
Theoretical Methods Laboratory (Second Year)

DEPARTMENT OF CHEMISTRY

Electronic Structure

(Staff contact: Ian Gould)

Notes and suggestions of the format of the write-up required and points for discussion are included at the end of the exercise. Look at the marking scheme carefully.

Background reading: *Atkins and de Paula*, Physical Chemistry 7ed, Chapter 14 (Molecular Structure) and references cited therein. The Chemical Bond*, Murrell, Kettle and Tedder*, Chapters 6 and 9. For the brave souls amongst you Molecular Quantum Mechanics 3ed, *Atkins and Friedman,* Chapters 8 and 9. Brief revision of last years course by Professor Klug.

Objectives

This 'experiment' consists of four exercises. Allow roughly equal time for each. As you progress the time required for the calculations to complete will increase, benzene will take of the order of ½ hour to perform the calculation and, therefore, you will be supplied with some data files to examine.

For exercises 1, part of 2 and all of 3 there is a common procedure with respect to creating the molecule of interest followed by geometry optimisation and determination of certain physical properties. It is also a good idea to look at page 14 which describes what is required for the write up in terms of the questions to be addressed.

Exercise 1: Examine the trend in the bond length, molecular orbitals and vibrational mode of the following homonuclear diatomics H_2, Li_2, N_2, O_2 and F_2. Ask a demonstrator about running O_2 as a triplet as well as a singlet. Investigate the following heteronuclear diatomics: LiH, LiF and CO with respect to the same parameters as for the homonuclear diatomics and also examine the charges. Comment on your findings in terms of the bonding in the systems.

Exercise 2: Examine the geometry, vibrational modes, molecular orbitals and charges for 1,3,5 hexatriene and benzene. Investigate the effect of replacing one carbon atom in benzene and naphthalene with a nitrogen, pyridine and quinoline, with respect to geometry, vibrational frequencies, charges and molecular orbitals. You will be supplied with the necessary data files, in the form of formatted checkpoint files, for naphthalene, pyridine and quinoline. Does the replacement cause a major or minor perturbation of the physical properties?

Exercise 3: Examine the geometry, vibrational modes, molecular orbitals and charges for the following substituted benzenes: NH_2, NO_2, F, Cl, OH and CN. As for exercise 2 you will be supplied with the data (.fchk) files for these molecules. Do you observe effects consistent with what you have learnt in organic chemistry, electron donating/withdrawing etc?

Exercise 4: Examine the geometry, vibrational modes, molecular orbitals and charges for Cis and Trans butadiene. Locate the transition state and determine the energetic barrier for the isomerization process and indicate which is the more stable conformation, does this correspond to what you'd expect? Comment on the vibrational modes of the transition state, how does this confirm you are at a maximum on the potential energy surface?

By the end of these exercises, you should be able to
* Determine the structure, vibrational spectra and molecular orbitals of small gas phase molecules using quantum mechanical techniques.
* Locate and characterise a transition state in a chemical transformation and be able to calculate the barrier height and the relevant stabilities of the species involved.

You will also have a better understanding of modern computation applications in chemistry.

Program Notes

The exercises run in the computer lab using Gaussview for Windows, which you have already seen last week.
(Programs menu).

The files you need are available in the Mac-PC/electronic folder.
(PC – Mac-PC icon on desktop)

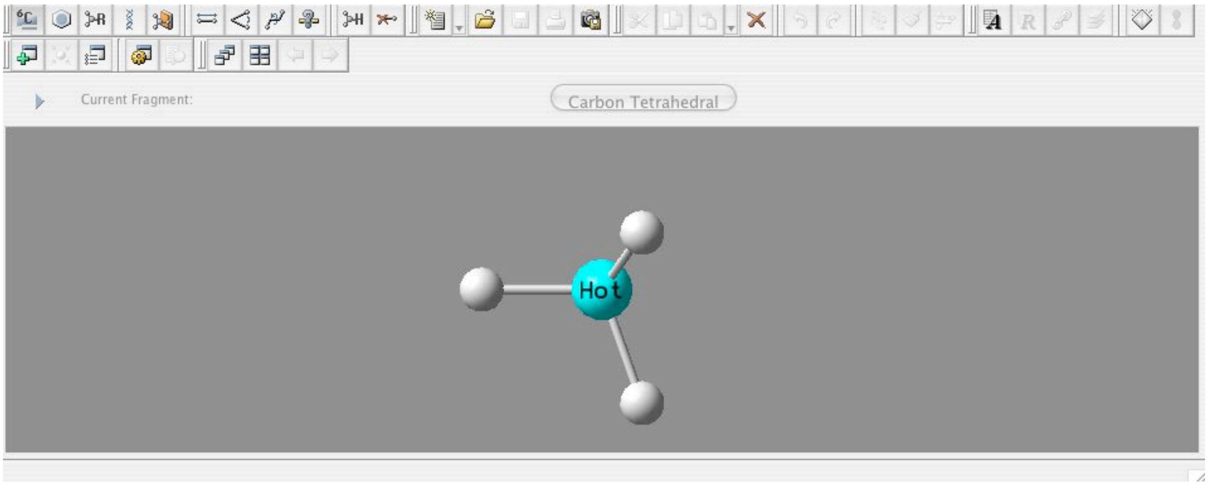
Copy the folders ex2 and ex3 to your network home directory first.

As part of the exercise, you will need to copy images from the Gaussview display. Two suggested ways of doing this:
1) Alt-Print Screen copies the current window to the clipboard. This can be pasted into e.g. PowerPoint or Word.
2) Gaussview can save graphics files in TIFF, JPEG (or BMP) format, which can be imported into another application.

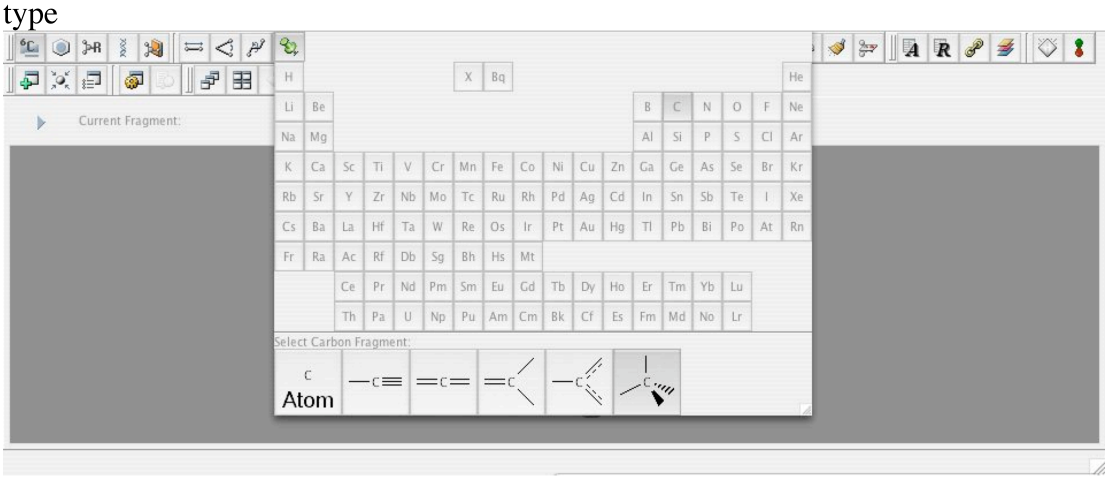
For the exercises where you need to create molecules that will subsequently be subjected to sophisticated quantum mechanical investigation you will need to adopt the following procedure as outlined by the example of methane below.

To familiarise you with the workings of the programme we will walk through an investigation of methane, optimising the geometry, looking at the molecular orbitals and charges, the essential components of all four exercises.

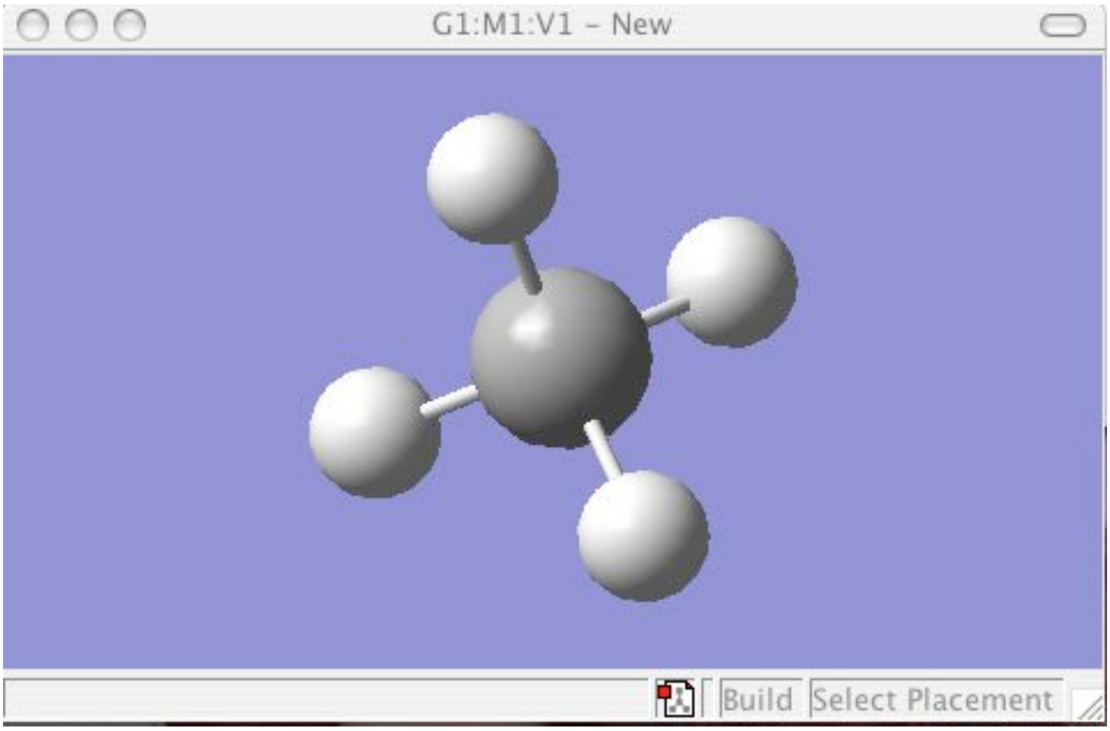
When you first launch Gaussview you are greeted with the following windows



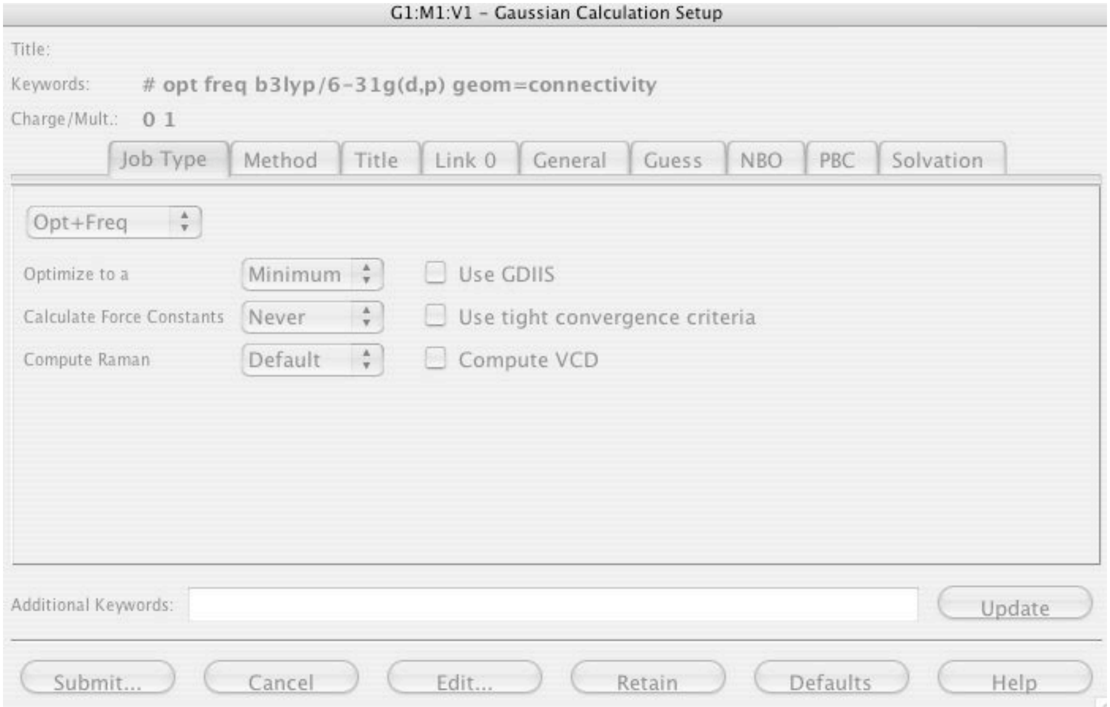
Clicking on the top left icon produces a panel from which it is possible to select an atom type



In the above example we have selected the carbon atom, you will notice that there are several different representations dependent on the Carbon’s environment, click on the tetrahedral one and click in the blue window and you should obtain the following picture.



You will use the graphics display of **Gaussview** to manipulate the molecule, scale, rotate etc, and to calculate the properties of the molecule that are of interest. This is achieved through the menu “Calculate” followed by selecting “Gaussian”. At which stage you should be presented with the following menu



G1:M1:V1 – Gaussian Calculation Setup

Title:

Keywords: # opt freq b3lyp/6-31g(d,p) geom=connectivity

Charge/Mult.: 0 1

Opt+Freq

Optimize to a: Minimum

Calculate Force Constants: Never

Compute Raman: Default

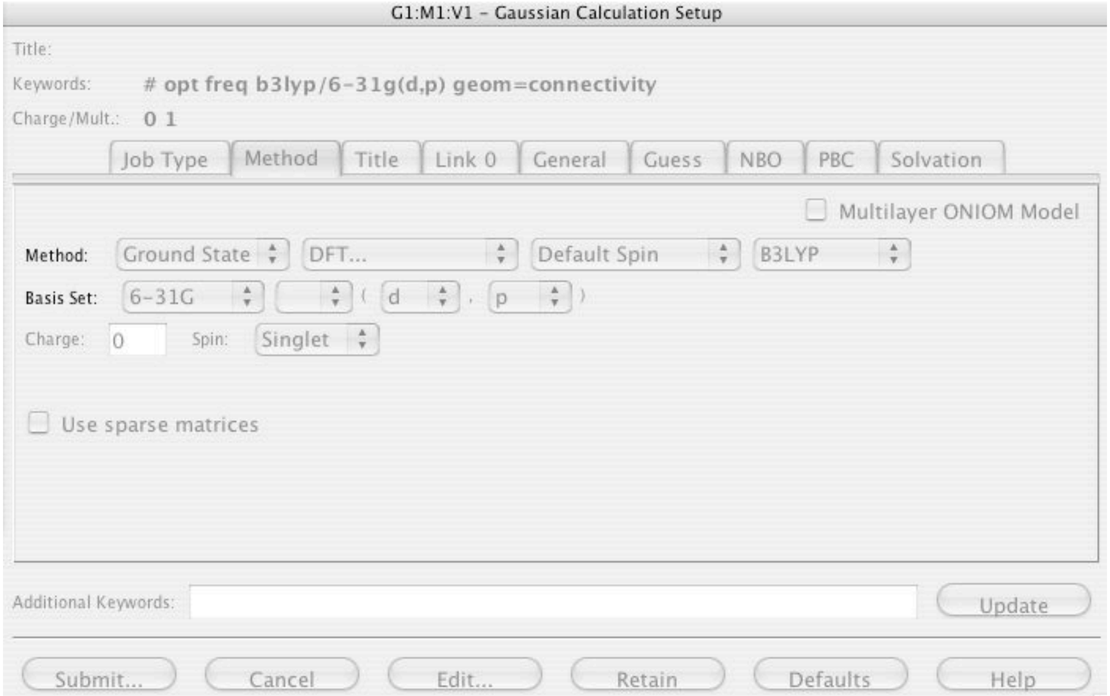
☐ Use GDIIS

☐ Use tight convergence criteria

☐ Compute VCD

Additional Keywords:

Check that the settings correspond to these in the previous diagram for the “Job Type”, then click on the method button and select the following



G1:M1:V1 – Gaussian Calculation Setup

Title:

Keywords: # opt freq b3lyp/6-31g(d,p) geom=connectivity

Charge/Mult.: 0 1

☐ Multilayer ONIOM Model

Method: Ground State, DFT..., Default Spin, B3LYP

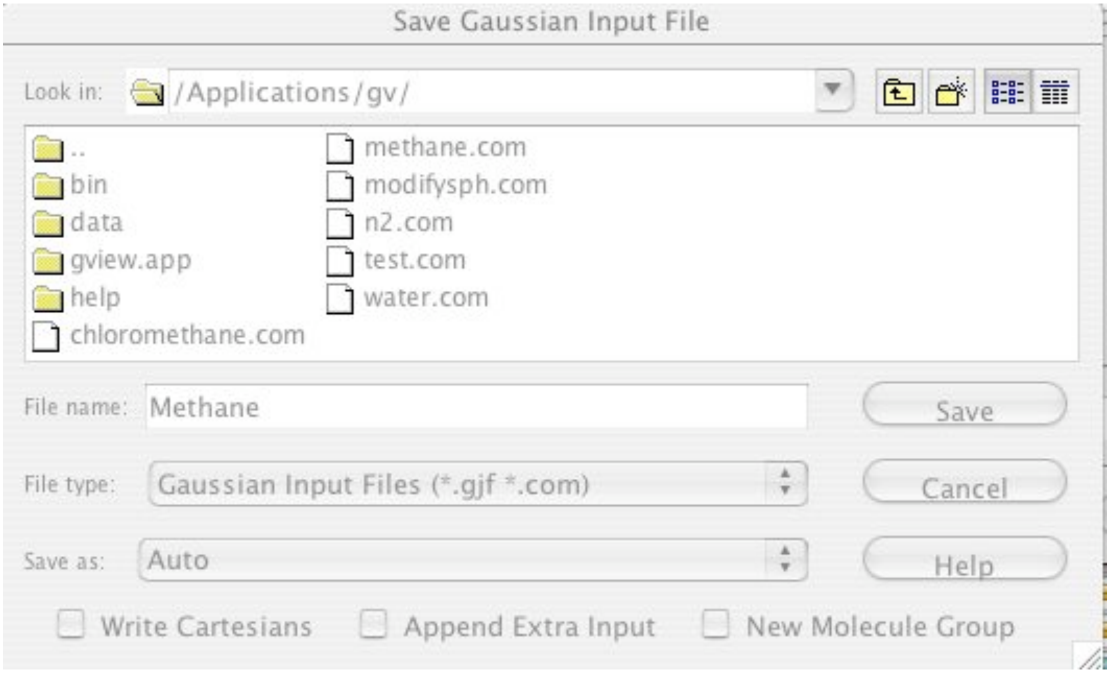
Basis Set: 6-31G, (d , p)

Charge: 0 Spin: Singlet

☐ Use sparse matrices

Additional Keywords:

At this stage you are almost ready to perform your first calculation, click on the Submit button, you will be asked to save the file, so go ahead and at the prompt save it as, in this instance, Methane.



Save Gaussian Input File

Look in: /Applications/gv/

..
bin
data
gview.app
help
chloromethane.com
methane.com
modifysph.com
n2.com
test.com
water.com

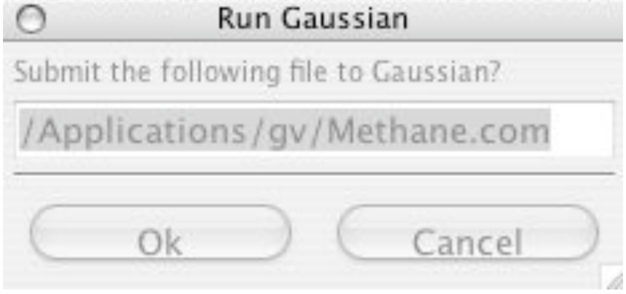
File name: Methane

File type: Gaussian Input Files (*.gjf *.com)

Save as: Auto

☐ Write Cartesians ☐ Append Extra Input ☐ New Molecule Group

This will be followed by

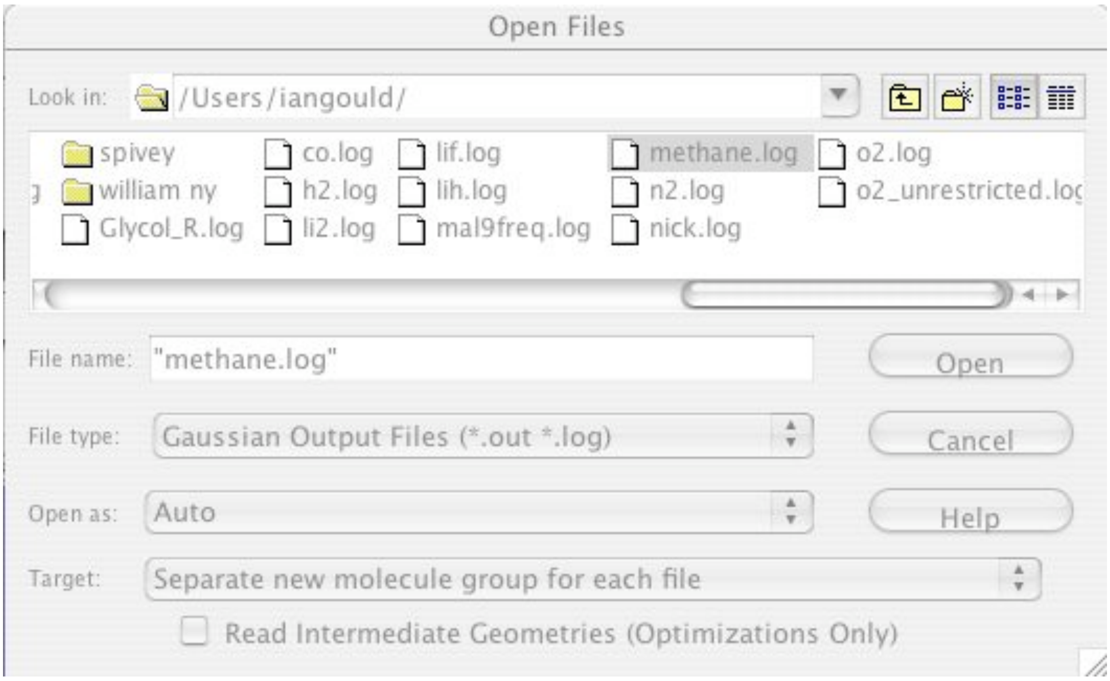


Run Gaussian

Submit the following file to Gaussian?

/Applications/gv/Methane.com

Click Ok, sit back and wait for the programme to report back that it has finished the calculation, it will ask you if you would like to open a result file. You are then presented with the following window



Look in: /Users/iangould/

File name: "methane.log"

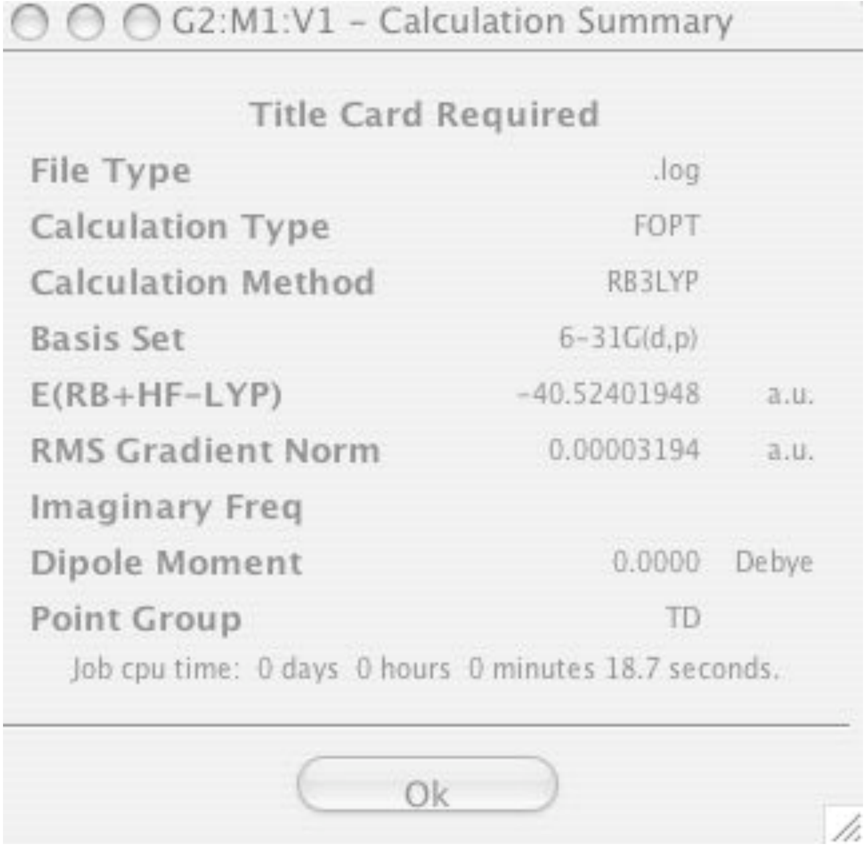
File type: Gaussian Output Files (*.out *.log)

Open as: Auto

Target: Separate new molecule group for each file

☐ Read Intermediate Geometries (Optimizations Only)

By default output files are appended with the .log extension, the job input files are known as .com's. Opening the .log file opens a window with the molecule displayed and you will now have access to the results menu bar, here you can get a summary of the job

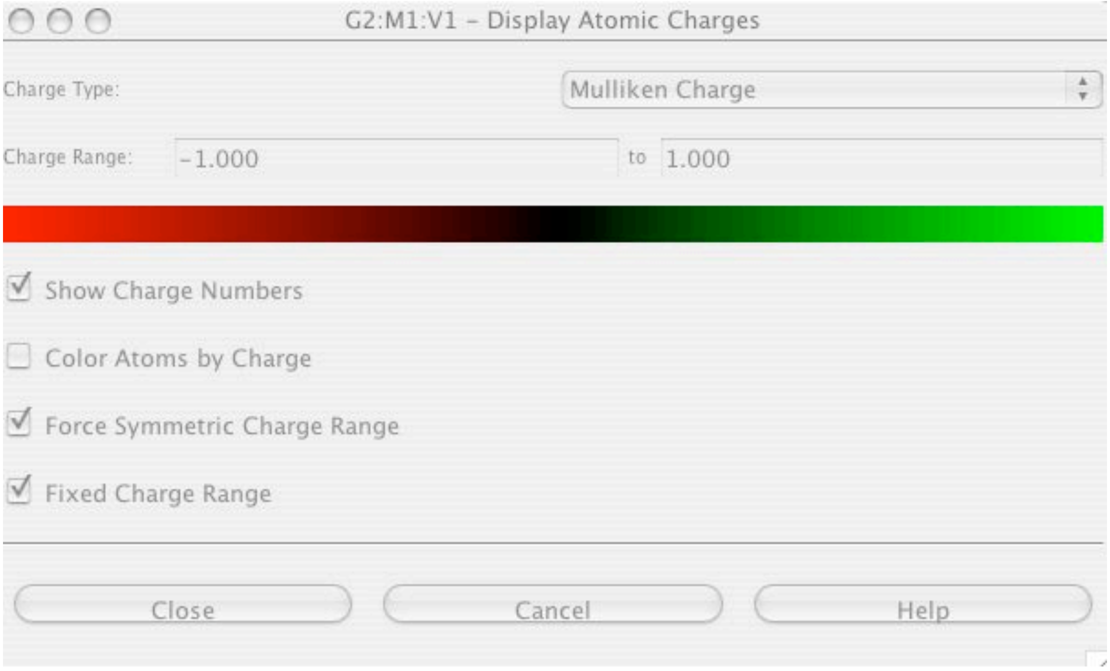


Title Card Required

File Type	.log	
Calculation Type	FOPT	
Calculation Method	RB3LYP	
Basis Set	6-31G(d,p)	
E(RB+HF-LYP)	-40.52401948	a.u.
RMS Gradient Norm	0.00003194	a.u.
Imaginary Freq		
Dipole Moment	0.0000	Debye
Point Group	TD	

Job cpu time: 0 days 0 hours 0 minutes 18.7 seconds.

This just tells you the job has run and what level of theory it has used. The line E(RB+HF-LYP) -40.52401948 a.u. gives the total energy of the molecule in atomic units, you will need this information for exercise 4 where you determine the energy difference between the Cis-Trans forms of butadiene and the transition state between them. You will need to look up the conversion factor for atomic units to kJ/Mol. Another property that you can investigate is the atomic charges of the molecule again from the results menu choose charges, there are a couple of options restrict yourself to Mulliken and ATP charges the later being the better choice.


G2:M1:V1 – Display Atomic Charges

Charge Type: Mulliken Charge

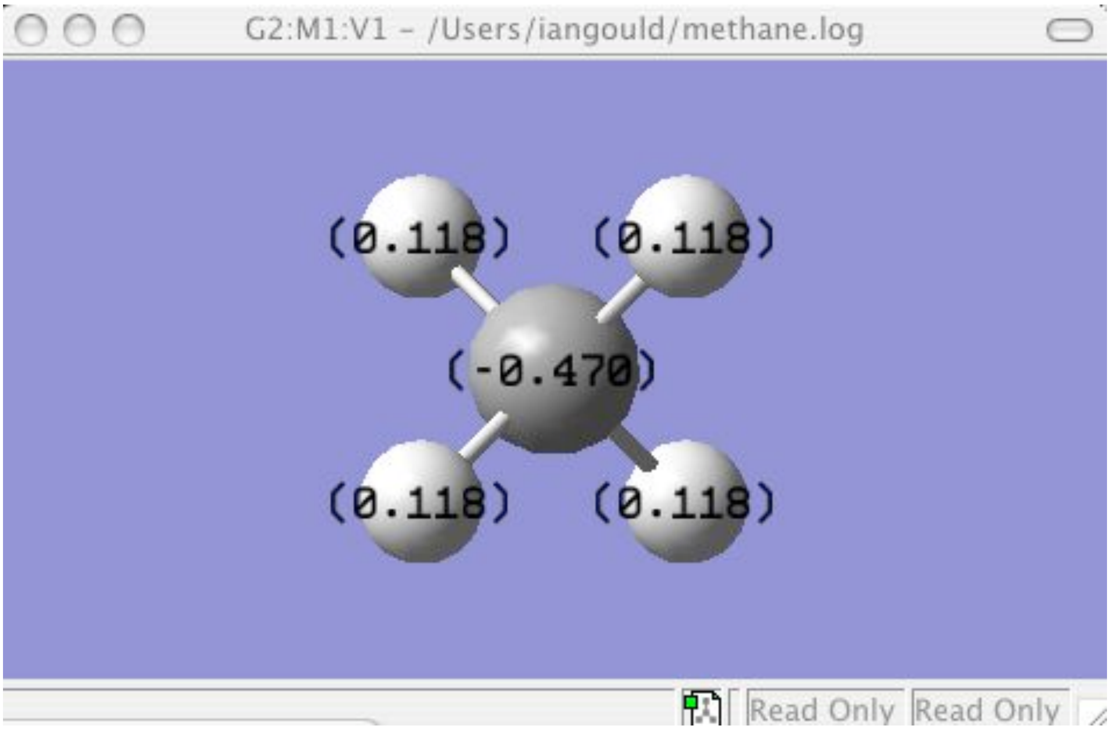
Charge Range: -1.000 to 1.000

☑ Show Charge Numbers

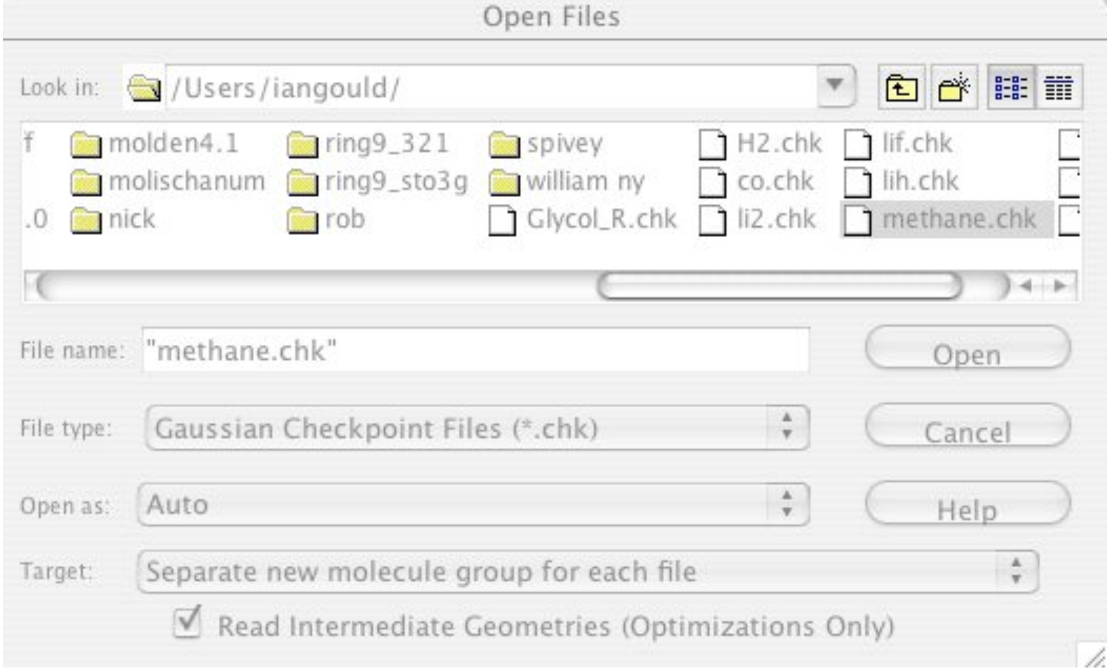
☐ Color Atoms by Charge

☑ Force Symmetric Charge Range

☑ Fixed Charge Range



For all of the exercises in this experiment you will need to visualise the molecular orbtitals and vibrational frequencies for the systems you are investigating. This is achieved by opening the checkpoint, .chk, file associated with the calculation you have just done.



Look in: /Users/iangould/

File name: "methane.chk"

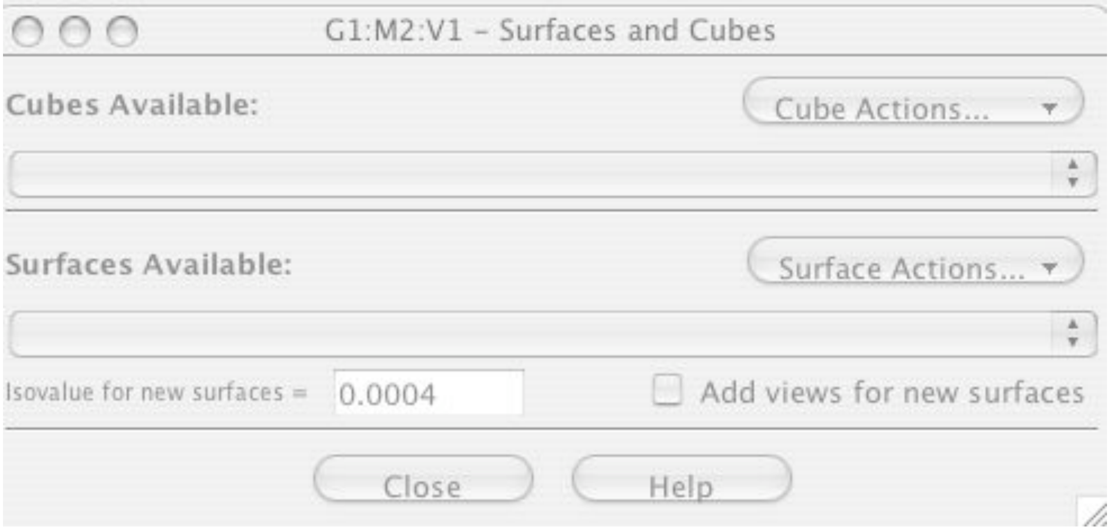
File type: Gaussian Checkpoint Files (*.chk)

Open as: Auto

Target: Separate new molecule group for each file

☑ Read Intermediate Geometries (Optimizations Only)

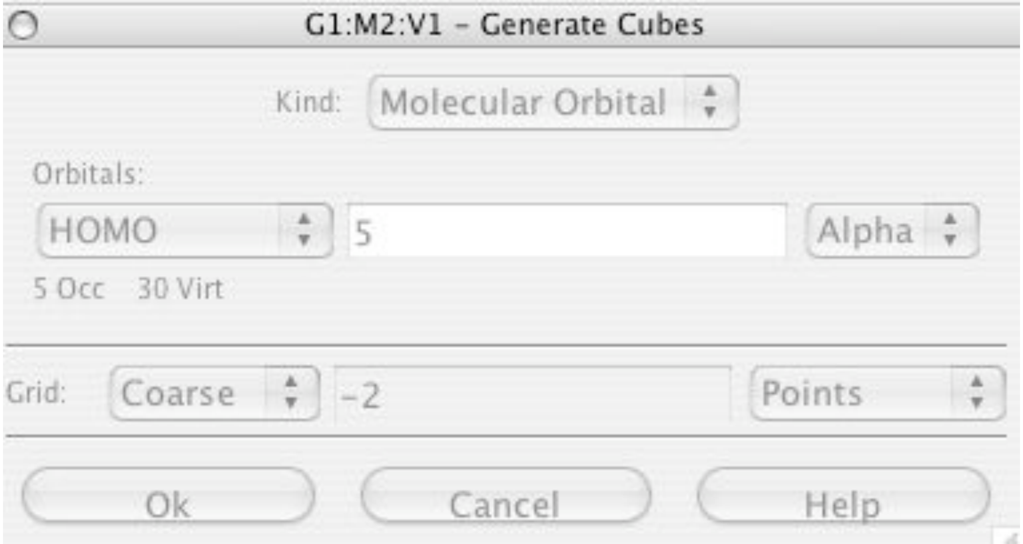
Once the molecule has loaded you will see from that the surfaces option is now active in the results menu bar, clicking on this produces the following and you need to select new cube from the cube action menu



Isovalue for new surfaces = 0.0004

☐ Add views for new surfaces

Then select the orbital you want to look at



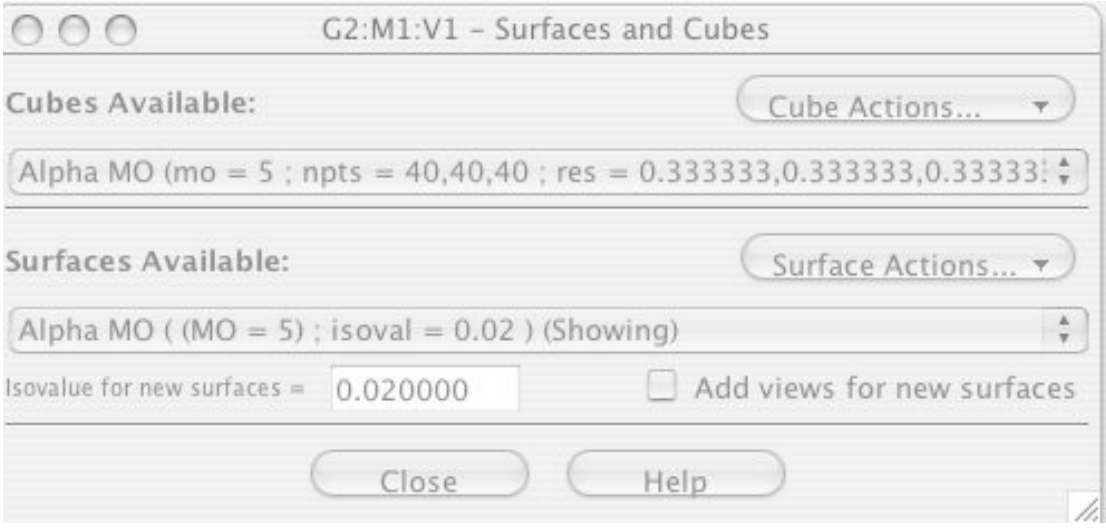
Kind: Molecular Orbital

Orbitals: HOMO 5 Alpha

5 Occ 30 Virt

Grid: Coarse -2 Points

You click Ok and then on the following


G2:M1:V1 – Surfaces and Cubes

Cubes Available:

Alpha MO (mo = 5 ; npts = 40,40,40 ; res = 0.333333,0.333333,0.33333

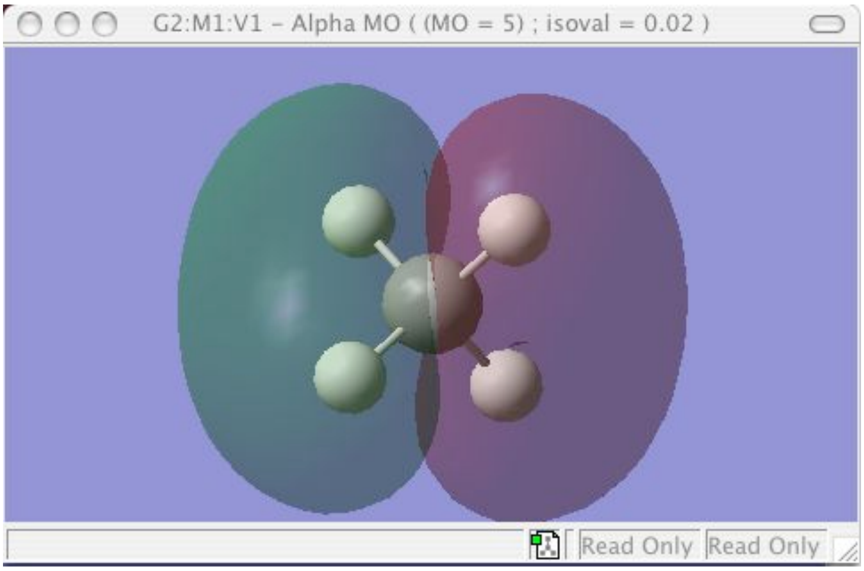
Surfaces Available:

Alpha MO ((MO = 5) ; isoval = 0.02) (Showing)

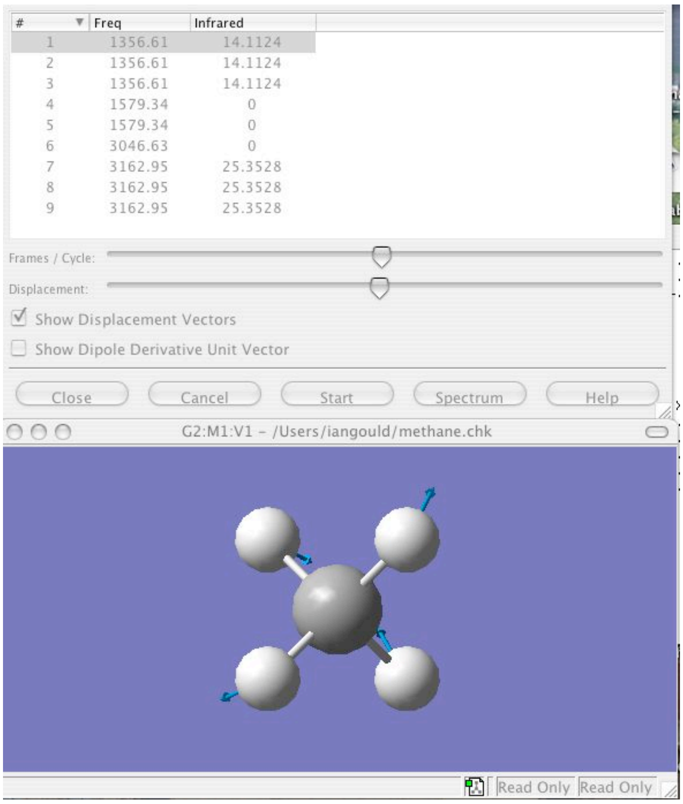
Isovalue for new surfaces = 0.020000

☐ Add views for new surfaces

Which yields the following image of the Homo orbital for methane



It is also useful to examine the vibrational spectra of the molecule under consideration, if the system is an optimised structure it will have only non-negative frequencies. To access the vibrational spectra you can either load the .log file and select the vibrations menu under results

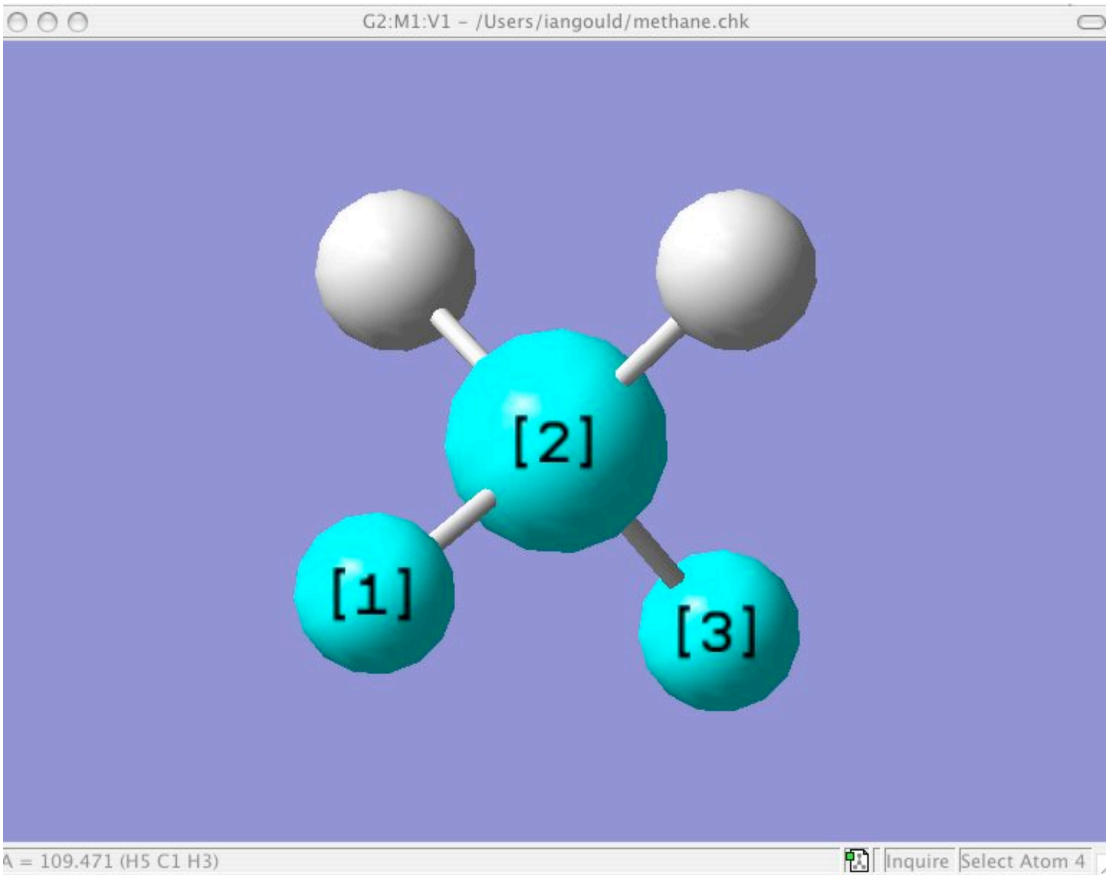


#	Freq	Infrared
1	1356.61	14.1124
2	1356.61	14.1124
3	1356.61	14.1124
4	1579.34	0
5	1579.34	0
6	3046.63	0
7	3162.95	25.3528
8	3162.95	25.3528
9	3162.95	25.3528

☑ Show Displacement Vectors

☐ Show Dipole Derivative Unit Vector

Finally, it is very useful to be able to interrogate the geometric parameters, bond lengths, angles and torsions, of optimised molecules. This is easily achieved by using the "inquire" facility in Gaussview, it is the symbol of a pencil with a question mark across it.



The above graphic gives the bond angle for HCH of 109.471^0 in pretty good agreement with experiment.

You are now equipped with the necessary tools to perform the exercises, the only area that has not been covered in any detail is the calculation of the transition state for exercise 4, when you are at this point in the experiment contact one of the demonstrators for assistance.

Electronic Structure

Suggested guide/template for write up 10-15 pages. Reports in excess of 15 pages will not be appreciated.
You should start by reading the discussions in e.g. Atkins.

Marks are given for correct results, but also for demonstrating that you understand the underlying concepts of how molecules are formed from their constituents.

With respect to Molecular Orbital pictures, restrict yourself to including in the write up just the Homo and Lumo's and only include them if there is something significant to illustrate. (Hint, you may actually require more than two for benzene)

Exercise 1:

Comment on the relationship between bond length, vibrational mode frequency and bond order of the homonuclear diatomics. Which is lower in energy the singlet or triplet O_2, comment on this observation. Describe the nature of the bonds in the heteronuclear diatomics, can you see whether LiH is covalent or ionic? What is the nature of the bond in LiF? CO has the same number of electrons as N_2, compare the two in terms of their physical properties that you have investigated.

Exercise 2:

Describe the fundamental differences between 1,3,5 hexatriene and benzene in terms of their bonding, molecular orbital distribution, charges etc. How does changing one C atom for an N atom in benzene and naphthalene change the properties you have investigated.

Exercise 3:
Do the properties that you observe for series of substituted benzenes mirror what you would expect? Illustrate you answer with respect to the charge distribution on the molecules, with reference to the ortho, meta and para positions. How do the different groups affect the molecular orbitals and the level of delocalisation.

Exercise 4:
Identify which isomer is the more stable and by how much, energy stabilisation in kJ/Mol please, do the molecular orbitals help you rationalise this result? How do you know the Transition state is the highest point on the potential energy surface, how do the molecular orbitals compare to those of the Cis and Trans conformations. Is there anything significant about the negative frequency of the transition state structure?

"Always look on the bright side of life...
If life seems jolly rotten,
There's something you've forgotten!
And that's to laugh and smile and dance and sing"
Monty Python's Life of Brian

2nd Year Lab 2005
Mark Scheme for Computer Experiments.

Electronic Structure

Imperial College Department of Chemistry

Please note reports should NOT exceed 15 pages in length.

Student Name: ………………………………………

Marker: ………………………………………..

Presentation	
- Legibility and Structure (is the report well laid out?)	/10
- Figures and Tables (are these well presented, labelled and clear?)	/10
Grammar	
- Spelling (deduct marks for persistent errors)	
- Grammatical construction (does it read well?)	
- Proof reading (has the report been properly proof read?)	
	/10
Content	
- Discussion of each exercise 4 x 15	/60
Bonus Points	
- Independent thought in interpretation.	/5
- Additional experiments / improvements to expt.	/5
TOTAL MARK	/100