MAGYARORSZÁG - ROMÁNIA
ÉS MAGYARORSZÁG - SZERBIA ÉS MONTENEGRÓ
Határon Átnyúló Együttműködési Program

INTERREG IIIA Community Initiative Program

Szegedi Tudományegyetem **Prirodno-matematički fakultet, Univerzitet u Novom Sadu**

„Computer-aided Modelling and Simulation in Natural Sciences“
University of Szeged,
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Molecular Design and Quantum Chemistry

edited by Béla Viskolcz

Contents:

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1 Introduction

Most of the organic compounds have a structurally well defined carbon skeleton, frequently denoted by R (the first letter of the word: Radical) and carry a single functional group (G)

$$\mathrm{R - G}$$

1.1.1—1. eq.

Simple examples of these molecular structures are:

$$\mathrm{R - Cl} \quad \text{An organic halide}$$

1.1.1—2. eq.

$$\mathrm{R - OH} \quad \text{An organic alcohol}$$

1.1.1—3. eq.

The purpose of classical organic chemistry is to study the structure of organic molecules and the reaction which interconverts one organic structure to another. These interconversions or chemical reactions need some reagents which may be inorganic or organic:

$$\text{Structure}_1 \xrightarrow{\text{Reagent}} \text{Structure}_2$$

1.1.1—4. eq.

$$\mathrm{R - G_1} \xrightarrow{\text{Reagent}} \mathrm{R - G_2}$$

1.1.1—5. eq.

$$\mathrm{R - Cl} \xrightarrow{\mathrm{OH^-}} \mathrm{R - OH + Cl^-}$$

1.1.1—6. eq.

When we are dealing with the structure of organic molecules we are concerned with the architecture of the molecule and the architecture is three dimensional. The 3D-structural chemistry is frequently referred to as stereochemistry.

Molecular structure is very important not only because it is pre-requisite knowledge for organic synthesis but also because it predetermines the physical property, chemical reactivity and biological activity of the organic molecule in question. In other words the architecture or the structure of the molecules is an independent variable, while

Physical properties

1.1.1—7. eq.

Chemical reactivities

1.1.1—8. eq.

Biological activities

1.1.1—9. eq.

are dependent variables. Consequently, we can specify symbolically such functional dependence:

Property=f(structure)

1.1.1—10. eq.

Reactivity=F(structure)

1.1.1—11. eq.

Activity=f(structure)

1.1.1—12. eq.

Yet, we are not sure, at this time, of the explicit functional dependence. Thus, we may only guess on the basis of accumulated experience what molecular structure will give us a bright red color, what structural feature of a plastic may enhance chemical or biodegradability and what drug candidate could perhaps have the desired pharmacological effect. In other words, at this point in history, we are not in the position to do precise molecular engineering, i.e. to design a molecular structure that delivers the desired physical, chemical and biological characteristics. One may anticipate, at this time, that a great deal of advancement along this line will occur in the 21st century.

1.1 Experimental Background

1.1.1 Stable structures and Transition States

The term stable structure refers to the structure of a molecule with the lowest (minimum) internal energy (E) over a range of geometrical distortions, which the molecule can have.

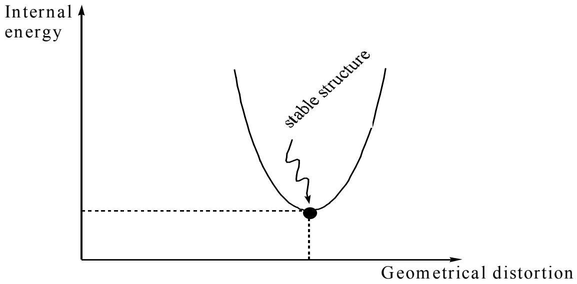

Figure. 1.1.1—1. A schematic illustration showing that a stable structure corresponds to a minimum of internal energy.

When comparing two different structures the energy difference (ΔE) is a measure of their relative stabilities.

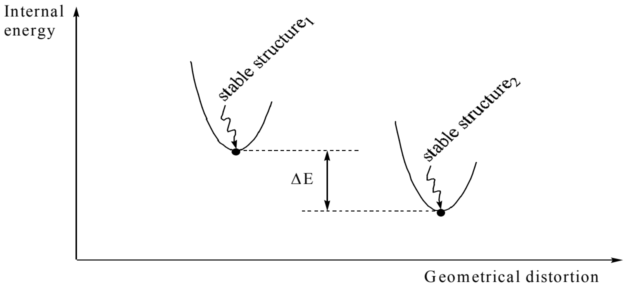

Figure. 1.1.1—2. A schematic illustration showing that the energy differences (ΔE) is a measure of relative stability.

If there is a path between the two minima, i.e. if the system can go from one minima to another, then ΔE is related to the equilibrium constant (K) between the two stable structures

$$\text{stable structure}_1 \xrightleftharpoons{K} \text{stable structure}_2$$

1.1.1—1. eq.

If there is a path between the two structures, the geometrical distortion necessary to go from stable structure_1 to stable structure_2 is called the reaction coordinate. The reaction coordinate measures the reaction's progress from one structure to another. In a one-step reaction the energy rises to a maximum value, then lowers as it passes along the reaction coordinate from the reactant state (R) to the product state (P). The energy maximum between R and P is normally referred to as the transition state and is frequently denoted as TS or ‡. [11] The variation in energy along the reaction coordinate is frequently called the energy profile of the chemical change from reactant to product.

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[1] Ruff, Csizmadia Fizikai szerves kémia

$$R \rightarrow [TS^{\ddagger}] \rightarrow P$$

1.1.1—2. eq.

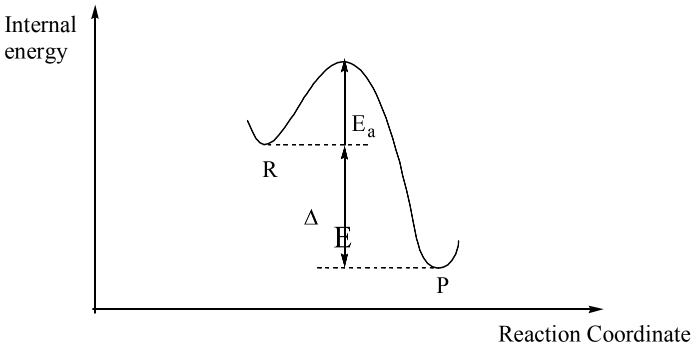


Figure 1.1.1—3. A schematic illustration showing the reaction profile for a one-step reaction.

While ΔE is related to the equilibrium constant (K), the energy of activation (E_a), or the barrier height, predetermines the specific rate (k), or specific velocity of the reaction

$$k = Ae^{-Ea/RT}$$

1.1.1—3. eq

where A is the frequency factor, R is the universal gas constant and T is the absolute temperature.

A reaction intermediate is also an energy minimum. Thus, for an overall reaction there must be two transition states, one proceeding and one following a reaction intermediate (I)

$$R \rightarrow [TS^{\ddagger}_{1}] \rightarrow I \rightarrow [TS^{\ddagger}_{2}] \rightarrow P$$

1.1.1—4. eq.

The corresponding reaction profile is shown in Figure 1.1.1—4

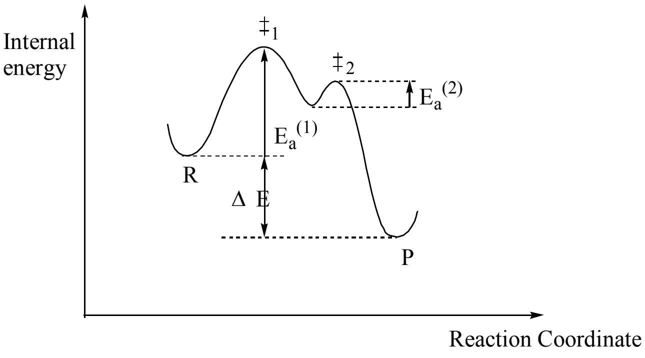


Figure 1.1.1—4. A schematic illustration showing the reaction profile for a two-step reaction.

Usually the first step, characterized by $E_a^{(1)}$, determines the overall rate of the reaction to a good degree of approximation. The possession of this information will enable us to consider the details, the mechanism, of the chemical reaction. Now we can expand on our description of what the purpose of organic chemistry is. The purpose of modern organic chemistry is to study the structure of organic molecules and their reactions as well as the mechanisms involved in converting one organic structure to another.

In order to illustrate this, let us reconsider the reaction presented in the Introduction as shown in 1.1.1—6. eq.:

$$\underset{\text{Bond breaking}}{HO^{-}+R\text{-}Cl} \longrightarrow \underset{\text{Bond makeing}}{HO\text{-}R+Cl^{-}}$$

1.1.1—5. eq.

In this reaction, we are breaking one bond and making another bond. In principle, we have two mechanisms, but if the bond breaking and bond making are occurring simultaneously, then we have a one-step or concerted mechanism:

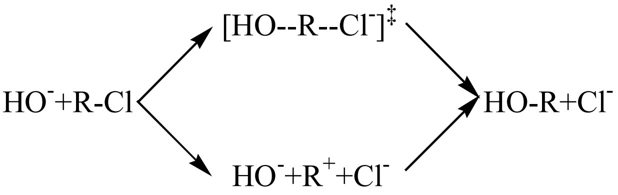
$$HO^{-}+R\text{-}Cl \longrightarrow [HO\text{--}R\text{--}Cl^{-}]^{\ddagger} \longrightarrow HO\text{-}R+Cl^{-}$$

1.1.1—6. eq.

Such a reaction is an example of a substitution (S), i.e. Cl is substituted by HO. Since the reagent $HO^{(-)}$ is negatively charged and, therefore, nucleophilic (N) or “nucleus-loving” and because two (2) molecules (i.e. $HO^{(-)}$ and R-Cl) are involved in the reaction, this reaction path is called an S_N2 mechanism. In this case the reaction profile will look something like the one shown in Figure 1.1.1—3

In contrast to the above, if the bond breaking precedes the bond making, then only one molecule is involved; and therefore this nonsynchronous or stepwise path is called an S_N1 mechanism. In this case, the bond breaking process clearly leads to a stable intermediate; thus, the reaction profile will be like the one shown in Figure 1.1.1—4.

The two mechanisms are shown together in1.1.1—7. eq.:



1.1.1—7. eq.

There are two questions associated with competing mechanisms such as the ones shown in1.1.1—7. eq. First of all "which mechanism will dominate the reaction?" The answer to this question is simple; the mechanism which is faster will dominate the reaction, and the one that has the smallest overall activation energy (E_a), i.e. the lowest barrier height, will be the faster one. The second question is "what makes one barrier lower than the other?" The answer to this question is "the molecular structure". This was hinted at in the Introduction in equation 11 eq. Three molecular structures are given below. In Case I, the S_N2 mechanism dominates. In Case II, a mixture of S_N1 and S_N2 mechanisms occurs side by side and in Case III the S_N1 mechanism dominates.

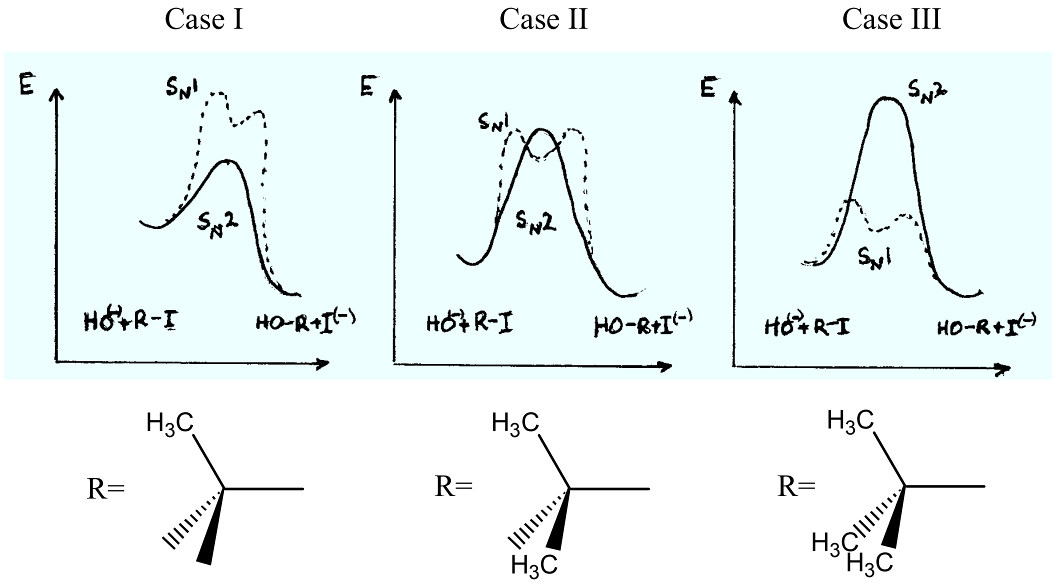


Figure 1.1.1—5. A schematic illustration of how structural change (i.e. a variation in R) can influence the dominating reaction mechanism. [See appendix 1]

1.1.2 Fundamentals of Thermodynamics and Kinetics

Both thermodynamics and kinetics are important in the elucidation of reaction mechanisms. The area of investigation of these two topics is illustrated by the figure below.

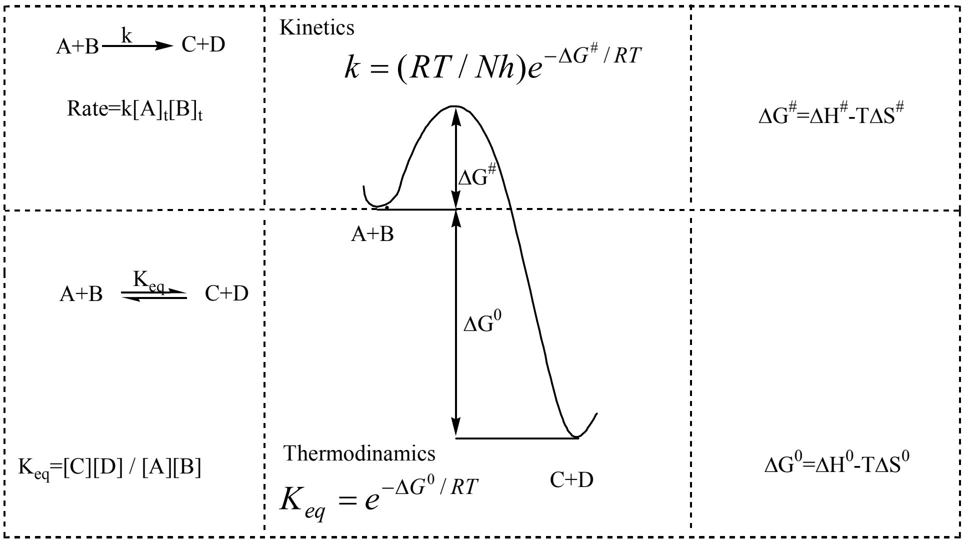
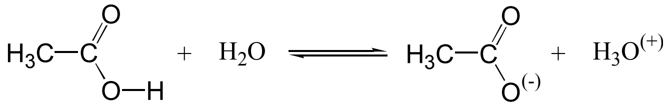


Figure1.1.2—1. A schematic illustration of the effective domain of thermodynamics and kinetics in studying chemical reactions.

Since not all reactions reach the equbrium we shall illustrate the thermodynamics of reactions via the ionization of acids, which almost always reach equilibrium within a short time.

The thermodynamics of equilibria

As may be inferred from **Hiba! A hivatkozási forrás nem található.**, proton transfer reactions are very fast because the energy barriers (‡$_1$ and ‡$_2$) along the reaction coordinates are very small. Consequently, proton transfer equilibrium is established almost immediately.



1.1.2—1. eq.

$$K_{eq}= \frac{[CH_3COO^{(-)}]\,[H_3O^{(+)}]}{[CH_3COOH]\,[H_2O]}$$

1.1.2—2. eq.

As 1.1.2—1. eq. indicates, the equilibrium in this case is shifted to the left; thus, less than 50% of acetic acid is dissociated in aqueous solution. The energetics of the process certainly predetermines the position of the equilibrium and, therefore, the equilibrium constant K_{eq}. For this reason, a review of the basic principles of thermodynamics (usually taught, but seldom learned in first year chemistry courses) is in order.

There are two ways to carry out an experiment, at constant pressure or at constant volume. Most of our experiments are done in open vessels and the atmospheric pressure is usually constant during the experiment. For a constant volume experiment, we need a sealed piece of equipment usually referred to as an autoclave, like a pressure cooker. The two modes of measurements, constant volume and constant pressure, yield slightly different results and we need to give different names to these thermodynamic functions.

At constant volume, the observed heat of the reaction corresponds to the energy change (ΔE) and at constant pressure the heat of the reaction corresponds to the enthalpy change (ΔH). These two quantities do not differ from each other by very much; fundamentally the difference is due to $\Delta(PV)$. Sometimes the difference is only RT which amounts to 0.6 kcal/mol at 300K. However, the distinction between ΔE and ΔH is important. Since most of our experiments are carried out at constant pressure, ΔH is quoted more often than ΔE. We might mention, in passing, that in Quantum Chemistry, ΔE needs to be augmented by a correction term to obtain ΔH.

Thermal energy or enthalpy cannot freely be converted to work. In other words, the conversion efficiency can never be 100%! The reason for this is due to the fact that thermal energy and enthalpy are partially disordered and only the ordered portion can be converted to work. The extent of disorder is proportional to the absolute temperature, T(K), and the proportionality constant is called the entropy change: ΔS

$$\text{Extent of disorder} = T\Delta S$$

1.1.2—3. eq.

This quantity, the extent of disorder, is the same for the energy and the enthalpy change. Consequently, the portion of the energy, which is freely convertible to work, the “free energy” or “Helmholz free energy”, corresponds to the following difference (Volume = const.):

$$\Delta A = \Delta E - T\Delta S$$

1.1.2—4. eq.

One may write a similar difference for the enthalpy (Pressure = const):

$$\Delta G = \Delta H - T\Delta S$$

1.1.2—5. eq.

This quantity (ΔG) denotes “free enthalpy”, but it is usually referred to as “Gibbs free energy” in honour of the great thermodynamicist Josiah W. Gibbs (1839-1903) who was professor at Yale from 1869 until 1903.

The equilibrium constant K_{eq}, such as the one given in 1.1.3-2 for the ionization of an acid, is related to ΔG° according to 1.1.3-7. Note that superscript ° in ΔG° implies standard Gibbs free energy at 1 atm pressure for gases and 1M concentration for solutions.

$$K_{eq} = e^{-\Delta G°/RT}$$

1.1.2—6. eq.

$$\Delta G° = -2.303RT \log K_{eq}$$
$$\text{or } \Delta G° = -RT \ln K_{eq}$$

1.1.2—7. eq.

where R = 1.987 cal/mol ≈ 0.002 kcal/mol/K and T is the absolute temperature in Kelvin units; [i.e., T(K) = 273.2 + t (°C)]. This equation clearly shows that the driving force for any reaction is ΔG°. If $\Delta G° \ll 0$ the reaction is driven to the right ($K_{eq} \gg 1$); if $\Delta G° \gg 0$ then $K_{eq} \ll 1$, and if $\Delta G°=0$ then $K_{eq}=1.0$. [For further exercise see appendix 5]

2 White papers

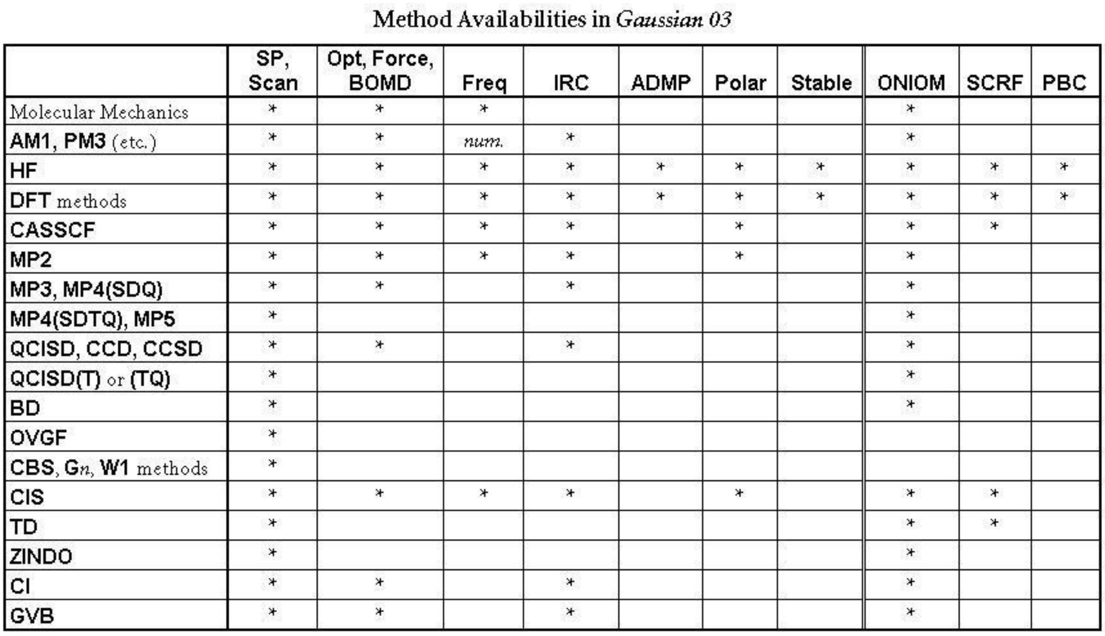
Gaussian 03 Online Manual

Last update: 2 October 2006

Model Chemistries

The combination of method and basis set specifies a model chemistry to *Gaussian*, specifying the level of theory. Every *Gaussian* job must specify both a method and basis set. This is usually accomplished via two separate keywords within the route section of the input file, although a few method keywords imply a choice of basis set.

The following table lists methods which are available in *Gaussian*, along with the job types for which each one may be used. Note that the table lists only analytic optimizations, frequencies, and polarizability calculations; numerical calculations are often available for unchecked methods (see the discussion of the specific keyword in question for details).



Method Availabilities in *Gaussian 03*

	SP, Scan	Opt, Force, BOMD	Freq	IRC	ADMP	Polar	Stable	ONIOM	SCRF	PBC
Molecular Mechanics	*	*	*					*		
AM1, PM3 (etc.)	*	*	*num.*	*				*		
HF	*	*	*	*	*	*	*	*	*	*
DFT methods	*	*	*	*	*	*	*	*	*	*
CASSCF	*	*	*	*		*		*	*	
MP2	*	*	*	*		*		*		
MP3, MP4(SDQ)	*	*		*				*		
MP4(SDTQ), MP5	*							*		
QCISD, CCD, CCSD	*	*		*				*		
QCISD(T) or (TQ)	*							*		
BD	*							*		
OVGF	*									
CBS, G*n*, W1 methods	*									
CIS	*	*	*	*		*		*	*	
TD	*							*	*	
ZINDO	*							*		
CI	*	*		*				*		
GVB	*	*		*				*		

If no method keyword is specified, HF is assumed. Most method keywords may be prefaced by **R** for closed-shell restricted wavefunctions, **U** for unrestricted open-shell wavefunctions, or **RO** for restricted open-shell wavefunctions: for example, **ROHF**, **UMP2**, or **RQCISD**. **RO** is available only for Hartree-Fock, all Density Functional methods, AM1, MINDO3 and MNDO and PM3 semi-empirical energies and gradients, and MP2 energies; note that analytic **ROMP2** gradients are not yet available.

In general, *only a single method keyword should be specified*, and including more than one of them will produce *bizarre* results. However, there are exceptions:

- **CASSCF** may be specified along with **MP2** to request a CASSCF calculation including electron correlation.
- **ONIOM** and **IRCMax** jobs require multiple method specifications. However, they are given as options to the corresponding keyword.
- The form *model*2 // *model*1 described previously may be used to generate an automatic optimization followed by a single point calculation at the optimized geometry.

Click here to go on to the next section.

Product Information
Last update: 15 March 2005

Gaussian 03:
Expanding the limits of Computational Chemistry

Gaussian 03 brings enhancements and performance boosts to existing methods along with new features applying electronic structure methods to previously inaccessible areas of investigation and types of molecules.

Introducing Gaussian 03

Gaussian 03 is the latest in the *Gaussian* series of electronic structure programs. *Gaussian 03* is used by chemists, chemical engineers, biochemists, physicists and others for research in established and emerging areas of chemical interest.

Starting from the basic laws of quantum mechanics, *Gaussian* predicts the energies, molecular structures, and vibrational frequencies of molecular systems, along with numerous molecular properties derived from these basic computation types. It can be used to study molecules and reactions under a wide range of conditions, including both stable species and compounds which are difficult or impossible to observe experimentally such as short-lived intermediates and transition structures. This article introduces several of its new and enhanced features.

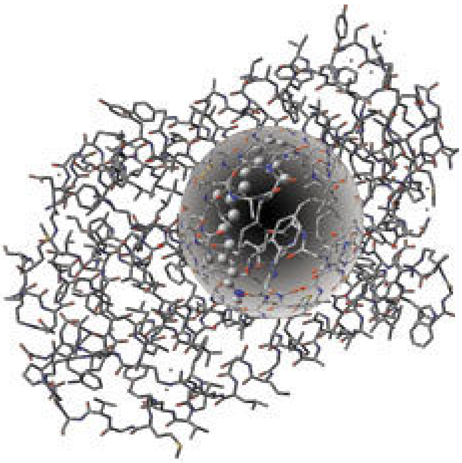
Investigating the Reactivity and Spectra of Large Molecules

Traditionally, proteins and other large biological molecules have been out of the reach of electronic structure methods. However, *Gaussian 03's* ONIOM method overcomes these limitations. ONIOM first appeared in *Gaussian 98*, and several significant innovations in *Gaussian 03* make it applicable to much larger molecules.

This computational technique models large molecules by defining two or three layers within the structure that are treated at different levels of accuracy. Calibration studies have demonstrated that the resulting predictions are essentially equivalent to those that would be produced by the high accuracy method.

The ONIOM facility in *Gaussian 03* provides substantial performance gains for geometry optimizations via a quadratic coupled algorithm and the use of micro-iterations. In addition, the program's option to include electronic embedding within ONIOM calculations enables both the steric and electrostatic properties of the entire molecule to be taken into account when modeling processes in the high accuracy layer (e.g., an enzyme's active site). These techniques yield molecular structures and properties results that are in very good agreement with experiment.

For example, researchers are currently studying excited states of bacteriorhodopsin (illustrated below) using an ONIOM(MO:MM) model, as a first step in understanding the means by which this species generates energy within a cell. In this two-layer approach, the active site is treated using an electronic structure method while the rest of the system is modeled with molecular mechanics. Electronic embedding, which includes the electrostatics of the protein environment within the QM calculation of the active site, is essential to accurate predictions of the molecule's UV-Visible spectrum.



Bacteriorhodopsin, set up for an ONIOM calculation (stylized). See T. Vreven and K. Morokuma, "Investigation of the $S_0 \rightarrow S_1$ *excitation in bacteriorhodopsin with the ONIOM(MO:MM) hybrid method," Theor. Chem. Acc. (2003).*

The ONIOM method is also applicable to large molecules in many other areas, including enzyme reactions, reaction mechanisms for organic systems, cluster models of surfaces and surface reactions, photochemical processes of organic species, substituent effects and reactivity of organic and organometallic compounds, and homogeneous catalysis.

***Other new ONIOM related features in Gaussian 03*:**

- Customizable molecular mechanics force fields.
- Efficient ONIOM frequency calculations.
- ONIOM calculation of electric and magnetic properties.

Determining Conformations via Spin-Spin Coupling Constants

Conformational analysis is a difficult problem when studying new compounds for which X-ray structures are not available. Magnetic shielding data in NMR spectra provides information about the connectivity between the various atoms within a molecule. Spin-spin coupling constants can aid in identifying specific conformations of molecules because they depend on the torsion angles with the molecular structure.

Gaussian 03 can predict spin-spin coupling constants in addition to the NMR shielding and chemical shifts available previously. Computing these constants for different conformations and then comparing predicted and observed spectra makes it possible to identify the specific conformations that were observed. In addition, the assignment of observed peaks to specific atoms is greatly facilitated.

Studying Periodic Systems

Gaussian 03 expands the range of chemical systems that it can model to periodic systems such as polymers and crystals via its periodic boundary conditions (PBC) methods. The PBC technique models these systems as repeating unit cells in order to determine the structure and bulk properties of the compound.

For example, *Gaussian 03* can predict the equilibrium geometries and transition structures of polymers. It can also study polymer reactivity by predicting isomerization energies, reaction energetics, and so on, allowing the decomposition, degradation, and combustion of materials to be studied. *Gaussian 03* can also model compounds' band gaps.

Other PBC capabilities in Gaussian 03:

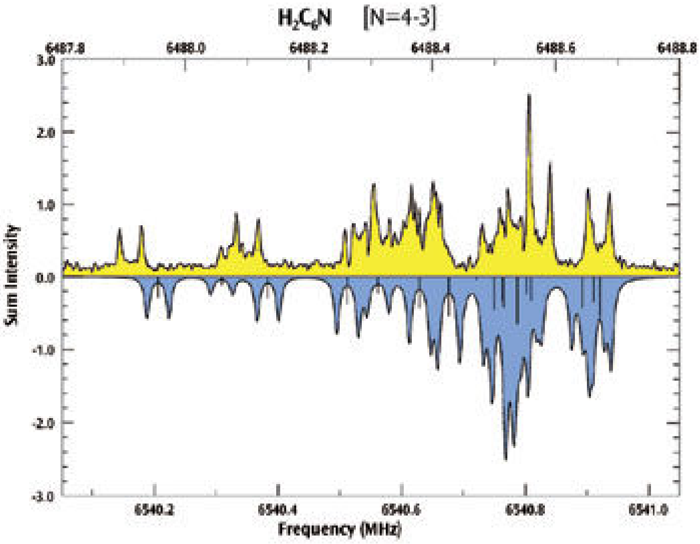
- 2D PBC methods can be used to model surface chemistry, such as reactions on surfaces and catalysis. In addition, using *Gaussian 03* allows you to study the same problem using a surface model and/or a cluster model, using the same basis set □and Hartree-Fock or DFT theoretical method in both cases. Using *Gaussian 03* enables you to choose the appropriate approach for the system you are studying, rather than being forced to frame the problem to fit the capabilities and limitations of a particular model.
- 3D PBC: The structures and available bulk properties of crystals and other three-dimensional periodic systems can be predicted.

Predicting Spectra

Gaussian 03 can compute a very wide range of spectra and spectroscopic properties. These include:

- IR and Raman
- Pre-resonance Raman
- UV-Visible
- NMR
- Vibrational circular dichroism (VCD)
- Electronic circular dichroism (ECD)
- Optical rotary dispersion (ORD)
- Harmonic vibration-rotation coupling
- Anharmonic vibration and vibration-rotation coupling
- *g* tensors and other hyperfine spectra tensors

For example, *Gaussian 03* computes many of the tensors which contribute to hyperfine spectra. These results are useful for making spectral assignments for observed peaks, something which is usually difficult to determine solely from the experimental data (see the example below). Using theoretical predictions to aid in interpreting and fitting observed results should make non-linear molecules as amenable to study as linear ones.



The observed (yellow) and computed (blue) hyperfine spectra for $H_2 C_6 N$ *(N=4-3). The predicted spectrum allows spectral assignments to be made for the observed peaks, a task which is often difficult or impossible from the experimental data alone due to spectral overlap. Experimental data provided by S. E. Novick, W. Chen, M. C. McCarthy and P. Thaddeus (article in preparation).*

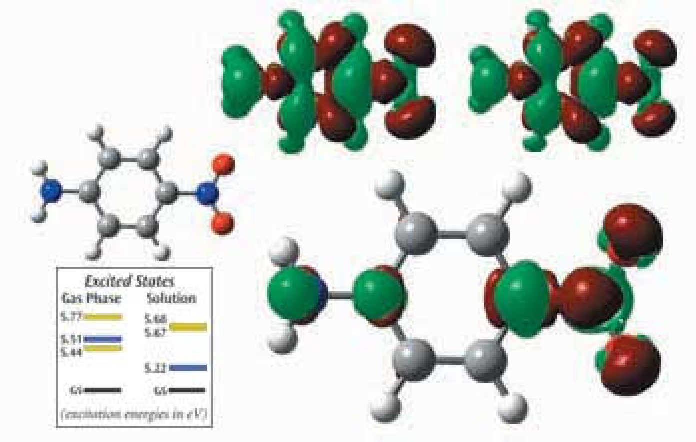
Modeling Solvent Effects on Reactions and Molecular Properties

Molecular properties and chemical reactions often vary considerably between the gas phase and in solution. For example, low lying conformations can have quite different energies in the gas phase and in solution (and in different solvents), conformation equilibria can differ, and reactions can take significantly different paths.

Gaussian 03 offers the Polarizable Continuum Model (PCM) for modeling system in solution. This approach represents the solvent as a polarizable continuum and places the solute in a cavity within the solvent.

The PCM facility in *Gaussian 03* includes many enhancement that significantly extend the range of problems which can be studied:

- Excitation energies and related properties of excited states can be calculated in the presence of a solvent (see the surfaces in the diagram below).
- NMR spectra and other magnetic properties.
- Vibrational frequencies, IR and Raman spectra, and other properties computed via analytic second derivatives of the energy.
- Polarizabilities and hyperpolarizabilities.
- General performance improvements.



$(\text{excited state-ground state})^{\text{solvated}} - (\text{excited state-ground state})^{\text{gas phase}}$

These surfaces represent the electron density difference between the ground state and the charge transfer excited state in paranitroaniline (the molecule is at the near right). The small surface at the top right shows the electron density difference in the gas phase, and the one to its left shows the difference in acetonitrile solution. Electron density moves from the green areas to the red areas in the excited state.

The larger surface below the small ones is the difference of these difference densities (solution minus gas phase), and it illustrates how the charge transfer from NH_2 to NO_2 from the ground state to the excited state is larger in solution than it is for the same gas phase transition. In addition, as the level diagrams indicate, the ordering of the lowest two excited states changes between the gas phase and in solution with acetonitrile (the yellow states have 0 oscillator strengths and are not observed in ordinary UV-Visible spectra).

Model Chemistries

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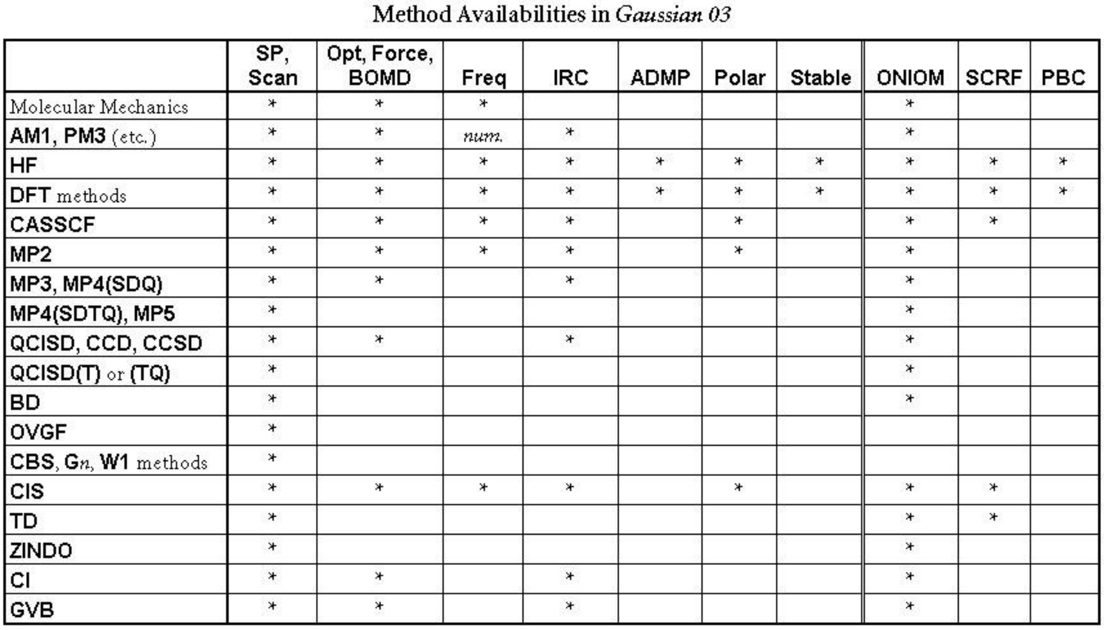

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Molecular Mechanics	*	*	*					*		
AM1, PM3 (etc.)	*	*	*num.*	*				*		
HF	*	*	*	*	*	*	*	*	*	*
DFT methods	*	*	*	*	*	*	*	*	*	*
CASSCF	*	*	*	*		*		*	*	
MP2	*	*	*	*		*		*		
MP3, MP4(SDQ)	*	*		*				*		
MP4(SDTQ), MP5	*							*		
QCISD, CCD, CCSD	*	*		*				*		
QCISD(T) or (TQ)	*							*		
BD	*							*		
OVGF	*									
CBS, G*n*, W1 methods	*									
CIS	*	*	*	*		*		*	*	
TD	*							*	*	
ZINDO	*							*		
CI	*	*		*				*		
GVB	*	*		*				*		

If no method keyword is specified, **HF** is assumed. Most method keywords may be prefaced by **R** for closed-shell restricted wavefunctions, **U** for unrestricted open-shell wavefunctions, or **RO** for restricted open-shell wavefunctions: for example, **ROHF**, **UMP2**, or **RQCISD**. **RO** is available only for Hartree-Fock, all Density Functional methods, AM1, MINDO3 and MNDO and PM3 semi-empirical energies and gradients, and MP2 energies; note that analytic **ROMP2** gradients are not yet available.

In general, *only a single method keyword should be specified*, and including more than one of them will produce *bizarre* results. However, there are exceptions:

- **CASSCF** may be specified along with **MP2** to request a CASSCF calculation including electron correlation.
- **ONIOM** and **IRCMax** jobs require multiple method specifications. However, they are given as options to the corresponding keyword.
- The form *model*2 // *model*1 described previously may be used to generate an automatic optimization followed by a single point calculation at the optimized geometry.

Click here to go on to the next section.

Vibrational Analysis in *Gaussian*

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Abstract

One of the most commonly asked questions about *Gaussian* is “What is the definition of reduced mass that *Gaussian* uses, and why is is different than what I calculate for diatomics by hand?” The purpose of this document is to describe how *Gaussian* calculates the reduced mass, frequencies, force constants, and normal coordinates which are printed out at the end of a frequency calculation.

Contents

1 The short answer

So why is the reduced mass different in *Gaussian*? The short answer is that Gaussian uses a coordinate system where the normalized cartesian displacement is one unit. This differs from the coordinate system used in most texts, where a unit step of one is used for the change in interatomic distance (in a diatomic). The vibrational analysis of polyatomics in *Gaussian* is not different from that described in “Molecular Vibrations” by Wilson, Decius and Cross. Diatomics are simply treated the same way as polyatomics, rather than using a different coordinate system.

2 The long answer

In this section, I'll describe exactly how frequencies, force constants, normal modes and reduced mass are calculated in *Gaussian*, starting with the Hessian, or second derivative matrix. I'll outline the general polyatomic case, leaving out details for dealing with frozen atoms, hindered rotors and the like.

I will try to stick close to the notation used in "Molecular Vibrations" by Wilson, Decius and Cross. I will add some subscripts to indicate which coordinate system the matrix is in.

There is an important point worth mentioning before starting. Vibrational analysis, as it's descibed in most texts and implemented in *Gaussian*, is valid only when the first derivatives of the energy with respect to displacement of the atoms are zero. In other words, the geometry used for vibrational analysis *must* be optimized at the same level of theory and with the same basis set that the second derivatives were generated with. Analysis at transition states and higher order saddle points is also valid. Other geometries are not valid. (There are certain exceptions, such as analysis along an IRC, where the non-zero derivative can be projected out.) For example, calculating frequencies using HF/6-31g* on MP2/6-31G* geometries is not well defined.

Another point that is sometimes overlooked is that frequency calculations need to be performed with a method suitable for describing the particular molecule being studied. For example, a single reference method, such as Hartree-Fock (HF) theory is not capable of describing a molecule that needs a multireference method. One case that comes to mind is molecules which are in a $^2\Pi$ ground state. Using a single reference method will yield different frequencies for the Π_x and Π_y vibrations, while a multireference method shows the cylindrical symmetry you might expect. This is seldom a large problem, since the frequencies of the other modes, like the stretching mode, are are still useful.

2.1 Mass weight the Hessian and diagonalize

We start with the Hessian matrix $\mathbf{f}_{\text{CART}}$, which holds the second partial derivatives of the potential V with respect to displacement of the atoms in cartesian coordinates (CART):

$$f_{\text{CART}ij} = \left(\frac{\partial^2 V}{\partial \xi_i \partial \xi_j}\right)_0 \tag{1}$$

This is a $3N \times 3N$ matrix (N is the number of atoms), where $\xi_1, \xi_2, \xi_3 \cdots \xi_{3N}$ are used for the displacements in cartesian coordinates, $\Delta x_1, \Delta y_1, \Delta z_1, \cdots \Delta z_N$. The $()_0$ refers to the fact that the derivatives are taken at the equilibrium positions of the atoms, and that the first derivatives are zero.

The first thing that *Gaussian* does with these force constants is to convert them to mass weighted cartesian coordinates (MWC).

$$f_{\text{MWC}ij} = \frac{f_{\text{CART}ij}}{\sqrt{m_i m_j}} = \left(\frac{\partial^2 V}{\partial q_i \partial q_j}\right)_0 \tag{2}$$

where $q_1 = \sqrt{m_1}\xi_1 = \sqrt{m_1}\Delta x_1$, $q_2 = \sqrt{m_1}\xi_2 = \sqrt{m_1}\Delta y_1$ and so on, are the mass weighted cartesian coordinates.

A copy of $\mathbf{f}_{\text{MWC}}$ is diagonalized, yielding a set of $3N$ eigenvectors and $3N$ eigenvalues. The eigenvectors, which are the normal modes, are discarded; they will be calculated again after the rotation and translation modes are separated out. The roots of the eigenvalues are the fundamental frequencies of the molecule. *Gaussian* converts them to cm^{-1}, then prints out the $3N$ (up to 9) lowest. The output for water HF/3-21G* looks like this:

```
Full mass-weighted force constant matrix:
Low frequencies ---   -0.0008    0.0003    0.0013   40.6275   59.3808   66.4408
Low frequencies --- 1799.1892 3809.4604 3943.3536
```

In general, the frequencies for for rotation and translation modes should be close to zero. If you have optimized to a transition state, or to a higher order saddle point, then there will be some negative frequencies which may be listed before the "zero frequency" modes. (Freqencies which are printed out as negative are really imaginary; the minus sign is simply a flag to indicate that this is an imaginary frequency.) There is a discussion about how close to zero is close enough, and what to do if you are not close enough in Section 4 of this paper.

You should compare the lowest real frequencies list in this part of the output with the corresponding frequencies later in the output. The later frequencies are calculated after projecting out the translational and rotational modes. If the corresponding frequencies in both places are not the same, then this is an indication that these modes are contaminated by the rotational and translational modes.

2.2 Determine the principal axes of inertia

The next step is to translate the center of mass to the origin, and determine the moments and products of inertia, with the goal of finding the matrix that diagonalizes the moment of inertia tensor. Using this matrix we can find the vectors corresponding to the rotations and translations. Once these vectors are known, we know that the rest of the normal modes are vibrations, so we can distinguish low frequency vibrational modes from rotational and translational modes.

The center of mass ($\mathbf{R}_{\text{COM}}$) is found in the usual way:

$$\mathbf{R}_{\text{COM}} = \frac{\sum_\alpha m_\alpha \mathbf{r}_\alpha}{\sum_\alpha m_\alpha} \tag{3}$$

where the sums are over the atoms, α. The origin is then shifted to the center of mass $\mathbf{r}_{\text{COM}\alpha} = \mathbf{r}_\alpha - \mathbf{R}_{\text{COM}}$. Next we have to calculate the moments of inertia (the diagonal elements) and the products of inertia (off diagonal elements) of the moment of inertia tensor ($\mathbf{I}$).

$$\mathbf{I} = \begin{pmatrix} I_{xx} & I_{xy} & I_{xz} \\ I_{yx} & I_{yy} & I_{yz} \\ I_{zx} & I_{zy} & I_{zz} \end{pmatrix} = \begin{pmatrix} \sum_\alpha m_\alpha(y_\alpha^2 + z_\alpha^2) & -\sum_\alpha m_\alpha(x_\alpha y_\alpha) & -\sum_\alpha m_\alpha(x_\alpha z_\alpha) \\ -\sum_\alpha m_\alpha(y_\alpha x_\alpha) & \sum_\alpha m_\alpha(x_\alpha^2 + z_\alpha^2) & -\sum_\alpha m_\alpha(y_\alpha z_\alpha) \\ -\sum_\alpha m_\alpha(z_\alpha x_\alpha) & -\sum_\alpha m_\alpha(z_\alpha y_\alpha) & \sum_\alpha m_\alpha(x_\alpha^2 + y_\alpha^2) \end{pmatrix} \tag{4}$$

This symmetric matrix is diagonalized, yielding the principal moments (the eigenvalues $\mathbf{I}'$) and a 3×3 matrix ($\mathbf{X}$), which is made up of the normalized eigenvectors of $\mathbf{I}$. The eigenvectors of the moment of inertia tensor are used to generate the vectors corresponding to translation and infinitesimal rotation of the molecule in the next step.

2.3 Generate coordinates in the rotating and translating frame

The main goal in this section is to generate the transformation $\mathbf{D}$ from mass weighted cartesian coordinates to a set of $3N$ coordinates where rotation and translation of the molecule are separated out, leaving $3N-6$ or $3N-5$ modes for vibrational analysis. The rest of this section describes how the Sayvetz conditions are used to generate the translation and rotation vectors.

The three vectors ($\mathbf{D_1}$, $\mathbf{D_2}$, $\mathbf{D_3}$) of length $3N$ corresponding to translation are trivial to generate in cartesian coordinates. They are just $\sqrt{m_i}$ times the corresponding coordinate axis. For example, for water (using $m_{\text{H}} = 1$ and $m_{\text{O}} = 16$) the translational vectors are:

$$\begin{aligned}
\mathbf{D_1} &= (1,0,0,4,0,0,1,0,0)^t \\
\mathbf{D_2} &= (0,1,0,0,4,0,0,1,0)^t \\
\mathbf{D_3} &= (0,0,1,0,0,4,0,0,1)^t
\end{aligned}$$

Generating vectors corresponding to rotational motion of the atoms in cartesian coordinates is a bit more complicated. The vectors for these are defined this way:

$$\begin{aligned}
D_{4j,i} &= ((P_y)_i X_{j,3} - (P_z)_i X_{j,2})/\sqrt{m_i} \\
D_{5j,i} &= ((P_z)_i X_{j,1} - (P_x)_i X_{j,3})/\sqrt{m_i} \\
D_{6j,i} &= ((P_x)_i X_{j,2} - (P_y)_i X_{j,1})/\sqrt{m_i}
\end{aligned} \tag{5}$$

where $j = x, y, z$; i is over all atoms and P is the dot product of $\mathbf{R}$ (the coordinates of the atoms with respect to the center of mass) and the corresponding row of $\mathbf{X}$, the matrix used to diagonalize the moment of inertia tensor $\mathbf{I}$.

The next step is to normalize these vectors. If the molecule is linear (or is a single atoms), any vectors which do not correspond to translational or rotational normal modes are removed. The scalar product is taken of each vector with itself. If it is zero (or very close to it), then that vector is not an actual normal mode and it is eliminated. (If the scalar product is zero, this mode will disappear when the transformation from mass weighted to internal coordinates is done, in Equation 6.) Otherwise, the vector is normalized using the reciprocal square root of the scalar product. *Gaussian* then checks to see that the number of rotational and translational modes is what's expected for the molecule, three for atoms, five for linear molecules and six for all others. If this is not the case, *Gaussian* prints an error message and aborts.

A Schmidt orthogonalization is used to generate $N_{vib} = 3N-6$ (or $3N-5$) remaining vectors, which are orthogonal to the five or six rotational and translational vectors. The result is a transformation matrix $\mathbf{D}$ which transforms from mass weighted cartesian coordinates $\mathbf{q}$ to internal coordinates $\mathbf{S} = \mathbf{D}\mathbf{q}$, where rotation and translation have been separated out.

2.4 Transform the Hessian to internal coordinates and diagonalize

Now that we have coordinates in the rotating and translating frame, we need to transform the Hessian, $\mathbf{f}_{\text{MWC}}$ (still in mass weighted cartesian coordinates), to these new internal coordinates (INT). Only the N_{vib} coordinates corresponding to internal coordinates will be diagonalized, although the full $3N$ coordinates are used to transform the Hessian.

The transformation is straightforward:

$$\mathbf{f}_{\text{INT}} = \mathbf{D}^{\dagger}\mathbf{f}_{\text{MWC}}\mathbf{D} \tag{6}$$

The $N_{vib} \times N_{vib}$ submatrix of $\mathbf{f}_{\text{INT}}$, which represents the force constants internal coordinates, is diagonalized yielding N_{vib} eigenvalues $\lambda = 4\pi^2\nu^2$, and N_{vib} eigenvectors. If we call the transformation matrix composed of the eigenvectors $\mathbf{L}$, then we have

$$\mathbf{L}^{\dagger}\mathbf{f}_{\text{INT}}\mathbf{L} = \mathbf{\Lambda} \tag{7}$$

where $\mathbf{\Lambda}$ is the diagonal matrix with eigenvalues λ_i.

2.5 Calculate the frequencies

At this point, the eigenvalues need to be converted frequencies in units of reciprocal centimeters. First we change from frequencies (ν_i) to wavenumbers ($\tilde{\nu}_i$), via the relationship $\nu_i = \tilde{\nu}_i c$, where c is the speed of light. Solving $\lambda = 4\pi^2\tilde{\nu}^2c^2$ for $\tilde{\nu}_i^2$ we get

$$\tilde{\nu}_i = \sqrt{\frac{\lambda_i}{4\pi^2c^2}} \tag{8}$$

The rest is simply applying the appropriate conversion factors: from a single molecule to a mole, from hartrees to joules, and from atomic mass units to kilograms. For negative eigenvalues, we calculate $\tilde{\nu}_i$ using the absolute value of λ_i, then multiply by -1 to make the frequency negative (which flags it as imaginary). After this conversion, the frequencies are ready to be printed out.

2.6 Calculate reduced mass, force constants and cartesian displacements

All the pieces are now in place to calculate the reduced mass, force constants and cartesian displacements. Combining Equation 6 and Equation 7, we arrive at

$$\mathbf{L}^{\dagger}\mathbf{D}^{\dagger}\mathbf{f}_{\text{MWC}}\mathbf{D}\mathbf{L} = \mathbf{\Lambda} = \mathbf{l}_{\text{MWC}}{}^{\dagger}\mathbf{f}_{\text{MWC}}\mathbf{l}_{\text{MWC}} \tag{9}$$

where $\mathbf{l} = \mathbf{DL}$ is the matrix needed to diagonalize $\mathbf{f}_{\text{MWC}}$. Actually, $\mathbf{l}_{\text{MWC}}$ is never calculated directly in *Gaussian*. Instead, $\mathbf{l}_{\text{CART}} = \mathbf{MDL}$ is calculated, where $\mathbf{M}$ is a diagonal matrix defined by:

$$M_{i,i} = 1/\sqrt{m_i} \tag{10}$$

and i runs over the x, y, and z coordinates for every atom. The individual elements of $\mathbf{l}_{\text{CART}}$ are given by:

$$l_{\text{CART}k,i} = \sum_{j}^{3N} \left(\frac{D_{k,j} L_{j,i}}{\sqrt{m_j}} \right). \tag{11}$$

The column vectors of these elements, which are the normal modes in cartesian coordinates, are used in several ways. First of all, once normalized by the procedure described below, they are the displacements in cartesian coordinates. Secondly, they are useful for calculating a number of spectroscopic properties, including IR intensities, Raman activies, depolarizations and dipole and rotational strengths for VCD.

Normalization is a relatively straight forward process. Before it is printed out, each of the $3N$ elements of $\mathbf{l}_{\text{CART}i}$ is scaled by normalization factor $\mathcal{N}_i$, for that particular vibrational mode. The normalization is defined by:

$$\mathcal{N}_i = \sqrt{\left(\sum_{k}^{3N} l_{\text{CART}k,i}^{\;2} \right)^{-1}} \tag{12}$$

The reduced mass μ_i for the vibrational mode is calculated in a similar fashion:

$$\mu_i = \left(\sum_{k}^{3N} l_{\text{CART}k,i}^{\;2} \right)^{-1} = \left(\sum_{k}^{3N} \left(\frac{l_{\text{MWC}k,i}}{\sqrt{m_j}} \right)^2 \right)^{-1} = \left(\sum_{k}^{3N} \left(\frac{l_{\text{MWC}k,i}^{\;2}}{m_j} \right) \right)^{-1} = \mathcal{N}_i^2 \tag{13}$$

Note that since $\mathbf{D}$ is orthonormal, and we can (and do) choose $\mathbf{L}$ to be orthonormal, then $\mathbf{l}$ is orthonormal as well. (Since $\mathbf{D}^\dagger\mathbf{D} = \mathbf{1}, \mathbf{L}^\dagger\mathbf{L} = \mathbf{1}$ then $\mathbf{l}^\dagger\mathbf{l} = (\mathbf{DL})^\dagger\mathbf{DL} = \mathbf{L}^\dagger\mathbf{D}^\dagger\mathbf{DL} = \mathbf{L}^\dagger\mathbf{1L} = \mathbf{1}$).

We now have enough information to explain the difference between the reduced mass *Gaussian* prints out, and the one calculated using the formula usually used for diatomics:

$$\frac{1}{\mu} = \frac{1}{m_1} + \frac{1}{m_2} \tag{14}$$

The difference is in the numerator of each term in the summation. Gaussian uses $l_{\text{MWC}k,i}^{\;2}$ rather than 1. Using the elements of $\mathbf{l}_{\text{MWC}}$ yields the consistent results for polyatomic cases, and automatically takes symmtery into consideration. Simply extending the formula from Equation 14 to $\frac{1}{\mu} = \sum_i^{atoms} \frac{1}{m_i}$ would (incorrectly) yield the same reduced mass for every mode of a polyatomic molecule.

The effect of using the elements of $\mathbf{l}_{\text{MWC}}$ in the numerator is to make the unit length of the coordinate system *Gaussian* uses be the normalized cartesian displacement. In other words, in the coordinate system that *Gaussian* uses, the sum of the squares of the cartesian displacements is 1. (You can check this in the output). In the more common coordinate system for diatomics, the unit length is a unit change in internuclear distance from the equilibrium value.

One of the consequences of using this coordinate system is that force constants which you think should be equal are not. A simple example is H_2 versus HD. Since the Hessian depends only on the electronic part of the Hamiltonian, you would expect the force constants to be the same for these to molecules. In fact, the force constant *Gaussian* prints out is different. The different masses of the atoms leads to a different set of Sayvetz conditions, which in turn, change the internal coordinate system the force constants are transformed to, and ultimately the resulting force constant.

The coordinates used to calculate the force constants, the reduced mass and the cartesian displacements are all internally consistent. The force constants k_i are given by $k_i = 4\pi^2\tilde{\nu}^2\mu_i$, since $\tilde{\nu} = \frac{1}{2\pi}\sqrt{\frac{k_i}{\mu_i}}$. The force constants are converted from atomic units to millidyne/angstrom.

3 Summary

To summarize, the steps *Gaussian* uses to perform vibrational analysis are:

1. Mass weight the Hessian

$$f_{\text{MWC}ij} = \frac{f_{\text{CART}ij}}{\sqrt{m_i m_j}}$$

2. Determine the principal axes of inertia

$$\mathbf{I}' = \mathbf{X}^\dagger \mathbf{I} \mathbf{X}$$

3. Generate coordinates in the rotating and translating frame

$$\mathbf{S} = \mathbf{D}\mathbf{q}$$

4. Transform the Hessian to internal coordinates and diagonalize

$$\mathbf{f}_{\text{INT}} = \mathbf{D}^\dagger \mathbf{f}_{\text{MWC}} \mathbf{D}$$

$$\mathbf{L}^\dagger \mathbf{f}_{\text{INT}} \mathbf{L} = \mathbf{\Lambda}$$

5. Calculate the frequencies

$$\tilde{\nu}_i = \sqrt{\frac{\lambda_i}{4\pi^2 c^2}}$$

6. Calculate reduced mass, force constants and cartesian displacements

$$\mu_i = \left(\sum_k^{3N} l_{\text{CART}}{}_{k,i}^2 \right)^{-1}$$

$$k_i = 4\pi^2 \tilde{\nu}_i^2 \mu_i$$

$$\mathbf{l}_{\text{CART}} = \mathbf{MDL}$$

Criteria	Low frequencies					
Opt	−0.0008	0.0003	0.0013	40.6275	59.3808	66.4408
Opt=Tight	0.0011	0.0013	0.0015	4.1908	−6.8779	12.4224
Opt=VeryTight	−0.0011	0.0014	0.0015	−0.9207	−1.1831	−1.6023

Table 1: The effect of optimization criteria on the low frequencies of water using HF/3-21G*. The frequencies are sorted by increasing absolute value, so that it's easier to distinguish rotational modes from vibrational modes.

4 A note about low frequencies

You'll find that the frequencies for the translations are almost always extremely close to zero. The frequencies for rotations are quite a bit larger. So, how "close to zero" is close enough? For most methods (HF, MP2, etc.), you'd like the rotational frequencies to be around 10 wavenumbers or less. For methods which use numerical integration, like DFT, the frequencies should be less than a few tens of wavenumbers, say 50 or so.

If the frequencies for rotations are not close to zero, it may be a signal that you need to do a tighter optimization. There are a couple of ways to accomplish this. For most methods, you can use Opt=Tight or Opt=Verytight on the route card to specify that you'd like to use tighter convergence criteria. For DFT, you may also need to specify Int=Ultrafine, which uses a more accurate numerical integration grid.

As an example, I reran the water HF/3-21G* calculation above, with both Opt=Tight and Opt=VeryTight. You can see in Table 1 that the rotational frequencies are an order of magnitude better for Opt=Tight than they were for just Opt. Using Opt=Verytight makes them even better. This raises the question of whether the you need to use tighter convergence. The answer is: it depends – different users will be interested in different results. There is a trade off between accuracy and speed. Using Opt=Tight or Int=Ultrafine makes the calulation take longer in addition to making the results more accurate. The default convergence criteria are set to give an accuracy good enough for most purposes without spending time to converge the results beyond this accuracy. You may find that you need to use the tighter criteria to compare to spectroscopic values, or to resolve a strucutre witha particularly flat potential energy surface.

In the water frequency calculation above, using tighter convergence criteria makes almost no difference in terms of energy or bond lengths, as Table 2 demonstrates. The energy is converged to less then 1 microHartree, and the OH bond length is converged to 0.0002 angstroms. Tightening up the convergence criteria is useful for getting a couple of extra digits of precision in the symmetric stretch frequency.

You can also see that the final geometry parameters obtained with the default optimization criteria depend somewhat on the initial starting geometry. Using Opt=VeryTight all but eliminates these differences. I've included the starting geometries in Table 3, for those who wish to reproduce these results. (Using the default convergence criteria may give somewhat different results than those I've shown if you use a different machine, or even the same machine using different libraries or a different version of the compiler).

With DFT, Opt=VeryTight alone is not necessarily enough to converge the geometry to

Criteria	Start Geom	Energy	R_{OH}	A_{HOH}	Bend	Symmetric Stretch	Antisymm. Stretch
Opt	A	−75.5859596012	0.9669	107.7241	1799.1892	3809.4604	3943.3536
Opt	B	−75.5859596488	0.9665	107.6348	1799.5957	3814.2216	3947.2011
Opt=Tight	A	−75.5859597578	0.9667	107.6784	1799.3335	3812.3499	3945.7723
Opt=Tight	B	−75.5859597580	0.9667	107.6811	1799.3156	3812.2440	3945.6938
Opt=Verytight	A	−75.5859597582	0.9667	107.6818	1799.2877	3812.3779	3945.8339
Opt=Verytight	B	−75.5859597582	0.9667	107.6820	1799.2854	3812.3847	3945.8418

Table 2: The default optimization settings yield results accurate enough for most purposes. Tighter optimizations make almost no difference for this HF/3-21G* frequency calculation on water.

Geometry A	Geometry B
O	O
H,1,R2	H,1,R2
H,1,R2,2,A3	H,1,R2,2,A3
R2=0.96	R2=1.0
A3=109.47122063	A3=109.5

Table 3: Initial geometries for water optimization calculations. Geometry A was produced by Geom=ModelA. Geometry B is a slightly modified version of Geometry A.

the point where the low frequencies are as close to zero as you would like. To demonstrate this, I have run B3LYP/3-21G* optimizations on water, starting with geometry B from Table 3, with Opt, Opt=Tight and Opt=VeryTight. The results are in Table 4. The low frequencies from these two jobs hardly change, and in fact get worse for the Tight and VeryTight optimizations.

Given the straight forward convergence seen with Hartree-Fock theory, this might not seem to make sense. However, it does make sense if you recall that DFT is done using a numerical integration on a grid of points. The accuracy of the default grid is not high enough for computing low frequency modes very precisely. The solution is to use a more numerically accurate grid. The tighter the optimzation criteria, the more accurate the grid needs to be. As you can see in Table 4, increasinfg the convergence criteria from Tight to VeryTight without increasing the numerical accuracy of the grid yields no improvement in the low frequencies. For Opt=Tight, we recommend using the Ultrafine grid. This is a good combination to use for systems with hindered rotors, or if exact conformation is of concern. If still more accuracy is necessary, then an unpruned 199974 grid can be used with Opt=VeryTight. Again, the higher accuracy comes at a higher cost in terms of CPU time. The VeryTight optimization with a 199974 grid is *very* expensive, even for medium sized molecules. The default grids are accurate enough for most purposes.

Criteria	Grid	Low frequencies					
Opt	FineGrid	−0.0005	−0.0011	0.0011	16.5776	17.8265	−38.2354
Opt=Tight	FineGrid	−0.0011	−0.0011	0.0005	25.8979	−29.0202	37.0170
Opt=VeryTight	FineGrid	−0.0006	−0.0007	−0.0008	25.8977	−29.0203	37.0168
Opt=Tight	UltraFine	0.0012	0.0022	0.0024	−1.5386	−4.8182	−9.0313
Opt=VeryTight	UltraFine	0.0012	0.0022	0.0024	−1.5386	−4.8182	−9.0313
Opt=VeryTight	Grid=199974	−0.0004	0.0010	0.0011	−4.8721	−5.3561	−6.3672

Table 4: The effect of grid size on the low frequencies from B3LYP/3-21G* on water with Opt, Opt=Tight and Opt=VeryTight. More accurate grids are necessary for a truly converged optimization. The frequencies are sorted by increasing absolute value, so that it's easier to distinguish rotational modes from vibrational modes.

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Thermochemistry in *Gaussian*

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Abstract

The purpose of this paper is to explain how various thermochemical values are computed in *Gaussian*. The paper documents what equations are used to calculate the quantities, but doesn't explain them in great detail, so a basic understanding of statistical mechanics concepts, such as partition functions, is assumed. *Gaussian* thermochemistry output is explained, and a couple of examples, including calculating the enthalpy and Gibbs free energy for a reaction, the heat of formation of a molecule and absolute rates of reaction are worked out.

Contents

1 Introduction

The equations used for computing thermochemical data in *Gaussian* are equivalent to those given in standard texts on thermodynamics. Much of what is discussed below is covered in detail in “Molecular Thermodynamics” by McQuarrie and Simon (1999). I’ve cross-referenced several of the equations in this paper with the same equations in the book, to make it easier to determine what assumptions were made in deriving each equation. These cross-references have the form [McQuarrie, §7-6, Eq. 7.27] which refers to equation 7.27 in section 7-6.

One of the most important approximations to be aware of throughout this analysis is that all the equations assume non-interacting particles and therefore apply *only* to an ideal gas. This limitation will introduce some error, depending on the extent that any system being studied is non-ideal. Further, for the electronic contributions, it is assumed that the first and higher excited states are entirely inaccessible. This approximation is generally not troublesome, but can introduce some error for systems with low lying electronic excited states.

The examples in this paper are typically carried out at the HF/STO-3G level of theory. The intent is to provide illustrative examples, rather than research grade results.

The first section of the paper is this introduction. The next section of the paper, I give the equations used to calculate the contributions from translational motion, electronic motion, rotational motion and vibrational motion. Then I describe a sample output in the third section, to show how each section relates to the equations. The fourth section consists of several worked out examples, where I calculate the heat of reaction and Gibbs free energy of reaction for a simple bimolecular reaction, and absoloute reaction rates for another. Finally, an appendix gives a list of the all symbols used, their meanings and values for constants I’ve used.

2 Sources of components for thermodynamic quantities

In each of the next four subsections of this paper, I will give the equations used to calculate the contributions to entropy, energy, and heat capacity resulting from translational, electronic, rotational and vibrational motion. The starting point in each case is the partition function $q(V,T)$ for the corresponding component of the total partition function. In this section, I’ll give an overview of how entropy, energy, and heat capacity are calculated from the partition function.

The partition function from any component can be used to determine the entropy contribution S from that component, using the relation [McQuarrie, §7-6, Eq. 7.27]:

$$S = Nk_B + Nk_B \ln\left(\frac{q(V,T)}{N}\right) + Nk_BT\left(\frac{\partial \ln q}{\partial T}\right)_V$$

The form used in *Gaussian* is a special case. First, molar values are given, so we can divide by $n = N/N_A$, and substitute $N_Ak_B = R$. We can also move the first term into the logarithm (as e), which leaves (with $N = 1$):

$$\begin{aligned} S &= R + R\ln\left(q(V,T)\right) + RT\left(\frac{\partial \ln q}{\partial T}\right)_V \\ &= R\ln\left(q(V,T)e\right) + RT\left(\frac{\partial \ln q}{\partial T}\right)_V \\ &= R\left(\ln(q_\mathrm{t}q_\mathrm{e}q_\mathrm{r}q_\mathrm{v}e) + T\left(\frac{\partial \ln q}{\partial T}\right)_V\right) \end{aligned} \tag{1}$$

The internal thermal energy E can also be obtained from the partition function [McQuarrie, §3-8, Eq. 3.41]:

$$E = Nk_BT^2\left(\frac{\partial \ln q}{\partial T}\right)_V, \tag{2}$$

and ultimately, the energy can be used to obtain the heat capacity [McQuarrie, §3.4, Eq. 3.25]:

$$C_V = \left(\frac{\partial E}{\partial T}\right)_{N,V} \tag{3}$$

These three equations will be used to derive the final expressions used to calculate the different components of the thermodynamic quantities printed out by *Gaussian*.

2.1 Contributions from translation

The equation given in McQuarrie and other texts for the translational partition function is [McQuarrie, §4-1, Eq. 4.6]:

$$q_\mathrm{t} = \left(\frac{2\pi mk_BT}{h^2}\right)^{3/2}V.$$

The partial derivative of q_t with respect to T is:

$$\left(\frac{\partial \ln q_\mathrm{t}}{\partial T}\right)_V = \frac{3}{2T}$$

which will be used to calculate both the internal energy E_t and the third term in Equation 1.

The second term in Equation 1 is a little trickier, since we don't know V. However, for an ideal gas, $PV = NRT = \left(\frac{n}{N_A}\right)N_Ak_BT$, and $V = \frac{k_BT}{P}$. Therefore,

$$q_\mathrm{t} = \left(\frac{2\pi mk_BT}{h^2}\right)^{3/2}\frac{k_BT}{P}.$$

which is what is used to calculate q_t in *Gaussian*. Note that we didn't have to make this substitution to derive the third term, since the partial derivative has V held constant.

The translational partition function is used to calculate the translational entropy (which includes the factor of e which comes from Stirling's approximation):

$$\begin{aligned} S_\mathrm{t} &= R\left(\ln(q_\mathrm{t}e) + T\left(\frac{3}{2T}\right)\right) \\ &= R(\ln q_\mathrm{t} + 1 + 3/2). \end{aligned}$$

The contribution to the internal thermal energy due to translation is:

$$\begin{aligned} E_{\mathrm{t}} &= N_A k_B T^2 \left(\frac{\partial \ln q}{\partial T}\right)_V \\ &= RT^2 \left(\frac{3}{2T}\right) \\ &= \frac{3}{2} RT \end{aligned}$$

Finally, the constant volume heat capacity is given by:

$$\begin{aligned} C_{\mathrm{t}} &= \frac{\partial E_{\mathrm{t}}}{\partial T} \\ &= \frac{3}{2} R. \end{aligned}$$

2.2 Contributions from electronic motion

The usual electronic partition function is [McQuarrie, §4-2, Eq. 4.8]:

$$q_{\mathrm{e}} = \omega_0 e^{-\epsilon_0/k_B T} + \omega_1 e^{-\epsilon_1/k_B T} + \omega_2 e^{-\epsilon_2/k_B T} + \cdots$$

where ω is the degeneracy of the energy level, ϵ_n is the energy of the n-th level.

Gaussian assumes that the first electronic excitation energy is much greater than $k_B T$. Therefore, the *first and higher excited states are assumed to be inaccessible* at any temperature. Further, the energy of the ground state is set to zero. These assumptions simplify the electronic partition function to:

$$q_{\mathrm{e}} = \omega_0,$$

which is simply the electronic spin multiplicity of the molecule.

The entropy due to electronic motion is:

$$\begin{aligned} S_{\mathrm{e}} &= R\left(\ln q_{\mathrm{e}} + T\left(\frac{\partial \ln q_{\mathrm{e}}}{\partial T}\right)_V\right) \\ &= R\left(\ln q_{\mathrm{e}} + 0\right). \end{aligned}$$

Since there are no temperature dependent terms in the partition function, the electronic heat capacity and the internal thermal energy due to electronic motion are both zero.

2.3 Contributions from rotational motion

The discussion for molecular rotation can be divided into several cases: single atoms, linear polyatomic molecules, and general non-linear polyatomic molecules. I'll cover each in order.

For a single atom, $q_{\mathrm{r}} = 1$. Since q_{r} does not depend on temperature, the contribution of rotation to the internal thermal energy, its contribution to the heat capacity and its contribution to the entropy are all identically zero.

For a linear molecule, the rotational partition function is [McQuarrie, §4-6, Eq. 4.38]:

$$q_{\mathrm{r}} = \frac{1}{\sigma_r}\left(\frac{T}{\Theta_r}\right)$$

where $\Theta_r = h^2/8\pi^2 I k_B$. I is the moment of inertia. The rotational contribution to the entropy is

$$\begin{aligned} S_{\mathrm{r}} &= R\left(\ln q_{\mathrm{r}} + T\left(\frac{\partial \ln q_{\mathrm{r}}}{\partial T}\right)_V\right) \\ &= R(\ln q_{\mathrm{r}} + 1). \end{aligned}$$

The contribution of rotation to the internal thermal energy is

$$\begin{aligned} E_{\mathrm{r}} &= RT^2\left(\frac{\partial \ln q_{\mathrm{r}}}{\partial T}\right)_V \\ &= RT^2\left(\frac{1}{T}\right) \\ &= RT \end{aligned}$$

and the contribution to the heat capacity is

$$\begin{aligned} C_{\mathrm{r}} &= \left(\frac{\partial E_{\mathrm{r}}}{\partial T}\right)_V \\ &= R. \end{aligned}$$

For the general case for a nonlinear polyatomic molecule, the rotational partition function is [McQuarrie, §4-8, Eq. 4.56]:

$$q_{\mathrm{r}} = \frac{\pi^{1/2}}{\sigma_r}\left(\frac{T^{3/2}}{(\Theta_{r,x}\Theta_{r,y}\Theta_{r,z})^{1/2})}\right)$$

Now we have $\left(\frac{\partial \ln q}{\partial T}\right)_V = \frac{3}{2T}$, so the entropy for this partition function is

$$\begin{aligned} S_{\mathrm{r}} &= R\left(\ln q_{\mathrm{r}} + T\left(\frac{\partial \ln q_{\mathrm{r}}}{\partial T}\right)_V\right) \\ &= R(\ln q_{\mathrm{r}} + \frac{3}{2}). \end{aligned}$$

Finally, the contribution to the internal thermal energy is

$$\begin{aligned} E_{\mathrm{r}} &= RT^2\left(\frac{\partial \ln q_{\mathrm{r}}}{\partial T}\right)_V \\ &= RT^2\left(\frac{3}{2T}\right) \\ &= \frac{3}{2}RT \end{aligned}$$

and the contribution to the heat capacity is

$$\begin{aligned} C_\mathrm{r} &= \left(\frac{\partial E_\mathrm{r}}{\partial T}\right)_V \\ &= \frac{3}{2}R. \end{aligned}$$

The average contribution to the internal thermal energy from each rotational degree of freedom is $RT/2$, while it's contribution to C_r is $R/2$.

2.4 Contributions from vibrational motion

The contributions to the partition function, entropy, internal energy and constant volume heat capacity from vibrational motions are composed of a sum (or product) of the contributions from each vibrational mode, K. Only the real modes are considered; modes with imaginary frequencies (i.e. those flagged with a minus sign in the output) are ignored. Each of the $3n_\mathrm{atoms} - 6$ (or $3n_\mathrm{atoms} - 5$ for linear molecules) modes has a characteristic vibrational temperature, $\Theta_\mathrm{v,K} = h\nu_K/k_B$.

There are two ways to calculate the partition function, depending on where you choose the zero of energy to be: either the bottom of the internuclear potential energy well, or the first vibrational level. Which you choose depends on whether or not the contributions arising from zero-point energy will be coputed separately or not. If they are computed separately, then you should use the bottom of the well as your reference point, otherwise the first vibrational energy level is the appropriate choice.

If you choose the zero reference point to be the bottom of the well (`BOT`), then the contribution to the partition function from a given vibrational mode is [McQuarrie, §4-4, Eq. 4.24]:

$$q_{\mathrm{v},K} = \frac{e^{-\Theta_{\mathrm{v},K}/2T}}{1 - e^{-\Theta_{\mathrm{v},K}/T}}$$

and the overall vibrational partition function is[McQuarrie, §4-7, Eq. 4.46]:

$$q_\mathrm{v} = \prod_K \frac{e^{-\Theta_{\mathrm{v},K}/2T}}{1 - e^{-\Theta_{\mathrm{v},K}/T}}$$

On the other hand, if you choose the first vibrational energy level to be the zero of energy (`V=0`), then the partition function for each vibrational level is

$$q_{\mathrm{v},K} = \frac{1}{1 - e^{-\Theta_{\mathrm{v},K}/T}}$$

and the overall vibrational partition function is:

$$q_\mathrm{v} = \prod_K \frac{1}{1 - e^{-\Theta_{\mathrm{v},K}/T}}$$

Gaussian uses the bottom of the well as the zero of energy (`BOT`) to determine the other thermodynamic quantities, but also prints out the `V=0` partition function. Ultimately, the only difference between the two references is the additional factor of $\Theta_{\mathrm{v},K}/2$, (which is the zero point vibrational energy) in the equation for the internal energy E_{v}. In the expressions for heat capacity and entropy, this factor disappears since you differentiate with respect to temperature (T).

The total entropy contribution from the vibrational partition function is:

$$\begin{aligned}
S_{\mathrm{v}} &= R\left(\ln(q_{\mathrm{v}}) + T\left(\frac{\partial \ln q}{\partial T}\right)_V\right) \\
&= R\left(\ln(q_{\mathrm{v}}) + T\left(\sum_K \frac{\Theta_{\mathrm{v},K}}{2T^2} + \sum_K \frac{(\Theta_{\mathrm{v},K}/T^2)e^{-\Theta_{\mathrm{v},K}/T}}{1-e^{-\Theta_{\mathrm{v},K}/T}}\right)\right) \\
&= R\left(\sum_K\left(\frac{\Theta_{\mathrm{v},K}}{2T} + \ln(1-e^{-\Theta_{\mathrm{v},K}/T})\right) + T\left(\sum_K \frac{\Theta_{\mathrm{v},K}}{2T^2} + \sum_K \frac{(\Theta_{\mathrm{v},K}/T^2)e^{-\Theta_{\mathrm{v},K}/T}}{1-e^{-\Theta_{\mathrm{v},K}/T}}\right)\right) \\
&= R\left(\sum_K \ln(1-e^{-\Theta_{\mathrm{v},K}/T}) + \left(\sum_K \frac{(\Theta_{\mathrm{v},K}/T)e^{-\Theta_{\mathrm{v},K}/T}}{1-e^{-\Theta_{\mathrm{v},K}/T}}\right)\right) \\
&= R\sum_K\left(\frac{\Theta_{\mathrm{v},K}/T}{e^{\Theta_{\mathrm{v},K}/T}-1} - \ln(1-e^{-\Theta_{\mathrm{v},K}/T})\right)
\end{aligned}$$

To get from the fourth line to the fifth line in the equation above, you have to multiply by $\frac{e^{\Theta_{\mathrm{v},K}/T}}{e^{\Theta_{\mathrm{v},K}/T}}$.

The contribution to internal thermal energy resulting from molecular vibration is

$$E_{\mathrm{v}} = R\sum_K \Theta_{\mathrm{v},K}\left(\frac{1}{2} + \frac{1}{e^{\Theta_{\mathrm{v},K}/T}-1}\right)$$

Finally, the contribution to constant volume heat capacity is

$$C_{\mathrm{v}} = R\sum_K e^{\Theta_{\mathrm{v},K}/T}\left(\frac{\Theta_{\mathrm{v},K}/T}{e^{-\Theta_{\mathrm{v},K}/T}-1}\right)^2$$

Low frequency modes (defined below) are *included* in the computations described above. Some of these modes may be internal rotations, and so may need to be treated separately, depending on the temperatures and barriers involved. In order to make it easier to correct for these modes, their contributions are printed out separately, so that they may be subtracted out. A low frequency mode in *Gaussian* is defined as one for which more than five percent of an assembly of molecules are likely to exist in excited vibrational states at room temperature. In other units, this corresponds to about 625 cm^{-1}, 1.9×10^{13} Hz, or a vibrational temperature of 900 K.

It is possible to use *Gaussian* to automatically perform some of this analysis for you, via the `Freq=HindRot` keyword. This part of the code is still undergoing some improvements, so I will not go into it in detail. See P. Y. Ayala and H. B. Schlegel, J. Chem. Phys. **108** 2314 (1998) and references therein for more detail about the hindered rotor analysis in *Gaussian* and methods for correcting the partition functions due to these effects.

3 Thermochemistry output from *Gaussian*

This section describes most of the *Gaussian* thermochemistry output, and how it relates to the equations I've given above.

3.1 Output from a frequency calculation

In this section, I intentionally used a non-optimized structure, to show more output. For production runs, it is *very* important to use structures for which the first derivatives are zero — in other words, for minima, transition states and higher order saddle points. It is occasionally possible to use structures where one of the modes has non-zero first derivatives, such as along an IRC. For more information about why it is important to be at a stationary point on the potential energy surface, see my white paper on "Vibrational Analysis in *Gaussian* ".

Much of the output is self-explanatory. I'll only comment on some of the output which may not be immediately clear. Some of the output is also described in "Exploring Chemistry with Electronic Structure Methods, Second Edition" by James B. Foresman and Æleen Frisch.

```
-------------------
- Thermochemistry -
-------------------
Temperature   298.150 Kelvin.  Pressure   1.00000 Atm.
Atom  1 has atomic number  6 and mass  12.00000
Atom  2 has atomic number  6 and mass  12.00000
Atom  3 has atomic number  1 and mass   1.00783
Atom  4 has atomic number  1 and mass   1.00783
Atom  5 has atomic number  1 and mass   1.00783
Atom  6 has atomic number  1 and mass   1.00783
Atom  7 has atomic number  1 and mass   1.00783
Atom  8 has atomic number  1 and mass   1.00783
Molecular mass:    30.04695 amu.
```

The next section gives some characteristics of the molecule based on the moments of inertia, including the rotational temperature and constants. The zero-point energy is calculated using only the non-imaginary frequencies.

```
Principal axes and moments of inertia in atomic units:
                          1         2         3
    EIGENVALUES --    23.57594  88.34097  88.34208
          X            1.00000   0.00000   0.00000
          Y            0.00000   1.00000   0.00001
          Z            0.00000  -0.00001   1.00000
THIS MOLECULE IS AN ASYMMETRIC TOP.
ROTATIONAL SYMMETRY NUMBER  1.
ROTATIONAL TEMPERATURES (KELVIN)      3.67381     0.98044     0.98043
```

```
ROTATIONAL CONSTANTS (GHZ)          76.55013    20.42926    20.42901
Zero-point vibrational energy     204885.0 (Joules/Mol)
                                  48.96870 (Kcal/Mol)
```

If you see the following warning, it can be a sign that one of two things is happening. First, it often shows up if your structure is not a minimum with respect to all non-imaginary modes. You should go back and re-optimize your structure, since all the thermochemistry based on this structure is likely to be wrong. Second, it may indicate that there are internal rotations in your system. You should correct for errors caused by this situation.

```
WARNING-- EXPLICIT CONSIDERATION OF   1 DEGREES OF FREEDOM AS
          VIBRATIONS MAY CAUSE SIGNIFICANT ERROR
```

Then the vibrational temperatures and zero-point energy (ZPE):

```
VIBRATIONAL TEMPERATURES:    602.31  1607.07  1607.45  1683.83  1978.85
         (KELVIN)           1978.87  2303.03  2389.95  2389.96  2404.55
                            2417.29  2417.30  4202.52  4227.44  4244.32
                            4244.93  4291.74  4292.31
```

```
Zero-point correction=                           0.078037 (Hartree/Particle)
```

Each of the next few lines warrants some explanation. All of them include the zero-point energy. The first line gives the correction to the internal thermal energy, $E_{\text{tot}} = E_{\text{t}} + E_{\text{r}} + E_{\text{v}} + E_{\text{e}}$.

```
Thermal correction to Energy=                    0.081258
```

The next two lines, respectively, are

$$H_{\text{corr}} = E_{\text{tot}} + k_B T$$

and

$$G_{\text{corr}} = H_{\text{corr}} - T S_{\text{tot}},$$

where $S_{\text{tot}} = S_{\text{t}} + S_{\text{r}} + S_{\text{v}} + S_{\text{e}}$.

```
Thermal correction to Enthalpy=                  0.082202
Thermal correction to Gibbs Free Energy=         0.055064
```

The Gibbs free energy includes $\Delta PV = \Delta NRT$, so when it's applied to calculating ΔG for a reaction, $\Delta NRT \approx \Delta PV$ is already included. This means that ΔG will be computed correctly when the number of moles of gas changes during the course of a reaction.

The next four lines are estimates of the total energy of the molecule, after various corrections are applied. Since I've already used E to represent internal thermal energy, I'll use $\mathcal{E}_0$ for the total electronic energy.

Sum of electronic and zero-point energies $= \mathcal{E}_0 + \mathcal{E}_{\text{ZPE}}$

Sum of electronic and thermal energies $= \mathcal{E}_0 + E_{\text{tot}}$

Sum of electronic and thermal enthalpies $= \mathcal{E}_0 + H_{\text{corr}}$

Sum of electronic and thermal free energies $= \mathcal{E}_0 + G_{\text{corr}}$

```
Sum of electronic and zero-point Energies=           -79.140431
Sum of electronic and thermal Energies=              -79.137210
Sum of electronic and thermal Enthalpies=            -79.136266
Sum of electronic and thermal Free Energies=         -79.163404
```

The next section is a table listing the individual contributions to the internal thermal energy (E_{tot}), constant volume heat capacity (C_{tot}) and entropy (S_{tot}). For every low frequency mode, there will be a line similar to the last one in this table (labeled `VIBRATION 1`). That line gives the contribution of that particular mode to E_{tot}, C_{tot} and S_{tot}. This allows you to subtract out these values if you believe they are a source of error.

```
                    E (Thermal)             CV                S
                     KCAL/MOL        CAL/MOL-KELVIN    CAL/MOL-KELVIN
TOTAL                  50.990              8.636            57.118
ELECTRONIC              0.000              0.000             0.000
TRANSLATIONAL           0.889              2.981            36.134
ROTATIONAL              0.889              2.981            19.848
VIBRATIONAL            49.213              2.674             1.136
VIBRATION  1            0.781              1.430             0.897
```

Finally, there is a table listing the individual contributions to the partition function. The lines labeled `BOT` are for the vibrational partition function computed with the zero of energy being the bottom of the well, while those labeled with `(V=0)` are computed with the zero of energy being the first vibrational level. Again, special lines are printed out for the low frequency modes.

```
                     Q            LOG10(Q)             LN(Q)
TOTAL BOT       0.470577D-25     -25.327369        -58.318422
TOTAL V=0       0.368746D+11      10.566728         24.330790
VIB (BOT)       0.149700D-35     -35.824779        -82.489602
VIB (BOT)  1    0.419879D+00      -0.376876         -0.867789
VIB (V=0)       0.117305D+01       0.069318          0.159610
VIB (V=0)  1    0.115292D+01       0.061797          0.142294
ELECTRONIC      0.100000D+01       0.000000          0.000000
TRANSLATIONAL   0.647383D+07       6.811161         15.683278
ROTATIONAL      0.485567D+04       3.686249          8.487901
```

3.2 Output from compound model chemistries

This section explains what the various thermochemical quantities in the summary out of a compound model chemistry, such as CBS-QB3 or G2, means.

I'll use a CBS-QB3 calculation on water, but the discussion is directly applicable to all the other compound models available in Gaussian. The two lines of interest from the output look like:

```
CBS-QB3 (0 K)=           -76.337451 CBS-QB3 Energy=             -76.334615
CBS-QB3 Enthalpy=        -76.333671 CBS-QB3 Free Energy=        -76.355097
```

Here are the meanings of each of those quantities.

- CBS-QB3 (0 K): This is the total electronic energy as defined by the compound model, including the zero-point energy scaled by the factor defined in the model.
- CBS-QB3 Energy: This is the total electronic energy plus the internal thermal energy, which comes directly from the thermochemistry output in the frequency part of the output. The scaled zero-point energy is included.
- CBS-QB3 Enthalpy: This is the total electronic energy plus H_{corr}, as it is described above with the unscaled zero-point energy removed. This sum is appropriate for calculating enthalpies of reaction, as described below.
- CBS-QB3 Free Energy: This is the total electronic energy plus G_{corr}, as it is described above, again with the unscaled zero-point energy removed. This sum is appropriate for calculating Gibbs free energies of reaction, also as described below.

4 Worked-out Examples

In this section I will show how to use these results to generate various thermochemical information.

I've run calculations for each of the reactants and products in the reaction where ethyl radical abstracts a hydrogen atom from molecular hydrogen:

$$C_2H_5 + H_2 \rightarrow C_2H_6 + H$$

as well as for the transition state (all at 1.0 atmospheres and 298.15K). The thermochemistry output from *Gaussian* is summarized in Table 1.

Once you have the data for all the relevant species, you can calculate the quantities you are interested in. Unless otherwise specified, all enthalpies are at 298.15K. I'll use $298K \approx 298.15K$ to shorten the equations.

	C_2H_5	H_2	C_2H_6	H	C
$\mathcal{E}_0$	-77.662998	-1.117506	-78.306179	-0.466582	-37.198393
$\mathcal{E}_{\text{ZPE}}$	0.070833	0.012487	0.089704	0.000000	0.000000
E_{tot}	0.074497	0.014847	0.093060	0.001416	0.001416
H_{corr}	0.075441	0.015792	0.094005	0.002360	0.002360
G_{corr}	0.046513	0.001079	0.068316	-0.010654	-0.014545
$\mathcal{E}_0 + \mathcal{E}_{\text{ZPE}}$	-77.592165	-1.105019	-78.216475	-0.466582	-37.198393
$\mathcal{E}_0 + E_{\text{tot}}$	-77.588501	-1.102658	-78.213119	-0.465166	-37.196976
$\mathcal{E}_0 + H_{corr}$	-77.587557	-1.101714	-78.212174	-0.464221	-37.196032
$\mathcal{E}_0 + G_{corr}$	-77.616485	-1.116427	-78.237863	-0.477236	-37.212938

Table 1: Calculated thermochemistry values from *Gaussian* for the reaction $C_2H_5 + H_2 \rightarrow C_2H_6 + H$. All values are in Hartrees.

4.1 Enthalpies and Free Energies of Reaction

The usual way to calculate enthalpies of reaction is to calculate heats of formation, and take the appropriate sums and difference.

$$\Delta_r H^\circ(298K) = \sum_{\text{products}} \Delta_f H^\circ_{\text{prod}}(298K) - \sum_{\text{reactants}} \Delta_f H^\circ_{\text{react}}(298K).$$

However, since Gaussian provides the sum of electronic and thermal enthalpies, there is a short cut: namely, to simply take the difference of the sums of these values for the reactants and the products. This works since the number of atoms of each element is the same on both sides of the reaction, therefore all the atomic information cancels out, and you need only the molecular data.

For example, using the information in Table 1, the enthalpy of reaction can be calculated simply by

$$\begin{aligned}
\Delta_r H^\circ(298K) &= \sum(\mathcal{E}_0 + H_{corr})_{\text{products}} - \sum(\mathcal{E}_0 + H_{corr})_{\text{reactants}} \\
&= ((-78.212174 + -0.464221) - (-77.587557 + -1.101714)) * 627.5095 \\
&= 0.012876 * 627.5095 \\
&= 8.08 \text{ kcal/mol}
\end{aligned}$$

The same short cut can be used to calculate Gibbs free energies of reaction:

$$\begin{aligned}
\Delta_r H^\circ(298K) &= \sum(\mathcal{E}_0 + G_{corr})_{\text{products}} - \sum(\mathcal{E}_0 + G_{corr})_{\text{reactants}} \\
&= ((-78.237863 + -0.477236) - (-77.616485 + -1.116427)) * 627.5095 \\
&= 0.017813 * 627.5095 \\
&= 11.18 \text{ kcal/mol}
\end{aligned}$$

4.2 Rates of Reaction

In this section I'll show how to compute rates of reaction using the output from *Gaussian*. I'll be using results derived from transition state theory in section 28-8 of "Physical Chemistry,

Compound	$\mathcal{E}_0$	$\mathcal{E}_0 + G_{corr}$
HF	-98.572847	-98.579127
HD	-98.572847	-98.582608
Cl	-454.542193	-454.557870
HCl	-455.136012	-455.146251
DCl	-455.136012	-455.149092
F	-97.986505	-98.001318
FHCl	-553.090218	-553.109488
FDCl	-553.090218	-553.110424

Table 2: Total HF/STO-3G electronic energies and sum of electronic and thermal free energies for atoms molecules and transition state complex of the reaction FH + Cl → F + HCl and the deuterium substituted analog.

A Molecular Approach" by D. A. McQuarrie and J. D. Simon. The key equation (number 28.72, in that text) for calculating reaction rates is

$$k(T) = \frac{k_B T}{hc^\circ} e^{-\Delta^\ddagger G^\circ / RT}$$

I'll use $c^\circ = 1$ for the concentration. For simple reactions, the rest is simply plugging in the numbers. First, of course, we need to get the numbers. I've run HF/STO-3G frequency calculation for reaction FH + Cl → F + HCl and also for the reaction with deuterium substituted for hydrogen. The results are summarized in Table 2. I put the total electronic energies of each compound into the table as well to illustrate the point that the final geometry and electronic energy are independent of the masses of the atoms. Indeed, the cartesian force constants themselves are independent of the masses. Only the vibrational analysis, and quantities derived from it, are mass dependent.

The first step in calculating the rates of these reactions is to compute the free energy of activation, $\Delta^\ddagger G^\circ$ ((H) is for the hydrogen reaction, (D) is for deuterium reaction):

$$\begin{aligned}
\Delta^\ddagger G^\circ(H) &= -553.109488 - (-98.579127 + -454.557870) \\
&= 0.027509 \text{ Hartrees} \\
&= 0.027509 * 627.5095 = 17.26 \text{ kcal/mol}
\end{aligned}$$

$$\begin{aligned}
\Delta^\ddagger G^\circ(D) &= -553.110424 - (-98.582608 + -454.557870) \\
&= 0.030054 \text{ Hartrees} \\
&= 0.030054 * 627.5095 = 18.86 \text{ kcal/mol}
\end{aligned}$$

Then we can calculate the reaction rates. The values for the constants are listed in the appendix. I've taken $c^\circ = 1$.

$$k(298, H) = \frac{k_B T}{hc^\circ} e^{-\Delta^\ddagger G^\circ / RT}$$

$$
\begin{aligned}
&= \frac{1.380662 \times 10^{-23}(298.15)}{6.626176 \times 10^{-34}(1)} \exp\left(\frac{-17.26 * 1000}{1.987 * 298.15}\right) \\
&= 6.2125 \times 10^{12} e^{-29.13} \\
&= 1.38\mathrm{s}^{-1}
\end{aligned}
$$

$$
\begin{aligned}
k(298, D) &= 6.2125 \times 10^{12} \exp\left(\frac{-18.86 * 1000}{1.987 * 298.15}\right) \\
&= 6.2125 \times 10^{12} e^{-31.835} \\
&= 0.0928\mathrm{s}^{-1}
\end{aligned}
$$

So we see that the deuterium reaction is indeed slower, as we would expect. Again, these calculations were carried out at the HF/STO-3G level, for illustration purposes, not for research grade results. More complex reactions will need more sophisticated analyses, perhaps including careful determination of the effects of low frequency modes on the transition state, and tunneling effects.

4.3 Enthalpies and Free Energies of Formation

Calculating enthalpies of formation is a straight-forward, albeit somewhat tedious task, which can be split into a couple of steps. The first step is to calculate the enthalpies of formation ($\Delta_f H^\circ(0K)$) of the species involved in the reaction. The second step is to calculate the enthalpies of formation of the species at 298K.

Calculating the Gibbs free energy of reaction is similar, except we have to add in the entropy term:

$$\Delta_f G^\circ(298) = \Delta_f H^\circ(298K) - T(S^\circ(M, 298K) - \sum S^\circ(X, 298K))$$

To calculate these quantities, we need a few component pieces first. In the descriptions below, I will use M to stand for the molecule, and X to represent each element which makes up M, and x will be the number of atoms of X in M.

- Atomization energy of the molecule, $\sum D_0(M)$:

  These are readily calculated from the total energies of the molecule ($\mathcal{E}_0(M)$), the zero-point energy of the molecule ($\mathcal{E}_{\mathrm{ZPE}}(M)$) and the constituent atoms:

  $$\sum D_0(M) = \sum_{\text{atoms}} x\mathcal{E}_0(X) - \mathcal{E}_0(M) - \mathcal{E}_{\mathrm{ZPE}}(M)$$

- Heats of formation of the atoms at 0K, $\Delta_f H^\circ(X, 0K)$:

  I have tabulated recommended values for the heats of formation of the first and second row atomic elements at 0K in Table 3. There are (at least) two schools of thought with respect to the which atomic heat of formation data is most appropriate. Some authors prefer to use purely experimental data for the heats of formation (Curtiss, et. al., J.

Chem. Phys. **106**, 1063 (1997)). Others (Ochterski, et. al., J. Am. Chem. Soc. **117**, 11299 (1995)), prefer to use a combination of experiment and computation to obtain more accurate values. The elements of concern are boron, beryllium and silicon. I have arranged Table 3 so that either may be used; the experimental results are on the top, while the computational results for the three elements with large experimental uncertainty are listed below that.

- Enthalpy corrections of the atomic elements, $H^\circ_X(298K) - H^\circ_X(0K)$:

  The enthalpy corrections of the first and second row atomic elements are also included in Table 3. These are used to convert the atomic heats of formation at 0K to those at 298.15K, and are given for the elements in their standard states. Since they do not depend on the accuracy of the heat of formation of the atom, they are the same for both the calculated and experimental data.

  This is generally *not* the same as the output from *Gaussian* for a calculation on an isolated gas-phase atom. These values are referenced to the standard states of the elements. For example, the value for hydrogen atom is 1.01 kcal/mol. This is $(H^\circ_{H_2}(298K) - H^\circ_{H_2}(0K))/2$, and not $H^\circ_H(298K) - H^\circ_H(0K)$, which is what *Gaussian* calculates.

- Enthalpy correction for the molecule, $H^\circ_M(298K) - H^\circ_M(0K)$:

  For a molecule, this is $H_{\text{corr}} - \mathcal{E}_{\text{ZPE}}(M)$, where H_{corr} is the value printed out in the line labeled "`Thermal correction to Enthalpy`" in *Gaussian* output. Remember, though, that the output is in Hartrees/particle, and needs to be converted to kcal/mol. The conversion factor is 1 Hartree = 627.5095 kcal/mol.

- Entropy for the atoms, $S^\circ_X(298K)$:

  These are summarized in Table 3. The values were taken from the JANAF tables (M. W. Chase, Jr., C. A. Davies, J. R. Downey, Jr., D. J. Frurip, R. A. McDonald, and A. N. Syverud, J. Phys. Ref. Data **14** Suppl. No. 1 (1985)). Again, these values are referenced to the standard states of the elements, and will disagree with values *Gaussian* calculates for the gas-phase isolated atoms.

- Entropy for the molecule, $S^\circ_M(298K)$:

  Gaussian calculates $G = H - TS$, and prints it out on the line labeled "`Thermal correction to Gibbs Free Energy`". The entropy can be teased out of this using $S = (H - G)/T$.

Putting all these pieces together, we can finally take the steps necessary to calculate $\Delta_f H^\circ(298K)$ and $\Delta_f G^\circ(298K)$:

1. Calculate $\Delta_f H^\circ(M, 0K)$ for each molecule:

$$\begin{aligned}\Delta_f H^\circ(M,0K) &= \sum_{\text{atoms}} x\Delta_f H^\circ(X,0K) - \sum D_0(M) \\ &= \sum_{\text{atoms}} x\Delta_f H^\circ(X,0K) - \left(\sum_{\text{atoms}} x\mathcal{E}_0(X) - \mathcal{E}_0(M)\right)\end{aligned}$$

Experimental^a			
Element	$\Delta_f H^\circ(0K)$	$H^\circ(298K) - H^\circ(0K)$	$S^\circ(298K)$
H	51.63±0.001	1.01	27.418±0.004
Li	37.69±0.2	1.10	33.169±0.006
Be	76.48±1.2	0.46	32.570±0.005
B	136.2 ±0.2	0.29	36.672±0.008
C	169.98±0.1	0.25	37.787±0.21
N	112.53±0.02	1.04	36.640±0.01
O	58.99±0.02	1.04	38.494±0.005
F	18.47±0.07	1.05	37.942±0.001
Na	25.69±0.17	1.54	36.727±0.006
Mg	34.87±0.2	1.19	8.237±^{d}
Al	78.23±1.0	1.08	39.329±0.01
Si	106.6 ±1.9	0.76	40.148±0.008
P	75.42±0.2	1.28	39.005±0.01
S	65.66±0.06	1.05	40.112±0.008
Cl	28.59±0.001	1.10	39.481±0.001
Calculated^b			
Element	$\Delta_f H^\circ(0K)$	$H^\circ(298K) - H^\circ(0K)$	$S^\circ(298K)$
Be	75.8 ±0.8	0.46	32.570±0.005
B	136.2 ±0.2	0.29	36.672±0.008
Si	108.1 ±0.5	0.76	40.148±0.008

Table 3: Experimental and calculated enthalpies of formation of elements (kcal mol^{-1}) and entropies of atoms (cal mol^{-1} K^{-1}) . ^{a} Experimental enthalpy values taken from J. Chem. Phys. **106**, 1063 (1997). ^{b} Calculated enthalpy values taken from J. Am. Chem. Soc. **117**, 11299 (1995). $H^\circ(298K) - H^\circ(0K)$ is the same for both calculated and experimental, and is taken for elements in their standard states. ^{c} Entropy values taken from JANAF Thermochemical Tables: M. W. Chase, Jr., C. A. Davies, J. R. Downey, Jr., D. J. Frurip, R. A. McDonald, and A. N. Syverud, J. Phys. Ref. Data **14** Suppl. No. 1 (1985). ^{d} No error bars are given for Mg in JANAF.

2. Calculate $\Delta_f H^\circ(M, 298K)$ for each molecule:

$$\begin{aligned} \Delta_f H^\circ(M, 298K) &= \Delta_f H^\circ(M, 0K) + (H^\circ_M(298K) - H^\circ_M(0K)) \\ &\quad - \sum_{\text{atoms}} x(H^\circ_X(298K) - H^\circ_X(0K)) \end{aligned}$$

3. Calculate $\Delta_f G^\circ(M, 298K)$ for each molecule:

$$\Delta_f G^\circ(M, 298K) = \Delta_r H^\circ(298K) - 298.15(S^\circ(M, 298K) - \sum S^\circ(X, 298K))$$

Here is a worked out example, where I've calculated $\Delta_f H^\circ(298K)$ for the reactants and products in the reaction I described above.

First, I'll calculate $\Delta_f H^\circ(0K)$ for one of the species:

$$\begin{aligned}
\Delta_f H^\circ(C_2H_6, 0K) &= 2 * 169.98 + 6 * 51.63 \\
&\quad -627.5095 * (2 * (-37.198393) + 6 * (-0.466582) - (-78.216475)) \\
&= 649.74 - 627.5095 * 1.020197 \\
&= 9.56
\end{aligned}$$

The next step is to calculate the $\Delta_f H^\circ(298K)$:

$$\begin{aligned}
\Delta_f H^\circ(C_2H_6, 298K) &= 9.56 + 627.5095 * (0.094005 - 0.089704) - (2 * 0.25 + 6 * 1.01) \\
&= 9.56 + 2.70 - 6.56 \\
&= 5.70
\end{aligned}$$

To calculate the Gibbs free energy of formation, we have (the factors of 1000 are to convert kcal to or from cal) :

$$\begin{aligned}
\Delta_f G^\circ(C_2H_6, 298K) &= 5.70 + 298.15(627.5095 * (0.094005 - 0.068316)/298.15 - \\
&\quad (2 * 37.787 + 6 * 27.418)/1000 \\
&= 5.70 + 298.15 * (0.054067 - 0.240082) \\
&= -49.76
\end{aligned}$$

5 Summary

The essential message is this: the basic equations used to calculate thermochemical quantities in *Gaussian* are based on those used in standard texts. Since the vibrational partition function depends on the frequencies, you must use a structure that is either a minimum or a saddle point. For electronic contributions to the partition function, it is assumed that the first and all higher states are inaccessible at the temperature the calculation is done at. The data generated by *Gaussian* can be used to calculate heats and free energies of reactions as well as absolute rate information.

Appendix

Symbols

C_{e} = contribution to the heat capacity due to electronic motion

C_{r} = contribution to the heat capacity due to rotational motion

C_{tot} = total heat capacity $(C_{\mathrm{t}} + C_{\mathrm{r}} + C_{\mathrm{v}} + C_{\mathrm{e}})$

C_{t} = contribution to the heat capacity due to translation

C_{v} = contribution to the heat capacity due to vibrational motion

E_{e} = internal energy due to electronic motion

E_{r} = internal energy due to rotational motion

E_{tot} = total internal energy $(E_{\mathrm{t}} + E_{\mathrm{r}} + E_{\mathrm{v}} + E_{\mathrm{e}})$

E_{t} = internal energy due to translation

E_{v} = internal energy due to vibrational motion

G_{corr} = correction to the Gibbs free energy due to internal energy

H_{corr} = correction to the enthalpy due to internal energy

I = moment of inertia

K = index of vibrational modes

N = number of moles

N_A = Avogadro's number

P = pressure (default is 1 atmosphere)

R = gas constant = 8.31441 J/(mol K) = 1.987 kcal/(mol K)

S_{e} = entropy due to electronic motion

S_{r} = entropy due to rotational motion

S_{tot} = total entropy $(S_{\mathrm{t}} + S_{\mathrm{r}} + S_{\mathrm{v}} + S_{\mathrm{e}})$

S_{t} = entropy due to translation

S_{v} = entropy due to vibrational motion

T = temperature (default is 298.15)

V = volume

$\Theta_{\mathrm{r}}, \Theta_{\mathrm{r,(xyz)}}$ = characteristic temperature for rotation (in the x, y or z plane)

$\Theta_{\mathrm{v,K}}$ = characteristic temperature for vibration K

k_B = Boltzmann constant = 1.380662×10^{-23} J/K

ϵ_n = the energy of the n-th energy level

ω_n = the degeneracy of the n-th energy level

σ_r = symmetry number for rotation

h = Planck's constant = 6.626176×10^{-34} J s

m = mass of the molecule

n = number of particles (always 1)

q_e = electronic partition function

q_r = rotational partition function

q_t = translational partition function

q_v = vibrational partition function

$\mathcal{E}_\mathrm{ZPE}$ = zero-point energy of the molecule

$\mathcal{E}_0$ = the total electronic energy, the MP2 energy for example

$H^\circ, S^\circ, G^\circ$ = standard enthalpy, entropy and Gibbs free energy — each compound is in its standard state at the given temperature

$\Delta^\ddagger G^\circ$ = Gibbs free energy of activation

c° = concentration (taken to be 1)

$k(T)$ = reaction rate at temperature T

Predicting Magnetic Properties with ChemDraw and Gaussian

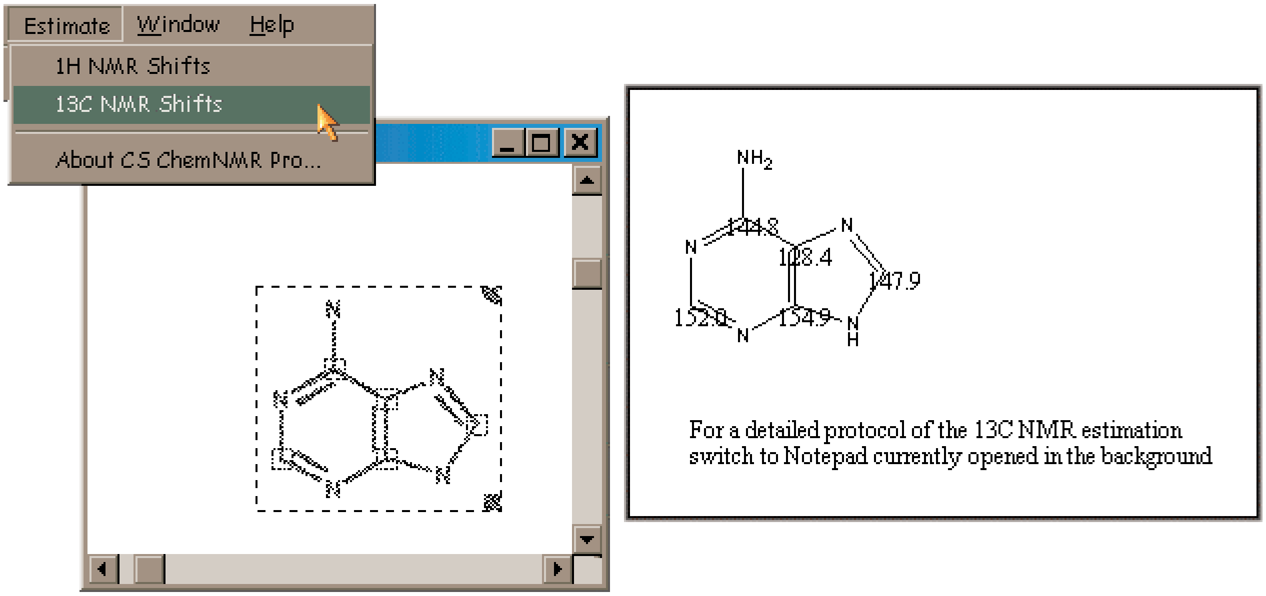
By James R. Cheeseman and Æleen Frisch

Introduction

NMR chemical shifts are an important tool in characterizing molecular systems and structures. Accordingly, predicting NMR spectra is an essential feature of computational chemistry software. In this article, we'll look at two very different NMR facilities, each of which is very useful when applied to the appropriate sort of molecules.

ChemDraw Ultra includes the CS ChemNMR Pro facility which can be used to estimate the ^{13}C and ^{1}H (proton) chemical shifts with respect to TMS. This facility is accessed from the **Estimate** menu within the product. When a molecule has been selected, the two items on the menu become active, and selecting one of them causes the NMR chemical shifts for the corresponding atom type to be calculated.

Figure 1 illustrates the use of this facility; here we estimate the ^{13}C chemical shifts with respect to TMS for adenine. The **Estimate** menu and selected molecule appear on the left in the figure, and the resulting graphic output appears on the right. The latter consists of another copy of the molecule to which numbers denoting the chemical shift (in ppm) have been added at each atom location. Note that numbers are ordinary ChemDraw text labels and thus may be moved as needed in order to make them fully legible. Additional output is presented in text form via a Notepad document (which is opened automatically by ChemDraw).



For a detailed protocol of the 13C NMR estimation switch to Notepad currently opened in the background

Figure 1. Example CS ChemNMR Pro Output

CS ChemNMR Pro uses a heuristically-driven procedure in order to estimate chemical shifts; it starts with a base value determined from the molecular mechanics atom type of the atom in question, and then applies corrections for each of the groups to which it is bonded in order to compute its final value. This process is illustrated in this excerpt from the textual output from a calculation on taxol:

```
Protocol of the 13C NMR Estimation

Node     Estim.     Base     Incr.     Comment (ppm rel. to TMS)
  C      138.5      123.3              1-ethylene
                             -8.9      1 -C-C-C-C
                             -7.4      1 -C
                             17.3      1 -C-C-C-C
                             14.2      1 -C-O
```

The main advantage of this approach to computing chemical shifts is its speed: chemical shifts can be computed almost instantaneously even for very large molecules. However, the method has an important weakness which must be kept in mind. Since it relies on a fixed set of parameters corresponding to atom types and subgroups, the method will be reliable only for molecules for which parameters are available and for which the assumptions about molecular structure and bonding which are built-in to the parameters are valid.

In simple terms, this NMR estimation method is appropriate only for ordinary organic molecules. It produces reasonable results for such systems, but becomes quite unreliable for systems with any unusual features: unusual bonding, strained systems, systems for which electron correlation is important for accurate modeling of the molecular structure or properties, and so on. In these cases, a more accurate computational method is required.

Systematic Prediction of Magnetic Properties

Gaussian 98 includes a facility for predicting magnetic properties, including NMR shielding tensors and chemical shifts. These calculations compute magnetic properties from first principles, as the mixed second derivative of the energy with respect to an applied magnetic field and the nuclear magnetic moment. As a result, they can produce high accuracy results for the entire range of molecular systems studied experimentally via NMR techniques.

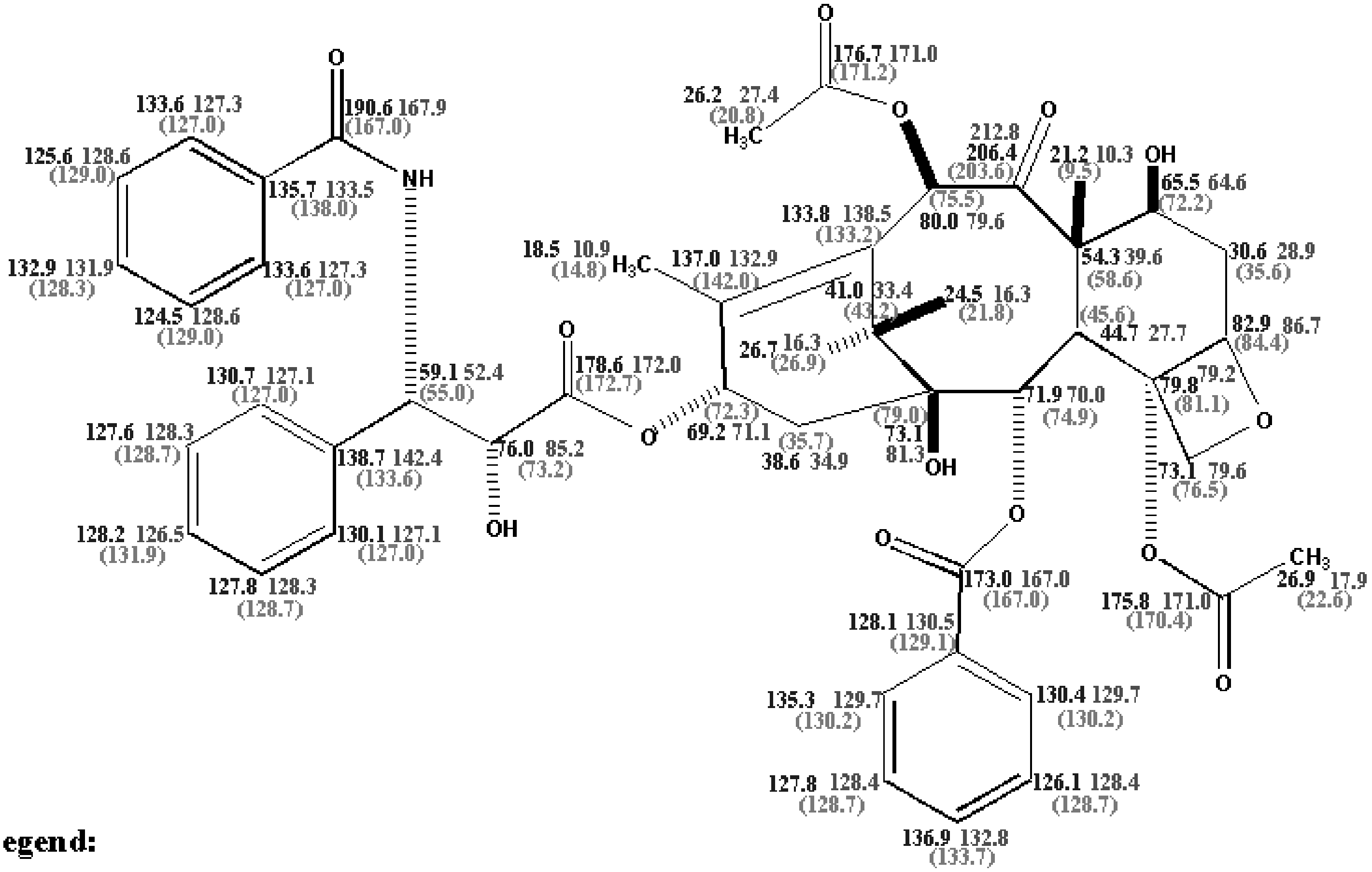
Thus, *Gaussian 98*'s facility has several important advantages over the simple computation procedure used by CS ChemNMR Pro:

- Accurate prediction of magnetic properties for all types of molecular systems
- Ability to predict chemical shifts for atoms other than hydrogen and carbon (nitrogen, phosphorous, boron, and so on).
- NMR properties can be computed as part of a systematic and self-consistent study of the molecule.

Some Sample Results

As we've noted, CS ChemNMR Pro does an adequate job of estimating chemical shifts for ordinary organic compounds. Taxol provides an example of this. For this molecule, CS ChemNMR Pro's mean absolute error with respect to the observed ^{13}C chemical shifts is 3.8 ppm, with a standard deviation of 4.6, and the largest error is 19.0 ppm. *Gaussian* also does well for this molecule: its mean absolute error is 4.2, with a standard deviation of 3.8 and a maximum error of 23.6.

Observed and Predicted ^{13}C Chemical Shifts for Taxol



Legend:

Gaussian 98 **Shift** CS ChemNMR Pro Shift
(Observed Shift)

Layout occasionally modified due to space constraints.

Chemical shifts are with respect to TMS.

Table 1 presents ^{13}C chemical shifts for adenine as computed by CS ChemNMR Pro and predicted by *Gaussian 98*, comparing them to the experimentally observed values. For this molecule, *Gaussian 98* performs slightly better than CS ChemNMR Pro. However, the errors that *Gaussian* makes are systematic, always over estimating the magnitude of the chemical shift. In contrast, the estimated shifts computed by CS ChemNMR Pro contain large errors with respect to the observed values in both directions.

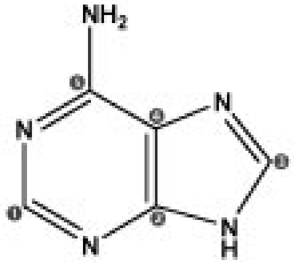


Table 1. Predicted ^{13}C Chemical Shifts for Adenine

Atom	CS ChemNMR Pro	ΔExperiment	*Gaussian 98*	ΔExperiment	Experiment
C1	150.2	-2.2	161.2	+9.2	152.4
C2	154.9	+3.6	156.8	+5.5	151.3
C3	147.9	+8.6	139.5	+0.2	139.3
C4	128.4	+10.8	124.8	+7.2	117.6
C5	144.8	-10.5	160.7	+5.4	155.3

Table 2 lists the estimated and predicted ^{13}C chemical shifts for a series of three strained system, cyclopropane, bicyclobutane and [1.1.1]propellane, and for another unusual system, oxaspiropentene (left to right in the illustration). Both values for the carbon shift in cyclopropane are reasonable, but with the larger molecules, the limitations of the heuristically-based approach become clear. CS ChemNMR Pro cannot estimate either the values of the chemical shifts nor the difference in shift between the two different types of carbon atoms within the molecule. Finally, the results for oxaspiropentene are only fair. In contrast, the values predicted by *Gaussian 98*agree very well with with the observed values in all cases.

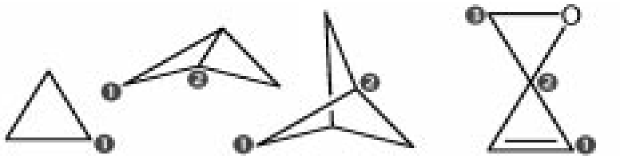


Table 2. Chemical Shifts for Three Strained Hydrocarbons

Molecule and Atom	**CS ChemNMR Pro**	***Gaussian 98***	**Experiment**
Cyclopane (C_3H_6)			
C1	-2.8	-6.7	-4.0
Bicyclobutane (C_5H_6)			
C1	6.6	26.6	32.0
C2	-0.2	-7.1	-5.7
Shift Difference	6.8	33.7	37.7

Molecule and Atom	**CS ChemNMR Pro**	***Gaussian 98***	**Experiment**
[1.1.1]Propellane(C_5H_6)			
C1	30.3	70.6	79.3
C2	26.0	-3.4	3.4
Shift Difference	4.3	74.0	82.7
Oxaspiropentene			
C1	46.0	39.2	38.9
C2	129.3	120.8	116.7
C3	44.6	31.13	30.76

Table 3 lists some sample results for predicted ^{15}N and ^{11}B chemical shifts as predicted by *Gaussian 98*. The predicted values are again in very good agreement with experimental observations.

Table 3. Predicted ^{15}N and ^{11}B Chemical Shifts

Molecule and Atom	***Gaussian 98***	**Experiment**
$C_2B_3H_5$		
C	99.9	103.3
B[b]	-0.1	3.5
CH_3CN		
C	-4.1	0.4
C	114.3	114.3
N[c]	290.8	272.6

[b] Shift with respect to B_2H_6.
[c] Shift with respect to NH_3.

Selected References

All reported *Gaussian 98* chemical shifts except those for taxol were computed via NMR calculations using the B3LYP/6-311+G(2d,p) level at the B3LYP/6-31G(d) optimized geometries. The taxol chemical shifts were computed from NMR calculations performed at the HF/6-31G(d) level using STO-3G optimized geometries.

“A comparison of models for calculating nuclear magnetic resonance shielding tensors,” James R. Cheeseman, Gary W. Trucks, Todd A. Keith and Michael J. Frisch, *J. Chem. Phys.* **104** (1996) 5497. [A discussion of the method used to predict magnetic properties as well as results for a wide variety of molecules. See the references to this paper for the sources of the experimental values cited here.]

“Synthesis of Oxaspiropentene,” W. E. Billups, Vladislav A. Litosh, Rajesh K. Saini and Andrew D. Daniels, *Org. Lett.* **1** (1999) 115. [NMR predictions are used to confirm the identiy of the synthesized compound.]

“NMR Chemical Shifts. 3. A Comparison of Acetylene, Allene, and the Higher Cumulenes,” Kenneth B. Wiberg, Jack D. Hammer, Kurt W. Zilm and James R. Cheeseman, *J. Org. Chem.* **64** (1999) 6394. [An example of a recent application study using the *Gaussian* NMR facility.]

“NMR Methods Blossom,” *Chemical and Engineering News*, 76:39, 28 September 1999. [Overview of a recent ACS symposium on NMR.]

Acknowledgments

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3 Practice

Gaussian 03 Online Manual

Last update: 2 October 2006

Gaussian 03 Input Overview

Gaussian 03 input consists of a series of lines in an ASCII text file. The basic structure of a *Gaussian* input file includes several different sections:

- *Link* 0 *Commands*: Locate and name scratch files (not blank line terminated).
- *Route section* (*# lines*): Specify desired calculation type, model chemistry and other options (blank line terminated).
- *Title section:* Brief description of the calculation (blank line terminated).
- *Molecule specification*: Specify molecular system to be studied (blank line terminated).
- *Optional additional sections:* Additional input needed for specific job types (usually blank line terminated).

Many *Gaussian 03* jobs will include only the second, third, and fourth sections. Here is an example of such a file, which requests a single point energy calculation on water:

```
# HF/6-31G(d)                   Route section

water energy                    Title section
0   1                           Molecule specification
O  -0.464   0.177   0.0
H  -0.464   1.137   0.0
H   0.441  -0.143   0.0
```

In this job, the route and title sections each consist of a single line. The molecule specification section begins with a line giving the charge and spin multiplicity for the molecule: 0 charge (neutral molecule) and spin multiplicity 1 (singlet) in this case. The charge and spin multiplicity line is followed by lines describing the location of each atom in the molecule; this example uses Cartesian coordinates to do so. Molecule specifications are discussed in more detail later in this chapter.

The following input file illustrates the use of Link 0 commands and an additional input section:

```
%Chk=heavy                                  Link 0 section
#HF/6-31G(d) Opt=ModRedundant               Route section

Opt job                                     Title section

 0    1                                      Molecule Specification section
atomic coordinates ...

3 8                                         Add a bond and an angle to the internal
2 1 3                                         coordinates used during the geom. opt.
```

This job requests a geometry optimization. The input section following the molecule specification is used by the **Opt=ModRedundant** keyword, and it serves to add an additional bond and angle in the internal coordinates used in the geometry optimization. The job also specifies a name for the checkpoint file.

Link 0 commands were introduced in the last chapter and are discussed individually in the penultimate section of this chapter. The remaining input sections are discussed in the subsequent subsections of this introductory section. For convenience, the table below lists all possible sections that might appear within a *Gaussian 03* input file, along with the keywords associated with each one.

Input Syntax

In general, *Gaussian* input is subject to the following syntax rules:

- Input is free-format and case-insensitive.
- Spaces, tabs, commas, or forward slashes can be used in any combination to separate items within a line. Multiple spaces are treated as a single delimiter.
- Options to keywords may be specified in any of the following forms:

  keyword = option
  keyword (*option*)
  keyword= (*option1, option2, ...*)
  keyword (*option1, option2, ...*)

- Multiple options are enclosed in parentheses and separated by any valid delimiter (commas are conventional and are shown above). The equals sign before the opening parenthesis may be omitted, or spaces may optionally be included before and/or after it.
- Note that some options also take values; in this case, the option name is followed by an equals sign: for example, **CBSExtrap**(**NMin=6**).
- All keywords and options may be shortened to their shortest unique abbreviation within the entire *Gaussian 03* system. Thus, the **Conventional** option to the **SCF** keyword may be abbreviated to **Conven**, but not to **Conv** (due to the presence of the **Convergence** option). This holds true whether or not both **Conventional** and **Convergence** happen to be valid options for any given keyword.
- The contents of an external file may be included within a *Gaussian 03* input file using the following syntax: *@filename*. This causes the entire file to be placed at the current location in the input stream. Appending **/N** to such commands will prevent the included file's contents from being echoed at the start of the output file.
- Comments begin with an exclamation point (**!**), which may appear anywhere on a line. Separate comment lines may appear anywhere within the input file.

Gaussian 03 Input Section Ordering

Section	**Keywords**	**Final blank line?**
Link 0 commands	**%** commands	no
Route Section (# lines)	all	yes
Extra Overlays	**ExtraOverlays**	yes
Title section	all	yes
Molecule specification	all	yes
Connectivity specifications	**Geom=Connect** or **ModConnect**	yes
Modifications to coordinates	**Opt=ModRedundant**	yes
2nd title and molecule specification	**Opt=QST2** or **QST3**	yes
Connectivity specifications for 2nd set of coordinates	**Geom=Connect** or **ModConnect** and **Opt=ModRedun** and **QST2** or **QST3**	yes
Modifications to 2nd set of coordinates	**Opt=ModRedun** and **QST2** or **QST3**	yes
3rd title and initial TS structure	**Opt=QST3**	yes for both

Connectivity specifications for 3rd set of coordinates	**Geom=Connect** or **ModConnect** **Opt=(ModRedun, QST3)**	yes
Modifications to 3rd set of coordinates	**Opt=(ModRedun, QST3)**	yes
Atomic masses	**IRC=ReadIsotopes**	yes
Frequency of interest	**CPHF=RdFreq**	yes
Molecular Mechanics parameters	**HardFirst, SoftFirst, SoftOnly, Modify**	yes
Initial force constants (Cartesian)	**Opt=FCCards**	yes
Accuracy of energy & forces	**Opt=ReadError**	no
BOMD/ADMP input (1 or more sections)	**ADMP** and **BOMD**	yes
Basis set specification	**Gen**, **GenECP**, **ExtraBasis**	yes
Basis set alterations	**Massage**	yes
Finite field coefficients	**Field=Read**	yes
ECP specification	**ExtraBasis**, **Pseudo=Cards**, **GenECP**	yes
Density fitting basis set specification	**Extra Density Basis**	yes
Background charge distribution	**Charge**	yes
Symmetry types to combine	**Guess=LowSymm**	no
Orbital specifications (separate α & β)	**Guess=Cards**	yes
Orbital alterations (separate α & β)	**Guess=Alter**	yes
Orbital reordering (separate α & β)	**Guess=Permute**	yes
PCM solvation model input	**SCRF=Read**	yes
Weights for CAS state averaging	**CASSCF=StateAverage**	no
States of interest for spin orbit coupling	**CASSCF=Spin**	no
# Orbitals/GVB pair	**GVB**	no
Atoms list for spin-spin coupling constants	**NMR=ReadAtoms**	yes
Alternate atomic radii	**Pop=ReadRadii** or **ReadAtRadii**	yes
Data for electrostatic properties	**Prop=Read** or **Opt**	yes
Cube filename (& **Cards** input)	**Cube**	yes
NBO input	**Pop=NBORead**	no
Orbital freezing information	**ReadWindow** options	yes
OVGF orbitals to refine	**OVGF=ReadOrbitals**	yes
Temperature, pressure, atomic masses	**Freq=ReadIsotopes**	no
PROAIMS/Pickett output filename	**Output=WFN** or **Pickett**	no

---

Click here to go on to the next section.

Gaussian 03 Online Manual
Last update: 2 October 2006

Constructing Z-Matrices

This page presents a brief overview of traditional Z-matrix descriptions of molecular systems.

Using Internal Coordinates

Each line of a Z-matrix gives the internal coordinates for one of the atoms within the molecule. The most-used Z-matrix format uses the following syntax:

Element-label, *atom* 1, *bond-length*, *atom* 2, *bond-angle*, *atom* 3, *dihedral-angle* [,*format-code*]

Although these examples use commas to separate items within a line, any valid separator may be used. *Element-label* is a character string consisting of either the chemical symbol for the atom or its atomic number. If the elemental symbol is used, it may be optionally followed by other alphanumeric characters to create an identifying label for that atom. A common practice is to follow the element name with a secondary identifying integer: C1, C2, etc.

*Atom*1, *atom*2, *atom*3 are the labels for previously-specified atoms and are used to define the current atoms' position. Alternatively, the other atoms' line numbers within the molecule specification section may be used for the values of variables, where the charge and spin multiplicity line is line 0.

The position of the current atom is then specified by giving the length of the bond joining it to *atom*1, the angle formed by this bond and the bond joining *atom*1 and *atom*2, and the dihedral (torsion) angle formed by the plane containing *atom*1, *atom*2 and *atom*3 with the plane containing the current atom, *atom*1 and *atom*2. Note that bond angles must be in the range 0º < *angle* < 180º. Dihedral angles may take on any value.

The optional format-code parameter specifies the format of the Z-matrix input. For the syntax being described here, this code is always **0**. This code is needed only when additional parameters follow the normal Z-matrix specification data, as in an **ONIOM** calculation.

As an initial example, consider hydrogen peroxide. A Z-matrix for this structure would be:

```
H
O 1 0.9
O 2 1.4 1 105.0
H 3 0.9 2 105.0 1 120.0
```

The first line of the Z-matrix simply specifies a hydrogen. The next line lists an oxygen atom and specifies the internuclear distance between it and the hydrogen as 0.9 Angstroms. The third line defines another oxygen with an O-O distance of 1.4 Angstroms (i.e., from atom 2, the other oxygen) and having an O-O-H angle (with atoms 2 and 1) of 105 degrees. The fourth and final line is the only one for which all three internal coordinates need be given. It defines the other hydrogen as bonded to the second oxygen with an H-O distance of 0.9 Angstroms, an H-O-O angle of 105 degrees and a H-O-O-H dihedral angle of 120 degrees.

Variables may be used to specify some or all of the values within the Z-matrix. Here is another version of the previous Z-matrix:

```
H
O 1 R1
O 2 R2 1 A
H 3 R1 2 A 1 D
  Variables:
R1 0.9
R2 1.4
A 105.0
D 120.0
```

Symmetry constraints on the molecule are reflected in the internal coordinates. The two H-O distances are specified by the same variable, as are the two H-O-O bond angles. When such a Z-matrix is used for a geometry optimization in internal coordinates (**Opt**=**Z-matrix**), the values of the variables will be optimized to locate the lowest energy structure. For a full optimization (**FOpt**), the variables are required to be linearly independent and include all degrees of freedom in the molecule. For a partial optimization (**POpt**), variables in a second section (often labeled **Constants**:) are held fixed in value while those in the first section are optimized:

```
  Variables:
R1 0.9
R2 1.4
A 105.0
  Constants:
D 120.0
```

See the examples in the discussion of the **Opt** keyword for more information about optimizations in internal coordinates.

Mixing Internal and Cartesian Coordinates

Cartesian coordinates are actually a special case of the Z-matrix, as in this example:

```
C   0.00   0.00   0.00
C   0.00   0.00   1.52
H   1.02   0.00  -0.39
H  -0.51  -0.88  -0.39
H  -0.51   0.88  -0.39
H  -1.02   0.00   1.92
H   0.51  -0.88   1.92
H   0.51   0.88   1.92
```

It is also possible to use both internal and Cartesian coordinates within the same Z-matrix, as in this example:

```
O 0 xo  0.  zo
C 0 0.  yc  0.
C 0 0. -yc  0.
```

```
N 0 xn  0.  0.
H 2 r1 3 a1 1  b1
H 2 r2 3 a2 1  b2
H 3 r1 2 a1 1 -b1
H 3 r2 2 a2 1 -b2
H 4 r3 2 a3 3  d3
  Variables:
xo -1.
zo  0.
yc  1.
xn  1.
r1 1.08
r2 1.08
r3 1.02
a1 125.
a2 125.
d3 160.
b1  90.
b2 -90.
```

This Z-matrix has several features worth noting:

- The variable names for the Cartesian coordinates are given symbolically in the same manner as for internal coordinate variables.
- The integer 0 after the atomic symbol indicates symbolic Cartesian coordinates to follow.
- Cartesian coordinates can be related by a sign change just as dihedral angles can.

Alternate Z-matrix Format

An alternative Z-matrix format allows nuclear positions to be specified using two bond angles rather than a bond angle and a dihedral angle. This is indicated by a **1** in an additional field following the second angle (this field defaults to **0**, which indicates a dihedral angle as the third component):

```
C4 O1 0.9 C2 120.3 O2 180.0 0
C5 O1 1.0 C2 110.4 C4 105.4 1
C6 O1 R C2 A1 C3 A2 1
```

The first line uses a dihedral angle while the latter two use a second bond angle.

Using Dummy Atoms

This section will illustrate the use of dummy atoms within Z-matrices, which are represented by the pseudo atomic symbol **X**. The following example illustrates the use of a dummy atom to fix the three-fold axis in C_{3v} ammonia:

```
N
X 1 1.
H 1 nh 2 hnx
H 1 nh 2 hnx 3  120.0
H 1 nh 2 hnx 3 -120.0

nh 1.0
hnx 70.0
```

The position of the dummy on the axis is irrelevant, and the distance 1.0 used could have been replaced by any other positive number. **hnx** is the angle between an NH bond and the threefold axis.

Here is a Z-matrix for oxirane:

```
X
C1  X halfcc
O   X     ox C1 90.
C2  X halfcc  O 90. C1 180.0
H1 C1     ch  X hcc  O  hcco
H2 C1     ch  X hcc  O -hcco
H3 C2     ch  X hcc  O  hcco
H4 C2     ch  X hcc  O -hcco

halfcc   0.75
ox       1.0
ch       1.08
hcc    130.0
hcco   130.0
```

This example illustrates two points. First, a dummy atom is placed at the center of the C-C bond to help constrain the cco triangle to be isosceles. **ox** is then the perpendicular distance from O to the C-C bond, and the angles oxc are held at 90 degrees. Second, some of the entries in the Z-matrix are represented by the negative of the dihedral angle variable hcco.

The following examples illustrate the use of dummy atoms for specifying linear bonds. Geometry optimizations in internal coordinates are unable to handle bond angles of l80 degrees which occur in linear molecular fragments, such as acetylene or the C_4 chain in butatriene. Difficulties may also be encountered in nearly linear situations such as ethynyl groups in unsymmetrical molecules. These situations can be avoided by introducing dummy atoms along the angle bisector and using the half-angle as the variable or constant:

```
N
C 1 cn
X 2 1. 1 90.
H 2 ch 3 90. 1 180.

cn 1.20
ch 1.06
```

Similarly, in this Z-matrix intended for a geometry optimization, **half** represents half of the NCO angle which is expected to be close to linear. Note that a value of **half** less than 90 degrees corresponds to a cis arrangement:

```
N
C 1 cn
X 2 1. 1 half
O 2 co 3 half 1 180.0
H 4 oh 2  coh 3   0.0

cn 1.20
co 1.3
oh 1.0
half 80.0
coh 105.
```

Model Builder Geometry Specifications

The model builder is another facility within *Gaussian* for quickly specifying certain sorts of molecular systems. It is requested with the **ModelA** or **ModelB** options to the **Geom** keyword, and it requires additional input in a separate section within the job file.

The basic input to the model builder is called a *short formula matrix*, a collection of lines, each of which defines an atom (by atomic symbol) and its connectivity, by up to six more entries. Each of these can be either an integer, which is the number of the line defining another explicitly specified atom to which the current atom is bonded, or an atomic symbol (e.g. H, F) to which the current atom is connected by a terminal bond, or a symbol for a terminal functional group which is bonded to the current atom. The functional groups currently available are OH, NH2, Me, Et, NPr, IPr, NBu, IBu, and TBu.

The short formula matrix also implicitly defines the rotational geometry about each bond in the following manner. Suppose atoms X and Y are explicitly specified. Then X will appear in row Y and Y will appear in row X. Let *I* be the atom to the right of X in row Y and *J* be the atom to the right of Y in row X. Then atoms *I* and *J* are put in the trans orientation about the X-Y bond. The short formula matrix may be followed by optional lines modifying the generated structure. There are zero or more of each of the following lines, which must be grouped together in the order given here:

AtomGeom,*I*,*Geom*
Normally the local geometry about an atom is defined by the number and types of bond about the atom (e.g., carbon in methane is tetrahedral, in ethylene is trigonal, etc.). All bond angles at one center must be are equal. The **AtomGeom** line changes the value of the bonds at center *I*. *Geom* may be the angle as a floating point number, or one of the strings **Tetr**, **Pyra**, **Trig**, **Bent**, or **Line**.

BondRot,*I*,*J*,*K*,*L*,*Geom*
This changes the orientations of the *I-J* and *K-L* bonds about the *J-K* bond. *Geom* is either the dihedral angle or one of the strings **Cis** (≥0), **Trans** (≥180), **Gaup** (≥+60), or **Gaum** (≥-60).

BondLen,*I*,*J*,*NewLen*
This sets the length of the *I-J* bond to *NewLen* (a floating point value).

The model builder can only build structures with atoms in their normal valencies. If a radical is desired, its extra valence can be "tied down" using dummy atoms, which are specified by a minus sign before the atomic symbol (e.g., -H). Only terminal atoms can be dummy atoms.

The two available models (A and B) differ in that model A takes into account the type (single, double, triple, etc.) of a bond in assigning bond lengths, while model B bond lengths depend only on the types of the atoms involved. Model B is available for all atoms from H to Cl except He and Ne. If Model A is requested and an atom is used for which no Model A bond length is defined, the appropriate Model B bond length is used instead.

4 Visualization tools

Viewing Gaussian Structures with GaussView

(GaussView Version: 3.09)

Gaussian '03	Download The Files Associated With This Example			
	Input File	Output File	Checkpoint File	Formatted Checkpoint File

In GaussView, there are several ways to visualize structures from a Gaussian output file. The log file, checkpoint file, and formatted checkpoint file can be read into GaussView.

Generating Formatted Checkpoint Files

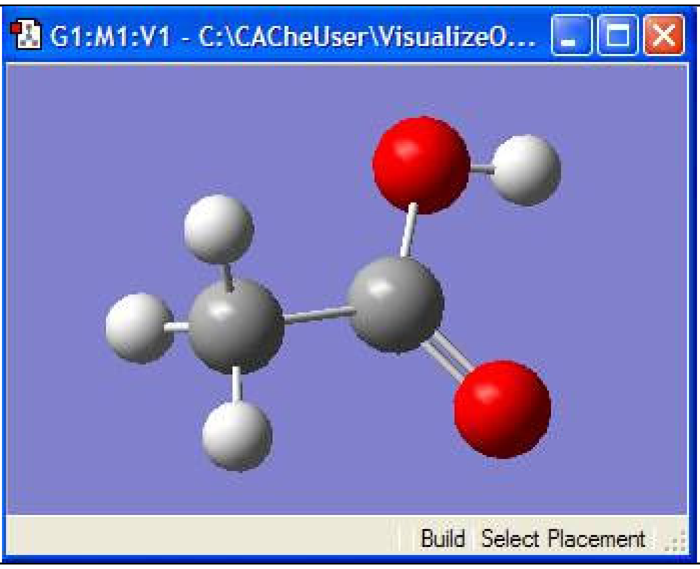
When running the Gaussian calculation there are two ways in which you can get the desired formatted checkpoint file.

1. As a keyword, enter formcheck. This will create a .FChk file when the Gaussian calculation is complete.
2. After the Gaussian calculation is complete, open Gaussian. Select **Utilities|FormChk**. In the dialog box that appears, browse for the checkpoint file that was previously created. Select it. This will create a formatted checkpoint file with the extension .fch that has the same name as the checkpoint file. (This is the preferred method.)

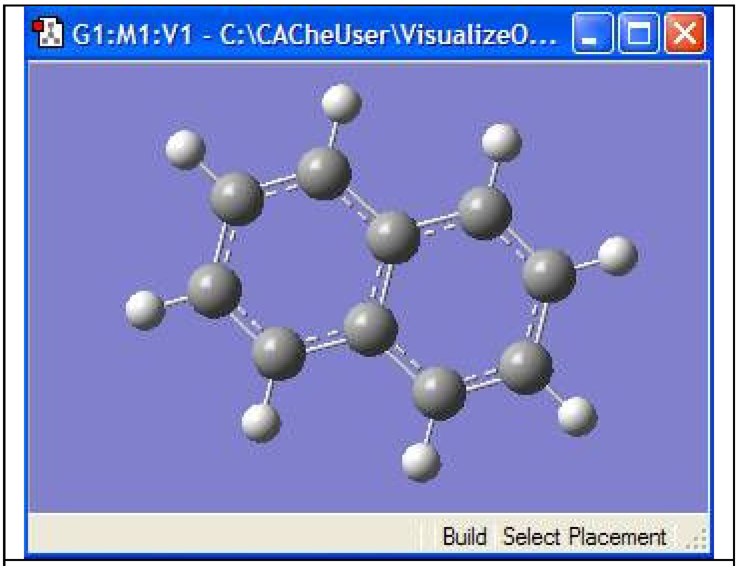
Viewing Structures with GaussView

- Open GaussView.
- Select **File|Open**. A new dialog box opens.
- Select the type of file you wish to open
  - .gjf
  - .log
  - .chk
  - .fch
- Select OK.

Note: Even if the calculation ends in an error, GaussView will still read in the last structure so that you are able to view what the calculation was doing at the time of termination.



Acetic Acid Gaussian Input File – Viewed in GaussView



Naphthalene Gaussian Formatted Checkpoint File – Viewed in GaussView

Viewing Molecular Orbitals with GaussView

(GaussView Version: 3.09)

Download The Files Associated With This Example			
Azulene	Input File	Output File	Formatted Checkpoint File
Naphthalene	Input File	Output File	Formatted Checkpoint File

GaussView has the ability to read any formatted checkpoint file to display the molecular orbitals of a molecule. Cube file generation is done behind the scenes from the GaussView interface. However, cube files can still be created using the Gaussian utility Cubegen and then loaded in GaussView by selecting **Results|Surfaces**. However, viewing the molecular orbitals is much easier now.

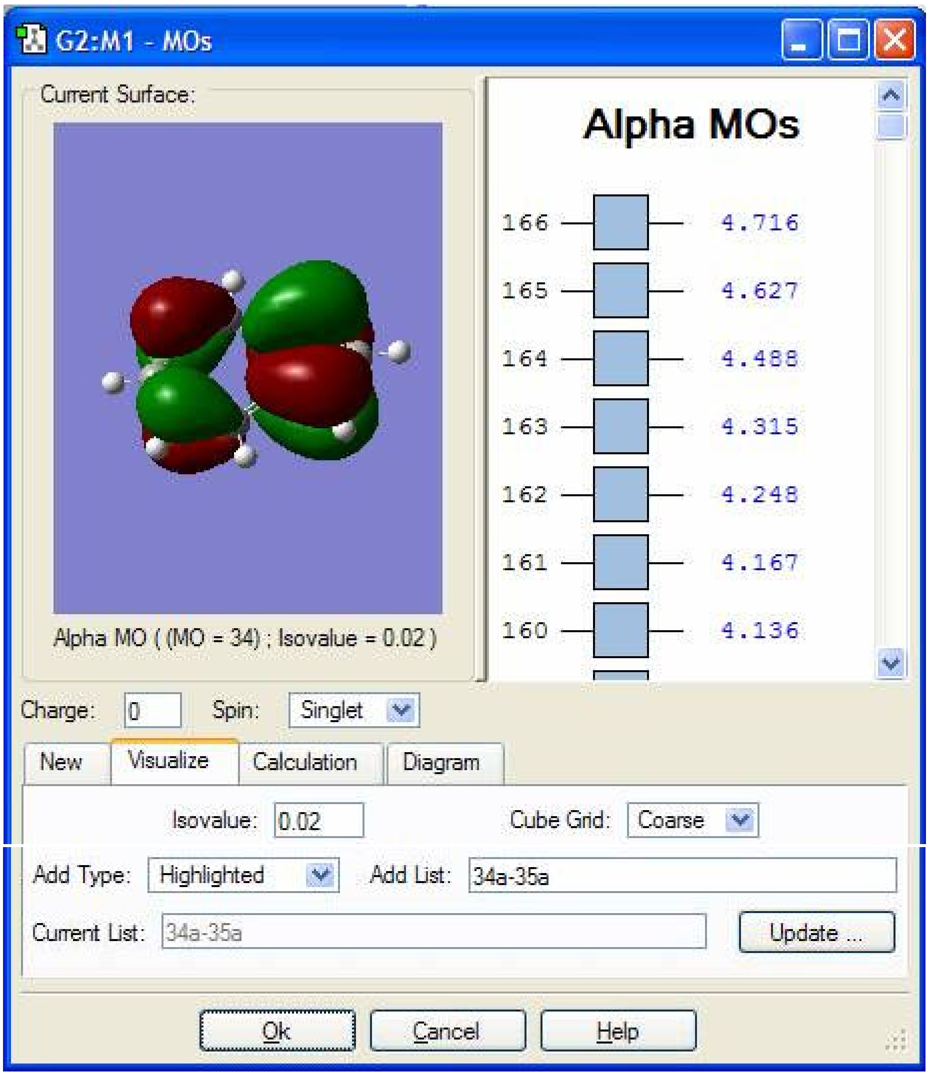
Generating Formatted Checkpoint Files

When running the Gaussian calculation there are two ways in which you can get the desired formatted checkpoint file.

1. As a keyword, enter formcheck. This will create a .FChk file when the Gaussian calculation is complete.
2. After the Gaussian calculation is complete, open Gaussian. Select **Utilities|FormChk**. In the dialog box that appears, browse for the checkpoint file that was previously created. Select it. This will create a formatted checkpoint file with the extension .fch that has the same name as the checkpoint file. (This is the preferred method.)

Visualizing the Orbitals in GaussView

- Select **File|Open**. Select the checkpoint file or formatted checkpoint file.
- Select OK.
- Select **Edit|MOs**
- A new window will open with a display of the molecule, and a list of Alpha MOs on the right
- Select the orbitals you want cube files generated for by clicking on the number of the orbital on the list to the right.
- Select the Visualize Tab from the bottom of the window, and then click the Update button.
- Cubegen will run in the background to generate cube files for the requested orbitals.
- After they are generated, you may select to view an orbital by selecting the box to the far right in the Alpha MOs list. The active orbital will have a red box (the inactive orbitals will have grey boxes). All visualization of the MO is done in the frame in the left of the MOs window.



Alpha MO ((MO = 34) ; Isovalue = 0.02)

166	4.716
165	4.627
164	4.488
163	4.315
162	4.248
161	4.167
160	4.136

Charge: 0

Spin: Singlet

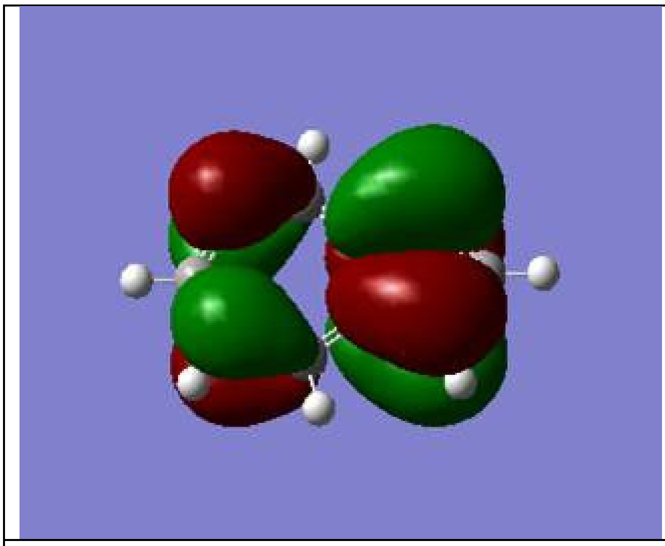
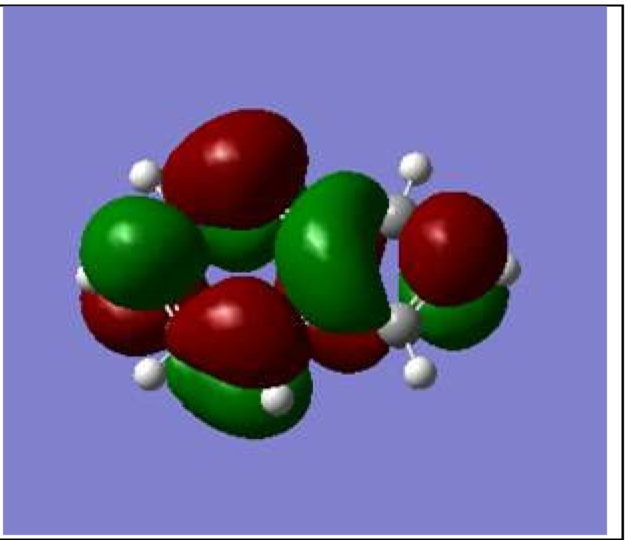
Isovalue: 0.02

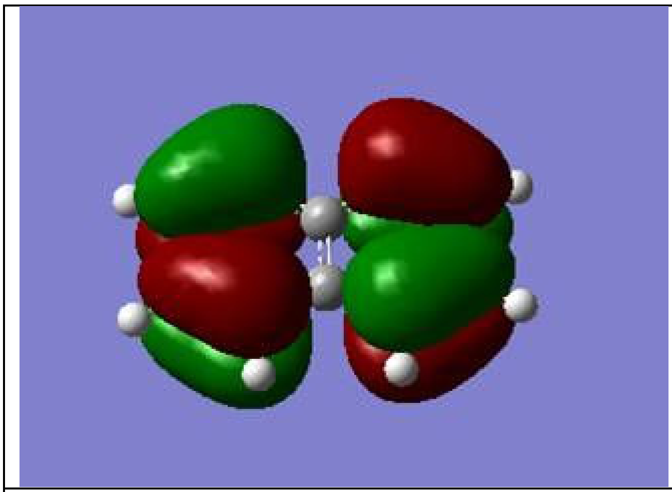
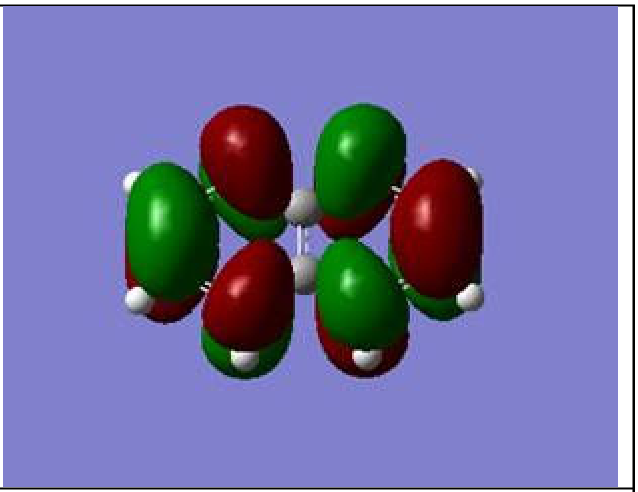
Cube Grid: Coarse

Add Type: Highlighted

Add List: 34a-35a

Current List: 34a-35a

	
Azulene HOMO (MO 34) at an isosurface of .02 (5-membered ring is on right)	Azulene LUMO (MO 35) at an isosurface of .02 (5-membered ring is on right)

	
Naphthalene HOMO (MO 34) at an isosurface of .02	Naphthalene LUMO (MO 35) at an isosurface of .02

TIPS:

- To rotate the molecule, click in the main window and move the mouse while holding down the left button.
- To enlarge the molecule, hold down the Control key and move the mouse while holding down the left button.
- To translate the molecule, hold down the Shift key and move the mouse while holding down the left button.

Viewing Electrostatic Potential with GaussView

(GaussView Version: 3.09)

Gaussian '03	Download The Files Associated With This Example			
	Azulene	Input File	Output File	Formatted Checkpoint File
	Naphthalene	Input File	Output File	Formatted Checkpoint File

GaussView has the ability to view painted isosurfaces. These painted isosurfaces require two input files. The isosurface of one value allows the second property to be displayed on it. This is particularly useful for examining electrostatic potential. The electrostatic potential is mapped onto a particular value of the total electron density. This can be done two ways in GaussView. The first way is to create the cube files using the Gaussian CubeGen utility and then reading the cube file into GaussView. The second way is to have GaussView generate the cube files internally from a previously created checkpoint file or formatted checkpoint file.

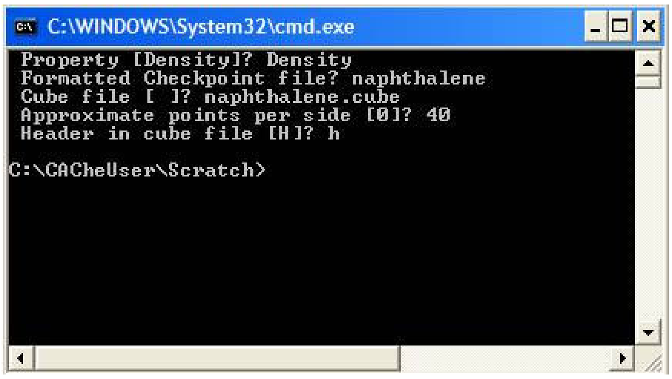
Generating Formatted Checkpoint Files

When running the Gaussian calculation there are two ways in which you can get the desired formatted checkpoint file.

1. As a keyword, enter formcheck. This will create a .FChk file when the Gaussian calculation is complete.
2. After the Gaussian calculation is complete, open Gaussian. Select **Utilities|FormChk**. In the dialog box that appears, browse for the checkpoint file that was previously created. Select it. This will create a formatted checkpoint file with the extension .fch that has the same name as the checkpoint file. (This is the preferred method.)

Generating Cube Files in Gaussian

- After the Gaussian calculation is complete, open Gaussian.
- Select **Utilities|CubeGen**.
- The following dialog box appears:



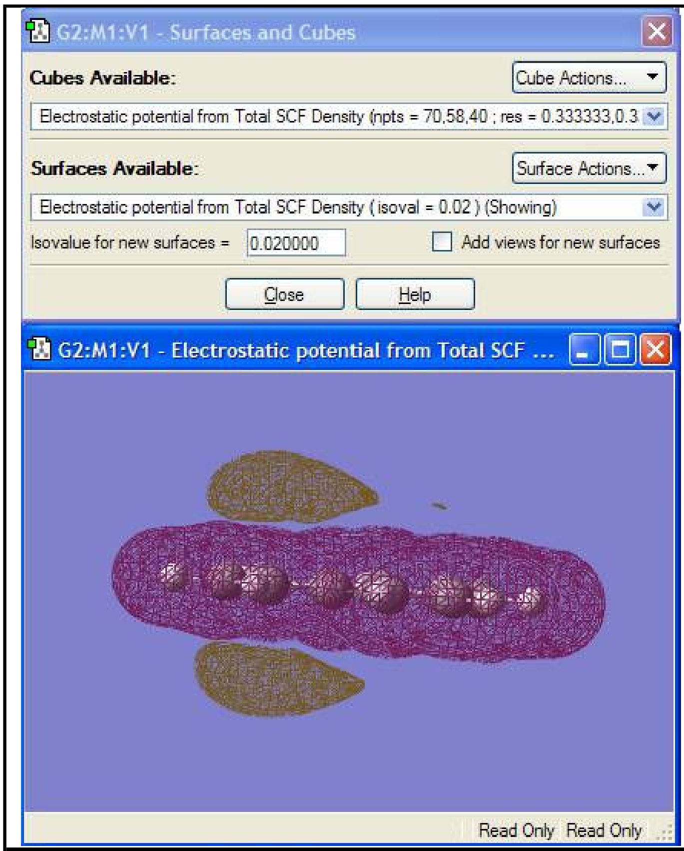
```
 Property [Density]? Density
 Formatted Checkpoint file? naphthalene
 Cube file [ ]? naphthalene.cube
 Approximate points per side [0]? 40
 Header in cube file [H]? h

C:\CACheUser\Scratch>
```

  - *Property[Density]?* Density
  - *Formatted Checkpoint File?* C:\Filename.fch (note that you will need to specify the path to your .fch file here)

    - *Cube File [ ]?* Filename.cub3 (this is the name of your cube file Cubegen will create)
    - *Approximate Points per Side [O]?* 40 (This puts roughly 40 points on each side of the cube, giving it 40^3 points)
    - *Header in cube file [H]?* H (make sure to have a header so you can get the exact dimensions of the cube file. T3D will require them)

Visualizing the Orbitals in GaussView

- Select **File|Open**. Select the checkpoint file or formatted checkpoint file. Select OK.
- Select **Results|Surfaces**. A Surfaces and Cubes window will appear.
- Select the Cube Actions drop down menu. Select New Cube.
    - In the Kind box using the drop down menu select Total Density.
        - Leave all options as the default.
    - Select OK.
    - A line of data will appear in the Cubes Available box.
- Select the Cube Actions drop down menu. Select New Cube.
    - In the Kind box using the drop down menu select ESP.
        - Leave all options as the default.
    - Select OK.
    - A second line of data will appear in the Cubes Available box.
- Select an appropriate isosurface value (such as 0.020)
    - Adjust the isosurface value until you obtain a visualization of the difference densities that is ideal.
- Using the drop down button under Cubes Available, select the line that says Electron Density from Total SCF Density.
    - Select the Surface Actions drop down menu. Select New Mapped Surface.
    - A Surface Mapping window appears. Select circle next to Use an Existing Cube. Under Cubes Available, make sure that Electrostatic Potential from Total SCF Density is selected. Select OK.
        - A line of data will appear in the Surfaces Available box.
        - This will generate a graphical window with the mapped electrostatic potential displayed.
        - If the visualization is not ideal, select the Surface Actions drop down menu. Select Remove Surface. Change the isosurface value. Select the Surface Actions drop down menu. Select New Surface.
            - Repeat these steps until the visualization for the molecular orbital is ideal.
- Using the drop down button under Cubes Available, select the line that says Electrostatic Potential from Total SCF Density.
    - Select the Surface Actions drop down menu. Select New Surface.
        - A line of data will appear in the Surfaces Available box.
        - This will generate a graphical window with the molecular orbitals displayed
        - If the visualization is not ideal, select the Surface Actions drop down menu. Select Remove Surface. Change the isosurface value. Select the Surface Actions drop down menu. Select New Surface.
            - Repeat these steps until the visualization for the molecular orbital is ideal.
- To change the display of the orbitals
    - Select **View|Display Format**.
    - Click on the Surface tab.
    - At the format drop down menu select either mesh, solid, or transparent.
    - The Z-Clip slider (min to max) can also be adjusted to alter the way the surface is viewed.
        - It may be used to remove the frontmost portions of the image to allow views into the interior of the molecular display.

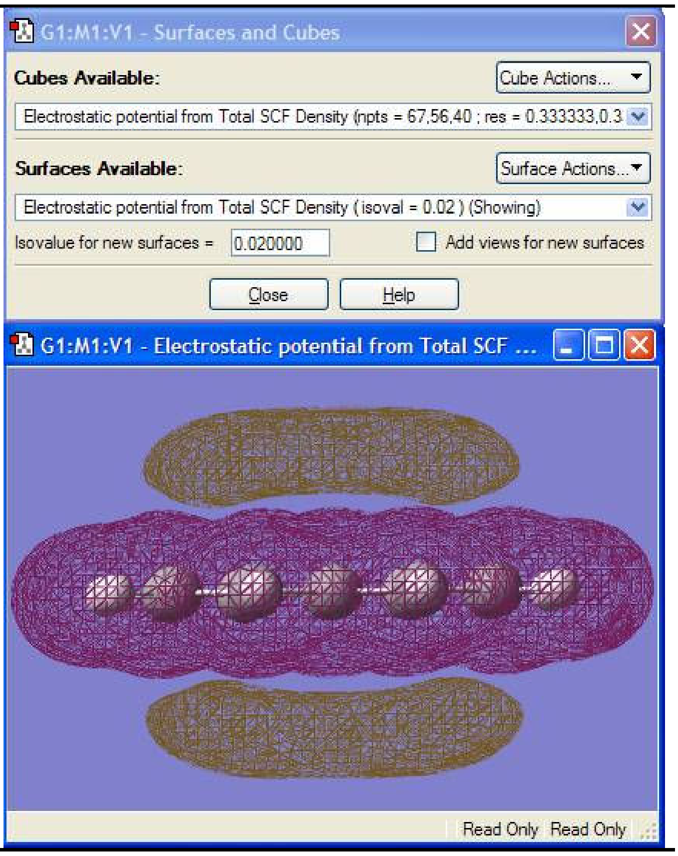


Cubes Available: Electrostatic potential from Total SCF Density (npts = 70,58,40 ; res = 0.333333,0.3

Surfaces Available: Electrostatic potential from Total SCF Density (isoval = 0.02) (Showing)

Isovalue for new surfaces = 0.020000 ☐ Add views for new surfaces

Azulene Electron Density – Viewed in GaussView

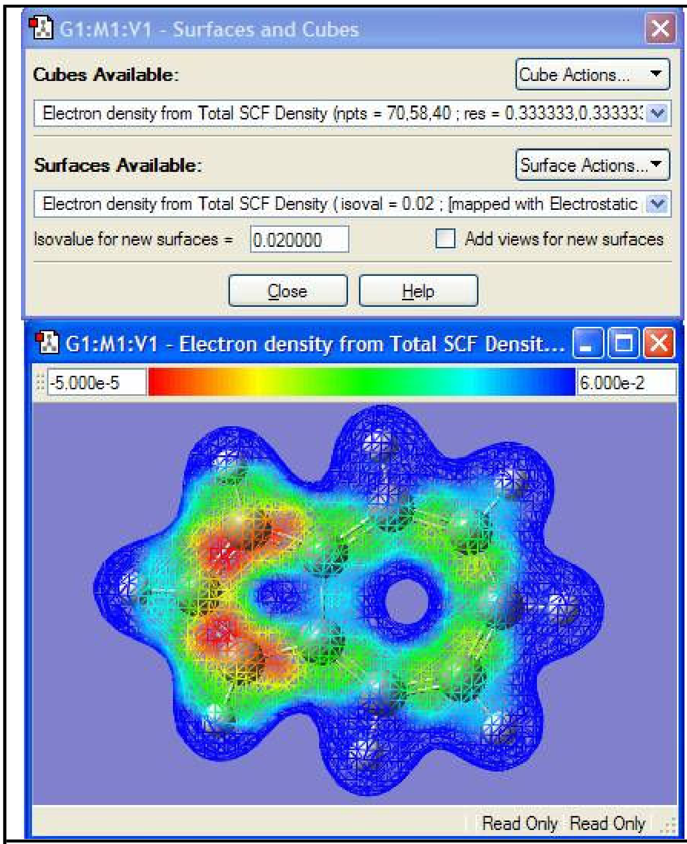


Cubes Available: Electrostatic potential from Total SCF Density (npts = 67,56,40 ; res = 0.333333,0.3

Surfaces Available: Electrostatic potential from Total SCF Density (isoval = 0.02) (Showing)

Isovalue for new surfaces = 0.020000 ☐ Add views for new surfaces

Naphthalene Electron Density– Viewed in GaussView

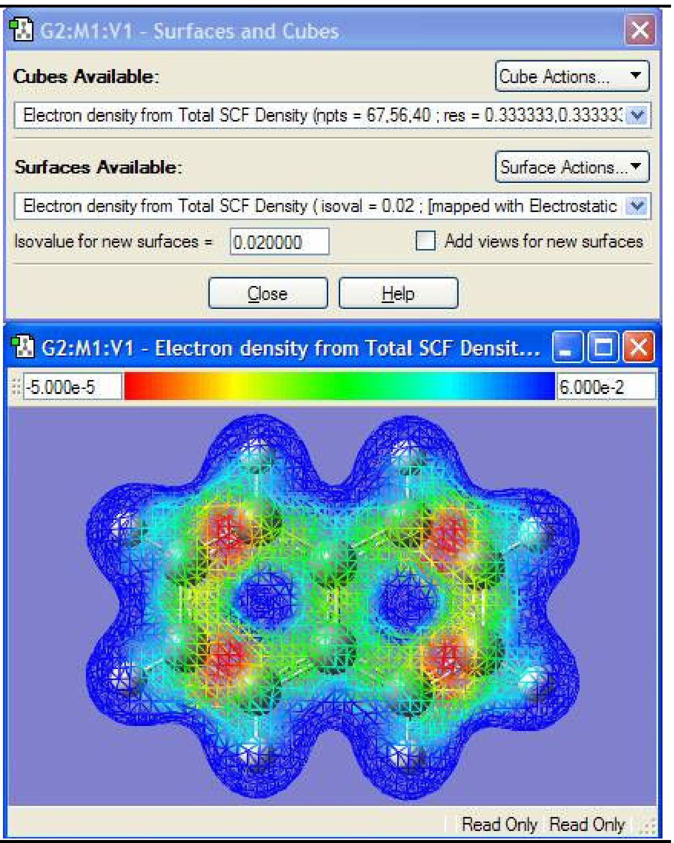


Cubes Available: Electron density from Total SCF Density (npts = 70,58,40 ; res = 0.333333,0.33333:

Surfaces Available: Electron density from Total SCF Density (isoval = 0.02 ; [mapped with Electrostatic

Isovalue for new surfaces = 0.020000 ☐ Add views for new surfaces

Azulene MEP – Viewed in GaussView



Cubes Available: Electron density from Total SCF Density (npts = 67,56,40 ; res = 0.333333,0.33333:

Surfaces Available: Electron density from Total SCF Density (isoval = 0.02 ; [mapped with Electrostatic

Isovalue for new surfaces = 0.020000 ☐ Add views for new surfaces

Naphthalene MEP – Viewed in GaussView

TIPS:

- To rotate the molecule, click in the main window and move the mouse while holding down the left button.
- To enlarge the molecule, hold down the Control key and move the mouse while holding down the left button.
- To translate the molecule, hold down the Shift key and move the mouse while holding down the left button.

Viewing Gaussian Difference Densities with GaussView

(GaussView Version: 3.09)

	Download The Files Associated With This Example			
	Ground State	Input File	Output File	Cube File
	Excited State 2	Input File	Output File	Cube File
	Excited State 3	Input File	Output File	Cube File

Gaussview can be utilized to view the total electron density difference between ground and excited states. The program reads the formatted checkpoint file or the cube file from a Gaussian calculation. This example looks at several of the excited states of acrolein.

Generating Cube Files

- For a Ground State Density
  - CIS/6-31G(d) density(SCF) cube=density NoSymm
  - At the end of input information
    - Blank line > filename_gs.cube > Blank line
- For an Excited State Density
  - Input information located directly below last blank line from Ground State Density input information
    - --link1--
    - %chk=filename.chk
    - # geom=allcheck guess(read, only) density(checkpoint,cis=n) cube=density NoSymm
      - Where n represents the number for the excited state (example: n=2 for the second excited state)
    - Blank line > filename_ex.cube > Blank line

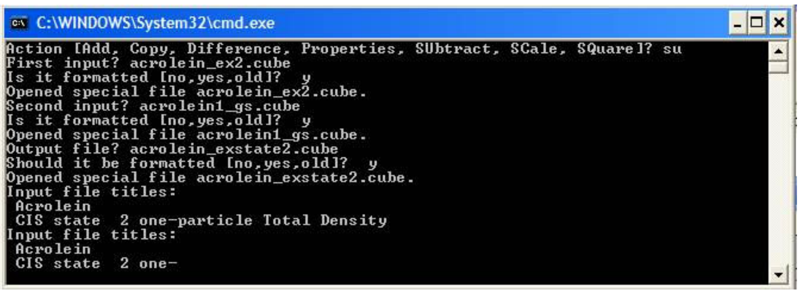
Note: There are numerous ways to generate cube files. The method instructed above is simply the way chosen for this particular demonstration. Also, the NoSymm keyword is included to ensure that Gaussian does not reorient the molecule between calculations due to symmetry. If this occurs, the cube files could have different coordinates and not line up properly when viewed.

Creating Difference Density Cube Files in Gaussian

- Select **Utilities|CubMan**. A small window will appear.
- Enter “su” for subtract at the initial prompt
  - This operation subtracts two cube files to produce a new cube file.
- For the first input file type the name of the excited state cube file (example: filename_ex.cube)
  - Is the file formatted? Answer “y” for yes.
- For the second input file type the name of the ground state cube file (example: filename_gs.cube)
  - Is the file formatted? Answer “y” for yes.
- For the output file type in the name desired for the difference density output file (example:

filename_diffex.cube)
  - Should it be formatted? Answer “y” for yes.

Follow the above procedure for each of the excited states that you want to visualize the difference densities for in GaussView.



```
Action [Add, Copy, Difference, Properties, SUbtract, SCale, SQuare]? su
First input? acrolein_ex2.cube
Is it formatted [no,yes,old]?  y
Opened special file acrolein_ex2.cube.
Second input? acrolein1_gs.cube
Is it formatted [no,yes,old]?  y
Opened special file acrolein1_gs.cube.
Output file? acrolein_exstate2.cube
Should it be formatted [no,yes,old]?  y
Opened special file acrolein_exstate2.cube.
Input file titles:
 Acrolein
 CIS state  2 one-particle Total Density
Input file titles:
 Acrolein
 CIS state  2 one-
```

Generating Formatted Checkpoint Files

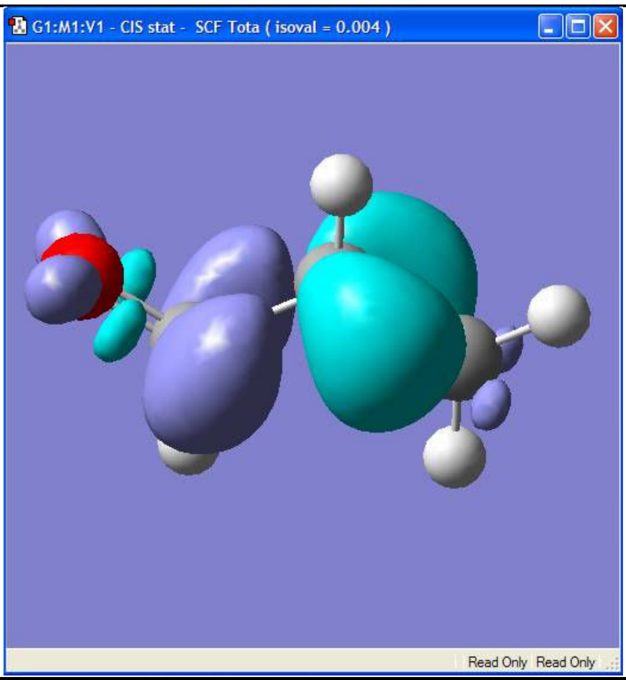
When running the Gaussian calculation there are two ways in which you can get the desired formatted checkpoint file.

1. As a keyword, enter formcheck. This will create a .FChk file when the Gaussian calculation is complete.
2. After the Gaussian calculation is complete, open Gaussian. Select **Utilities|FormChk**. In the dialog box that appears, browse for the checkpoint file that was previously created. Select it. This will create a formatted checkpoint file with the extension .fch that has the same name as the checkpoint file. (This is the preferred method.)

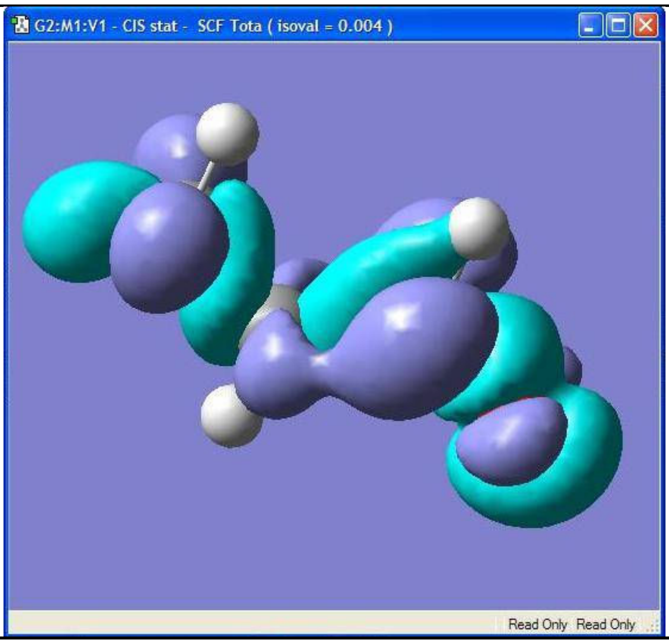
Visualizing Difference Densities in GaussView

GaussView can be used to read in two formatted checkpoint files or two cube files, take the difference, and create an isosurface rendering of the result.

- Select **File|Open**. Select the formatted checkpoint file for the excited state that you want to visualize the difference density for in GaussView. Select OK.
- Select **Results|Surfaces**. A Surfaces and Cubes window will appear.
- Select the Cube Actions drop down menu. Select Load Cube. Find the cube file that represents the difference density calculated with CubMan. Select OK.
  - A line of data will appear in the Cubes Available box.
- Select an appropriate isosurface value (such as 0.004)
  - Adjust the isosurface value until you obtain a visualization of the difference densities that is ideal.
- Select the Surface Actions drop down menu. Select New Surface.
  - A line of data will appear in the Surfaces Available box.
  - This will generate a graphical window with the molecule and difference density for your excited state.
    - The blue represents where the electrons are coming from, and the purple represents where the electrons are going.
  - If the visualization is not ideal, select the Surface Actions drop down menu. Select Remove Surface. Change the isosurface value. Select the Surface Actions drop down menu. Select New Surface.
    - Repeat these steps until the visualization for the difference density is ideal.



Acrolein Difference Density (Excited State 2 and Ground State) – Viewed in GaussView



Acrolein Difference Density (Excited State 3 and Ground State) – Viewed in GaussView

TIPS:

- To rotate the molecule, click in the main window and move the mouse while holding down the left button.
- To enlarge the molecule, hold down the Control key and move the mouse while holding down the left button.
- To translate the molecule, hold down the Shift key and move the mouse while holding down the left button.

Viewing Vibrational Frequencies in GaussView

(GaussView Version: 3.09)

Gaussian '03	Download The Files Associated With This Example	
	Input File	Output File

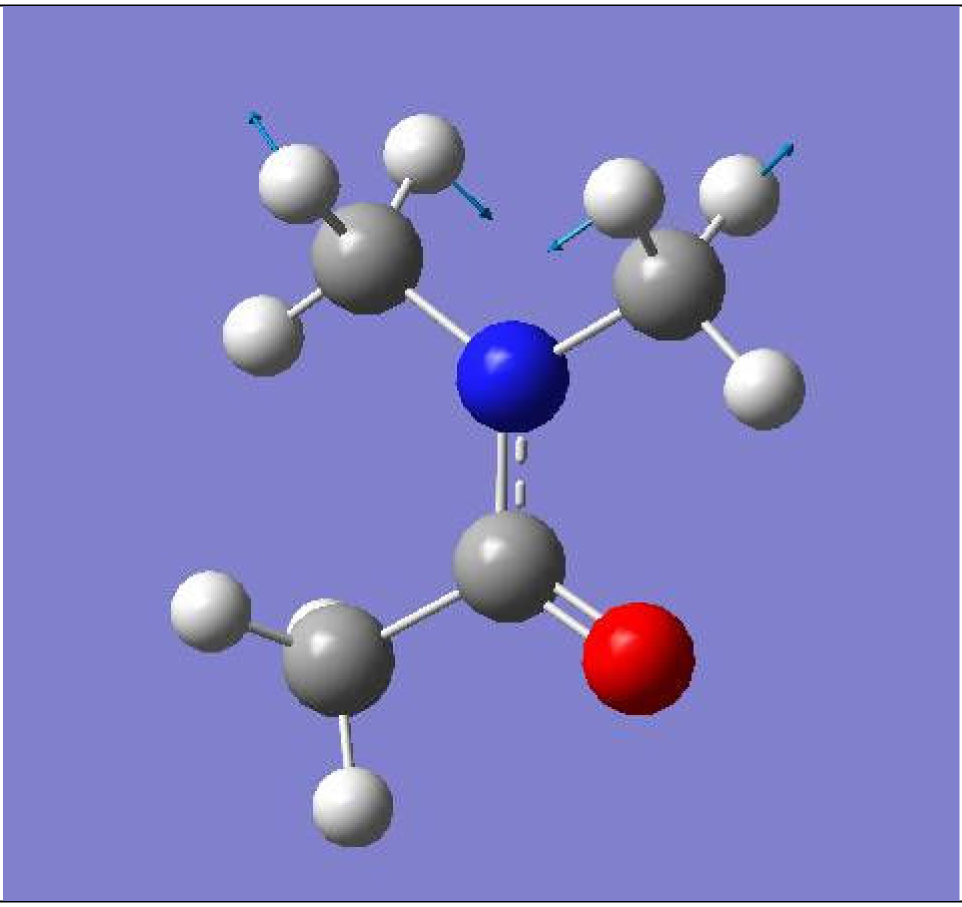
The Vibrational Frequencies and IR Spectra of a molecule can be read by GaussView from any Gaussian output file resulting from a Vibrational Frequencies calculation. This means either a file with the extension .out or .log can be used.

Steps:

- Open GaussView
- Select File|Open
- Locate an output file from the Gaussian calculation (.out or .log)
- The molecule will appear in a new window
- Select Results|Vibrations
- A new window titled “Display Vibrations” will appear
- Select a Frequency and click Start

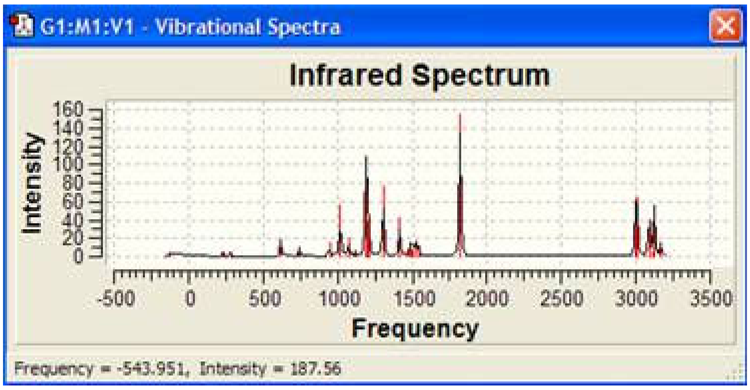
The molecule will now animate the vibrations associated the frequency selected. You can change the frequency at any time during the animation by simply clicking on another frequency in the “Display Vibrations” window.

There is no easy way to capture the vibrations from GaussView. However, there is the option of showing displacement vectors, which displays arrows pointing the in direction each atom is moving. This could be useful for displaying online or on paper to illustrate. To view displacement vectors, simply click the “show displacement vectors” checkbox in the “Display Vibrations” window mentioned previously.



Picture of N,N-dimethylacetamide with displacement vectors

Similarly, The infrared spectra can be viewed by clicking the “Spectrum” button in the “Display Vibrations” window. Sections of the IR Spectrum can be enlarged by selecting the IR Spectrum window, the clicking and dragging a box around the region of interest. After selecting a region, you can return to the full spectrum by right clicking in the window and selecting “Zoom Out”



Frequency = -543.951, Intensity = 187.56

Viewing NMR Tensors with GaussView

(GaussView Version: 3.09)

Download The Files Associated With This Example			
Ethane:	Input	Output	Formatted Checkpoint File
Ethene:	Input	Output	Formatted Checkpoint File
Ethyne:	Input	Output	Formatted Checkpoint File

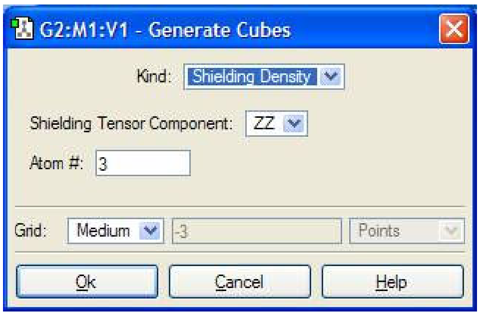
NMR Tensors can be viewed in GaussView if you have generated cube files from either the checkpoint file or the formatted checkpoint file. The process for doing so is described below:

The first step in this process is to format the checkpoint file from the NMR Gaussian job.

- In Gaussian 03, select **Utilities|FormChk**
- Using the File Browser that opens, locate the checkpoint file from the NMR calculation and click OK
- A command line window will open, and the checkpoint file will be formatted

Next you must use this file to generate Cube Files

- Open GaussView
- Select **File|Open**
- Open the formatted checkpoint file resulting from the Gaussian NMR calculation
- Select **Results|Surfaces**
- A window titled Surfaces and Cubes will spawn
- Click on the Cube Actions pulldown and select "New Cube"
  - Kind: Current Density
  - Shielding Tensor Component: Z
  - Grid: Medium
- A command line will open in the background and run Cubegen, a Gaussian utility, to create the cube file which is now available in the list of available cubes in the "Surfaces and Cubes" window
- The next two cubes will be Shielding Density cubes. Creating Shielding Density cubes requires that you specify an atom. To help you choose the correct atom number, you can select **View|Display Format** and under the General tab, click "Show Tags". This will number each atom for you.
  - First Cube
    - Kind: Shielding Density
    - Shielding Tensor Component: ZZ
    - Grid: Medium
    - Atom: 1 (Carbon)
  - Second Cube
    - Kind: Shielding Density
    - Shielding Tensor Component: ZZ
    - Grid: Medium
    - Atom: 3 (Hydrogen)


G2:M1:V1 - Generate Cubes

Kind: Shielding Density

Shielding Tensor Component: ZZ

Atom #: 3

Grid: Medium -3 Points

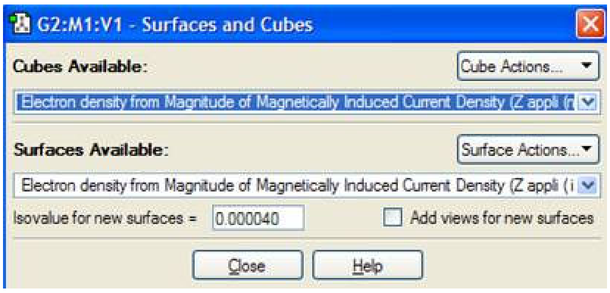
- You can save the cube files by selecting them in the pulldown menu and then going to the Cube Actions pulldown menu and selecting "Save Cube"

Now you are ready to view the newly generated cube files

- To show an isosurface of the current density, select the Current Density cube under the Available Cubes heading, and type an isosurface value at the bottom of the window. Then click on the Surface Actions pulldown menu and select “New Surface”. The isosurface of current density will appear.
- Once you have an appropriate value for the isosurface, pull down the Surface Actions pulldown and either hide or remove that surface.

To Map Shielding Density on the Current Density Isosurface

- Select the Current Density Cube file from the available cubes pulldown menu, and then enter an isosurface value at the bottom of the window. Go to the Surface Actions pulldown menu and select “New Mapped Surface”. Choosing the Current Density cube before selecting this option signifies that the Current Density isosurface is the surface that will be use to map on.


G2:M1:V1 - Surfaces and Cubes

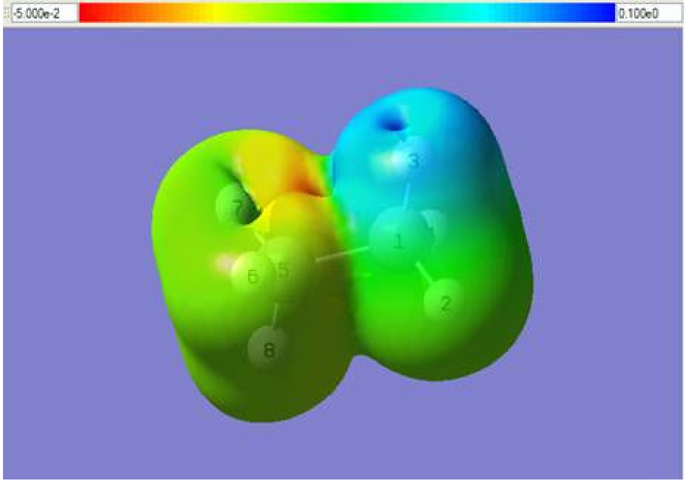
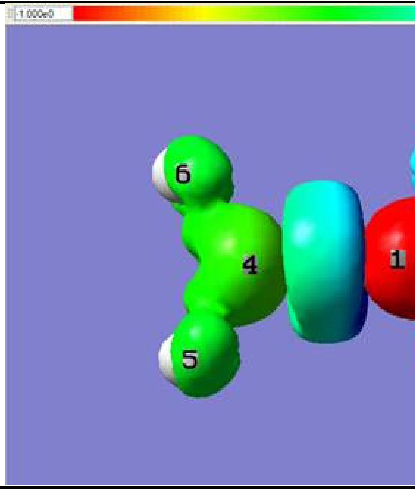
Cubes Available: Electron density from Magnitude of Magnetically Induced Current Density (Z appli (r

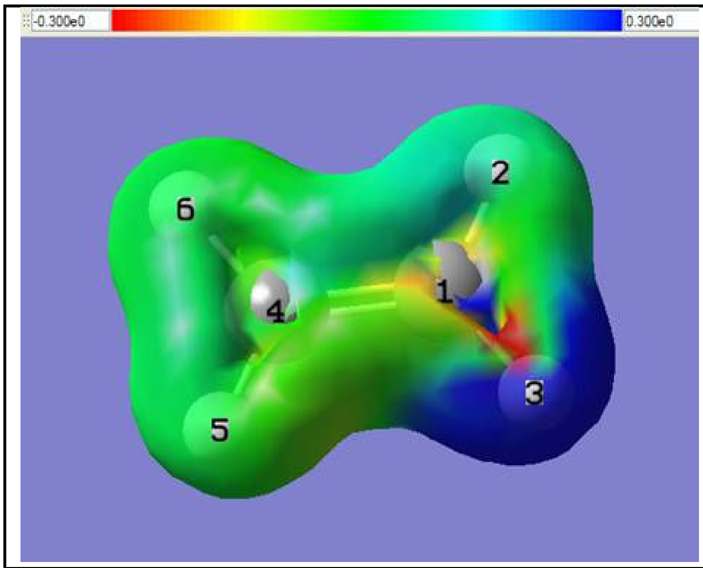
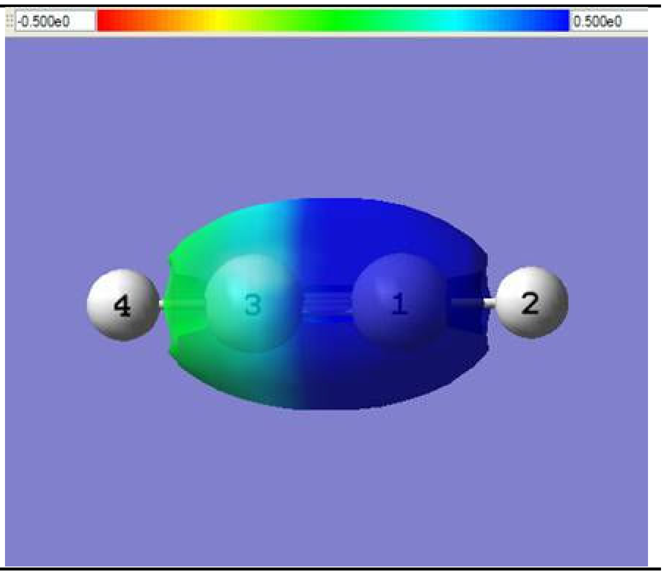
Surfaces Available: Electron density from Magnitude of Magnetically Induced Current Density (Z appli (i

Isovalue for new surfaces = 0.000040

☐ Add views for new surfaces

- Select “New Mapped Surface” and then select one of the Shielding Density cube files from the pulldown menu. Click OK
- The Shielding Density will now map onto the Current Density Isosurface. There will be a color map at the top of the molecule window. You can adjust the range of the color map by changing the values in either end of the color map.

<table>
<tr><td colspan="2">Note: In the pictures below, the negative values represent deshielding while the positive valu</td></tr>
<tr><td>
</td><td>
</td></tr>
<tr><td>Ethane
Shielding Density as seen by Nucleus 3 (H) in the ZZ direction mapped between the values of -.05 to .1 on the Current Density=Z isosurface at a value of .00004</td><td>E
Shielding Density as seen by
mapped between the values c
isosurface a</td></tr>
</table>

	
Ethene Shielding Density seen by Nucleus 3 (H) in the ZZ direction mapped between the values of -.3 to .3 on the Current Density=Z isosurface at a value of .0002	Ethyne Shielding Density seen by Nucleus 1 (C) in the ZZ direction mapped between values of -.5 to .5 onto the Current Density=Z isosurface at a value of .0004

Viewing a Reaction Path with GaussView

(GaussView Version: 3.09)

<table>
<tr><td rowspan="2">Gaussian '03</td><td colspan="3">Download the Files Associated With This Example</td></tr>
<tr><td>Input File</td><td>Output File</td><td>Formatted Checkpoint File</td></tr>
</table>

Gaussview can be utilized to view the reaction pathway. The program reads the formatted checkpoint file or the output file from a Gaussian calculation. This example looks at the reaction pathway of H_2 and acetone.

Generating Formatted Checkpoint Files

When running the Gaussian calculation there are two ways in which you can get the desired formatted checkpoint file.

1. As a keyword, enter formcheck. This will create a .FChk file when the Gaussian calculation is complete.
2. After the Gaussian calculation is complete, open Gaussian. Select **Utilities|FormChk**. In the dialog box that appears, browse for the checkpoint file that was previously created. Select it. This will create a formatted checkpoint file with the extension .fch that has the same name as the checkpoint file. (This is the preferred method.)

Preparing to Visualize Reaction Path

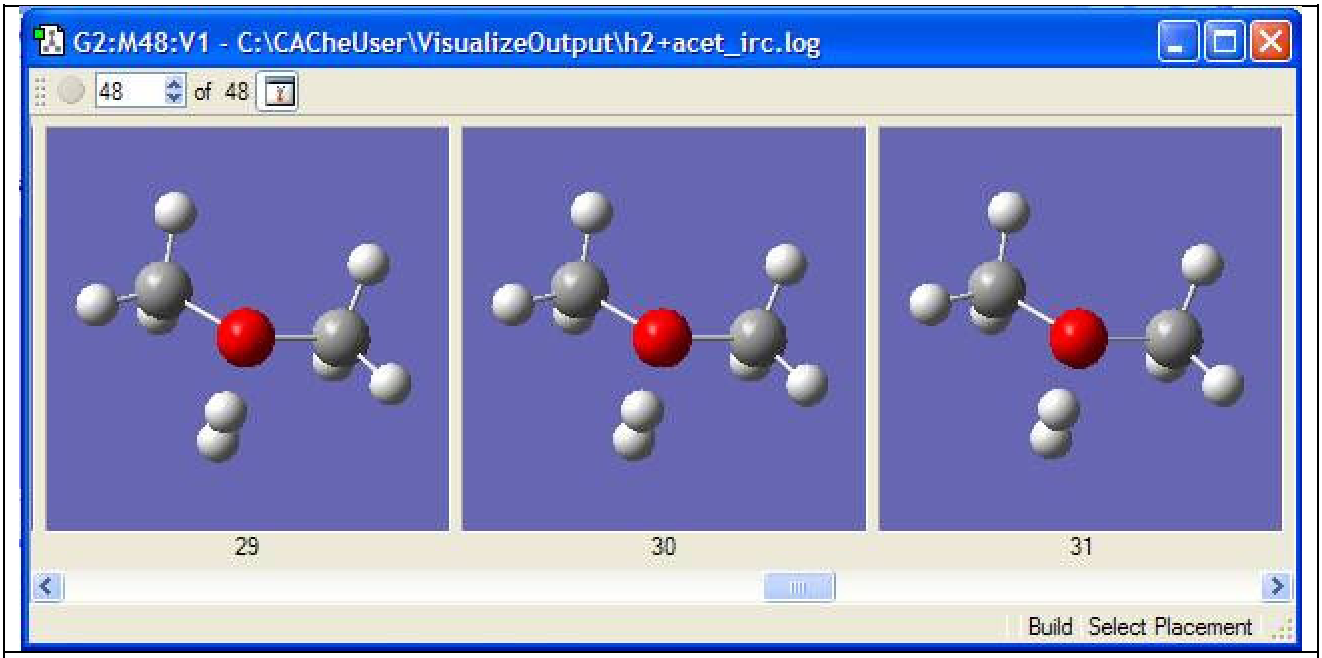
- Create reactants, products, and an educated guess at the transition structure
- Run these through a Gaussian optimization job
  - Use additional keywords opt (QST3, CalcFC)
    - QST3 is a search for a transition structure
      - This option requires the reactant, product, and initial transition structure structures as input
    - CalcFC specifies that the force constants be computed at the first point
  - Create a formatted checkpoint file
- Next, run these through a Gaussian frequency job
  - Create a formatted checkpoint file
- Finally, run these through a Gaussian Reaction Path job (IRC)
  - Use additional keywords IRC (Maxpoints=24, RCFC, phase=(1,2)) NOSYMM
    - IRC requests that a reaction path be followed
    - Maxpoints represents the number of points along the reaction path to be examined
    - RCFC specifies that the computed force constants in Cartesian coordinates from a frequency calculation be read from the checkpoint file
    - Phase defines the phase for the transition vector
      - If two atom numbers are given, the coordinate is a bond stretch between the two atoms
  - Create a formatted checkpoint file

Note: IRC Calculations require initial force constants to proceed. These must be provided to the calculation in some way. The usual method is to save the checkpoint file from the preceding frequency calculation (used to verify that the optimized geometry to be used in the IRC calculation is in face a transition state).

Visualizing Reaction Paths in GaussView

- Select **File|Open**. Select either the formatted checkpoint file or the output file that was created from the IRC Calculation. Select OK.
- A window will appear with the selected structure displayed with the option of showing all the steps along the reaction pathway.
  - The formatted checkpoint file will have 1 of 49 steps of the reaction pathway
  - The output file will have 1 of 48 steps of the reaction pathway

- To view each of the steps along the reaction pathway, simply click on the up or down arrow located next to the first number.
- To view a timeline of all the steps along the reaction pathway, click on the button that shows a split screen with two molecules located next to the second number (the one that is fixed). The button will now only show one molecule. To view only one step at a time, click on the same button.
- To view a slideshow of all the stops along the reaction pathway, click on the green button located next to the first number. The green button will turn into a red “X”. To stop the slideshow, click on the red “X”.



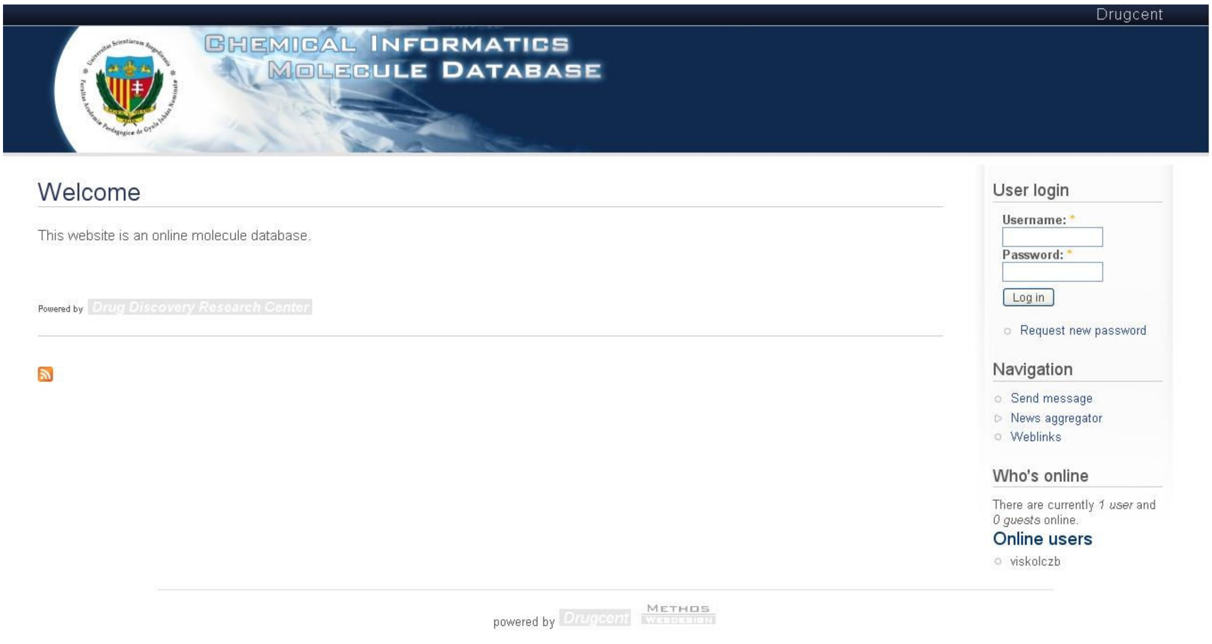
Reaction Pathway Timeline – Viewed in GaussView

TIPS:

- To rotate the molecule, click in the main window and move the mouse while holding down the left button.
- To enlarge the molecule, hold down the Control key and move the mouse while holding down the left button.

- To translate the molecule, hold down the Shift key and move the mouse while holding down the left button.

Webtools



Welcome

This website is an online molecule database.

Powered by Drug Discovery Research Center

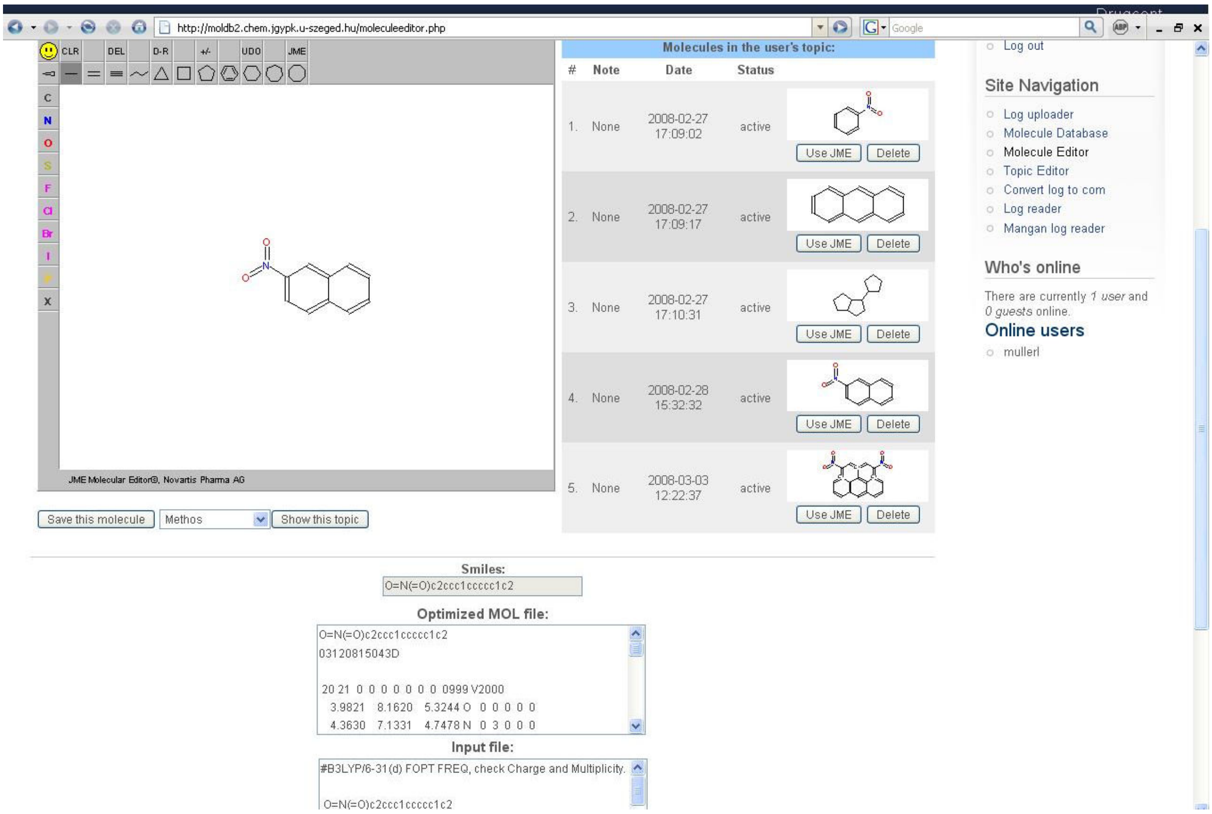
Username: *

Password: *

There are currently *1 user* and *0 guests* online.

viskolczb

Mainpage of the molecule database



Molecules in the user's topic:

#	Note	Date	Status
1.	None	2008-02-27 17:09:02	active
2.	None	2008-02-27 17:09:17	active
3.	None	2008-02-27 17:10:31	active
4.	None	2008-02-28 15:32:32	active
5.	None	2008-03-03 12:22:37	active

There are currently *1 user* and *0 guests* online.

mullerl

Smiles:

O=N(=O)c2ccc1ccccc1c2

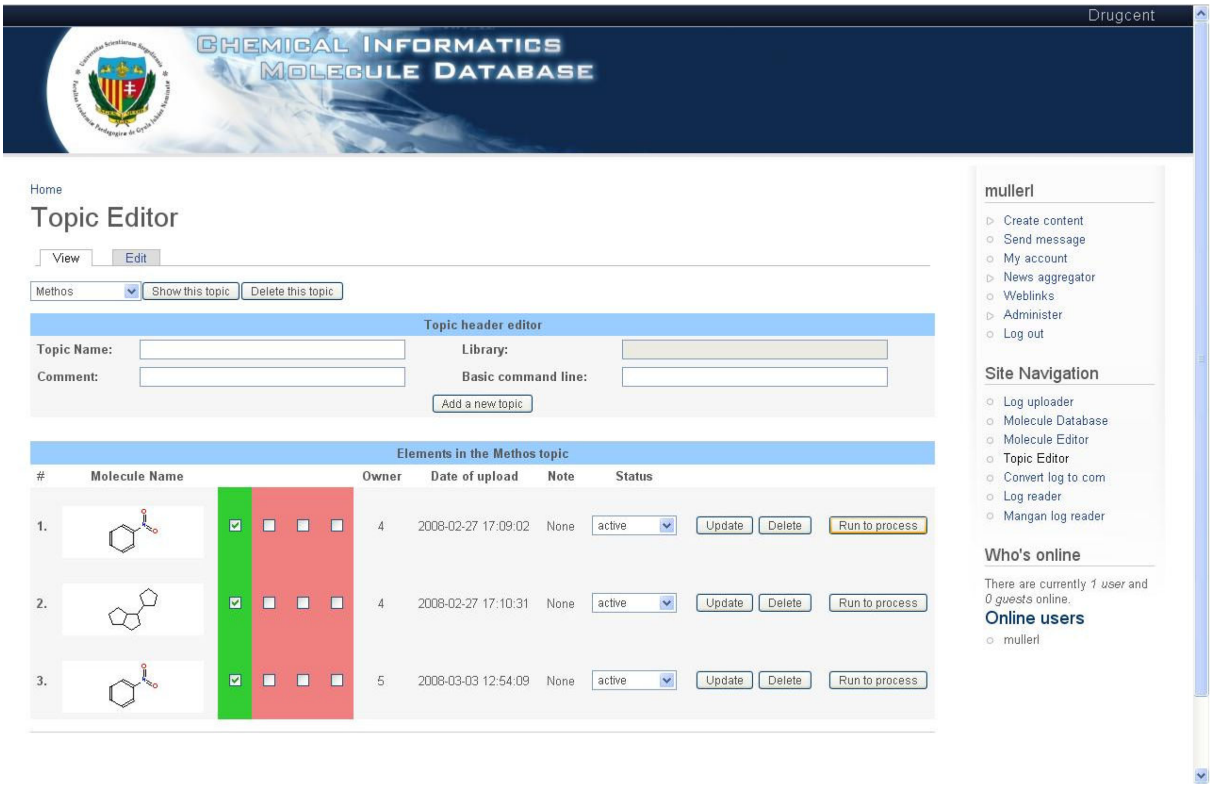
Optimized MOL file:

```
O=N(=O)c2ccc1ccccc1c2
03120815043D

 20 21  0  0  0  0  0  0  0  0999 V2000
    3.9821    8.1620    5.3244 O   0  0  0  0  0
    4.3630    7.1331    4.7478 N   0  3  0  0  0
```

Input file:

```
#B3LYP/6-31(d) FOPT FREQ, check Charge and Multiplicity.

 O=N(=O)c2ccc1ccccc1c2
```

Molecule editor interface



Topic header editor

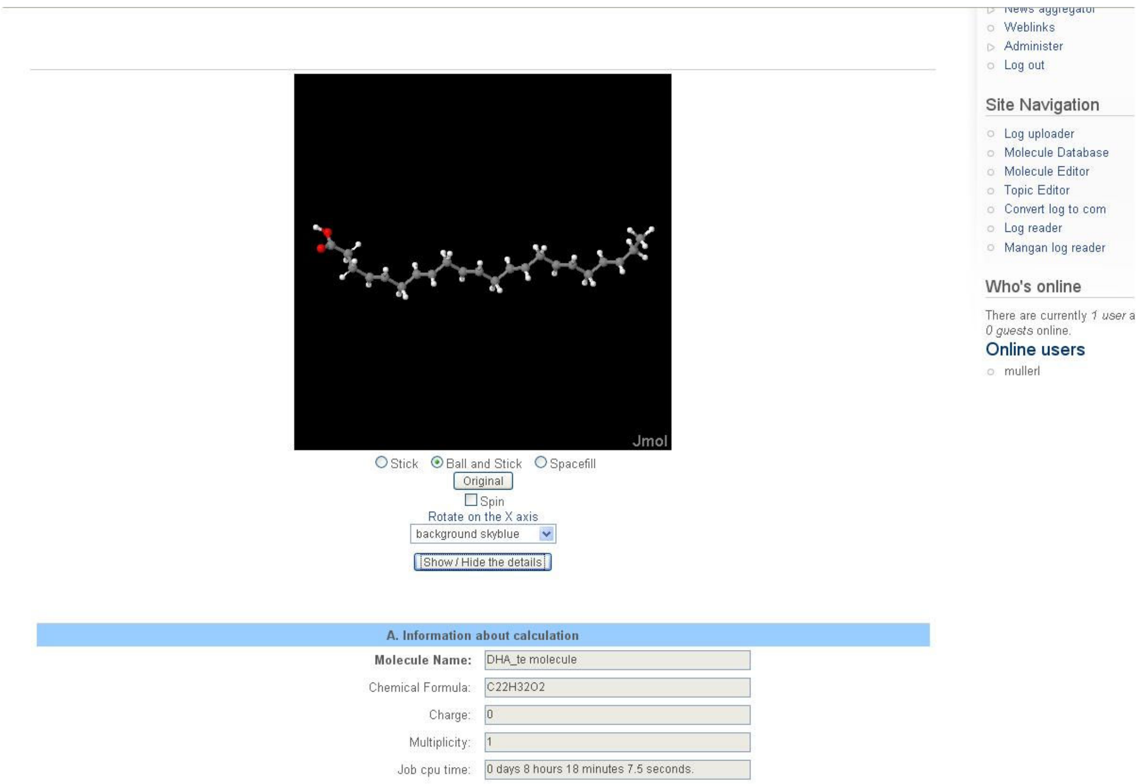
Topic Name:		**Library:**	
Comment:		**Basic command line:**	

Elements in the Methos topic

#	Molecule Name					Owner	Date of upload	Note	Status			
1.		☑	☐	☐	☐	4	2008-02-27 17:09:02	None	active	Update	Delete	Run to process
2.		☑	☐	☐	☐	4	2008-02-27 17:10:31	None	active	Update	Delete	Run to process
3.		☑	☐	☐	☐	5	2008-03-03 12:54:09	None	active	Update	Delete	Run to process

There are currently 1 *user* and 0 *guests* online.

Topic editor interface



○ Stick ● Ball and Stick ○ Spacefill

☐ Spin

There are currently 1 *user* a
0 *guests* online.

A. Information about calculation

Molecule Name:	DHA_te molecule
Chemical Formula:	C22H32O2
Charge:	0
Multiplicity:	1
Job cpu time:	0 days 8 hours 18 minutes 7.5 seconds.

Visualization of the molecular database

Appendix

To solve exercises we used Gaussian03 ab-initio program package. Other ab-initio programs and free demos can be found in the next location
http://www.theochem.uni-stuttgart.de/theolinks/links.html below the
Program Packages and Documentations Ab initio program packages
titles

Appendix 1

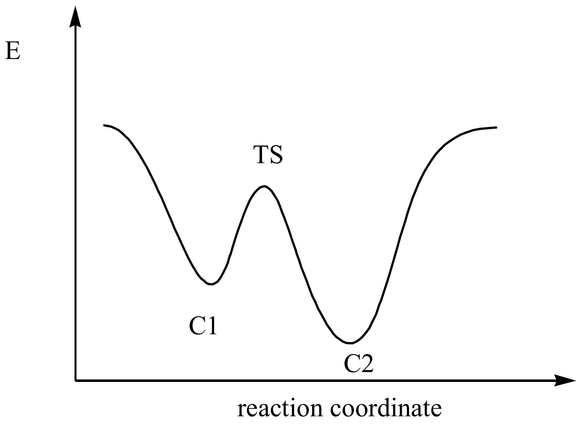
Problem

Compute the energy profile of the concreted (A) and stepwise (B) mechanism of reaction between metil-cloride and Brom ion.

Solution of S_N2 (concreted) reaction.

To solve this problem we use Gaussian 03 and gview programs.

As we calculate the energy in gas phase the energy profile is similar to the next



First we have to optimize the starting complex (C1) and product complex (C2). One of the input files is below

```
%chk=SNopt.chk
%mem=6MW
%nproc=1
#p opt hf/3-21g                                              optimization at 3-21g basis set

Metilklorid - bromide ion kiindulasi complex(C1) optimizacioja   note
```

charge -1, multiplicity singlet

atomic coordinates in Cartesian frame

```
-1 1
 C          0.61552264   0.78757807   0.54621719
 H          0.97217707  -0.22123193   0.54621719
 H          0.97219548   1.29197626   1.41986870
 H          0.97219548   1.29197626  -0.32743431
 Cl        -1.14447736   0.78759976   0.54621719
 Br         3.84149447   0.83548548   0.70019980
```

Then we make a redundant coordinate between the Brom ion and carbon atom of metil-cloride. During the optimization we increase the distance between the two atoms with 0.01Å in each step.

optimization at 3-21g basis set

```
%chk=
%mem=6MW
%nproc=1
#p opt=modredundant hf/3-21g geom=connectivity

SN reakció scan a szén-bromion tavolsag csökkentésével

-1 1

 C
 H        1      B1
 H        1      B2   2      A1
 H        1      B3   2      A2   3      D1
 Cl       1      B4   4      A3   3      D2
 Br       1      B5   4      A4   3      D3

   B1        1.06717105
   B2        1.06718052
   B3        1.06716759
   B4        1.99526909
   B5        3.11779504
   A1      114.18106258
   A2      114.19157479
   A3      104.19767784
   A4       75.81809217
   D1      133.94956808
   D2      113.03179128
   D3      -66.94632404

 1 2 1.0 3 1.0 4 1.0
 2
 3
 4
 5
 6

B 6 1 S 150 -0.010000
```

atomic coordinates in Z-matrix form

redundant parameters: Bond between atom no.6 and 1

step no.150

step -0.010000Å

You can see the results in the gwiev. You have to choose in the open dialog box read intermediate geometries and open the out file. If in the results dialog box you choose the scan option you will get a diagram of C-Br distance versus Energy of molecule. The diagram is false after the second minima, because the C-Br distance too short, so we have to calculate with other redundant coordinate.

Appendix 2

Problem: Use Gaussian X program package to compute the dipole momentum of following species: CH_4, C_2H_6, C_3H_8, Butan (4 conformers), MeCl, MeBr, MeF, MeOH, MeSH, $MeNH_2$, MeMgCl.

Solution: Input file for methane:

```
%chk=metan.chk
%mem=6MW
%nproc=1
#p opt hf/3-21g

Methan dipole moment

0 1
 C
 H                 1             B1
 H                 1             B2     2                 A1
 H                 1             B3     3                 A2     2
D1
 H                 1             B4     3                 A3     2
D2

   B1             1.07000000
   B2             1.07000000
   B3             1.07000000
   B4             1.07000000
   A1           109.47120255
   A2           109.47125080
   A3           109.47121829
   D1          -119.99998525
   D2           120.00000060
```

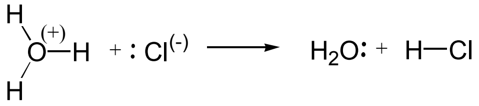
Results:

Species	Computed
Metane	0 debey
Ethane	0 debey
Propane	0 debey

Butane	
Syn-periplanar	0.0570 debey
Syn kinalis	0.0446 debey
Anti kinalis	0.0627 debey
Anti-periplanar	0.0 debey
Metilcloride	2.8641 debey
Metilbromide	2.1624 debey
Metilfluoride	2.3393 debey
Metilhidroxide	2.1227 debey
Metilsulfit	2.1178 debey
Metilamin	1.4401 debey
Metilmagnezium klorid	3.5176 debey

Apppendix 3

Problem: Compute the energy of species involving in the following reaction:



Solution:
Input file for H_3O^+

```
%chk=h3o.chk
%mem=6MW
%nproc=1
#p opt=gdiis hf/3-21g

Oxonium ion molecule energy cal.

1 1
 O
 H                  1             B1
 H                  1             B2     2                A1
 H                  1             B3     2                A2     3
D1

   B1             0.96000000
```

```
B2              0.96000000
B3              0.96000000
A1            109.47122063
A2            109.47122063
D1            120.00000000
```

Species	Energy in a.u.
H_3O^+	-75.89122771
Cl^-	-457.35358538
H_2O	-75.58580978
HCl	-457.86943112