

## **Appendix C—Calculating Excited States using Gaussian**

This appendix contains methods for using Gaussian 03<sup>78</sup> and Gaussian 09<sup>121</sup> to calculate excited states of molecules. Such methods are useful for estimating the electronic transition frequencies of molecules, particularly for the open shell peroxy radicals studied in our lab. In particular, these methods have been used to study hydroxymethylperoxy (HMP), described in Part 3 of this thesis. Testing and verification of these methods was performed on alkyl peroxy radicals, since extensive experimental and computational work has been performed on these species.<sup>44</sup>

Methods described in this appendix:

- 1) Configuration Interaction Singles (CIS)
- 2) Time-Dependent HF and DFT (TD-HF and TD-DFT)
- 3) Exploiting Orbital Symmetry
- 4) Freezing the Initial Orbital Guess Using `Guess=(Alter, Always)`
- 5) Scaling of Transition Frequencies
- 6) Composite Quantum Chemistry Methods: G2, CBS-QB3, and W1
- 7) Generating Potential Energy Surfaces
- 8) A Caution on Using EOM-IP

### **1) Configuration Interaction Singles (CIS)**

The Configuration Interaction Singles method (CIS) is a “zeroth order method” to approximate excited state energies.<sup>196</sup> Excited states are determined by combinations of single excitations from the Hartree Fock wavefunction. CIS calculations tend to give

very rough estimates of transition frequencies ( $\pm 4000 \text{ cm}^{-1}$ ). In general, one should select a more accurate method to estimate electronic transition frequencies. On the other hand, CIS calculations are very cheap, and can be used on larger molecules where *ab initio* or DFT methods would be unfeasible.

A CIS calculation can be requested using the following route line in Gaussian:

```
#p opt CIS/6-31+g(d,p) geom=connectivity Density=Current
```

There are a few things to point out in this route line. First, CIS calculations cannot be paired with a higher level of theory (such as CCSD). Specifying both CIS and a level of theory will default to a CIS calculation. Second, a CIS calculation should always be run with the `Opt` keyword to ensure that the excited state analysis is performed on an optimized geometry. Finally, note that the `Density=Current` command requests that all analysis be done on the CIS wavefunction, rather than the HF wavefunction. **As a general rule, `Density=Current` should be included in all calculations where the dipole moment integrals are needed.**

The relevant CIS data are found near the end of the output file. These data include transition dipole moments, transition frequencies, oscillator strengths, and information on which orbitals are involved in the excitation. Shown below is the output for a CIS calculation on the HMP radical (discussed in Part 3 of this thesis).

```
*****
Excited states from <AA, BB:AA, BB> singles matrix:
*****

1PDM for each excited state written to RWF 633
Ground to excited state Transition electric dipole moments (Au):
```

state	X	Y	Z	Osc.
1	0.0043	0.0068	0.0048	0.0000
2	-0.0526	-0.1119	-0.1460	0.0058
3	-0.0183	0.0033	-0.0028	0.0001

Ground to excited state transition velocity dipole Moments (Au):

state	X	Y	Z	Osc.
1	0.0005	-0.0027	-0.0022	0.0003
2	0.0069	0.0121	0.0247	0.0023
3	-0.0109	-0.0028	0.0108	0.0006

Ground to excited state transition magnetic dipole Moments (Au):

state	X	Y	Z
1	-0.5531	0.7356	-0.3320
2	-0.7098	-0.2665	0.6301
3	0.0279	0.0486	0.0881

$\langle 0 | \text{del} | b \rangle * \langle b | r x \text{del} | 0 \rangle$  (Au), Rotatory Strengths (R) in  
cgs ( $10^{*-40}$  erg-esu-cm/Gauss)

state	X	Y	Z	R(velocity)
1	-0.0003	-0.0020	0.0007	-12.7346
2	-0.0049	-0.0032	0.0156	7.4106
3	-0.0003	-0.0001	0.0010	0.4657

$\langle 0 | r | b \rangle * \langle b | r x \text{del} | 0 \rangle$  (Au), Rotatory Strengths (R) in  
cgs ( $10^{*-40}$  erg-esu-cm/Gauss)

state	X	Y	Z	R(length)
1	-0.0024	0.0050	-0.0016	-0.2556
2	0.0374	0.0298	-0.0920	5.8450
3	-0.0005	0.0002	-0.0002	0.1418

$\langle 0 | \text{del} | b \rangle * \langle b | r | 0 \rangle$  (Au)

state	X	Y	Z	Osc.(frdel)
1	0.0000	0.0000	0.0000	0.0000
2	-0.0004	-0.0014	-0.0036	0.0036
3	0.0002	0.0000	0.0000	-0.0001

Ground to excited state transition densities written to RWF 633

Excitation energies and oscillator strengths:

Excited State	1:	?Spin	-A	0.7752 eV	1599.45 nm	f=0.0000
12B -> 17B			0.13373			
14B -> 17B			-0.27905			
14B -> 18B			0.19594			
14B -> 19B			0.16934			
14B -> 20B			-0.14236			
14B -> 21B			0.11446			
14B -> 26B			-0.11191			
15B -> 17B			0.23868			
15B -> 18B			-0.16647			
15B -> 19B			-0.14434			
15B -> 20B			0.12165			
16B -> 17B			-0.44498			
16B -> 18B			0.31356			
16B -> 19B			0.26832			
16B -> 20B			-0.22451			
16B -> 21B			0.17976			
16B -> 26B			-0.16624			
16B -> 29B			-0.12826			
16B -> 30B			0.11778			

This state for optimization and/or second-order correction.  
Total Energy, E(CIS) = -264.047852507

In this case, the HMP A-X frequency is predicted to be 0.7752 eV (1599.45 nm, or 6252  $\text{cm}^{-1}$ ). This is 1100  $\text{cm}^{-1}$  less than the experimental frequency, determined by CRDS (7391  $\text{cm}^{-1}$ ). It is predicted to have an oscillator strength of 0.0000, but Gaussian predicts this for many peroxy radicals ( $\text{HO}_2$ ,  $\text{CH}_3\text{O}_2\bullet$ , etc.). This is because the minimum oscillator strength that Gaussian will report is 0.0001, corresponding to an integrated cross section of  $8.85 \times 10^{-17} \text{ cm molec}^{-1}$ . Electronic transitions with integrated cross sections less than this will appear to have an oscillator strength of 0, a reasonable result for the weak A-X transition in peroxy radicals.<sup>44</sup>

Table C.1 shows a comparison of CIS A-X transition frequency to experiment for  $\text{HO}_2$ ,  $\text{CH}_3\text{OO}\bullet$ , and HMP. The quantitative and qualitative agreement between theory and experiment is absolutely terrible. CIS calculations underestimate the A-X frequency by 1000–1500  $\text{cm}^{-1}$ . Additionally, the CIS calculation places the A-X transition frequency of  $\text{CH}_3\text{OO}\bullet$  lower than  $\text{HO}_2$ , while experiment shows the A-X transition frequency of  $\text{CH}_3\text{OO}\bullet$  is higher than  $\text{HO}_2$ .

**Table C.1.** Comparison of CIS/6-31+G(d,p) to experiment for A-X electronic transitions of peroxy radicals

Molecule	A-X, CIS ( $\text{cm}^{-1}$ )	A-X, Experiment ( $\text{cm}^{-1}$ )
$\text{HO}_2$	6331	7029 <sup>54,55</sup>
$\text{CH}_3\text{OO}\bullet$	5857	7382 <sup>44</sup>
$\text{HOCH}_2\text{OO}\bullet$	6252	7391

## 2) Time-Dependent HF and DFT (TD-HF and TD-DFT)

The time-dependent versions of Hartree-Fock and Density Functional Theory (TD-HF and TD-DFT) can also predict excited state energies. Both methods are extensions of the respective time-independent theories (HF and DFT). While the

time-independent methods do not report excited state frequencies, the time dependent formulations do.

To request a time-dependent calculation in Gaussian, simply append the TD keyword to the rest of the route section. The program will automatically select TD-HF or TD-DFT based on the level of theory requested. Shown below is the route line for a TD-DFT calculation.

```
#p Opt B3LYP/6-31+G(d,p) TD geom=connectivity
```

The relevant section of the output looks similar to the CIS output. Shown below is the result of a TD-B3LYP calculation on HO<sub>2</sub>.

```
*****
Excited states from <AA,BB:AA,BB> singles matrix:
*****

1PDM for each excited state written to RWF 633
Ground to excited state Transition electric dipole moments (Au):
  state      X      Y      Z      Osc.
  1          0.0000  0.0000 -0.0198  0.0000
  2         -0.0400 -0.5619  0.0000  0.0418
  3          0.0159  0.1112  0.0000  0.0017
Ground to excited state transition velocity dipole Moments (Au):
  state      X      Y      Z      Osc.
  1          0.0000  0.0000  0.0043  0.0003
  2          0.0078  0.1050  0.0000  0.0374
  3         -0.0041 -0.0206  0.0000  0.0015
Ground to excited state transition magnetic dipole Moments (Au):
  state      X      Y      Z
  1         -0.0795 -0.8866  0.0000
  2          0.0000  0.0000  0.0309
  3          0.0000  0.0000 -0.0447
<0|del|b> * <b|rxdel|0> (Au), Rotatory Strengths (R) in
cgs (10**-40 erg-esu-cm/Gauss)
  state      X      Y      Z      R(velocity)
  1          0.0000  0.0000  0.0000  0.0000
  2          0.0000  0.0000  0.0000  0.0000
  3          0.0000  0.0000  0.0000  0.0000
<0|r|b> * <b|rxdel|0> (Au), Rotatory Strengths (R) in
cgs (10**-40 erg-esu-cm/Gauss)
  state      X      Y      Z      R(length)
```

```

1          0.0000      0.0000      0.0000      0.0000
2          0.0000      0.0000      0.0000      0.0000
3          0.0000      0.0000      0.0000      0.0000
<0|del|b> * <b|r|0> (Au)
state      X          Y          Z          Osc.(frdel)
1          0.0000      0.0000     -0.0001     0.0001
2         -0.0003     -0.0590      0.0000     0.0395
3         -0.0001     -0.0023      0.0000     0.0016
Ground to excited state transition densities written to RWF 633

Excitation energies and oscillator strengths:

Excited State  1:  ?Spin -A"      0.9919 eV 1249.97 nm f=0.0000
8B -> 9B      1.08132
This state for optimization and/or second-order correction.
Total Energy, E(RPA) = -150.876870963
Copying the excited state density for this state as the 1-particle
RhoCI density.

Excited State  2:  ?Spin -A'      5.3799 eV 230.46 nm f=0.0418
7A -> 10A     -0.17402
8A -> 13A      0.11876
9A -> 10A     -0.19873
7B -> 9B      0.95400

Excited State  3:  ?Spin -A'      5.4896 eV 225.85 nm f=0.0017
9A -> 10A     -0.63390
9A -> 11A      0.25689
9A -> 14A     -0.15605
7B -> 9B     -0.17966
8B -> 10B      0.65845
8B -> 11B     -0.35617
8B -> 14B      0.20378
Leave Link 914 at Tue Apr 06 09:17:52 2010, MaxMem= 167772160 cpu:
4.0
(Enter C:\G03W\l114.exe)

```

There are a couple of things to note about the TD-DFT calculations. Similar to the CIS calculation, dipole moment integrals, excited state frequencies, oscillator strengths, and the molecular orbitals involved in excitation are reported. The above output reports the A-X frequency of HO<sub>2</sub> to be 0.9919 eV (1249.97 nm, or 8000 cm<sup>-1</sup>). This overestimates the A-X frequency by 1000 cm<sup>-1</sup> (experimental value of 7029 cm<sup>-1</sup>).<sup>54, 55</sup> Additionally, the TD-DFT calculations are very computationally expensive when paired with the `Opt` keyword. One workaround is to optimize the geometry using

time-independent DFT, and then run a single point TD-DFT calculation. While this method will reduce the computational expense, it is also less accurate than a full TD-DFT optimization.

Table C.2 shows a comparison of TD-DFT A-X transition frequency to experiment for HO<sub>2</sub>, CH<sub>3</sub>OO•, and HMP. TD-DFT values were calculated both with and without the `Opt` keyword, as described above. When the `Opt` keyword was used on the calculations of CH<sub>3</sub>OO• and HMP, Gaussian would crash after a few optimization steps, reporting that the Hessian structure was not correct. We do notice that the single point TD-DFT calculations are able to correctly predict the trend in A-X frequency amongst the three radicals, suggesting that the single point TD-DFT method can be used to predict relative positions in peroxy radicals.

**Table C.2.** Comparison of TD-DFT to experiment for A-X electronic transitions of peroxy radicals (TD-B3LYP/6-31+G(d,p))

Molecule	A-X, TDDFT SP (cm <sup>-1</sup> )	A-X, TDDFT Opt (cm <sup>-1</sup> )	A-X, Experiment (cm <sup>-1</sup> )
HO <sub>2</sub>	8932	8000	7029 <sup>54, 55</sup>
CH <sub>3</sub> OO•	9287	not computed	7382 <sup>44</sup>
HOCH <sub>2</sub> OO•	9303	not computed	7391

The authors of NWChem,<sup>197</sup> a computational chemistry program published by Pacific Northwest National Laboratories, offer a comment on the accuracy of TD-DFT:

“The accuracy of TDDFT may vary depending on the exchange-correlation functional. In general, the exchange-correlation functionals that are widely used today and are implemented in NWChem work well for low-lying valence excited states. However, for high-lying diffuse excited states and Rydberg excited states in particular, TDDFT employing these conventional functionals breaks down and the excitation energies are substantially underestimated.”

TD-HF is roughly comparable in accuracy to CIS. My experience with TD-DFT is absolute accuracy of  $\pm 1000 \text{ cm}^{-1}$  (based on the above calculations on  $\text{HO}_2$ ,  $\text{CH}_3\text{OO}\cdot$ , and HMP). In general, I would not ever run a TD-HF calculation, since the CIS calculation will be of comparable accuracy and less expensive. TD-DFT can be thought of as one step more accurate than CIS. However, the computational expense of TD-DFT calculations makes them generally unsuitable for anything with more than a few carbons.

### 3) Exploiting Orbital Symmetry

The optimization algorithm in Gaussian will do its best to keep the same molecular symmetry as the input geometry.<sup>79</sup> Thus, if the input file contains a molecule in  $C_s$  symmetry, the optimized structure will also be  $C_s$ . The same idea holds true for the symmetry of the electronic wavefunction. If the input file contains an electronic wavefunction with  $A''$  symmetry, then the optimization will attempt to keep the electronic wavefunction in  $A''$  symmetry at every step.

The idea of restricting symmetries can be exploited to obtain excited state geometries. Consider, for example, the first two states of  $\text{HO}_2$ . The ground state has  $A''$  symmetry, while the first excited state has  $A'$  symmetry. Suppose that the input file requests a geometry optimization, with an initial electronic state guess of  $A'$  symmetry. During the optimization, Gaussian will always keep the electronic state symmetry as  $A'$ . The result of the optimization will be the lowest energy structure with  $A'$  electronic symmetry, i.e., the first excited state.

The initial orbital population can be changed using `Guess=Alter` in the route line. This command allows users to switch pairs of orbitals that are to be populated. (For



example, switching orbitals 4 and 5 will cause Gaussian to populate the orbitals in this order: 1, 2, 3, 5, 4, 6, 7, ...) Switching two core orbitals will have no effect. (However, such an operation is not completely useless; it may be necessary to switch core orbital filling in a CASSCF job.) Switching a core or valence orbital with a virtual orbital will allow the user to change the electronic symmetry. These pairs of orbitals are listed at the end of the input file.

If the calculation uses a restricted method (RHF, RCCSD, etc.), then only one line is necessary to change orbitals. If the calculation uses an unrestricted method (UHF, UCCSD, etc.), then separate lines are necessary for  $\alpha$  and  $\beta$  electrons. Both lines must be present in the input file. If no electrons of one type are to be changed, then the line should be blank.

The following example file calculates the first excited state of HO<sub>2</sub>. Since HO<sub>2</sub> has 17 electrons (9  $\alpha$ , 8  $\beta$ ), we will change the order of  $\beta$  orbitals 8 and 9. Since no  $\alpha$  electrons are being altered, we put a blank line before the  $\beta$  orbital line (**this is in addition to a blank line needed to separate the connectivity section from the orbital alteration section**).

```

%chk=HO2 B3LYP A Opt.chk
%nproc=1
#p opt B3LYP/6-31+g(d,p) geom=connectivity Guess=Alter

HO2 A State
MKS, 4/6/10

0 2
O
H          1          B1
O          1          B2      2          A1

B1=0.98052408
B2=1.33330037
A1=105.52948981

1 2 1.0 3 1.0
2
3

8 9

```

The output file will look exactly like a normal optimization file. **However, the user should ensure that the final symmetry is the excited state electronic symmetry, and not the ground state.** Sometimes, the optimization will “relax” down to the ground state symmetry. I am not sure what the reason for this is, but it does happen from time to time. The symmetry can be found in the final output (highlighted below).

```

(Enter C:\G03W\19999.exe)
Final structure in terms of initial Z-matrix:
O
H,1,B1
O,1,B2,2,A1
Variables:
B1=0.97637273
B2=1.39529609
A1=103.55791628
1|1|UNPC-UNK|FOpt|UB3LYP|6-31+G(d,p)|H1O2(2)|PCUSER|06-Apr-2010|4||#P
OPT B3LYP/6-31+G(D,P) GEOM=CONNECTIVITY GUESS=ALTER|Title Ca
rd Required||0,2|O,-0.6348300196,0.,0.1172381389|H,-0.6030213526,0.,1.
0930925935|O,0.7102076887,0.,-0.253874713|||8,9||Version=IA32W-G03RevC
.01|State=2-A'|HF=-150.8824122|S2=0.753042|S2-1=0.|S2A=0.750007|RMSD=3
.483e-009|RMSF=8.428e-005|Dipole=-0.1481518,0.,0.8045714|PG=CS [SG(H1O
2)]||@

```

In this case, the electronic state is listed as  $2-A'$ , which is the electronic symmetry of the first excited state. The final energy can be compared to the ground state (calculated separately), and the A-X frequency can be computed. For HO<sub>2</sub> at B3LYP/6-31+G(d,p), the A-X frequency is computed as 7251 cm<sup>-1</sup>, 222 cm<sup>-1</sup> higher than the experimental value.

#### **4) Freezing the Initial Orbital Guess Using `Guess=(Alter,Always)`**

Note: The paper on alkyl peroxy spectra by Sharp et al. describe populating the electronic orbitals in a low level calculation, then running a high level calculation using the orbitals obtained from the previous calculation.<sup>44</sup> It is unknown to me whether Sharp uses a separate script or the method described below. As will be shown, our method can reproduce Sharp's results, and is, at a minimum, equivalent to their method. The discussion below should help future students perform these calculations.

Most conformations of the molecules that we are interested in do not have any point group symmetry (i.e., they belong to the C<sub>1</sub> point group). As such, there is no electronic wavefunction symmetry to take advantage of, and simply using the keyword `Guess=Alter` will result in the optimization relaxing back to the ground state. However, by changing this command to `Guess=(Alter,Always)`, Gaussian 03W will repopulate the electron orbitals at each step of the SCF calculation. The result of this is "freezing" the electrons in a non-ground-state configuration. Such a calculation will allow for the excited state energy of any molecule to be computed. Unlike a CIS calculation, the geometry and orbitals are optimized in the excited state as opposed to the

ground state, and thus the energies obtained should be vastly more accurate than a CIS calculation.

The syntax and output are the same as described in the previous section, with the exception of changing `Guess=Alter` to `Guess=(Alter,Always)`. The A-X transition frequencies obtained on  $C_1$  conformers of a molecule are consistent with results obtained from  $C_s$  conformers (i.e., exploiting orbital symmetry as described in the previous section). This can be illustrated by mapping out the full potential energy surfaces, and showing that the  $C_s$  transition frequencies agree with the surrounding  $C_1$  transition frequencies, as has been done for HMP (see the surfaces presented in Part 3 of this thesis). This consistency strongly implies that this method of obtaining excited states is valid for molecules with no symmetry.

Table C.3 shows a comparison of `Guess=(Alter,Always)` A-X transition frequency to experiment for  $\text{HO}_2$ ,  $\text{CH}_3\text{OO}\cdot$ , and HMP. The absolute transition frequencies are too high by 100–200  $\text{cm}^{-1}$ , though this represents a vast improvement over CIS or TD-DFT. For the most part, the transition frequencies qualitatively follow the experimental trends. `Guess=(Alter,Always)` is able to predict the transition frequencies of both  $\text{CH}_3\text{OO}\cdot$  and  $\text{HOCH}_2\text{OO}\cdot$  to be higher than the transition frequency of  $\text{HO}_2$ . Unfortunately, it also predicts  $\text{HOCH}_2\text{OO}\cdot$  to have a lower frequency than  $\text{CH}_3\text{OO}\cdot$ . Sharp et al. make similar observations: the `Guess=(Alter,Always)` calculations become less accurate as the peroxy radical of interest becomes more complicated (either additional functional groups, or a longer carbon chain).

**Table C.3.** Comparison of the *Guess=(Alter, Always)* method to experiment for A-X electronic transitions of peroxy radicals (B3LYP/6-31+G(d,p))

Molecule	A-X, <i>Alter, Always</i> ( $\text{cm}^{-1}$ )	A-X, Experiment ( $\text{cm}^{-1}$ )
HO <sub>2</sub>	7251	7029 <sup>54,55</sup>
CH <sub>3</sub> OO•	7622	7382 <sup>44</sup>
HOCH <sub>2</sub> OO•	7501	7391

### 5) Scaling of Transition Frequencies

The calculation methods presented above can often get the correct qualitative behavior for the transition frequencies. For example, the *Guess=(Alter, Always)* method at B3LYP/6-31+G(d,p) is able to predict that CH<sub>3</sub>OO• and HOCH<sub>2</sub>OO• both have a higher A-X transition frequency than HO<sub>2</sub>. However, the quantitative agreement between calculated and experimental transition frequencies is not very good, ranging in accuracy from  $\pm 300 \text{ cm}^{-1}$  (*Guess=Alter, Always*) to  $\pm 1500 \text{ cm}^{-1}$  (single point TD-DFT). As presented so far, the computed transition frequencies are of limited aid for predicting electronic transitions that have not yet been detected.

A careful look at Tables C.1–C.3 reveals that each particular method tends to overestimate or underestimate the transition frequency by a similar amount, regardless of the specific peroxy radical being studied. This observation suggests that if we scale the calculated frequencies to a well-studied peroxy radical, such as HO<sub>2</sub>, we will be able to obtain quantitatively accurate transition frequencies. Scaling should eliminate systematic errors from the level of theory and basis being used. Additionally, if the reference molecule is chemically similar to the molecules of interest, we expect that the electronic surfaces will have similar curvature and harmonic frequencies. Thus, we will also account for any changes in the zero point vibrational energy (ZPVE).

Table C.4 contains the scaled A-X transition frequencies for  $\text{CH}_3\text{OO}\cdot$  and  $\text{HOCH}_2\text{OO}\cdot$ , using each of the methods to obtain this frequency described above (CIS, TD-DFT, `Guess=Alter, Always`). The frequencies are scaled to the experimentally determined A-X transition of  $\text{HO}_2$  of  $7029\text{ cm}^{-1}$ .<sup>54, 55</sup> The scaled frequencies are in general closer to the experimental values than the unscaled frequencies. While CIS still gives a poor prediction for the transition frequency, TD-DFT and `Guess=(Alter, Always)` are able to predict the A-X frequency within  $100\text{ cm}^{-1}$ . Although this is still considered considerable error, both TD-DFT and `Guess=(Alter, Always)` can be used to aid in experimental detection of A-X transitions in peroxy radicals. In order to obtain better quantitative agreement, we must move on to more sophisticated (and thus more expensive) methods, described in the next section.

**Table C.4.** Comparison of scaled frequencies to experiment for A-X electronic transitions of peroxy radicals. Frequencies scaled to A-X ( $\text{HO}_2$ ) =  $7029\text{ cm}^{-1}$ . (B3LYP/6-31+G(d,p))

Molecule	CIS ( $\text{cm}^{-1}$ )	TD-DFT, no opt ( $\text{cm}^{-1}$ )	<code>Guess=Alter, Always</code> ( $\text{cm}^{-1}$ )	Expt. ( $\text{cm}^{-1}$ )
$\text{HO}_2$	—	—	—	$7029$ <sup>54, 55</sup>
$\text{CH}_3\text{O}_2\cdot$	6503	7309	7390	$7382$ <sup>44</sup>
$\text{HOCH}_2\text{O}_2\cdot$	6942	7321	7272	7391

## 6) Composite Quantum Chemistry Methods: G2, CBS-QB3, and W1

Composite quantum chemistry methods are designed for high-accuracy thermochemical calculations. The purpose of these calculations is to approximate the energy at a high level of theory and large basis by performing many smaller calculations

(high level and small basis, or low level and large basis). Three methods used in the current chemical literature are G2,<sup>123, 198-201</sup> CBS-QB3,<sup>202-205</sup> and W1.<sup>206-211</sup> Of these, G2 has been used frequently in calculations of alkyl peroxy radicals. It has been shown to predict the A-X transition frequencies within  $\pm 50 \text{ cm}^{-1}$  without the need for scaling.<sup>44</sup> Sharpe et al. show that as the alkyl chain gets larger, the frequencies predicted by the G2 method become less accurate. The accuracy may or may not get worse when additional functional groups are present.

The purpose of the G2 method is to estimate the QCISD(T)/6-311+G(3df,2p) energy by computing less expensive energies at lower levels of theory, or smaller basis sets. These energies are used to estimate the contributions to the energy due to increasing the basis set. A G2 calculation consists of the following steps:

- 1) Geometry optimization at HF/6-31G(d)
- 2) Frequency calculation at the geometry from step 1, to obtain the zero point energy
- 3) Geometry optimization at MP2(Full)/6-31G(d)
- 4) Using the geometry from step 3, single point calculations at
  - a) QCISD(T,E4T)/6-311G(d,p) (see below for explanation of “E4T”)
  - b) MP4(SDTQ)/6-311G(2df,p)
  - c) MP4(SDTQ)/6-311+G(d,p)
  - d) MP2/6-311+G(3df,2p)

Note that the MP4(SDTQ) and QCISD(T) calculations will also provide MP2 and MP4 energies, at no additional cost. **The user must request for triples to be calculated during the QCISD(T) calculation by using the method QCISD (T , E4T) .**

The G2 energy can then be computed from Equation C.1, as defined in Pople's G1 and G2 papers:<sup>123, 198, 201</sup>

$$\begin{aligned}
 E(\text{G2}) = & \{ \text{QCISD(T)/6-311G(d,p)} \} \\
 & + [ \{ \text{MP4/6-311G(2df,p)} \} - \{ \text{MP4/6-311G(d,p)} \} ] \\
 & + [ \{ \text{MP4/6-311+G(d,p)} \} - \{ \text{MP4/6-311G(d,p)} \} ] \\
 & + [ \{ \text{MP2/6-311+G(3df,2p)} \} - \{ \text{MP2/6-311G(2df,p)} \} ] \quad (\text{C.1}) \\
 & + [ \{ \text{MP2/6-311G(d,p)} \} - \{ \text{MP2/6-311+G(d,p)} \} ] \\
 & + 0.8929 \times \text{ZPVE} \\
 & + \text{HLC},
 \end{aligned}$$

where the terms labeled {xx/yy} denote the single point energy at xx/yy//MP2(Full)/6-31G(d), ZPVE is the zero point vibrational energy, 0.8929 is the HF/6-31(d) scaling factor for the harmonic frequencies, and HLC is a "high level correction." The HLC is defined as

$$\text{HLC} = (-4.81 \text{ mhartree}) \times N_V - (-0.19 \text{ mhartree}) \times N_U, \quad (\text{C.2})$$

where  $N_V$  is the total number of valence electrons, and  $N_U$  is the number of unpaired valence electrons. For example, in HMP, there are 33 total electrons. 8 of these 33 are core (1s) electrons, leaving 25 valence electrons ( $N_V$ ), 1 of which is unpaired ( $N_U$ ). The HLC is -60.19 mhartree.

For ground state molecules, the G2 method can be directly requested in G03W, via the following route line:

```
#p G2 geom=connectivity
```

Gaussian will automatically carry out the calculations described above. The end of the output file contains information on the G2 energies. Shown below is the output for a G2 calculation on HMP:



Temperature=	298.150000	Pressure=	1.000000
E(ZPE)=	0.047510	E(Thermal)=	0.051972
E(QCISD(T))=	-264.903868	E(Empiric)=	-0.073870
DE(Plus)=	-0.015881	DE(2DF)=	-0.141516
G1(0 K)=	-265.087624	G1 Energy=	-265.083162
G1 Enthalpy=	-265.082218	G1 Free Energy=	-265.115071
E(Delta-G2)=	-0.017592	E(G2-Empiric)=	0.013680
<b>G2(0 K)=</b>	<b>-265.091536</b>	G2 Energy=	-265.087074
G2 Enthalpy=	-265.086130	G2 Free Energy=	-265.118983
DE(MP2)=	-0.166853		
G2MP2(0 K)=	-265.083401	G2MP2 Energy=	-265.078938
G2MP2 Enthalpy=	-265.077994	G2MP2 Free Energy=	-265.110847

The G2 energy is listed as G2 (0 K). In this case, the G2 energy is  $-265.091536$  au.

It is not possible to use the built in G2 method for calculating excited states, because Gaussian will not pass the `Guess=(Alter,Always)` command correctly to each step. Instead, the user must manually request the calculations described above (steps 1-4), and extract the correct energies from each file. I wrote a G2 calculator in Excel to automatically calculate the G2 energy: the user types in the energies from each part, and the program determines the G1 and G2 energies (Figure C.1 shows a screenshot of the calculator). Typically, the G2 energy obtained through the calculator only differs from the G2 energy directly reported by G03W by a few microhartree ( $<1 \text{ cm}^{-1}$ ). Once the X and A states have been calculated, the energy difference should be used directly as the transition frequency. No further energy scaling is required (such as the scaling described in the previous section), because differences in the ZPVE for the X and A states have already been accounted for.

HMP G2 through Gaussian						
A1	A	B	C	D	E	G
1	HMP G2 through Gaussian					
2						
3	Level	Basis	E (au)		Molecule	
4	QCISD(T)	6-311G(d,p)	-264.9038679		ncore	8
5	MP4	6-311G(2df,p)	-265.0426343		nalpha	13
6	MP4	6-311G(d,p)	-264.9011185		nbeta	12
7	MP4	6-311+G(d,p)	-264.9169993			
8	MP2	6-311+G(3df,2p)	-265.0151013			
9	MP2	6-311G(d,p)	-264.8482486			
10	MP2	6-311G(2df,p)	-264.9827944			
11	MP2	6-311+G(d,p)	-264.8629634			
12						
13	ZPVE	HF/6-31G(d)	0.053212			
14						
15		E(G1, 0K)	-265.0876215			
16		E(G2, 0K)	-265.0915336			
17						
18						
19	G1:	MP4(Full)/6-311G**/MP2(Full)/6-31G*				-264.9011185
20	(Pople 89)	dE(+)=MP4/6311+G** - MP4/6-311G**				-0.0158808 DE(Plus)
21		dE(2df) = MP4/6-311G**(2df) - MP4/6-311G**				-0.1415158 DE(2DF)
22		dE(QCJ) = QCISD(T)/6-311G** - MP4/6-311G**				-0.0027494
23		E combined				-265.0612645
24		dE(HLC) = -0.00019*nalpha+val-0.00595*nbeta+val				-0.07387 (E Empiric)
25		0.8929*ZPE				0.047512995 E(ZPE)
26		E(G1)				-265.0876215 G1 (0K)
27						
28						
29						

**Figure C.1.** Screenshot of the G2 energy calculator spreadsheet. The calculated G1 and G2 energies are circled.

Table C.5 shows a comparison of G2 A-X transition frequency to experiment for  $\text{HO}_2$ ,  $\text{CH}_3\text{OO}\cdot$ , and  $\text{HOCH}_2\text{OO}\cdot$ . The quantitative agreement between calculation and experiment is quite good.  $\text{HO}_2$  and  $\text{HOCH}_2\text{OO}\cdot$  are calculated to within  $40\text{ cm}^{-1}$  of their experimental values, while  $\text{CH}_3\text{OO}\cdot$  is calculated to better than  $10\text{ cm}^{-1}$ . It should be

noted that G2 is generally a much more expensive method than using `Guess=(Alter, Always)`, although this depends on the level of theory and basis used. It may be unfeasible to run G2 calculations on larger alkyl peroxies without access to a supercomputer.

**Table C.5.** Comparison of G2 calculated frequencies to experiment for A-X electronic transitions of peroxy radicals

Molecule	A-X (G2) (cm <sup>-1</sup> )	A-X, Experiment (cm <sup>-1</sup> )
HO <sub>2</sub>	7060	7029 <sup>54, 55</sup>
CH <sub>3</sub> OO•	7375	7382 <sup>44</sup>
HOCH <sub>2</sub> OO•	7424	7391

As shown in Part 3 of this thesis, the G2 method cannot locate all three conformers (local minima) of the HMP radical. The MP2(Full)/6-31+G(d,p) potential energy surface of HMP reveals that one of the local minima from CCSD and B3LYP calculations becomes a shelf at MP2(Full). Because the CCSD calculation is likely more accurate than the MP2(Full) calculation, my thought is that the G2 method is inadequate for conformer searches of substituted peroxy radicals.

Two other composite chemistry methods are also available in Gaussian 03: the complete basis set methods by Petersson (denoted as CBS methods),<sup>202-205</sup> and the Weizmann-1 method (W1).<sup>206-211</sup> In particular, two methods of interest are CBS-QB3 (based on a B3LYP geometry optimization) and W1U (based on a UB3LYP geometry optimization and UCCSD energy corrections). The work described in Part 3 of this thesis shows that the B3LYP and CCSD potential energy surfaces of HMP are in qualitative agreement. Furthermore, both methods are able to predict the A-X transition of HMP to within  $\pm 80$  cm<sup>-1</sup> when scaled to HO<sub>2</sub> (as seen in the previous section). Thus, composite

chemistry methods based on these levels of theory could lead to improvements in A-X transition predictions.

I wrote a CBS-QB3 energy calculator in Excel (similar to the G2 calculator described above), allowing for the computation of A-X transition frequencies. Table C.6 contains the CBS-QB3 calculated A-X transition frequencies for HO<sub>2</sub>, CH<sub>3</sub>OO•, and HOCH<sub>2</sub>OO•. CBS-QB3 is able to calculate both HO<sub>2</sub> and CH<sub>3</sub>OO• to within 20 cm<sup>-1</sup> of the experimental values. However, the accuracy is worse with substituted alkyl peroxies. The calculated A-X transition for HMP is 90 cm<sup>-1</sup> higher than the experimental frequency. It is unclear at the moment whether the accuracy will be better or worse than G2.

**Table C.6.** Comparison of CBS-QB3 calculated frequencies to experiment for A-X electronic transitions of peroxy radicals

Molecule	A-X (CBS-QB3) (cm <sup>-1</sup> )	A-X, Experiment (cm <sup>-1</sup> )
HO <sub>2</sub>	7042	7029 <sup>54, 55</sup>
CH <sub>3</sub> OO•	7411	7382 <sup>44</sup>
HOCH <sub>2</sub> OO•	7479	7391

W1U calculations make use of a B3LYP geometry and use CCSD(T) calculations to obtain complete basis set corrections. I've already written a calculator in Excel for W1U calculations, and I can reproduce the W1U energies for H<sub>2</sub> and OH. The W1U calculated A-X frequency for HMP is within 60 cm<sup>-1</sup> of the experimental value (7443 cm<sup>-1</sup> calculated, 7391 cm<sup>-1</sup> experimental). More expensive (and more accurate) methods are available (W2, W3, W4); however, these are likely out of range of our computational resources without access to a supercomputer.

It should be noted that the 32-bit version of Gaussian cannot perform a W1 calculation on HO<sub>2</sub> (or anything larger), due to the CCSD and CCSD(T) calculations exceeding the 16 GB scratch space limit for 32-bit programs. There are no problems running the W1 calculations on the 64-bit version of Gaussian in Linux. Furthermore, other 64-bit programs are also capable of these calculations (CFour, Molpro, Q-Chem, etc.). Significant amounts of memory are required for these calculations: the W1 calculation on HMP exceeded the 10 GB of RAM that I initially had allocated to Gaussian.

## **7) Generating Potential Energy Surfaces**

It is generally useful to determine the potential energy surface (PES) of a molecule as a function of molecular coordinates (bond distances, bond angles, dihedral angles). These potential energy functions can be used to assess energy barriers to molecular motion or reaction, coupling of vibrational and torsional normal modes due to intramolecular interactions such as hydrogen bonding, and explicit calculation of wavefunctions and quantum energy levels. As has been shown repeatedly in this thesis (HOONO, HMP, 2-HIPP), normal mode coupling causes additional complexity in the IR spectra, and must be explicitly modeled in order to correctly simulate the spectra.

Two types of potential energy scans can be requested in Gaussian: a rigid scan in which all other molecular coordinates remain fixed, or a relaxed scan in which all other molecular coordinates are optimized at each step. Rigid scans are useful in the adiabatic approximations: fast vibrational modes can be completely separated from slow modes. This is true when separating OH stretch motions from torsional motions in many

molecules, including HOONO and HMP. Relaxed scans are useful when an adiabatic approximation cannot be made. This is true when scanning over dihedral angles in a molecule: the torsional normal modes associated with these angles are typically of low frequency, and many other low frequency modes are generally present.

Scans are typically performed across internal coordinates rather than a Cartesian coordinate; therefore, it is easiest to request the potential energy scan directly from the Z-matrix input. The following example requests a relaxed potential energy scan across the two torsional angles (HOCO, OOCO) on the A state of the 2-HIPP radical, with the essential parts of requesting the scan highlighted.

```
%chk=C:\G09W\MKS\2-HIPP PES\2-HIPP A B3LYP PES.chk
#p Opt=Z-matrix B3LYP/6-31+g(d,p) Guess=(Alter,Always) NoSymm
```

Title Card Required

0 2

C							
C	1	B1					
H	2	B2	1	A1			
H	2	B3	1	A2	3	D1	0
H	2	B4	1	A3	4	D2	0
C	1	B5	2	A4	5	D3	0
H	6	B6	1	A5	2	D4	0
H	6	B7	1	A6	2	D5	0
H	6	B8	1	A7	2	D6	0
O	1	B9	2	A8	6	D7	0
H	10	B10	1	A9	2	D8	0
O	1	B11	10	A10	11	HOCO	0
O	12	B12	1	A11	10	OOCO	0

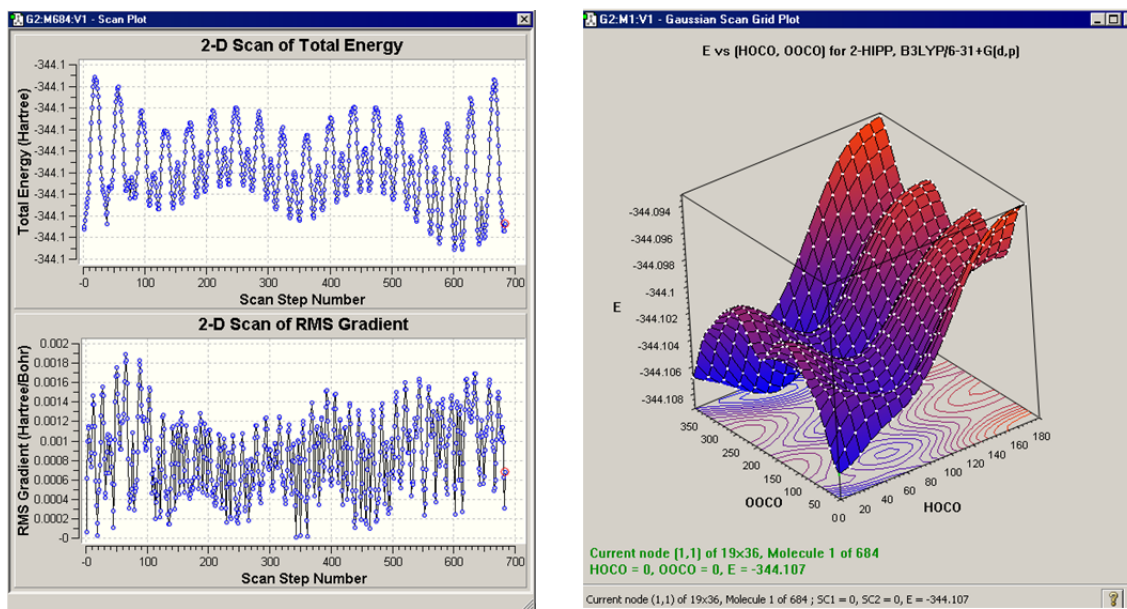
```
B1=1.52722762
B2=1.0933087
B3=1.09422741
B4=1.09247629
B5=1.51904907
B6=1.09171903
B7=1.09207247
B8=1.09289496
B9=1.39714561
B10=0.96792656
B11=1.48479112
B12=1.37990918
A1=109.09594428
A2=111.00707754
A3=110.52283361
A4=114.39312339
A5=110.61869101
A6=109.68521782
A7=108.76323525
A8=112.59779458
A9=109.77029369
A10=109.73656718
A11=112.28122574
D1=119.77962987
D2=120.04129575
D3=-60.2624729
D4=55.87981057
D5=176.84253762
D6=-64.27682433
D7=-123.2116855
D8=-120.0
HOCO=0.0 S 18 10.0
OOCO=0.0 S 35 10.0
```

24 25

There are four essential features to this input file. First, the keyword `Opt=Z-matrix` must be entered in the route line. This ensures that all optimization proceeds using Z-matrix coordinates. If only `Opt` is entered, the scan will fail. Second, the command `NoSymm` must be entered in the route line. If the scan breaks point group symmetry and `NoSymm` has not been requested, the scan will fail and Gaussian will exit with an error message. Third, all of the coordinates within the Z-matrix have been entered as variables (R1, A1, D1, etc.). The variables of interest have been specially labeled (HOCO and OOCO for the dihedral angles). Although this is not strictly necessary, it is good practice to highlight which variables are being scanned. Fourth, the entries for the variables being scanned over are not a single number; rather, they specify the initial parameter, number of steps, and step size. For example, the line `HOCO=0.0 S 18 10.0` requests that the variable HOCO start at a value 0.0, and then be scanned (S) with 18 steps of size 10.0 (final value of 180.0).

Gaussian will run all of the geometries consecutively and print the energies at the end of the file. It is more useful to compile all of the energies into one text file for further use in Excel (for data manipulation) and SigmaPlot (for surface plotting). GaussView can compile all of the energies, although versions 3 and 5 do this differently. Version 3 compiles the energies in the same order in which Gaussian ran them, while version 5 reorders them in ascending order by coordinate. Additionally, GaussView 5 will display a 3-dimensional surface for multidimensional scans. Figure C.2 shows the graphical output of GaussView 3.09 and GaussView 5.09 for scans of the X state of 2-HIPP.





**Figure C.2.** Visualization of energies generated from a 2-D potential energy scan of 2-HIPP in GaussView 3.09 (left) and GaussView 5.09 (right). GaussView 3.09 simply displays the energies in the order in which they were calculated, while GaussView 5.09 generates a contour plot.

The 2-dimensional potential energy surfaces presented in this thesis were generated in SigmaPlot. SigmaPlot requires a periodic arrangement of data. In other words, to generate a plot across 2 dihedral angles of  $360^\circ$  apiece, the input data must be arranged in the form  $(-180^\circ, -180^\circ)$ ,  $(-180^\circ, -170^\circ)$ , ...,  $(-180^\circ, 180^\circ)$ ,  $(-170^\circ, -180^\circ)$ ,  $(-170^\circ, -170^\circ)$ , etc. For many scans, only half of these points are explicitly calculated (the other half are equal in energy by symmetry). Before inputting energies into SigmaPlot, the user must generate all of the necessary energies in Excel by exploiting symmetry. Afterwards, the energies should be sorted into a periodic form, typically achieved by sorting one variable followed by a second variable. Finally, the sorted values can be copied into SigmaPlot to generate a contour plot similar to the ones presented in Parts 2 and 3 of this thesis.

## 8) A Caution on Using Equation of Motion (EOM) Methods

Note that a full discussion of Equation of Motion (EOM) methods is not included here because Gaussian 03 does not contain these methods. Gaussian 09 as well as many other programs (such as CFour and Q-Chem) do support EOM methods. These methods may prove useful for future calculations; however, future students are advised to use caution with these methods. Terry Miller's group found that EOM-IP overestimated the A-X transition frequency for alkyl peroxies by  $\sim 1000 \text{ cm}^{-1}$ .<sup>44</sup> Even if these values are scaled to experimental results on HO<sub>2</sub> or CH<sub>3</sub>OO•, the transition frequencies do not follow the experimental trends any better than the previously described methods. The Miller group attributes the poor agreement to EOM methods not properly accounting for electron correlation.

## Acknowledgements

We thank J. Sigrid Barklund and Leah G. Dodson for suggestions on how to improve the readability and utility of this appendix.