e

Ammonia + pyridinium cation = ammonia cation + pyridine

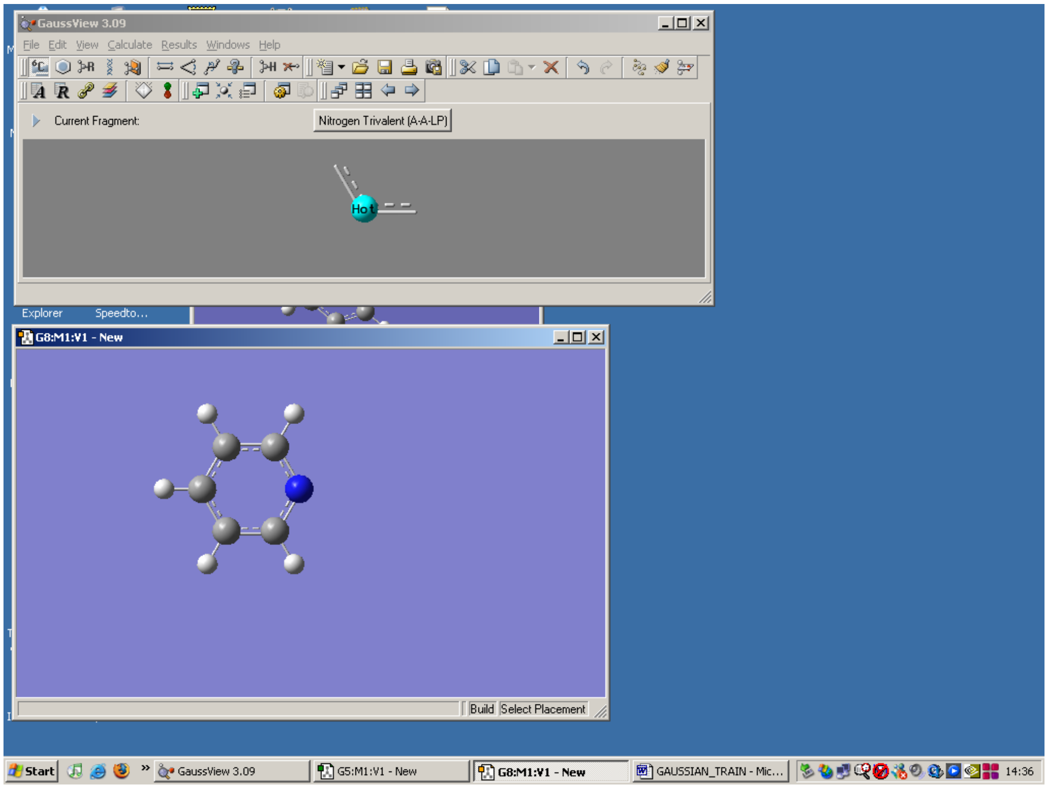
This equilibrium describes a competition by ammonia and pyridine for the proton. If ammonia is the stronger base the right side of the equilibrium will be favoured (ΔGrxn < 0) If pyridine is the stronger base the left-side will be favoured (ΔG rxn > 0). ΔG can be very difficult to calculate so in many cases one uses enthalpy especially when entropic effects are negligible.

The enthalpy is related to the energy value calculated in an electronic structure calculation and the enthalpy change can be evaluated by the difference between the energy of the products and the reactants. In the specific case here

Energy Change = {Energy (pyridine + ammonium cation)} – {Energy (ammonia + pyridinium cation)}

In this exercise we will calculate the energy of each of the reactants and products and thereby obtain the energy change for the reaction. We will then perform the same calculations in the presence of a water solvent and see if any change has occurred.

Build each molecule and ion as previously described. For the pyridine molecule an easy procedure is to first use the benzene ring template. Then select a nitrogen aromatic atom type. By clicking on any position on the benzene ring a nitrogen atom will be inserted as shown below.



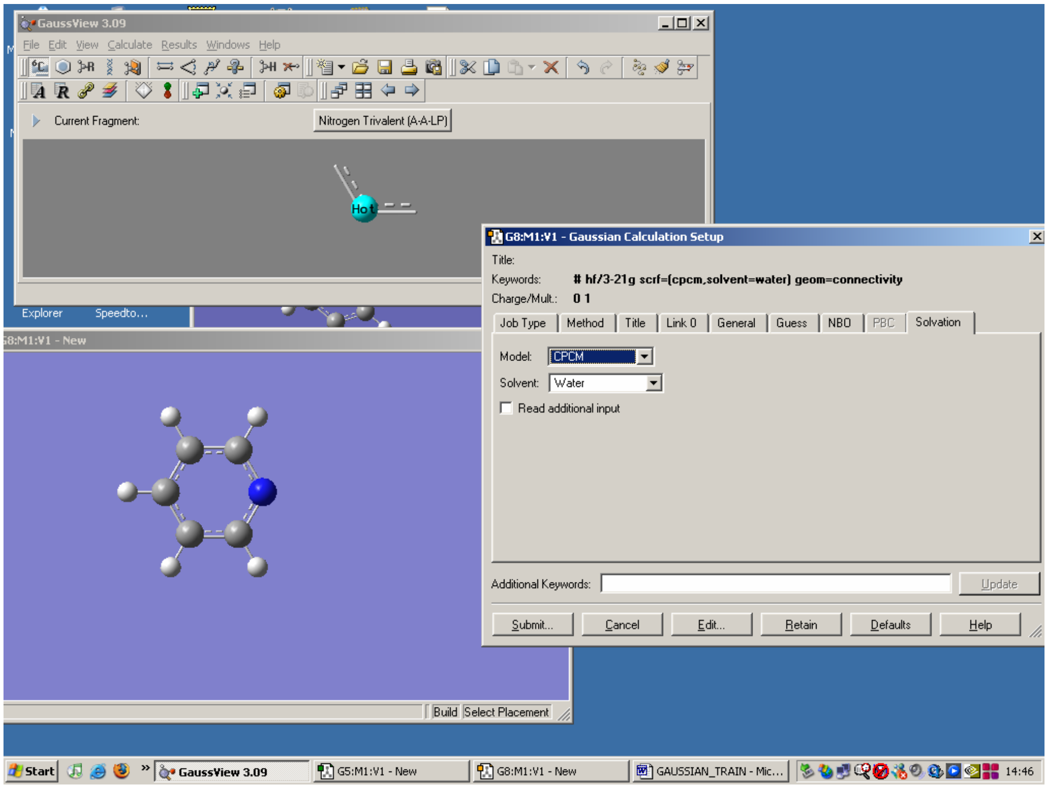
Current Fragment: Nitrogen Trivalent (A-A-LP)

Build all molecules and ions and submit for a HF/3-21G geometry optimisation.

The energy can be obtained by scrolling down the .log file or alternatively can be obtained using **RESULTS/SUMMARY** where the total energy is listed in hartrees.

Record the energy for each and calculate the reaction energy in kcal/mole. Do you have agreement with the experimental observation that pyridine is the stronger base in the gas phase?

Now you will proceed to model each reactant and product in aqueous solution. The same level of calculation will be used i.e HF/3-21G. One can select the solvent phase under the **CALCULATE** menu. For this calculation we will choose the Conductor-like Polarisable Continuum Model (CPCM) and choose water as the solvent.



Title:

Keywords: # hf/3-21g scrf=(cpcm,solvent=water) geom=connectivity

Charge/Mult.: 0 1

Model: CPCM

Solvent: Water

☐ Read additional input

Additional Keywords:

Choose Geometry optimisation and submit all four calculations. When completed calculate the energy of reaction, and again supply the answer as to which molecule is the stronger base in water. Do you find any significant difference between the gas phase and aqueous phase result. Provide an explanation for any conclusions reached. It will be instructive to compare the differences between the aqueous phase energy for each species and the gas phase values. This gives an estimation of the solvation energy for each species. How do they compare and how might they explain your observations?

Exercises

1. Using the same level of theory as the practice exercise, assess the influence of the methanol solvent on the relative base strength of ammonia and pyridine.

2. Using the same level of theory as the practice exercise predict the relative acidities of sulphuric and ethanoic acid in the gas and aqueous phases.