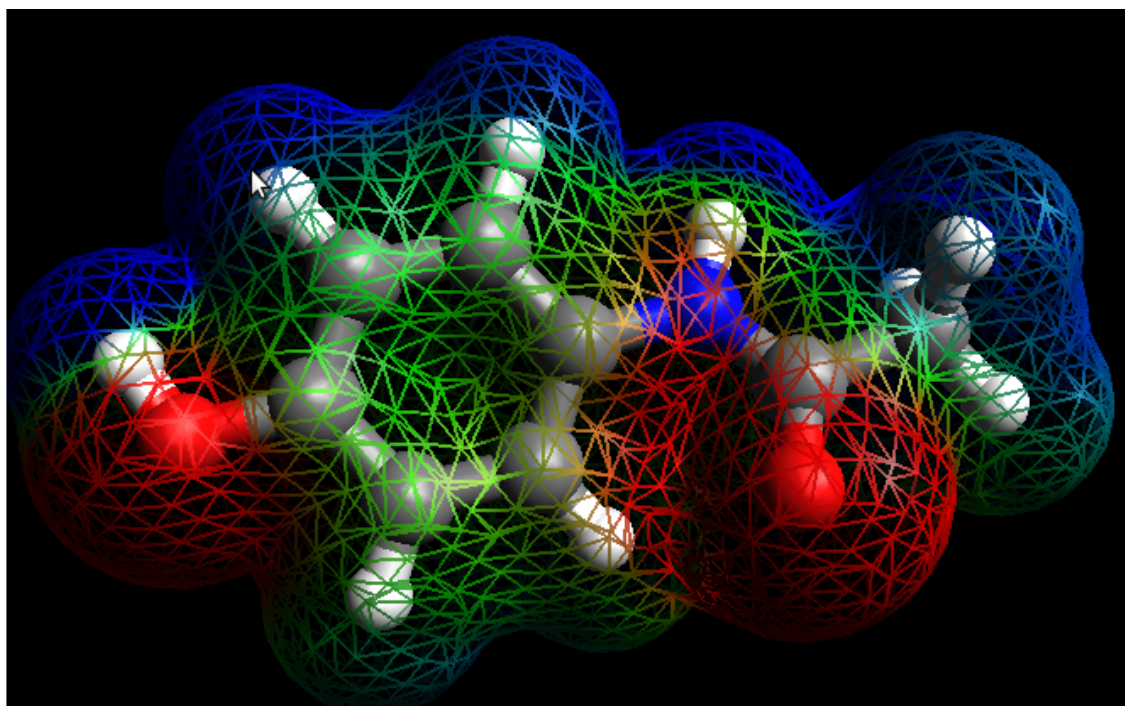


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Chapter 1

Introduction

Computational models are important parts of scientific research. Numerical simulations are used in chemistry, physics, biology, and even places where you wouldnt expect (like the stock market) to better understand real-life experiments and to test the prediction of theoretical models. If a particular model contains an accurate description of the essential processes that are crucial for subsequent predictions then simulations from such a model should reproduce the main aspects of the corresponding physical experiment.

Chemists are interested in such a variety of processes that the number of models available is extremely large. Chemical models may be aesthetically pleasing and physically tangible, such as the colorful plastic chemistry model kits. They may be visual, such as the lines and dots that organic chemists use to describe chemical reactions and placement of electrons, or even conceptual, such as the pages of equations describing physical chemistry. Computational and theoretical chemists use physics as well as mathematical and computational techniques to investigate the various chemical processes which interest them. These models are often able to provide valuable information about chemical species which are difficult to analyze experimentally, or explain certain strange phenomena. Experiment and theory are therefore linked and while both are valuable to explore independently, ultimately they exist to aide each other.

1.1 UNIX Shell and Commands

The UNIX shell is a command-line interface (CLI) of UNIX-like operating systems. While a graphic user interfaces (GUI) may seem to be more user-friendly, a command-line interface is more customizable and more efficient for performing repetitive tasks, as in the case of scientific computing. In a UNIX shell, we can type a command to tell the computer to perform a certain task.

To look up the usage of a particular command, we can type “man” followed by the command that we are interested in:

```
man (command)
```

For example, to find the manual page for the command “ls”, the command that lists the contents of a directory, type in “man ls” in the terminal and the manual pages for ls will show up(1.2). The manual pages of a command will show the name of the command, a brief synopsis of how to use the command, a description of its extensions, a description of the author of the command, an email to correspond to when reporting bugs, the copyright information and a see also section. Type “q” to exit viewing the manual and return to entering commands in the terminal.

A few other commonly used commands include pwd (print name of current/working directory)(Figure ??), mkdir (make directories), rmdir (remove empty directories), rm (remove files

```

LS(1)                                User Commands                                LS(1)
NAME
  ls - list directory contents
SYNOPSIS
  ls [OPTION]... [FILE]...
DESCRIPTION
  List information about the FILES (the current directory by default). Sort
  entries alphabetically if none of -cftuvSUX nor --sort.

  Mandatory arguments to long options are mandatory for short options too.

  -a, --all
      do not ignore entries starting with .

  -A, --almost-all
      do not list implied . and ..

  --author
      with -l, print the author of each file

  -b, --escape
      print octal escapes for nongraphic characters

  --block-size=SIZE
      use SIZE-byte blocks

Manual page ls(1) line 1

```

Figure 1.1: Beginning of the manual command page for ls

or directories), cd (change directory), and mv (move and rename files). The pwd command will show the present directory the user is entering commands (Figure 1.3).

Figures 1.4 and 1.5 demonstrates a couple of commonly used terminal command sequences. Figure 1.6 shows one method of completing a practice exercise.

1.2 Keeping Records

Keeping records in a computational project is as important and necessary as keeping a journal in a real laboratory. Organization is crucial in computational chemistry because files and results can easily get lost. You should organize your data in a clear systematic fashion with subdirectories that can be easily understood and accessed. For example, do not put the calculations of two different molecules in the same directory. Do not place all the calculations with the same basis set in the same directory. Remember to never type results into documents by hand. Copy and paste results into your documents to avoid typos. Make it a habit to copy the results of your finished calculations to a location under your home directory where it is saved and will automatically be backed up.

One method of organizing your results is by using an OpenOffice.org Spreadsheet document to document your work. The OpenOffice.org Spreadsheet program can be accessed by clicking on the Applications button on the top left corner of the screen and is located under the Office tab. An example of a way to keep your data organized is demonstrated in Figure ???. For every computational project created, the spreadsheet document should contain the following information:

1. What has been done, e.g., what method, basis set, which isomer?
2. Where is the data located?
3. What are the main results?

```

peihsuay@model6:~$ ls
control Desktop Documents Pictures texput.log tmp.input Work
peihsuay@model6:~$ ls -l
total 16
-rw-r--r-- 1 peihsuay furche 40 2010-06-28 10:03 control
drwx--S--- 4 peihsuay furche 31 2010-07-19 21:27 Desktop
drwxr-sr-x 8 peihsuay furche 114 2010-07-19 13:17 Documents
drwxr-sr-x 2 peihsuay furche 28 2010-07-19 21:24 Pictures
-rw-r--r-- 1 peihsuay furche 675 2010-07-19 15:25 texput.log
-rw-r--r-- 1 peihsuay furche 40 2010-06-28 10:03 tmp.input
drwxr-sr-x 22 peihsuay furche 4096 2010-07-15 15:06 Work
peihsuay@model6:~$ ls -al
total 56992
drwxr-x--T 44 peihsuay furche 16384 2010-07-20 14:16 .
drwxr-xr-x 4 root root 0 2010-07-19 15:08 ..
drwx----- 3 peihsuay furche 20 2010-04-12 16:01 .adobe
drwxr-sr-x 6 peihsuay furche 81 2010-07-02 01:22 .avogadro
-rw----- 1 peihsuay furche 6044 2010-07-20 13:39 .bash_history
-rw-r--r-- 1 peihsuay furche 220 2008-05-12 11:36 .bash_logout
-rw-r--r-- 1 peihsuay furche 3107 2009-02-20 18:28 .bashrc
drwx--S--- 4 peihsuay furche 4096 2010-07-09 13:00 .cache
drwx--S--- 3 peihsuay furche 20 2010-04-05 16:06 .compiz
drwxr-sr-x 7 peihsuay furche 150 2010-06-28 08:33 .config
-rw-r--r-- 1 peihsuay furche 40 2010-06-28 10:03 control
drwx--S--- 3 peihsuay furche 24 2010-04-05 16:04 .dbus
-rw-r--r-- 1 peihsuay furche 0 2010-04-12 16:09 .definerc
drwx--S--- 4 peihsuay furche 31 2010-07-19 21:27 Desktop
-rw----- 1 peihsuay furche 28 2010-07-20 10:56 .dmrc
drwxr-sr-x 8 peihsuay furche 114 2010-07-19 13:17 Documents
-rw----- 1 peihsuay furche 16 2010-04-05 16:04 .esd_auth
drwxr-xr-x 7 peihsuay furche 134 2010-07-07 16:55 .evolution
drwxr-sr-x 3 peihsuay furche 21 2010-06-15 15:07 .fltk
drwxr-sr-x 2 peihsuay furche 4096 2010-07-06 17:09 .fontconfig
drwx--S--- 4 peihsuay furche 31 2010-07-20 10:56 .gconf
drwx--S--- 2 peihsuay furche 24 2010-07-20 14:35 .gconfd

```

Figure 1.2: A simple example of using the “-l” and “-al” options (or flags) of ls. The “-l” option lists the files including permissions, owners, size and when they were last modified. The “-al” option lists the “-l” option to all files in addition to listing including those that are hidden.

```

peihsuay@model6:~$ pwd
/modfac/home/peihsuay
peihsuay@model6:~$ █

```

Figure 1.3: The command pwd

```

@model6:~/Documents$ cd ~
@model6:~$ ls
control Desktop Documents Pictures texput.log tmp.input Work
@model6:~$ mkdir NewFolder
@model6:~$ ls
control Desktop Documents NewFolder Pictures texput.log tmp.input Work
@model6:~$ mv NewFolder/ Documents/
@model6:~$ ls
control Desktop Documents Pictures texput.log tmp.input Work
@model6:~$ cd Documents/
@model6:~/Documents$ ls
Chem137 COSMOS GroupPresentations Practice
Chem137LManual COSMOSWebsite NewFolder
@model6:~/Documents$ rm NewFolder/
rm: cannot remove `NewFolder/': Is a directory
@model6:~/Documents$ rm -r NewFolder/
@model6:~/Documents$ ls
Chem137 Chem137LManual COSMOS COSMOSWebsite GroupPresentations Practice
@model6:~/Documents$

```

Figure 1.4: This terminal does the following: change into the home directory, ls, make a new folder called NewFolder, ls the home directory to see the NewFolder, then remove the new folder with the “rm -r” command

```

@model6:~$ pwd
/modfac/home/peihsuay
@model6:~$ ls
control Desktop Documents Pictures texput.log tmp.input Work
@model6:~$ mkdir NewDirectory
@model6:~$ ls
control Documents Pictures tmp.input
Desktop NewDirectory texput.log Work
@model6:~$ cd NewDirectory/
@model6:~/NewDirectory$ ls
@model6:~/NewDirectory$ cd ..
@model6:~$ ls
control Documents Pictures tmp.input
Desktop NewDirectory texput.log Work
@model6:~$ rm -r NewDirectory/
@model6:~$ ls
control Desktop Documents Pictures texput.log tmp.input Work
@model6:~$ cd Documents/
@model6:~/Documents$ ls
Chem137 Chem137LManual COSMOS COSMOSWebsite GroupPresentations Practice
@model6:~/Documents$ cd ~
@model6:~$ ls
control Desktop Documents Pictures texput.log tmp.input Work

```

Figure 1.5: This terminal does the following: show the present working directory, make a new folder called NewDirectory, change directory into the NewDirectory, change directory back to home, remove NewDirecotry, change into Documents and then change back to the home directory


```

@model6:~$ pwd
/modfac/home/peihsuay
@model6:~$ ls
control Desktop Documents Pictures texput.log tmp.input Work
@model6:~$ mkdir NewDirectory
@model6:~$ ls
control Documents Pictures tmp.input
Desktop NewDirectory texput.log Work
@model6:~$ cd NewDirectory/
@model6:~/NewDirectory$ ls
@model6:~/NewDirectory$ cd ..
@model6:~$ ls
control Documents Pictures tmp.input
Desktop NewDirectory texput.log Work
@model6:~$ rm -r NewDirectory/
@model6:~$ ls
control Desktop Documents Pictures texput.log tmp.input Work
@model6:~$ cd Documents/
@model6:~/Documents$ ls
Chem137 Chem137LManual COSMOS COSMOSWebsite GroupPresentations Practice
@model6:~/Documents$ cd ~
@model6:~$ ls
control Desktop Documents Pictures texput.log tmp.input Work
@model6:~$

```

Figure 1.6: One method of completing Exercise 1

	A	B	C	D
1	Assignment No. 6: Inversion Barrier of Methethylamine			
2	By Name			
3				
4				
5				
6	Hartree			
7		Transition State Energy	Ground State Energy	Barrier Heights
8	BP86/SV(P)	-174.325509097	-174.331417424	.005908327
9	BP86/TZVP	-174.536954504	-174.544220169	.007265664
10	TPSS/TZVP	-174.557739890	-174.566643430	.008903540
11				
12				
13	Conversion (Hartree to Kcal/mol)		627.5	
14				
15	Kcal/mol			
16		Transition State Energy	Ground State Energy	Barrier Heights
17	BP86/SV(P)	-109389.256958368	-109392.964433686	3.707475318
18	BP86/TZVP	-109521.938951524	-109526.498155909	4.559204386
19	TPSS/TZVP	-109534.981781013	-109540.568752093	5.586971080

Figure 1.7: Organizing work with OpenOffice.org Spreadsheet.

1.3 Your UNIX User Account

You will receive a username (typically your UCINetID) and a password at the beginning of this course. The first thing to do in the lab is to log on a workstation and to change your password. Your new password should have at least 8 characters, include at least two numbers and two special characters. Your password should not contain your user name or any other words or personal information that can be easily found out (e.g. doing an internet search on your name), but you should be able to remember it. UNIX passwords are case-sensitive. To change your password, open up a shell terminal (clicking on the terminal icon on your application panel) and type:

```
passwd
```

You are personally responsible for your account including damage caused by abuse, so make sure your password is safe and do not share it with anyone. Please note that while you are free to use all installed software on the Modeling Facility workstations, it is illegal to copy or download installed proprietary software, even for your personal use.

Any computational project should be run on a local disc to avoid excessive network traffic. The default location is the so-called work disk. Create this directory and access it by doing the following:

```
mkdir work  
cd work
```

1.4 Basic UNIX Shell Commands

Table 1.1 lists some basic shell commands. For a more complete introduction to Linux see Ref. [3].

The default shell you will be using is the Bourne-again shell (bash). bash has a number of very useful command-line features listed in Table 1.2 you should familiarize yourself with.

1.5 The Vi and Emacs Editors

Vi is a basic UNIX text editor that is available in almost any UNIX environment. There are two basic modes in Vi, the command mode and the append mode. Table 1.3 summarizes useful vi commands.

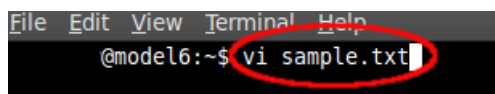


Figure 1.8: Starting Vi

A more user-friendly editor is Emacs (and its X-windows version, Xemacs). Emacs has many options and modes, and Table 1.6 displays only a small number of commands you need to get started with Emacs. You can access Emacs tutorials by clicking on “Help”.

There are a number of other text editors available. If you are used to Microsoft Word, try OpenOffice, which has word compatibility.

Another useful package is Open Babel [1] which is able to read, write and convert over ninety chemical file formats. This is particularly useful if the user wishes to open a certain file with different packages. For example, users could use OPEN BABEL when they wish convert a Protein Data Bank file (.pdb, standard format used by RCSB) that can normally be viewed with the VMD package to a XMOL molecule model file (XYZ, graphical coordinates) that can

Command	Description
pwd	Print working directory
ls	List all files in the current directory
ls -l	List all files in current directory with more details
cp file1 file2	Copy “file1” to “file2”
cp -r dir1 dir2	Recursively copy directory “dir1” to directory “dir2”
mkdir chemistry	Create directory “chemistry”
rmdir chemistry	Remove directory “chemistry”
cd chemistry/	Change working directory to “chemistry”
cd ..	Go to parent directory (..)
rm file1	Remove file1. Warning: once it’s gone, it’s gone
mv file1 file2	Rename “file1” to “file2”. Warning: if file 2 already exists it will be lost
mv * chemistry/	Move all files into the directory chemistry
find * -name *.pdf -print	Find all .pdf files in all directories and their subdirectories
cat file1	Print contents of file1 on screen
less file1	Pager that allows you to scroll through file1 pressing <space>
grep “string” file1	Search file1 for “string” and print matching lines
which openoffice	Shows location of executable “openoffice”
man (command)	Shows manual page for “command”
bzip2 file, bunzip2 file.bz2	Compresses/Uncompresses ‘file’
tar -vcjf dir.tar.bz2 *	Copy all files into compressed tape archive “dir.tar.bz2”
ps auwx	Print list of all running processes and their process IDs (PIDs)
kill <PID>	Kill (terminate) process
vi file1	Creates or opens file1 in the vi text editor
emacs file1	Creates or opens file1 in the emacs editor

Table 1.1: Basic shell commands

Command	Description
<UP>, <DOWN>	Scroll through command history
<CTRL>-r	Search command history
<TAB>	Automatic completion
<CTRL>-c	Abort present command
<CTRL>-z	Stop present command
<CTRL>-a, <CTRL>-e	Jump to beginning/end of line
<CTRL>-d, <ALT>-d	Delete character/word
ls -l — less	Combine or pipe two commands (pipe is “—”)
dscf > dscf.out	run program dscf and directs the output to “dscf.out”
dscf >> dscf.out	run program dscf and appends the output to “dscf.out”
define < define.input	run program define and redirects interactive input from file “define.input”
dscf &	Run program dscf in the background
nohup jobex &	Run program jobex in the background and continue running it even if the present shell is terminated
bg <PID>	Run (stopped) foreground process in the background
fg <PID>	Run (stopped) background process in the foreground

Table 1.2: Command-line features of bash

Command	Description
a	Enter append mode
i, I	Insert text before cursor position (goes into append mode)
<Esc>	Leave append mode
o, O	Open new line below/before the current line in append mode
x	Delete character under cursor
dd	Delete whole line
D	Delete line from cursor position to the end of the line
r	Replace character under cursor
R	Enter replace mode
:w (file1)	Save current contents (in file1)
:wq	Save file and exit vi
:q!	Exit without saving changes

Table 1.3: Table: Basic Vi commands.

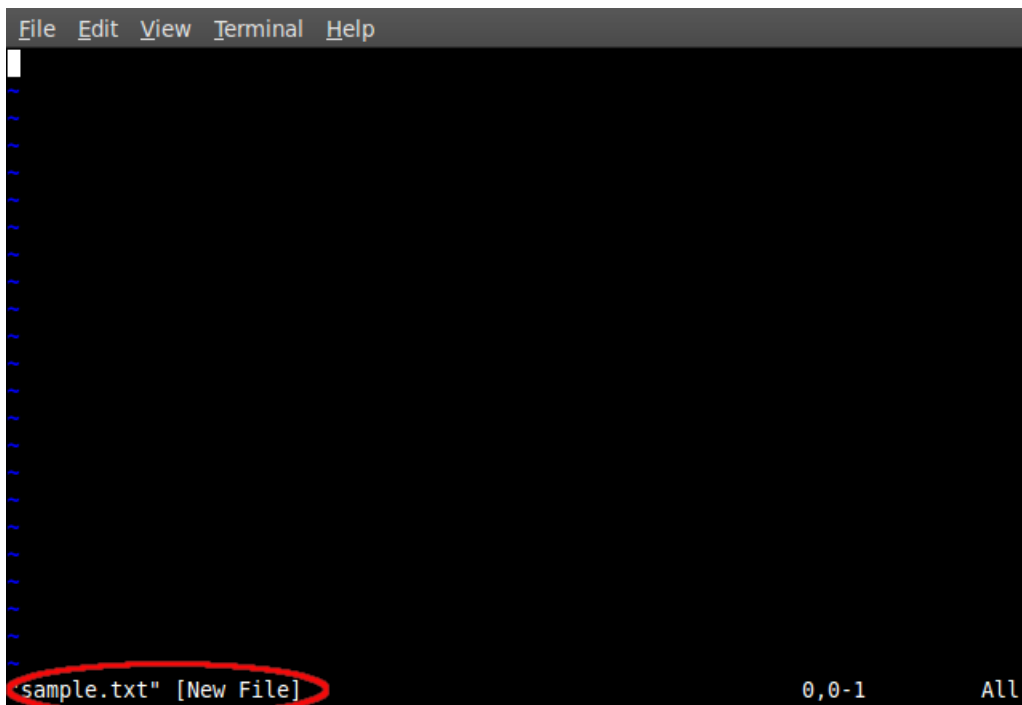
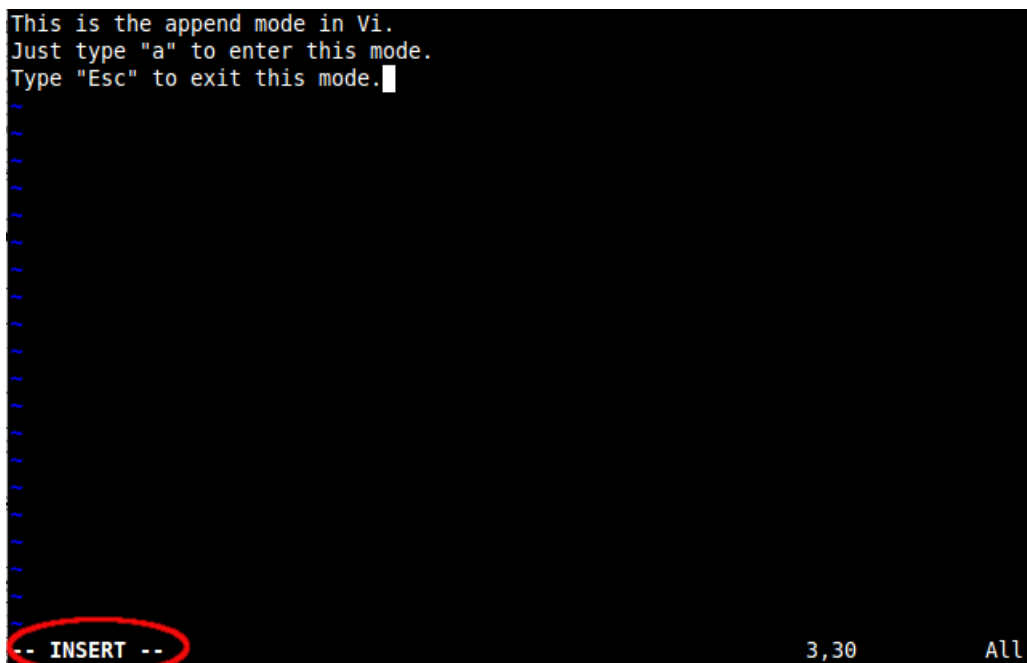


Figure 1.9: At start up, vi will enter the command mode, this mode can be verified by looking at the bottom left corner of the screen where the title of the document will be shown. In this case, sample.txt, is the new file that was created and is currently in the command mode of vi

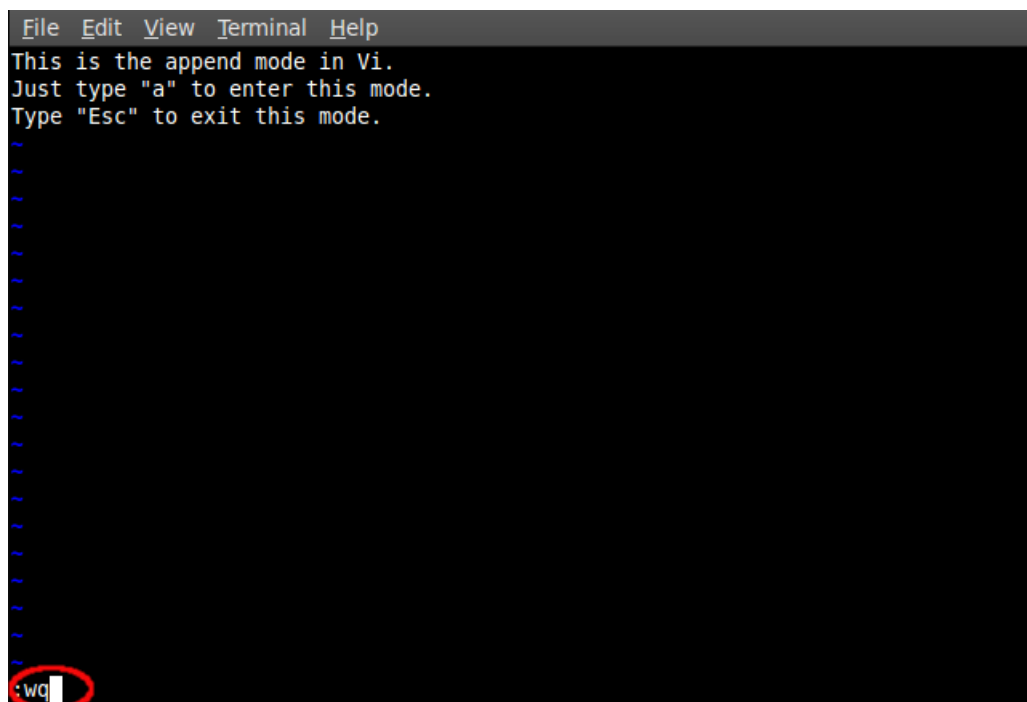
Command	Description
<CTRL>-x <CTRL>-a	Save file and exit emacs
<CTRL>-x <CTRL>-c	Exit emacs
<CTRL>-u	Undo
<CTRL>-k	Delete line from cursor on to the end of line
<CTRL>-<space>	Mark beginning of a selected region
<CTRL>-y	Paste region

Table 1.4: Useful key-combinations for the emacs editor



```
This is the append mode in Vi.  
Just type "a" to enter this mode.  
Type "Esc" to exit this mode.█  
  
-- INSERT -- 3,30 All
```

Figure 1.10: In order to start typing, enter the append mode by typing a. Type Esc to leave this mode. When using the append mode, INSERT will be shown on the bottom left corner of the screen



```
File Edit View Terminal Help  
This is the append mode in Vi.  
Just type "a" to enter this mode.  
Type "Esc" to exit this mode.  
  
:wq█
```

Figure 1.11: to save the document and exit the editor when finished, exit the append mode by entering the Esc key and :wq to save and quit the Vi editor.

be opened with AVOGADRO. The users could use Open Babel to convert the PDB file to an XYZ file through using the terminal 1.12 and then opening the files with the respective packages. A sample sequence of the result of this is shown in 1.13 and 1.14.

```
peihsuay@c2l6:~/Documents/Practice/PDB$ ls
3M4A.pdb  3M4A.pdb.gz
peihsuay@c2l6:~/Documents/Practice/PDB$ babel 3M4A.pdb 3M4A.xyz
1 molecule converted
174 audit log messages
peihsuay@c2l6:~/Documents/Practice/PDB$ ls
3M4A.pdb  3M4A.pdb.gz  3M4A.xyz
peihsuay@c2l6:~/Documents/Practice/PDB$
```

Figure 1.12: Using OPEN BABEL to convert a PDB file to a XYZ file

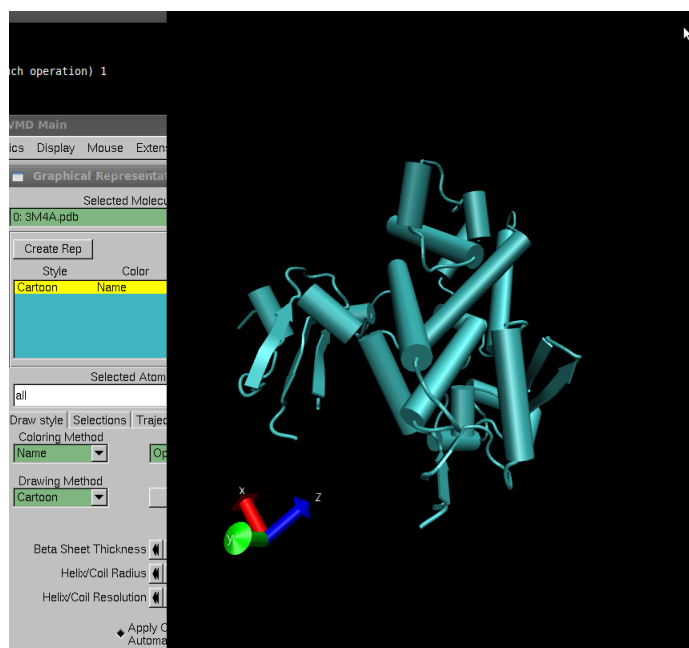


Figure 1.13: Opening the 3M4A.pdb file with VMD

1.6 UNIX File Systems

Unix keeps all files (including directories) using what is called a file system. After logging into your account, you will be placed in your home directory. Here you can create files, directories, and subdirectories. Your home directory is “mounted” on all Modeling Facility workstations and physically resides on the Modeling Facility Server. Your home directory (and all subdirectories) are backed-up in regular intervals.

Disk allocation is very important especially when dealing with I/O intensive calculations. The command “df -h” will print out the system hard disk space usage. This shows how much space is available and how much is being used in your main locations. The command “du -h” will list the disk usage in the current directory.

Any computational project should be run on a local disc to avoid excessive network traffic. The default location is the so-called work disk. Create this directory and access it by doing the following:

```
mkdir work
cd work
```

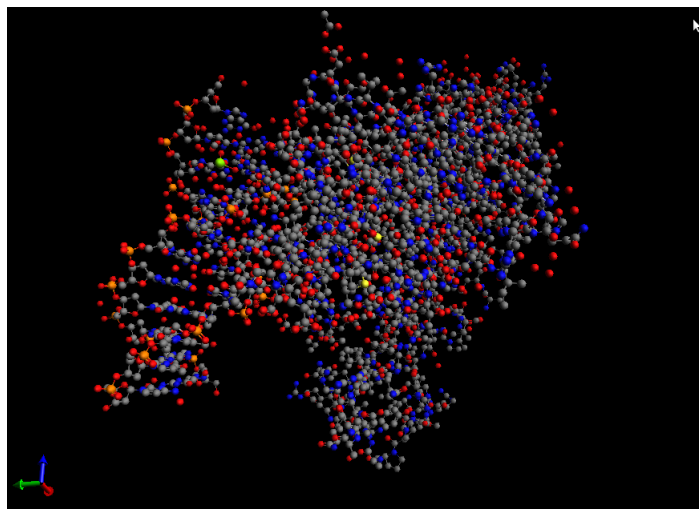


Figure 1.14: Opening the 3M4A.xyz file with AVOGADRO

Note that scratch disks are not backed up and may be lost in case of a hardware problem.

Organization is key in computational chemistry since files and results can easily get lost. You should organize your data using plenty and systematically clearly named subdirectories that can be easily understood and accessed. For example, don't put the calculations of two different molecules in the same directory and place all calculations with the same basis set in the same directory, etc.

1.7 The Builder Avogadro

The first step in a computational project is to build three-dimensional starting structures of the systems to be studied. These structures do not need to be accurate, but they should be a reasonable first guess to avoid convergence difficulties during subsequent structure optimizations. For example, a linear HOH molecule with O-H bond lengths of 200 pm is *not* a reasonable first guess for a water molecule.

The result of a build are files containing the Cartesian coordinates of all atoms. A common file format for Cartesian coordinates is the XYZ format. An example is shown in Fig. 1.15.

```
3
Energy = -75.93843413735
O    0.0000000    0.0000000   -0.0637470
H    0.7607968    0.0000000    0.5059245
H   -0.7607968    0.0000000    0.5059245
```

Figure 1.15: Cartesian coordinates of water [HF/SV(P)] in XYZ format. The units are Å. The first line contains the number of atoms. The second line is optional.

A molecular builder is a graphical interface that makes it easy to generate starting structures. There are various builders available in the Modeling Facility, including MOLDEN, ECCE, PYMOL, GAUSSVIEW, and SPARTAN. In this lab, we will use AVOGADRO [2], a free, easy-to-use molecular builder available for Linux, Mac, and Windows. It is started by entering

```
avogadro &
```

in a terminal. A screenshot of the graphical interface that should pop up is shown in Figure 1.16.

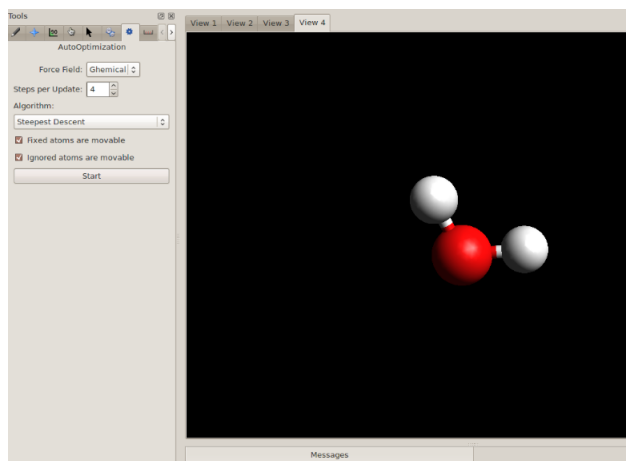


Figure 1.16: Screenshot of a molecular build using AVOGADRO.


Command	Description
Draw Tool	Create replace, and delete atoms and bonds
Navigation Tool	Rotate, zoom, and move molecule
Bond Centric Tool	Change bond lengths and angles
Manipulation Tool	Change atomic positions
Selection Tool	Select one or several atoms
Auto Rotation Tool	Rotate automatically
Auto Optimization Tool	Optimize structure using a force field
Measure Tool	Display bond lengths, angles and dihedral angles

Table 1.5: Basic AVOGADRO commands

By clicking on Help > Tutorials, you can access step-by-step tutorials explaining basic tasks. The most important functions are summarized in Table 1.5.

Another useful skill to learn with Avogadro is how to adjust bonds. Click on the Bond Centric Manipulate tool. Left click on the bond between either atom to change the angle on the other. Right click to elongate or to shorten the bond. Right or left click on the adjacent bond to adjust (Figure 1.17).

1.8 Bond Length and Angle Between Bonds

There are two ways to find the bond length depending on the number of significant figures desired (Figure: 1.19). The first way is to use the bond length inside tmolex3 which will give you a four significant figure value. To do this, click on the  show/build molecule button (the ladybug button) to open the TmoleX Visualization box and click on the bond of interest. The TmoleX Visualization will show the bond length (Å) in Bond properties box in the top right hand corner of the screen. The second way to find the bond length is through using the terminal window that you opened Tmolex3 with the command

```
tmolex3 &
```

On the terminal, change directory (cd) into the folder that contains the Tmolex3 job of interest. This folder should contain the coordinate (coord) and control files of the molecule. Then, type

```
dist _ _
```

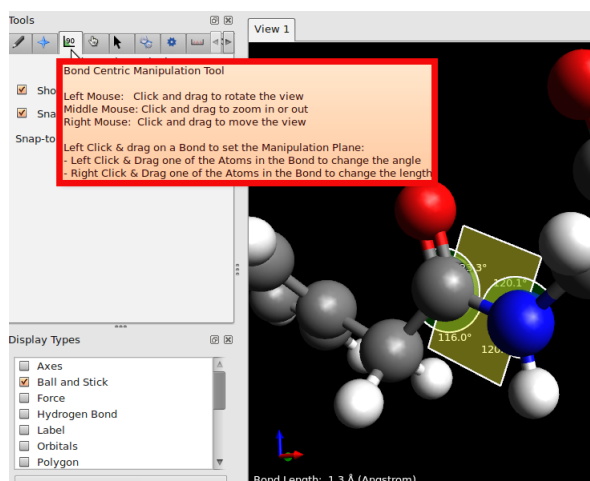



Figure 1.17: Adjusting bonds with AVOGADRO.

where the $_i$'s stand for the atom number Tmolex3 assigns to the specific atoms of interest in your molecule. The atom numbers can be found in the tab next to Objects when you click on the atom on the top right hand side of the TmoleX Visualization box (Figure: 1.18).

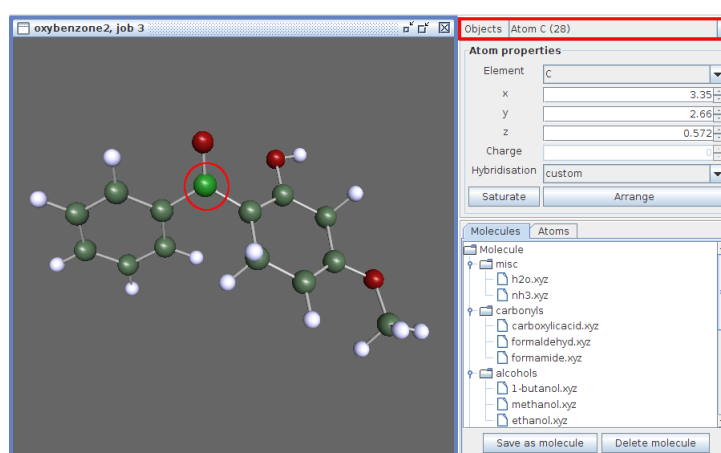



Figure 1.18: Selecting atoms on Tmolex3

There are a few methods of finding the bond angle between atoms. The first two ways listed here will be through using Tmolex3 and the other way will be with Avogadro. One way of obtaining the bond length is by clicking on the  show/build molecule button to open the TmoleX Visualization box, then select the bond lengths of the angle of interest (click one, hold shift, and click on the other one), and then clicking on Measure. This method will grant you a value with 5 significant digits. Another way to find the bond angle is through using the terminal window that you opened Tmolex3 with the command

```
tmolex3 &
```

Change directory into the folder that contains your calculations, make sure it contains the coordinate and control files. Then type

```
bend _ _ _
```

where the $_i$'s stand for the atom number Tmolex3 assigns to the specific atoms of interest in your molecule. Once again, the atom numbers can be found in the tab next to Objects when you

click on the atom on the top right hand side of the TmoleX Visualization box. With Avogadro: open molecule of interest, select the Bond Centric Manipulate Tool, and click on the bond angle of interest. This method will yield a value with 4 significant digits.

```
@model6:~$ ls
control Desktop Documents Pictures tmp.input Work
@model6:~$ cd Work/
@model6:~/Work$ ls
Benzene job_GEO_1 job_GEO_4 job_GEO_9 penicillin6
Benzene2 job_GEO_10 job_GEO_5 job_SP_8 water
carbon job_GEO_2 job_GEO_6 oxybenzone Work.backup
Ethene job_GEO_3 job_GEO_7 oxybenzone2 Work.tmole
@model6:~/Work$ cd oxybenzone2
@model6:~/Work/oxybenzone2$ ls
gsopt gsopt-correctedstruc oxybenzone2.tmole UvVisSpec
gsopt2 oxybenzone2.backup singleptenergy
@model6:~/Work/oxybenzone2$ cd gsopt-correctedstruc/
@model6:~/Work/oxybenzone2/gsopt-correctedstruc$ ls
auxbasis converged GEO_OPT CONVERGED job.last mos
basis coord gradient job.start statistics
control energy hessapprox message.output
@model6:~/Work/oxybenzone2/gsopt-correctedstruc$ dist 28 29
dist 28 c -- 29 o = 2.3227 au = 122.91 pm
@model6:~/Work/oxybenzone2/gsopt-correctedstruc$ bend 4 28 22
bend 4 c -> 28 c <- 22 c = 118.07 deg
@model6:~/Work/oxybenzone2/gsopt-correctedstruc$
```

Figure 1.19: Bend and Dist commands on the terminal.

1.9 Problems

Problem 1.1 (Terminal Commands). Do the following in a terminal and save the screenshot: Start at the home directory, check the present working directory, make a new folder called NewDirectory in the home directory, change into NewDirectory, change back into the home directory, remove the NewDirectory, change into the Documents folder, change directory back to the home folder.

Problem 1.2 (Initial Structures). Build reasonable initial structures of the following molecules.

1. B_2H_6
2. Adamantane
3. S_4N_4
4. P_4O_{10}
5. Bis(benzene)chromium

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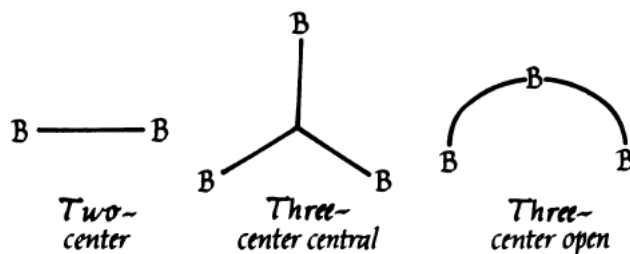
Chapter 2

Geometric and Electronic Structure of Boranes

2.1 Introduction

Boranes B_xH_y are among the most prominent examples of electron deficient compounds. These are molecules where the number of valence electrons is smaller than the number of accessible orbitals. A typical result of electron deficiency is delocalization of electron pairs over more than two atoms, leading to an unusual electronic structure that cannot be described with localized two-electron, two-center bonds. The tendency of boranes to form cages and clusters is also a direct consequence of this electron deficiency.

Explanation and prediction of the electronic structure of boranes was one of the early success stories of molecular orbital theory. Longuet-Higgins, the pioneer of theoretical borane chemistry, explained the unusual bridged structure of B_2H_6 in his undergraduate work with Bell [4]. Later Lipscomb and others used a combination of theoretical and experimental methods to establish a systematic theory of boranes (see Ref. [3] for a review). Over the past few decades, the scope of boron hydride chemistry has grown to include cages containing atoms other than boron, such as carbon in the carboranes and metals in the metallaboranes, where one or more boron atoms are substituted by metal atoms. Again, theoretical and computational chemistry has been vital for this development [8]. The success of theory in borane chemistry was bolstered by the fact that many boranes are difficult to characterize experimentally due to their instability and toxicity, and that electron correlation effects are relatively unimportant. Applications of boranes range from fuels to new carborane-based materials.



The three types of bonds within the boron framework of a borane structure, or an equivalent carborane structure, are a BB bond and the two types of three-center bonds. The open three-center bond is known only for BCB bonds, not BBB bonds.

Reference: Lipscomb, W. N., *Science* **196** (1977), 1047.

Figure 2.1: Three Center Bonds.

The simplest two-electron multi-center bonds occurring in boranes are:

1. Bridging BHB three-center bonds, which may be imagined to result from constructive interference of two B sp^2 hybrid and one H s orbitals
2. Closed BBB three-center bonds, resulting from constructive interference of three B sp^2 hybrid orbitals
3. Open BBB three-center bonds, resulting from constructive interference of two B sp^2 hybrid orbitals with a p orbital of the bridging B atom

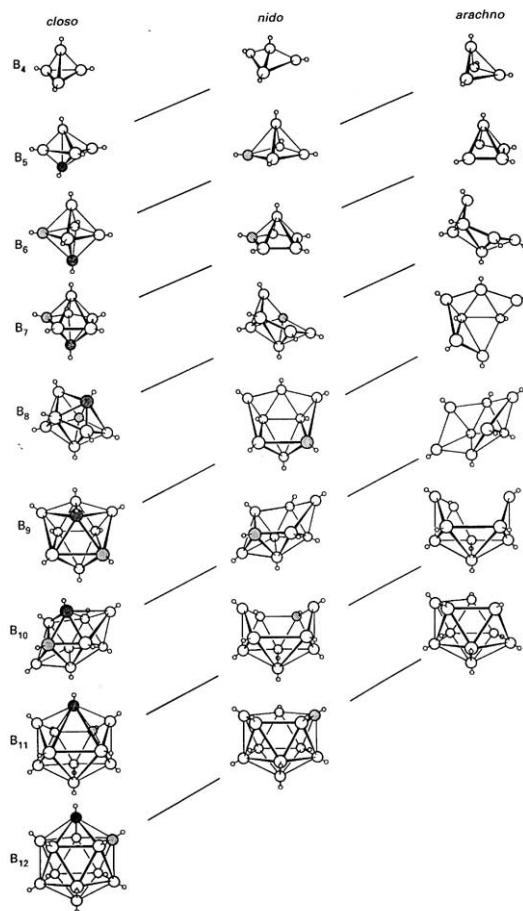


Figure 2.2: *Closo*, *nido*- and *arachno*-boranes

2.2 Wade's Rules

The structures of larger borane clusters can be predicted using Wade's rules. The boron cage is assumed to form a deltahedron, i.e. a polyhedron with triangular faces, see Tab. 2.1. Depending on the number of skeletal electron pairs, the deltahedral boranes are classified as *closo*-, *nido*-, or *arachno*- based on whether they represent a complete deltahedron, a deltahedron that is missing one or two vertices, see Fig. 2.2.

The general methodology to be followed when applying Wade's rules is:

1. Determine the total number of valence electrons from the chemical formula, i.e., 3 electrons per B, and 1 electron per H

Number of Vertices	Polyhedra
4	Tetrahedron
5	Trigonal Bipyramid
6	Octahedron
7	Pentagonal Bipyramid
8	Dodecahedron
9	Tricapped Trigonal Prism
10	Bicapped Square Antiprism
11	Octadecahedron
12	Icosahedron

Table 2.1: Deltahedral polyhedra with 4 to 12 vertices.

2. Subtract 2 electrons for each B-H unit.
3. Divide the number of remaining electrons by 2 to get the number of skeletal electron pairs (SEP).
4. A cluster with n vertices (i.e., n boron atoms) and $n + 1$ SEP for bonding has a *closo* structure.
5. A cluster with $n - 1$ vertices (i.e., $n - 1$ boron atoms) and $n + 1$ SEP for bonding has a *nido* structure.
6. A cluster with $n - 2$ vertices (i.e., $n - 2$ boron atoms) and $n + 1$ SEP for bonding has an *arachno* structure.

Example: Structure of B_5H_{11}

1. Total number of valence electrons: $5 \times 3 + 11 \times 1 = 26$
2. Number of electrons for each B-H unit: $5 \times 2 = 10$
3. Number of skeletal electrons: $26 - 10 = 16$
4. Number of SEP: $16/2 = 8$
5. $n + 1 = 8$ and $n - 2 = 5$ boron atoms, so $n = 7$
6. Structure of $n = 7$ is pentagonal bipyramid, therefore B_5H_{11} is *arachno*: Pentagonal bipyramid with two apexes missing

To explain how MO theory underlies Wade's rules we consider the anionic *closo* cluster $(B_6H_6)^{2-}$, see Fig. 2.4. The six boron atoms sit at the vertices of an octahedron. Each terminal hydrogen is bonded to boron in a normal two-electron two-center bond, where we conveniently assume *sp* hybridization of B here. If one *sp* hybrid is used for the terminal BH bonds, there are 3 B orbitals remaining to describe the skeletal electrons: One *sp* hybrid pointing radially into the center of the cage and 2 *p* orbitals tangential to the surface. The radial orbitals can form one low-lying totally symmetric molecular orbital which is strongly bonding. The 12 tangential orbitals can combine to 6 bonding and 6 antibonding MOs. 7 SEPs occupy exactly these 7 bonding orbitals, which explains the stability of the *closo* cage with 14 skeletal electrons.

Key assumptions of the Wade concept are:

- The use of a minimal valence basis with 2 tangential and one radial orbital per cluster atom

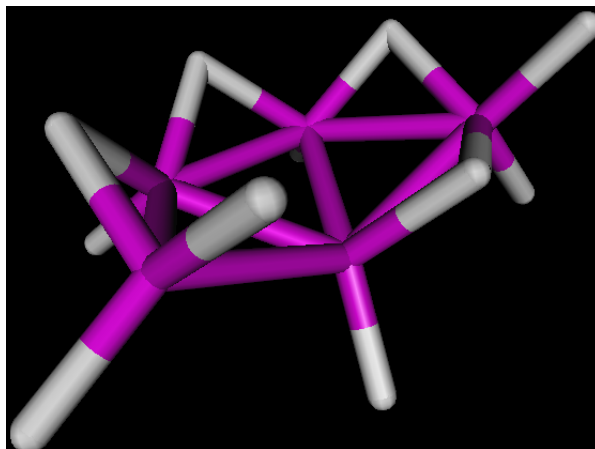
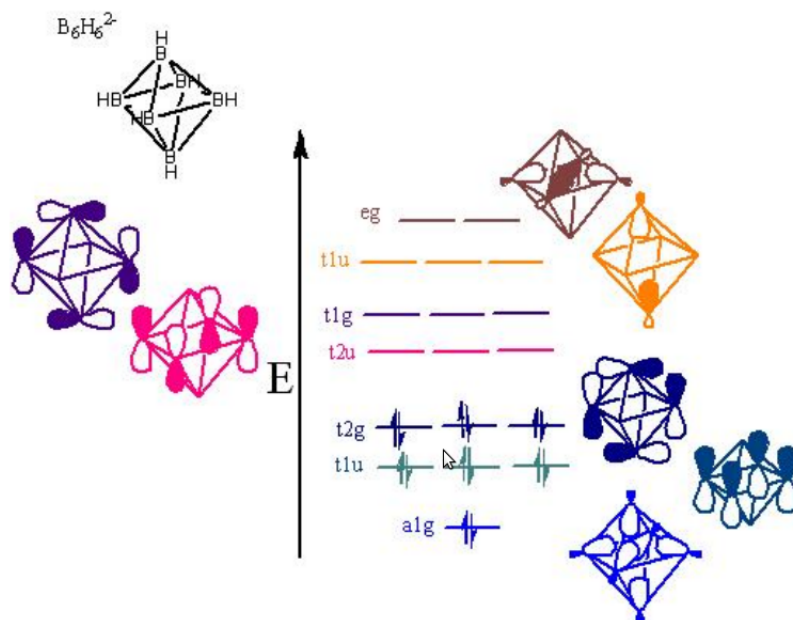
Figure 2.3: *Closo*, *nido*- and *arachno*-boranes

Figure 2.4: Qualitative MO diagram for $(B_6H_6)^{2-}$ [1]. Two p orbitals and an sp orbital are used as a basis for each boron vertex. Each Boron has three valence electrons one of which forms a bond with hydrogen. The remaining two electrons on each boron and the double negative charge contribute 14 electrons to the diagram

- The validity of the one-electron picture

Wade's rules have been applied to many other electron-deficient cluster compounds, including metal clusters and even main group clusters [5]. It is important to keep in mind that the Wade rules are a qualitative concept and exceptions are common.

Question: Structure of $B_6H_6^{-2}$ Apply Wade's rules to this structure to confirm that it corresponds to a closo structure

2.3 Diborane


We will perform an electronic structure calculations to investigate the geometry and the bonding in diborane using the TURBOMOLE package. A convenient tool to set up a TURBOMOLE calculation is the TMOLEX graphical user interface, which is invoked by the command:


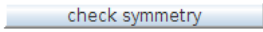

```
tmolex3 &
```

Before the session starts, you need to specify a project directory. This directory should be on the local /work partition under your user name. When you generate new directories make sure you follow good computational practice as outlined in Chapter 1.

2.3.1 The Geometry Menu

The first step is to establish the molecular geometry. In this menu, you can add atoms and enter their coordinates manually, or delete selected atoms from the list using the right mouse button. Although TMOLEX has some building capabilities, it is often advantageous to build the coordinates using an external program and import them. In other situations, you might start from a set of experimental coordinates, e.g. from X-ray analysis.


To import B_2H_6 atomic coordinates in XYZ format, use the  button in the left upper corner. A list of all atoms should show up on the screen.

You can check the structure by clicking the  button. Before proceeding, it is always a good idea to check for molecular symmetry. If your starting structure already has (approximately) the right symmetry, clicking  should automatically detect the correct symmetry elements and display the correct Schönflies symbol. You can also enforce a certain symmetry using . This option will automatically add symmetry equivalent atoms as needed.

2.3.2 The Atomic Attributes Menu

Here you can choose the basis sets and establish non-default charges or atomic masses (e.g. for isotope effects in IR spectra). The default basis set SV(P), is fine for an initial structure optimization.

2.3.3 The Molecular Attributes Menu

In this menu you can generate the initial set of molecular orbitals (MOs) and occupation numbers. By clicking , an extended Hückel theory (EHT) calculation will be performed, and the results will be displayed on the screen. While EHT works quite well in determining the correct occupation for many large-gap molecules, it can fail for small-gap cases, e.g. transition metal clusters. It is important to check at least that the spin multiplicity determined from EHT is physically reasonable.

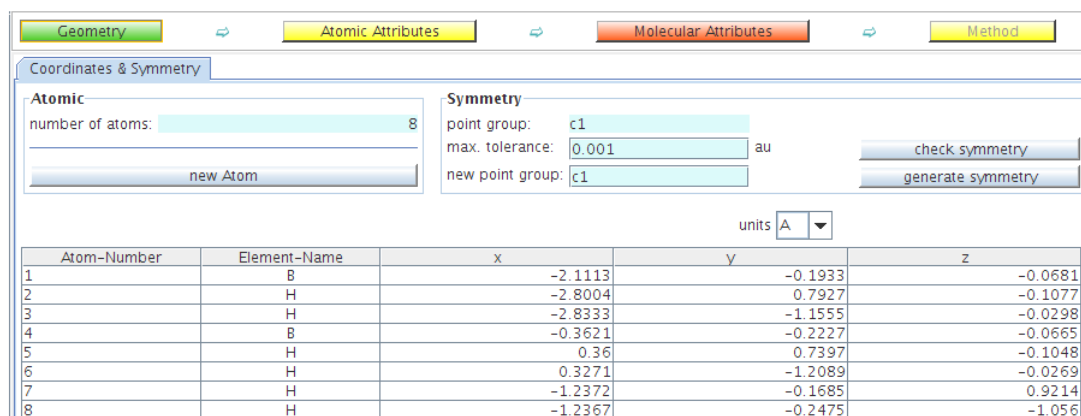


Figure 2.5: The TMOLEX geometry menu

2.3.4 The Method Menu

Here you can choose the actual electronic structure method. For our present purpose, the default (density functional theory using the Becke-Perdew86 functional) is sufficient. The RI approximation should be used whenever possible.

2.3.5 Running Your Job

In the **Start Job** menu you can choose between a single-point calculation or a complete geometry optimization. Typically, you start with a geometry optimization with default convergence criteria.

Once you have a converged geometry, you should check whether you have found a minimum or a transition state using the “frequency analysis” option. For a minimum, all vibrational frequencies of the molecule should be positive.

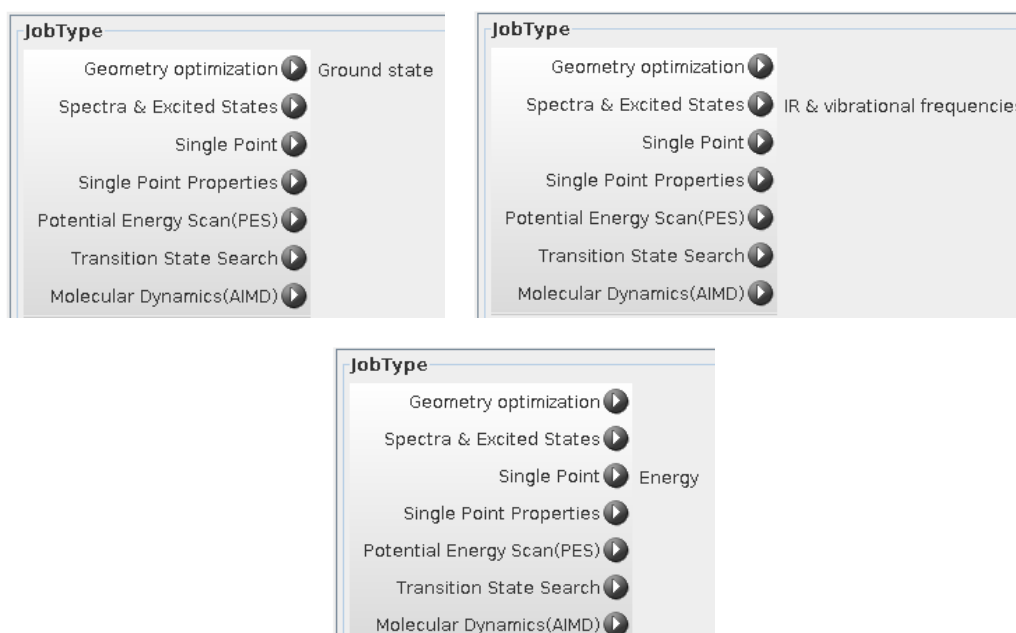



Figure 2.6: Location of the three types of calculations needed

2.3.6 Analyzing the Results

Most geometric properties can be displayed using the  function. This function also allows you to view and plot molecular orbitals (under “orbital viewer”) and visualize molecular vibrations, if they have been computed.

2.4 Problems

Problem 2.1 (Electronic Structure of Diborane). Perform a structure optimization of diborane using the TURBOMOLE default density functional and basis set (BP/SV(P)/RI).

1. Compare the optimized structure to the following accurate coupled cluster calculation and experiment.

	B–B	B–H _b	B–H _t	∠(H _t BH _t)
CCSD(T)	174.7	132.8	118.2	122.08
Exp.	173.3	131.4	118.4	121.5

Table 2.2: Structure parameters of B₂H₆. Bond lengths are in pm, bond angles in degrees. Coupled cluster (CCSD(T)/cc-pVTZ) results are from Ref. [6]. Experimental data (rotational spectroscopy) are from Ref. [2].

2. Visualize the molecular orbitals and identify the two bonding orbitals responsible for the two BHB bridges. Determine the orbital energies.

Problem 2.2 (Electronic Structure of B₆H₆²⁻). Build this molecule, perform a ground state geometry optimization, and visualize the orbitals. Compare these computed orbitals to the qualitative MO diagram 2.4. Can you find any orbitals that look exactly like the ones in the figure? If not, then why are these qualitative diagrams still used?

Problem 2.3 (Closed BBB Three-Center Bonds). In Ref. [7], Subotnik, Sodt, and Head-Gordon claim that ammonia triborane, see Fig. 2.7, is the smallest stable molecule supporting a closed, three-center BBB bond. Perform an electronic structure calculation using TURBOMOLE defaults (BP86/ SV(P)/RI) to investigate this claim. Visualize and plot the relevant molecular orbital(s).

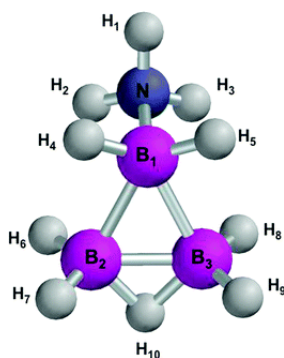


Figure 2.7: Structure of ammonia triborane, NH₃B₃H₇.

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Chapter 3

Introduction to Thermochemistry

3.1 Introduction

Theoretical thermochemistry aims to predict thermodynamic functions such as energies, enthalpies, and free energies and their changes in chemical reactions and any physical transformations, such as phase transitions. Often, thermochemical calculations are performed for a single molecule in the gas phase at 0 K; corrections for thermal and other effects are usually much smaller and can be added later. Tab. 3.1 lists the contributions to a typical experimental reaction enthalpy.

Contribution to ΔH_r°	Order of magnitude (kcal/mol)
Electronic	10-100
Zero point vibrational energy (ZPVE)	1-2
Thermal	1-2
Post Born-Oppenheimer	< 1
Relativistic	< 1 (light elements)

Figure 3.1: Contributions to gas phase reaction enthalpies and their typical order of magnitude

Thermodynamic functions such as enthalpies are typically dominated by electronic contributions. We will focus on purely electronic reaction energies in this chapter.

3.2 Important Reaction Types

3.2.1 Atomization Reactions

Any reaction energy can be computed from differences of atomization energies. However, the practical value of atomization energies is somewhat limited by the difficulties in measuring and calculating these quantities.

Measurement of atomization energies typically involves nebulizing the chemical and torching it at high temperatures or using arch discharges. The actual atomization energy is obtained from mass spectrometry and photoionization spectroscopy or a combination of both. Compared to conventional calorimetry experimental errors in these methods tend to be large.

Calculation of atomization energies involves free atoms. Especially open-shell atoms are difficult for many single-reference methods such as Hartree-Fock, since they have small gaps and low-lying excited states.

Whereas errors in computed atomization energies are often systematic and tend to cancel in reaction energies, this is not necessarily true for experimental errors.

3.2.2 Isogyric, Isodesmic, and Homodesmotic Reactions

Following Pople and co-workers [2], we may define special classes of reactions particularly suitable for thermochemical purposes [3]:

- Isogyric reactions: The number of electron pairs is conserved
- Isodesmic reactions: Isogyric reactions that conserve the number and type of bonds
- Homodesmotic reactions: Isodesmic reactions that conserve the hybridization and number of bonds of each atom

The concept of homodesmotic reactions is mostly limited to organic reactions in the literature. Examples are shown in Fig. 3.2.2.

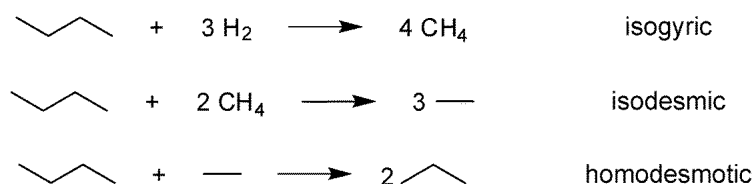
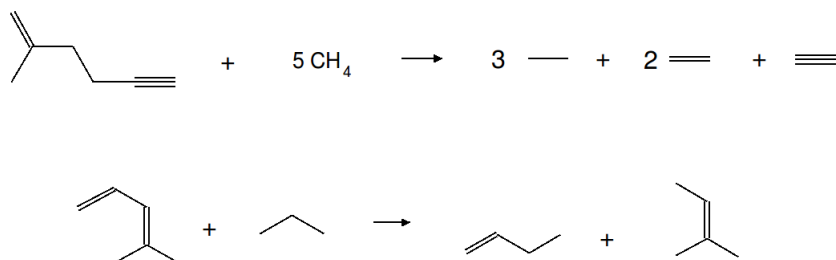


Figure 3.2: Isogyric, isodesmic, and homodesmotic decomposition of butane

The advantage of these reactions is that their reaction enthalpies can be computed with high accuracy using common electronic structure methods. This may be used to compute accurate enthalpies of formation and other thermochemical data. For example, if the enthalpies of formation of ethane and propane are accurately known, the third reaction in Fig. 3.2.2 can be used to compute the enthalpy of formation of butane accurately.

Question: Categorize the following two reactions



3.3 Theoretical Models

A model chemistry is a method and basis set combination that

1. is fully specified by choosing the method and basis set, and allows no other user choices (e.g. parameters),
2. can be applied indifferently to a range of systems (ideally the entire periodic table),
3. is size consistent,
4. yields energies and their derivatives for all nuclear positions.

Model chemistries are the most useful theoretical methods for chemistry, because

- they can be evaluated rigorously,
- they can be applied to a variety of systems and properties,
- they do not require excessive expertise (e.g. in choosing certain parameters to get “good” results),
- they have the highest predictive power.

Using a well-established and validated model chemistry is generally a much better approach than attempts to engineer a method (e.g. by arbitrarily changing parameters) to give “perfect agreement” with experiment.

The first step in a computational project is often to build a hierarchy of model chemistries. This is usually done by validation for a small model compounds that reflect key aspects of the system of interest.

Usually, a method and basis set combination is denoted by “method/basis set”, e.g. HF/SV(P). Additional information, e.g. use of the RI approximation, may be added with another slash.

3.4 Problems

Problem 3.1 (Model Chemistries for Reaction Energies). Consider the reactions and experimental reaction energies in Table

3.1.

Reaction	Exp.
$\text{HOOH} + \text{H}_2 \rightarrow 2 \text{H}_2\text{O}$	83
$\text{C}_2\text{H}_4 + 2 \text{CH}_4 \rightarrow 2 \text{C}_2\text{H}_6$	-17
$\text{CH}(\text{CH}_3)_3 + 3 \text{CH}_4 \rightarrow 3 \text{C}_2\text{H}_6$	7.5
$\text{CH}_3\text{F} \rightarrow \text{CH}_3 + \text{F}$	114

Table 3.1: Experimental reaction energies (kcal/mol; extrapolated to 0 K and corrected for zero point vibrational energy) from Ref. [1].

1. Optimize the structures of all occurring species using BP86/SV(P)/RI. Confirm that your structures are minima by frequency analysis.
2. Compare the BP86 results to single-point Hartree-Fock, B3LYP, and TPSSH energy calculations using the same structures and basis sets. Report the results in a table.
3. Perform single point BP86/def2-TZVP calculations to check the basis set dependence of your results. Report the results in a table.

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Chapter 4

Structure and Properties of Carbenes

4.1 Introduction

Carbenes $RR'C$ are electron deficient compounds formally containing a carbon atom with six rather than eight valence electrons. The prototypical carbene is methylene, CH_2 .

Carbenes can have singlet or triplet ground states. In singlet carbenes, the sextet carbon is approximately sp^2 hybridized, with one sp^2 hybrid occupied by two spin-paired electrons. The remaining p orbital is unoccupied. The RCR' angle is typically around 100° , see Fig. 4.1.

Carbenes with a triplet ground state are either linear or bent, corresponding to sp or sp^2 hybridization of the sextet carbon. The two unpaired electrons occupy two (different) orbitals. The RCR' angle in most triplet carbenes varies between 125 and 140° , see Fig. 4.1.

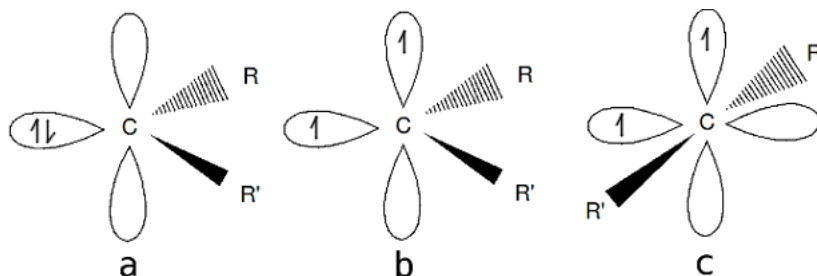


Figure 4.1: Electronic structure of singlet, bent triplet, and linear triplet carbenes

While methylene has a triplet ground state, π donating substituents (e.g. halogens) stabilize the singlet ground state. In inorganic carbene analogues such as Silylenes or Germylenes, the increasing s - p separation tends to stabilize the singlet ground state which has a higher total s occupation.

Although most carbenes are short-lived intermediates, they play an important role in preparative organic chemistry. In inorganic chemistry, transition metal carbene complexes have attracted much attention. Partly due to the elusive nature of most carbenes, theoretical chemistry contributed crucially to many aspects of carbene chemistry. For example, the bent structure of methylene was first predicted by accurate calculations [2].

A number of stable carbenes (also called persisten or Arduengo carbenes) are known [1]. Stable carbenes include diaminocarbenes $(R_2N)_2C$. The R groups can be bridged resulting in a heterocyclic carbene. Typically, R are bulky alkyl or aryl substituents that sterically hinder dimerization and other reactions. Stable singlet carbenes can be isolated and stored. A fairly stable triplet carbene was reported in 2001 [3].

4.2 Heavy Carbene Analogs and the Trinquier-Malrieu Rule

Carbenes and their heavier analogues dimerize forming unsaturated (pseudo) alkenes,



Despite the formal analogy with alkenes, silaalkenes ($X=Si$) and germaalkenes ($X=Ge$) are typically not planar, exhibiting pyramidalization of the X atom.

Using semi-empirical valence bond and MO arguments, Trinquier and Malrieu explained this unusual behavior by the tendency of heavier carbene analogues to have singlet ground states: While triplet carbenes can dimerize forming a π and a σ bond, singlet carbenes should dimerize in a fashion reminiscent of dative bonds, see Fig. 4.2, leading to pyramidalization.



Figure 4.2: Dimerization of triplet and singlet carbenes.

Trinquier and Malrieu proposed the following simple rule to decide whether a pseudoalkene is planar or bent [4]:

1. Determine

$$\Delta = \frac{1}{2}E_{\sigma+\pi} - \sum \Delta E_{ST}, \quad (4.1)$$

where $E_{\sigma+\pi}$ is the $X=X$ $\sigma + \pi$ bond energy and ΔE_{ST} is the sum of the singlet-triplet energy differences of the fragments.

2. For $\Delta > 0$, the dimer is planar, for $\Delta \leq 0$, the dimer is bent.

4.3 Computing Singlet-Triplet Gaps

Generally, the lowest state of a given spin multiplicity can be computed self-consistently using HF or density functional methods. It is important to pay attention to the occupation numbers and resulting spin multiplicities when setting up a calculation.

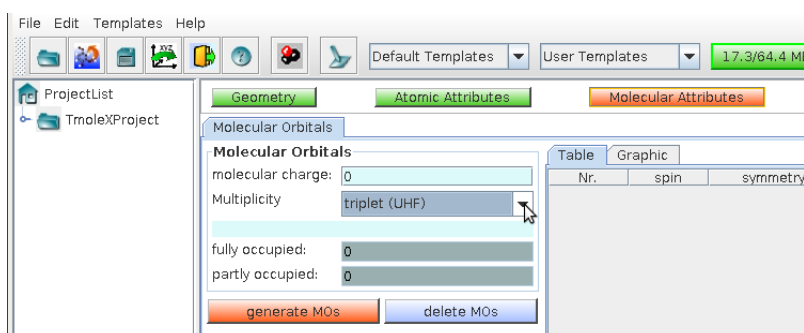


Figure 4.3: Choosing a triplet occupation in the TMOLEX molecular orbital menu. This option can only be changed before generating orbitals..

Figure 4.3 shows a screenshot of the TMOLEX molecular orbital menu where a triplet occupation has been selected for CH_2 . Once the occupation numbers are specified, the geometry optimization proceeds as in the spin-restricted case.

4.4 Problems

Problem 4.1 (Trinquier-Malrieu Rules).

1. Determine the adiabatic singlet-triplet splittings of CH_2 , SiH_2 , and GeH_2 at the B3LYP/def2-TZVP level. Explain the observed trend.
2. Optimize the structures of $\text{H}_2\text{C}=\text{CH}_2$, $\text{H}_2\text{Si}=\text{SiH}_2$, and $\text{H}_2\text{Ge}=\text{GeH}_2$ using the same method. If the structure is non-planar, compute the planarization barrier. Compare your results to the predictions of the Trinquier-Malrieu rule.

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Chapter 5

Vibrational Spectroscopy of Transition Metal Nitrosyls

5.1 Introduction

Nitrosyl complexes have attracted much attention due to their rich redox chemistry and their biological importance [3]. Density functional calculations are a well-established tool to investigate the structure and properties of transition metal nitrosyls [2]. In this chapter we will investigate the electronic structure of a simple dinuclear transition metal nitrosyl by vibrational spectroscopy.

5.2 Electronic Structure of the NO ligand

Figure 5.1 shows a qualitative MO diagram of NO. The binding of NO to metal atoms may be

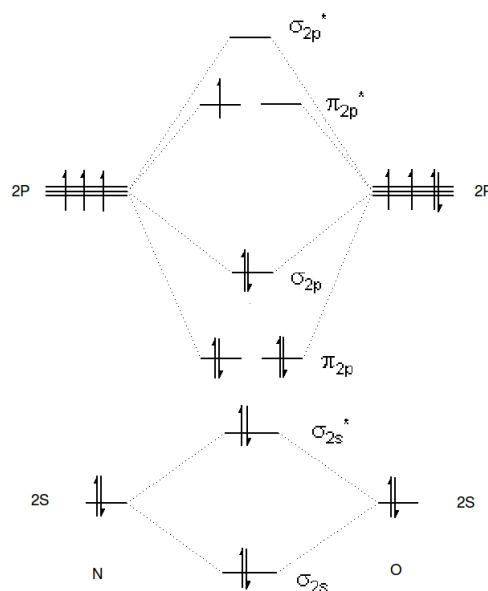


Figure 5.1: Simple MO diagram of NO

explained in terms of the following two mechanisms:

1. The occupied 5σ (denoted σ_{2p} in the figure) orbital can donate electron density into empty metal orbitals (“ σ donation”)

2. The empty 2π (denoted π^*_{2p} in the figure) orbitals can accept electron density from occupied metal orbitals) (“ π back-donation”)

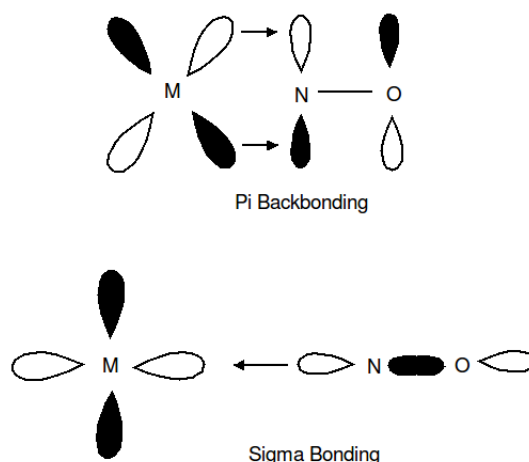


Figure 5.2: Bonding schemes

For an effective bonding, the ligand and the metal orbitals must have the right symmetry, they must overlap, and be similar in energy.

π back-donation leads to a decrease of the N–O bond order which can be correlated to the N–O bond length and stretching frequency.

Question: Bonding and backbonding

- Which diatomic ligand would not be able to backbond to a metal?
- When would it be energetically unfavorable for a metal to accept backbonding electrons?
- Show how an H_2 ligand could potentially form a bond with a metal and the direction of electron donation?
- How is the angle of the M–N–O correlated to the amount of backbonding present in the system?

5.3 The 18 Electron Rule

Transition metal complexes tend to form stable closed-shell configurations if the metal atoms have an 18 valence electron environment. This 18 electron rule is analogous to the octet rule in main group chemistry. It is motivated by the fact that Kr has 18, not 8 valence electrons if the 10 $3d$ electrons are included. There are many exceptions from the 18 electron rule, but it is a useful basic concept to understand the stability of certain transition metal complexes.

Table 5.1 contains some common ligands in organometallic chemistry and their valence electron count for coordinative bonds. Metal atoms are considered neutral in this model.

For example, both $Cr(C_6H_6)_2$ and $Fe(CO)_5$ satisfy the 18 electron rule.

Question: 18 electron rule Using the 18 electron rule, answer the following

- What is the oxidation state of Iron in Iron pentacarbonyl?
- What is the structure of Nickel carbonyl and Chromium carbonyl?

Ligand	Valence Electrons
CO	2
PR ₃	2
N ₂ (term.)	2
Carbene	2
η^2 -alkene	2
η^3 -allyl	3
NO	3
C ₅ H ₅	5
C ₆ H ₆	6

Table 5.1: Valence electron count for ligands.

5.4 Infrared Vibrational Spectroscopy

In a classical picture, the nuclei satisfy Newton's Equations of motion,

$$M_I \ddot{\mathbf{R}}_I - \mathbf{F}_I = 0. \quad (5.1)$$

At a minimum of the potential energy surface, the potential energy has the following Taylor expansion:

$$V = V_0 + \frac{1}{2} \sum_{\alpha, \beta=x,y,z} \sum_{IJ} \frac{\partial^2 V}{\partial R_{I\alpha} \partial R_{J\beta}} R_{I\alpha} R_{J\beta} + O(R^3) \quad (5.2)$$

V_0 is simply the total electronic energy at the bottom of the potential well. All first-order derivatives vanish at a minimum. The matrix of second derivatives, also called nuclear Hessian,

$$H_{I\alpha J\beta} = \frac{\partial^2 V}{\partial R_{I\alpha} \partial R_{J\beta}}, \quad (5.3)$$

is the central quantity for harmonic vibrational analysis. TURBOMOLE and other quantum chemistry codes include methods to compute the Hessian analytically or by finite differences.

De-coupling of the equations of motion (5.1) is achieved by solving the eigenvalue problem

$$\mathbf{H}\mathbf{X} = \mathbf{T}\mathbf{X}\boldsymbol{\lambda}, \quad (5.4)$$

where

$$T_{I\alpha J\beta} = M_I \delta_{IJ} \delta_{\alpha\beta} \quad (5.5)$$

contains the atomic masses and $\boldsymbol{\lambda}$ is diagonal. The eigenvectors \mathbf{X}_i are called vibrational normal modes, and the corresponding vibrational frequencies are

$$\omega_i = \sqrt{\lambda_i}. \quad (5.6)$$

5.5 Problems

Problem 5.1 (Nitrosyl Complexes). Dicyclopentadienyldichromium tetranitrosyl was synthesized and characterized by X-ray analysis and vibrational spectroscopy in 1974 [1].

1. Perform a BP86/SV(P) calculation of the structure and vibrational frequency of free NO for reference.
2. Optimize the structure of this dinuclear chromium complex at the BP86/SV(P) level using C_i symmetry. Compare the result to the X-ray data in Tab. 5.2.

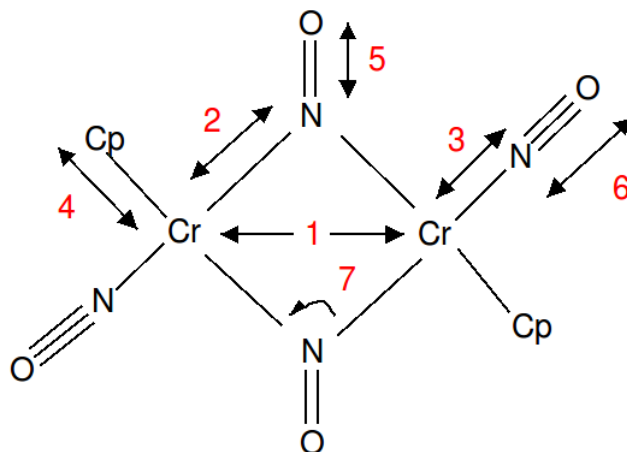


Figure 5.3: Dicyclopentadienyldichromium tetranitrosyl

Label	Parameter	Value
1	Cr–Cr	261.5
2	Cr– η^2 -NO	196.0
3	Cr– η^1 -NO	169.0
4	Cr–C	220.9
5	η^2 -N–O	119.3
6	η^1 -N–O	118.1
7	Cr– η^2 -NO–Cr	86.7

Table 5.2: X-ray structure parameters of Dicyclopentadienyldichromium tetranitrosyl. Bond distances are in pm, bond angles in degrees.

3. Perform a BP86/SV(P) harmonic vibrational frequency calculation. Use `tmolx3` to identify the bridging and terminal N–O stretching vibrational frequencies. Compare to the experimental results of 1518 and 1677 cm^{-1} . Why are there *four* N–O stretching frequencies in the computed spectrum?
4. Explain the observed trend in N–O distances and vibrational frequencies going from free over terminal to bridging NO ligands.

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Chapter 6

Inversion Barrier of Amines

6.1 Introduction

Due to the pyramidal coordination of nitrogen, organic amines $\text{NR}_2\text{R}'\text{R}''$ are chiral. The two enantiomers are related to each other by inversion of the N configuration. The goal of this lab is to determine the nitrogen inversion barrier computationally by a transition state optimization.

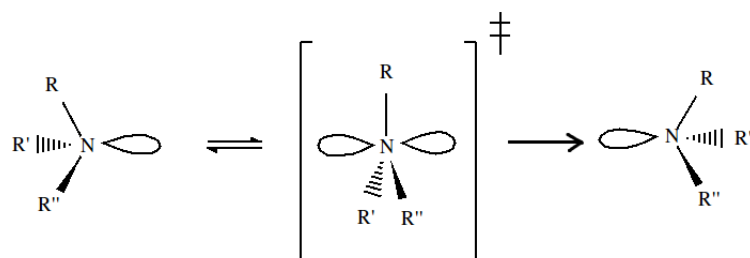


Figure 6.1: Inversion of an amine displaying a planar transition state

6.2 Transition State Theory

Transition state theory assumes that every elementary chemical reaction step proceeds through a “transition state” which is higher in energy than both the reactants and products[1].

A transition state is a first-order saddle point on the molecular potential energy surface, defined as follows:

- The energy is stationary, i.e., the energy gradients are zero corresponding to no net force on the nuclei
- There is *exactly one* imaginary harmonic vibrational frequency, which belongs to the reaction coordinate.

According to transition state theory, there exist a “quasistable” intermediate that exists in a small region of the reaction coordinate between the reactants and products [2].



Where AB^\ddagger is the transition state. An equilibrium constant can be defined based on the following concentrations.

$$K_C^\ddagger = \frac{[AB^\ddagger]/c^o}{[A]/c^o[B]/c^o} = \frac{[AB^\ddagger]/c^o}{[A][B]} \quad (6.2)$$

where c^o is the standard-state concentration. Expressing this formula in terms of the partition function gives the following relation. [1]

$$K_C^\ddagger = \frac{(q^\ddagger/V)c^o}{(q_A/V)(q_B/V)} \quad (6.3)$$

The rate law for this reaction is given by

$$\frac{d[P]}{dt} = k[A][B] = \nu_c[AB^\ddagger] \quad (6.4)$$

meaning that the rate constant k times the concentration of either starting reactants is equal to the concentration of the activated transition state times ν_c the frequency at which the system crosses over the saddle point.

Using the previous relations and some algebra

$$k[A][B] = \nu_c \frac{[A][B]K_C^\ddagger}{c^o} \quad (6.5)$$

or

$$k = \frac{\nu_c K_C^\ddagger}{c^o} \quad (6.6)$$

The translational part of the partition function [2] can be separated from q^\ddagger as a multiplicative value.

$$q^\ddagger = q_{int}q_{trans} = q_{int} \frac{(2\pi m^\ddagger k_B T)^{1/2}}{h} \delta \quad (6.7)$$

Where m^\ddagger is the mass of the transition state, δ is the infinitesimal region in the saddle point where the transition state resides q_{trans} is the translational part of the partition function, and q_{int} is the partition function of the remaining internal degrees of freedom. Applying this relation to the reaction rate gives the following expression

$$k = \nu_c \frac{(2\pi m^\ddagger k_B T)^{1/2}}{h} \delta \frac{(q_{int}^\ddagger/V)c^o}{(q_A/V)(q_B/V)} \quad (6.8)$$

δ and ν_c as a product can be defined as the average speed of crossing through the transition state barrier. This expression is found using the Maxwell-Boltzmann distribution.[3]

$$u_{ave} = \nu_c \delta = \frac{k_b T}{hc^o} K^\ddagger \quad (6.9)$$

adding this to the rate equation gives

$$k = \frac{K_B T}{hc^o} \frac{(q_{int}^\ddagger/V)c^o}{(q_A/V)(q_B/V)} = \frac{K_B T}{hc^o} K^\ddagger \quad (6.10)$$

Now that an equation that relates the rate constant to the equilibrium constant of the transition state has been found, The Gibbs free energy of transition state activation can be defined as

$$\Delta^\ddagger G^o = -RT \ln K^\ddagger \quad (6.11)$$

Therefore

$$k(T) = \frac{K_B T}{h c^o} e^{-\Delta^\ddagger G^o / (RT)} \quad (6.12)$$

Here $\Delta^\ddagger G^o$ denotes the Gibbs free activation energy, R is the ideal gas constant, h is planck's constant, T is temperature in Kelvin, and K_B is Boltzmann constant. $\Delta^\ddagger G^o$ may be computed from the Gibbs free energy difference of the transition state and the reactant. A problem that arises is that the energy $\Delta^\ddagger G^o$ is not the same as the activation energy, that is, the energy obtained from the difference in potential energies of the transition state and reactants $\Delta^\ddagger E^o$. Fortunately at low temperatures, $\Delta^\ddagger G^o$ is dominated by $\Delta^\ddagger E^o$ [4]

Question: Thermodynamic potentials

- Why is it not possible to obtain the Gibbs free energy from single molecule transition state energy calculation?

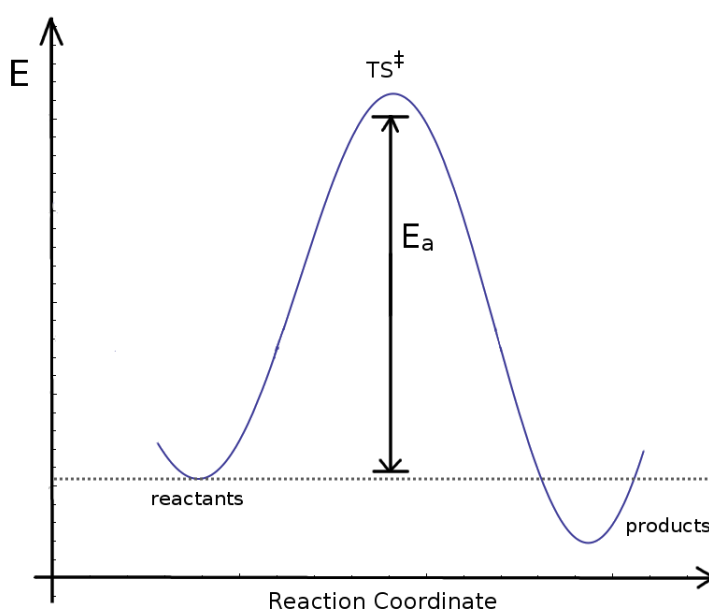


Figure 6.2: Inversion Reaction

6.3 Finding Transition States

The main task in a barrier height calculation is optimization of the structure of the relevant transition state(s). This is more difficult than finding a minimum on a potential energy surface because the transition state represents a maximum with respect to the reaction coordinate.

Transition state optimization generally proceeds as follows:

1. Optimize the structures of the reactant and the product
2. Guess the structure of the transition state, e.g. by constrained optimization
3. Perform a transition state search
4. Characterize the resulting transition state by vibrational analysis

The key to success is to guess an internal coordinate close to the true reaction coordinate. If this coordinate is well chosen, constrained optimization will lead to a suitable starting structure for the subsequent transition state search.

6.4 Problem: Inversion Barrier of Methylethylamine

Chiral methylethylamine racemises by nitrogen inversion. Is it possible to separate the enantiomers of methylethylamine at room temperature?

1. Perform a BP86/SV(P) optimization of methylethylamine.
2. Constrain a C-N-C angle to a value you expect to find in the transition state for the nitrogen inversion and optimize using BP86/SV(P).
3. Perform a transition state search using the same method and verify that you have found a transition state by vibrational analysis.
4. Compute the barrier height from your converged BP86/SV(P) results as well as single point BP86/TZVP and TPSS/TZVP calculations. Compare to experimentally determined barrier heights for similar amines, which are in the range of 8-9 kcal/mol [D. A. Forsyth, S. M. Johnson, *J. Am. Chem. Soc.* 116 (1994), 11481].
5. In view of your results, is it worth trying to separate the enantiomers of methylethylamine at room temperature?

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Chapter 7

UV Spectroscopy of Aromatic Hydrocarbons

7.1 Introduction

So far, this course has been concerned with properties of the electronic ground state. When molecules are electronically excited, their physical and chemical properties often change dramatically. Molecules often can be electronically excited by electromagnetic radiation in the visible (VIS) or ultraviolet (UV) spectrum [2].

According to the Franck-Condon principle, electronic excitations are *vertical*, i.e., there is no nuclear relaxation during an electronic transition. In the simplest case, the absorption maximum in a UV-VIS spectrum is located at the vertical transition energy,

$$E_n(X) - E_0(X) = \frac{hc}{\lambda}, \quad (7.1)$$

where X denotes the nuclear coordinates of the electronic ground state minimum, h is Planck's constant, c the speed of light, and λ the absorption wavelength.

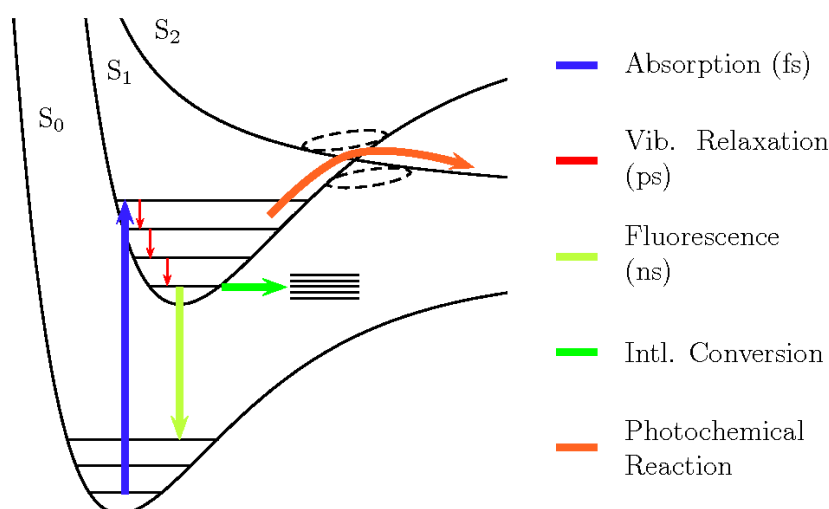


Figure 7.1: Elementary photochemical processes

7.2 Selection Rules

Within the dipole approximation, the transition probability for an electronic excitation from the ground to the n -th excited electronic state is proportional to the square of the electric transition dipole moment,

$$\boldsymbol{\mu}_{0n} = - \int d\tau \Psi_0^* \mathbf{r} \Psi_n. \quad (7.2)$$

$\boldsymbol{\mu}_{0n}$ is non-zero if the direct product of the electronic ground and the excited state irreducible representations of the molecular point group contain the dipole representation.

The frequency integral of an absorption band is proportional to the oscillator strength

$$f_{on} = \frac{2}{3} (E_n - E_0) |\boldsymbol{\mu}_{0n}|^2. \quad (7.3)$$

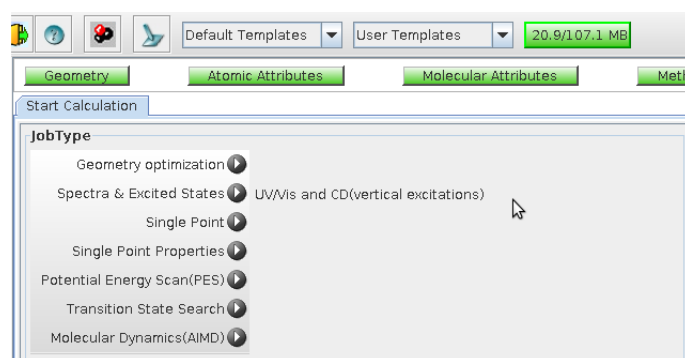
7.3 Time-Dependent Response Theory

Molecular UV-VIS spectra can be efficiently computed using time-dependent response theory [1]. The underlying idea is to apply a monochromatic external perturbation (e.g. by an electric field) of frequency ω , and to consider the time-dependent response of a system variable such as the dipole moment. When the frequency ω equals an electronic excitation energy of a dipole-allowed transition, the linear response diverges (resonance catastrophe).

7.4 Problems

Problem 7.1 (UV Spectroscopy of a Sunscreen Dye). The benzophenone derivative oxyphenone [(2-Hydroxy-4-methoxyphenyl)- phenylmethanone] is widely used in commercial sunscreen due to its strong absorption in the UV.

1. Optimize the structure of oxyphenone at the BP86/SV(P)/RI level.
2. Generate PBE0/SV(P) molecular orbitals (MOs) in a single-point calculation.
3. Perform a vertical excitation energy calculation using PBE0/SV(P). Include 5 excited states. *Hint*: Detailed results are displayed when you press the “output” button.



4. Assign the first band at 330 nm in the experimental absorption spectrum of oxybenzone [3] using your results: First, determine which excited state(s) is/are mainly responsible for the band. Remember that the SV(P) basis set is rather small, so one expects a slight overestimation of the computed excitation energies. Second, extract the involved single-orbital transitions from the output and analyze the MOs graphically.


```

4 singlet a excitation
Total energy: -764.7591765316365
Excitation energy: 0.1727565754634497
Excitation energy / eV: 4.700947615908430
Excitation energy / nm: 263.7430878550837
Excitation energy / cm^(-1): 37915.68560083730

Oscillator strength:
velocity representation: 0.9241673073759383E-02
length representation: 0.7357280209624003E-02
mixed representation: 0.8241712393870853E-02

Rotatory strength:
velocity representation: -0.1450615410760845E-03
velocity rep. / 10^(-40)erg*cm^3: -9.371674228828130
length representation: -0.1282512892966877E-03
length rep. / 10^(-40)erg*cm^3: -8.285650998877363

Dominant contributions:
occ. orbital energy / eV virt. orbital energy / eV |coeff.|^2*100
57 a -7.63 61 a -1.98 77.1
58 a -7.45 61 a -1.98 7.9
56 a -7.83 61 a -1.98 5.6

```

Figure 7.2: Example of the fourth singlet excitation in the output file showing the energy, oscillator strength, and orbital-orbital excitations. In this example, electrons in orbitals 57 58 and 56 with coefficients 77.1,7.9, and 5.6 are making a transition into orbital 61. In order for the contribution of this excitation to be significant, the oscillator strength should be at the order of 0.01

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Appendix A

Appendix I: Software

A.1 Molecular Builders

There are various builders available in the Modeling Facility, including Molden, Ecce, Pymol, GaussView, Spartan, Avogadro and Visual Molecular Dynamics (VMD). These programs all have their advantages and disadvantages.

A.2 File Conversion Tool

Open Babel is a useful file conversion tool that is able to read, write and convert over 90 chemical file formats.

A.3 TURBOMOLE

TURBOMOLE is a licensed software by GmbH developed by Prof. Dr. Reinhart Ahlrichs, Prof. Dr. Philipp Furche, Prof. Dr. Christof Hättig, Prof. Dr. Willem M. Klopper, PD Dr. Marek Sierka, and PD Dr. Florian Weigend. There are two main methods of running this program: through the terminal (through using define) or through using the graphical user interface (tmolex3). As with terminal commands, it is essential to learn how to use the terminal method during research. For more information on TURBOMOLE, see the Official TURBOMOLE GmbH Website, Turbomole Manual, and the Turbomole Tutorial Version 5-10.

Appendix B

Additional Resources

B.1 Computational Chemistry

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B.2 Physical Chemistry

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B.3 Other

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