

Computational Chemistry Lab

Addis Ababa University
School of Graduate Studies
Department of Chemistry

For M.Sc program in Physical Chemistry

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What is Computational Chemistry?

- is the application of computer based models to the simulation of chemical processes and the computation of chemical properties.

- **Computational chemistry is a valuable tool for experimental chemists to bypass tedious, time consuming, costly and some times dangerous experiments.**

- too unstable molecules to be studied experimentally

- Properties which are not experimentally observable

Computational Chemistry

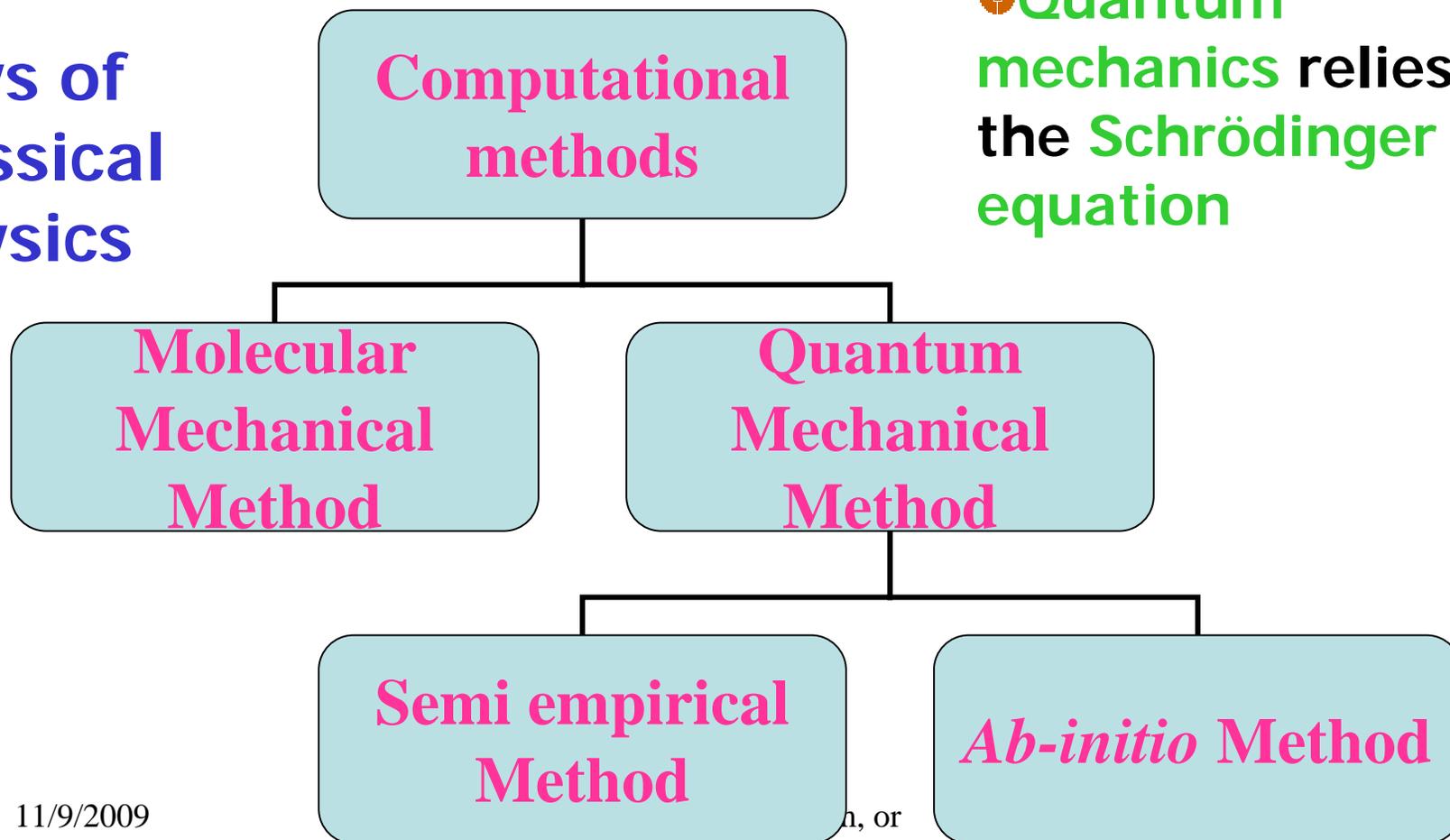
The field of Chemistry that focuses on

☞ **Theoretical Aspects** and

☞ **Computer program**

laws of
classical
physics

● **Quantum
mechanics** relies on
the **Schrödinger
equation**



Gaussian and Gaussview

Gaussian (www.gaussian.com):

- **computational chemistry software package**
- performs molecular mechanics, *ab initio*, density functional theory, and semi-empirical molecular orbital calculations
- calculates a wide range of properties
- performs geometry optimizations and frequency calculations

Gaussview (www.gaussian.com):

- **graphical user interface for Gaussian**
- can build molecules, set-up input files, submit Gaussian calculations, and visualize results

Gaussian Input File

the Gaussian input file has the following form (http://www.gaussian.com/g_ur/m_input.htm):

1. Link 0 Commands: -set up memory limits, etc. Line starts with %. Optional.
2. Route Section: -specifies the details of the calculation
 - can be multiple lines with max. 80 characters
 - each line in Route Section must start with #
3. Blank Line: -tells program Route Section is done
4. Title
5. Blank Line: -tells program Title is done
6. Charge and Multiplicity
7. Molecular Geometry: -provide the atomic coordinates
 - Cartesian or Z-matrix format
8. Blank Line: -tells program the input file is done

Gaussian Input File

example input for water

```
%chk=h2o_scan.chk  
%mem=6MW  
%nproc=1  
# hf/3-21g opt
```

} link 0 commands
← route line

Title

```
0 1  
O 0.0 0.0 0.0  
H 1.0 0.0 0.0  
H 0.0 1.0 0.0
```

← charge and multiplicity
} geometry in cartesian coordinates

Output

- gaussian output files will usually end with .log or .out
- contains a lot of information → contents depend on type of calculation
- units are usually Hartree for energy and Angstrom for distance (but not always)

1 Hartree = 627.51 kcal/mol

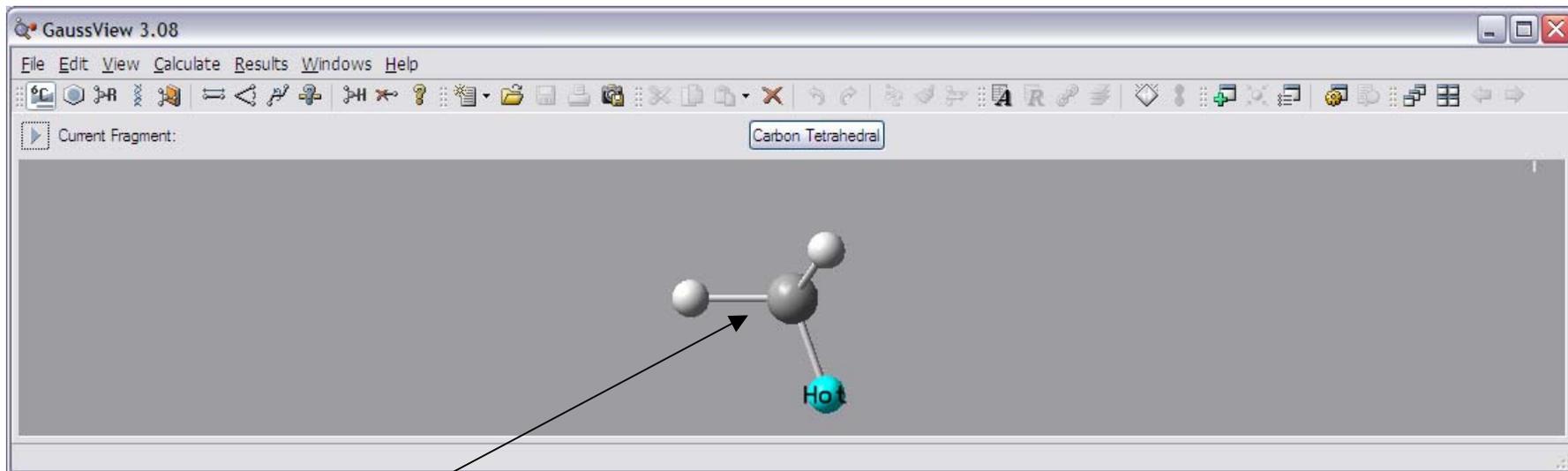
1 Angstrom = 1.0×10^{-10} m

Things to look for in the output:

- molecular structure → look for a line saying “Input orientation:”
- molecular energy → look for a line saying “SCF Done:”
- convergence in optimization → look for a line saying “Maximum Force”
- summary of a rigid scan → look for a line saying “Summary of the potential surface scan”
- summary of a relaxed scan → look for a line saying “Summary of Optimized Potential Surface Scan”
- frequency information → look for a line saying “Harmonic frequencies”

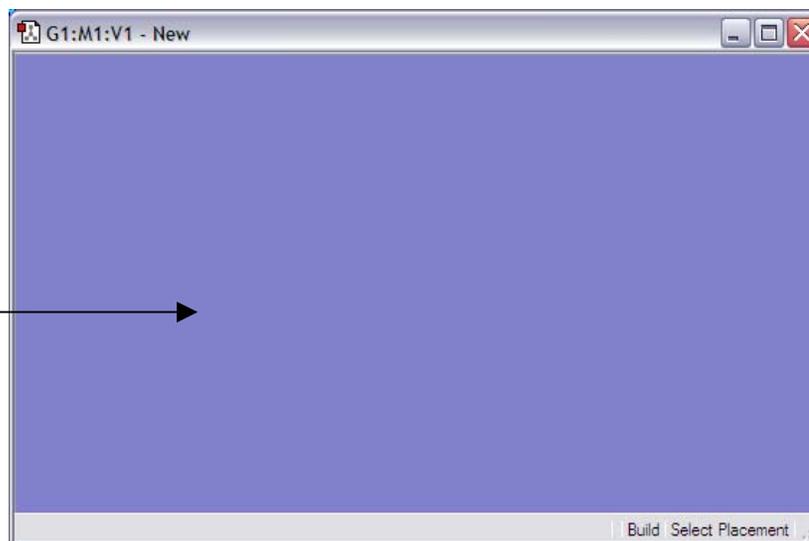
Gaussview

- graphical user interface to Gaussian
- builds molecules
- sets up input files
- submits calculations
- visualizes output



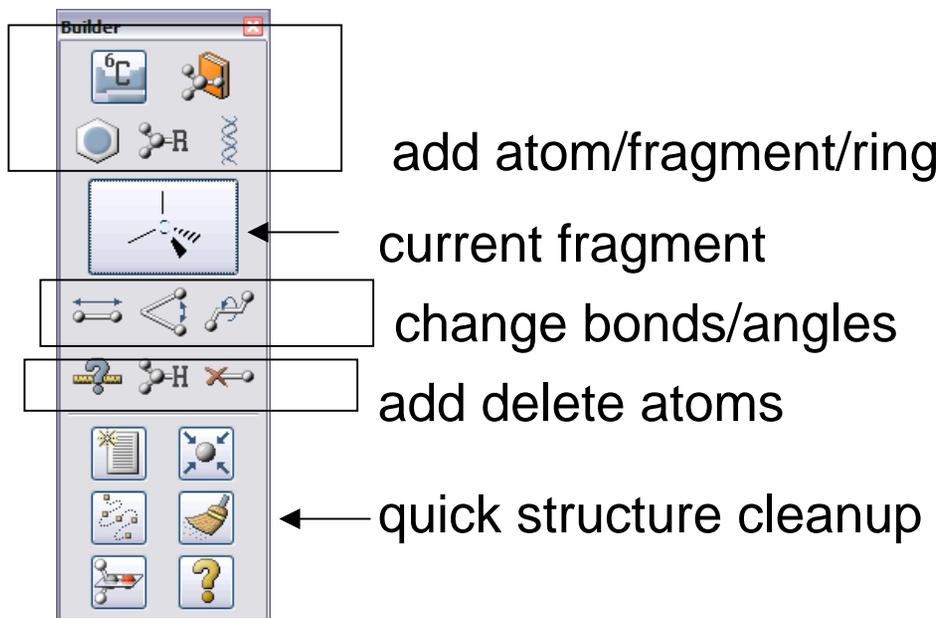
current fragment

structure window

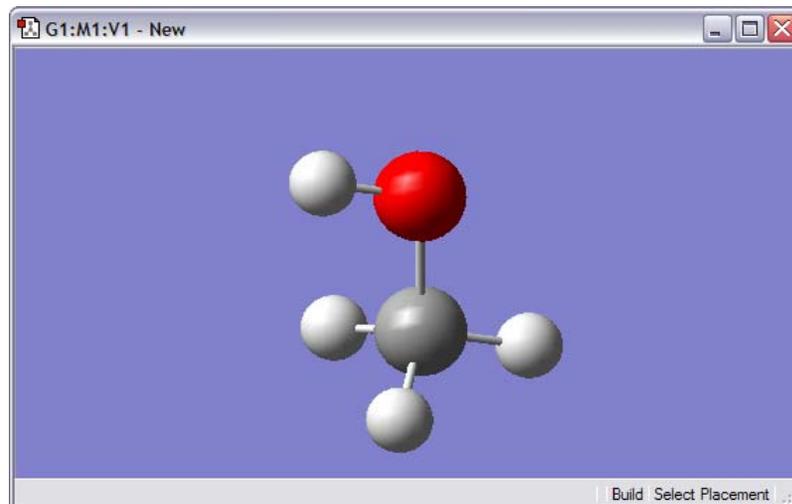


- shows molecule for current calculation
- © 2009 Gaussian, Inc. or
sene3095@yahoo.com

Open the builder menu by selecting: View → Builder



structure window



- use builder toolbar to select atoms/fragments to add to molecule
- add fragments by clicking in structure window
- run a quick structure cleanup to get a structure with reasonable bond lengths/angles
- can modify structure by selecting appropriate tool in builder toolbar and applying tool in structure window

Gaussview – Calculation Setup

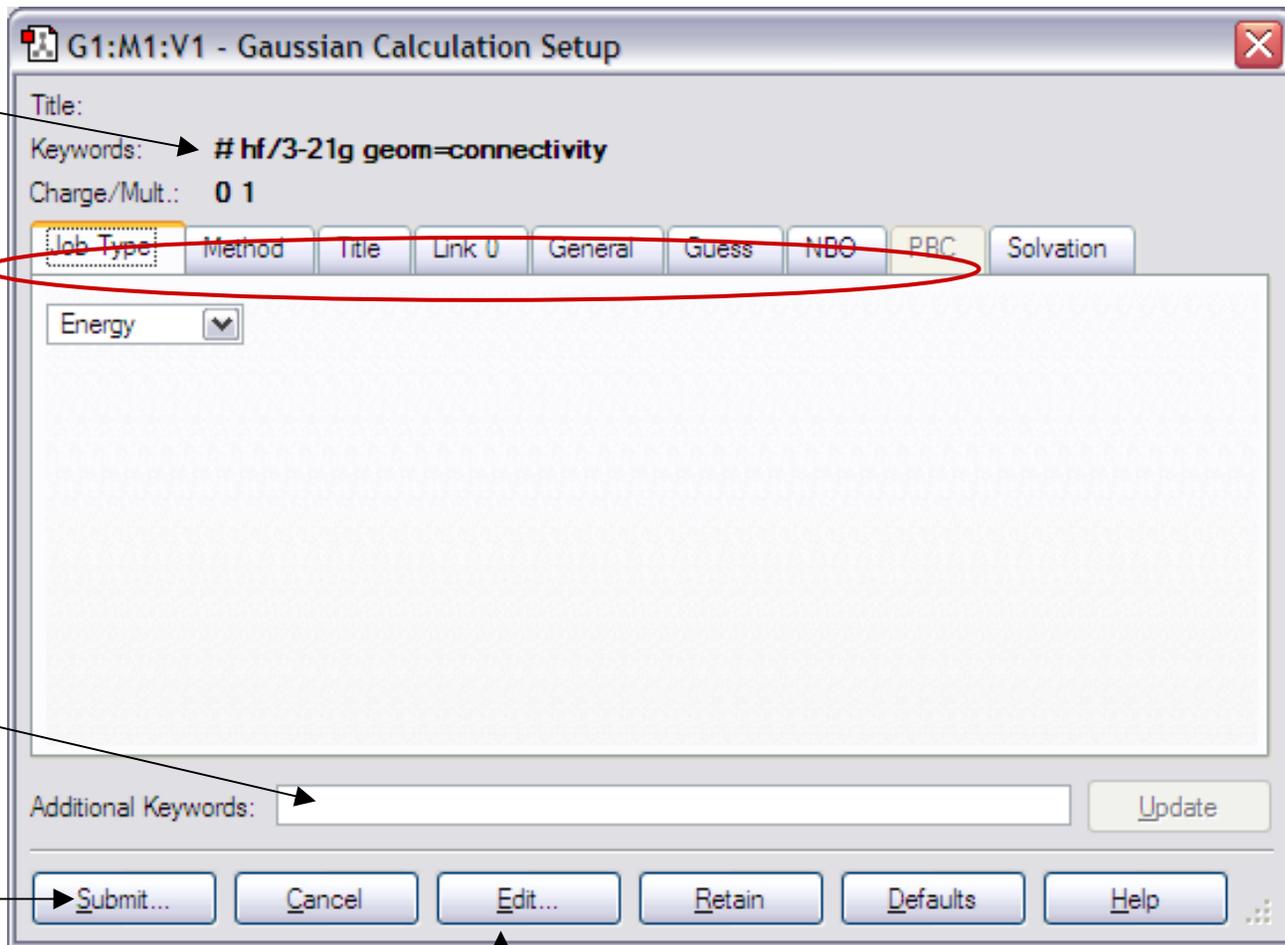
Set up a Gaussian input file by: Calculate → Gaussian...

current route line for calculation

menus to specify various job options

keywords not accessible with gaussview menus

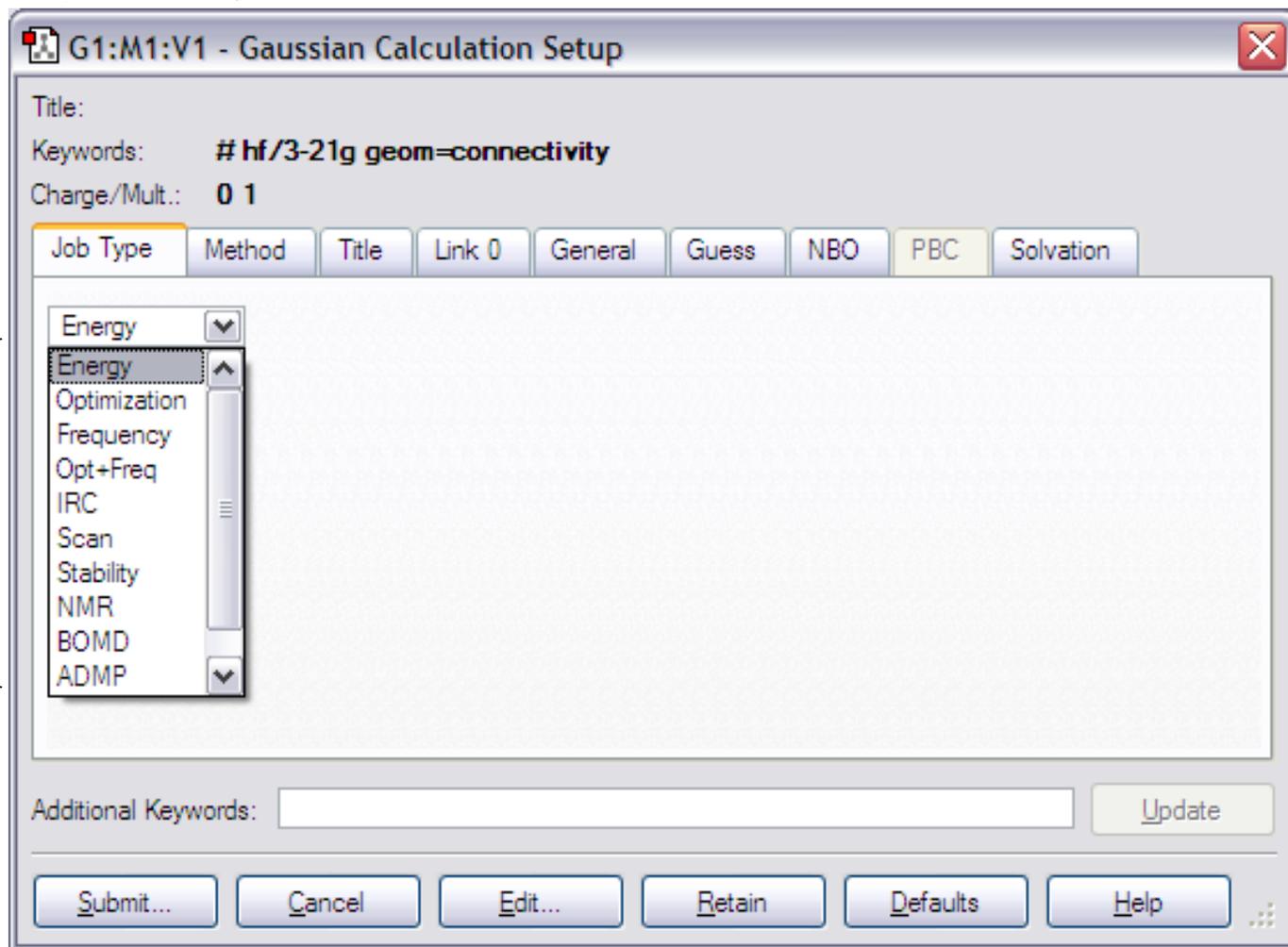
submit a Gaussian calculation



view and edit input file
in wordpad

Set up a Gaussian input file by: Calculate → Gaussian...

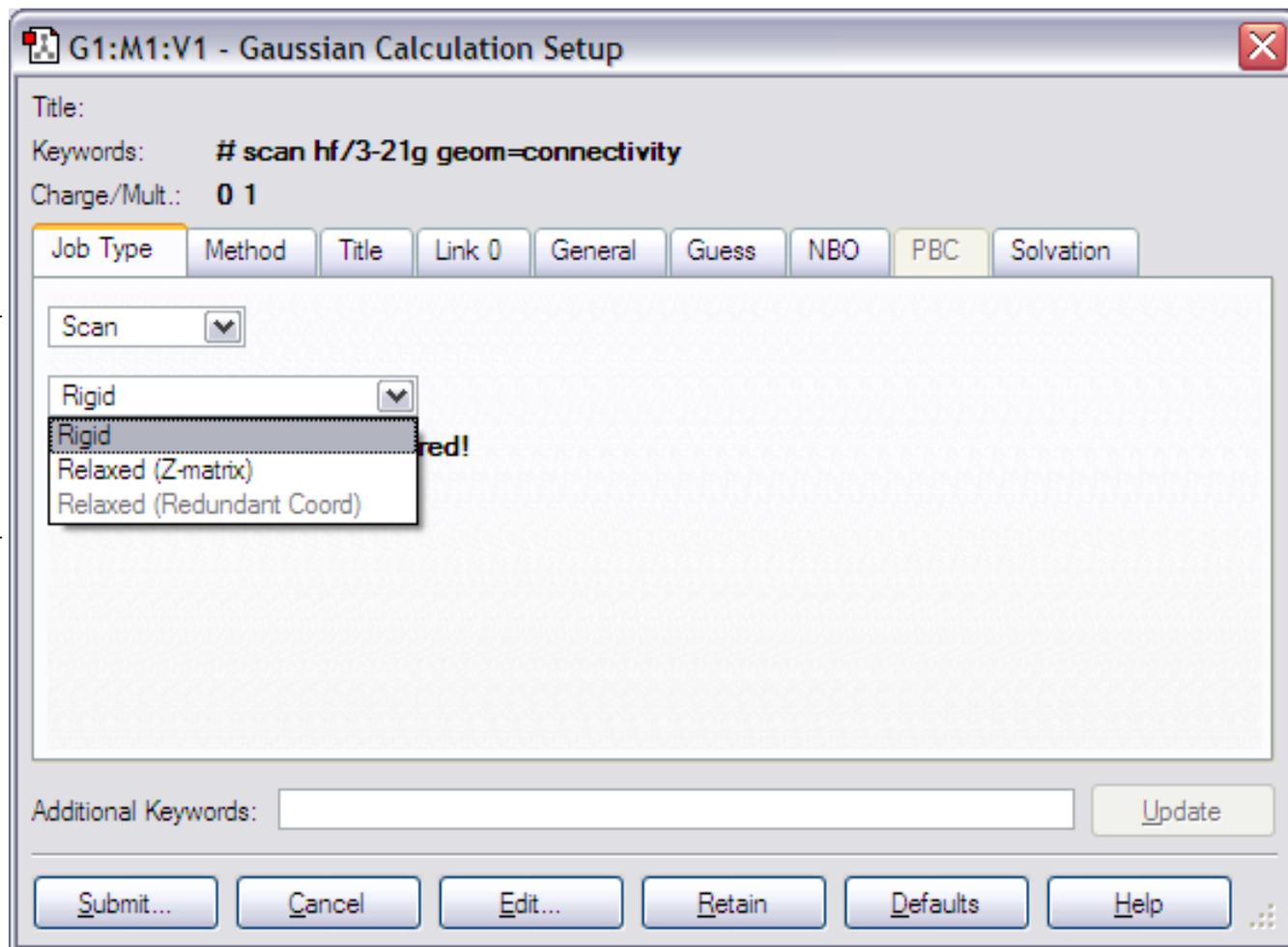
Job Type
click on job type
in drop-down list



Set up a Gaussian input file by: Calculate → Gaussian...

Job Type

some keywords
require you specify
additional options



Set up a Gaussian input file by: Calculate → Gaussian...

Method

specify the method used to calculate the energy

specify the basis set

set the charge and multiplicity

G1:M1:V1 - Gaussian Calculation Setup

Title:

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

Charge/Mult.: **0 1**

Job Type Method Title Link 0 General Guess NBO PBC Solvation

Multilayer ONIOM Model

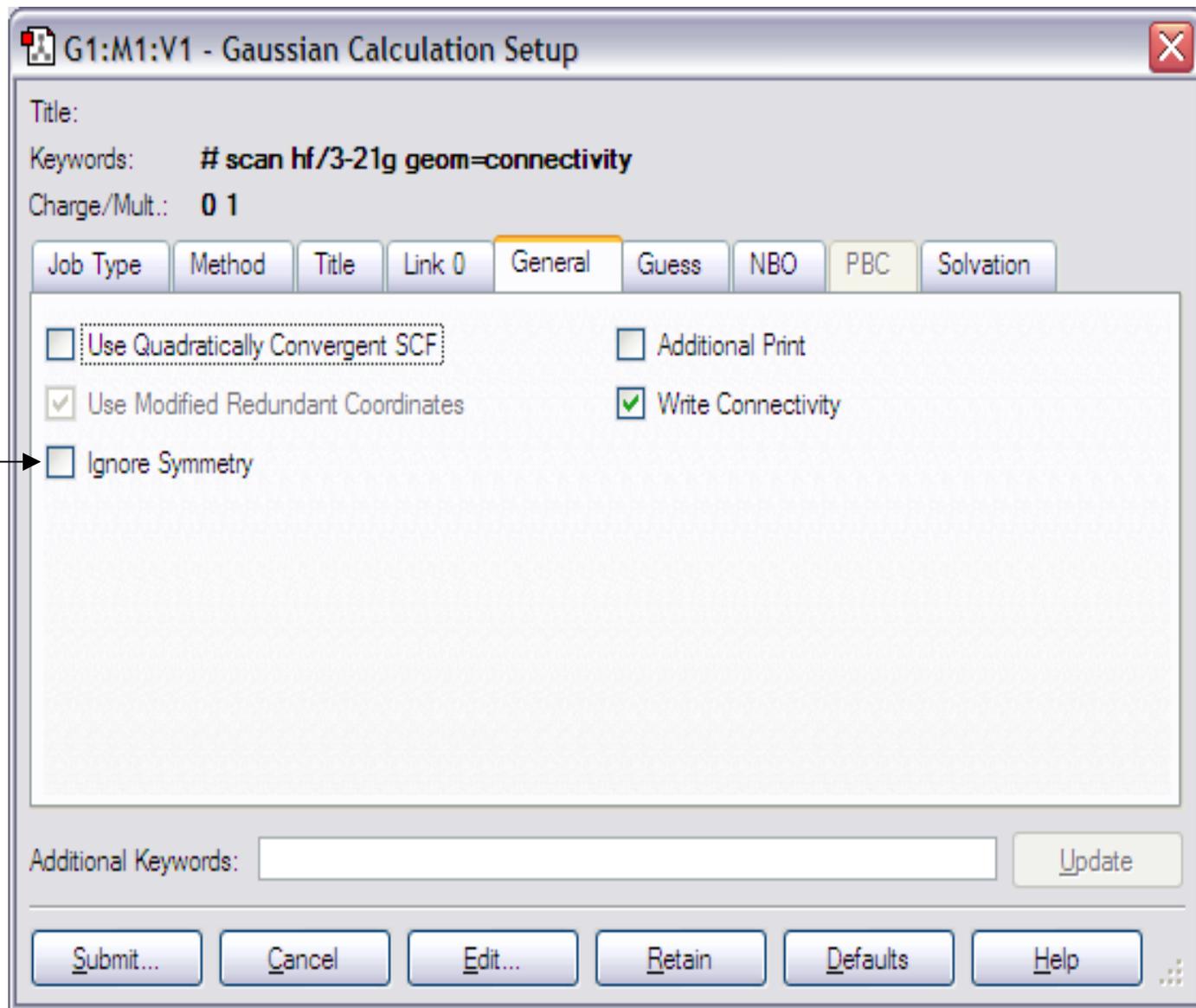
Method: Ground State Hartree-Fock Default Spin

Basis Set: 3-21G

Charge: 0 Spin: Singlet

Additional Keywords: Update

Submit... Cancel Edit... Retain Defaults Help



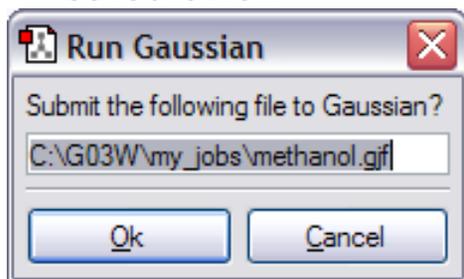
General

click here to set the symmetry to C1

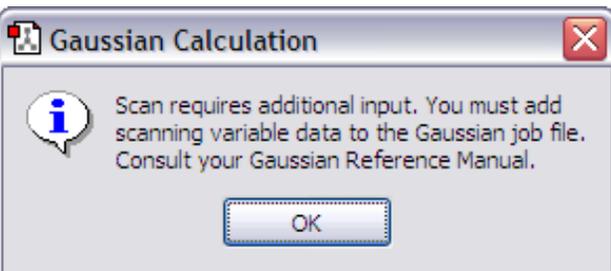
Set up a Gaussian input file by: Calculate → Gaussian...

Submit

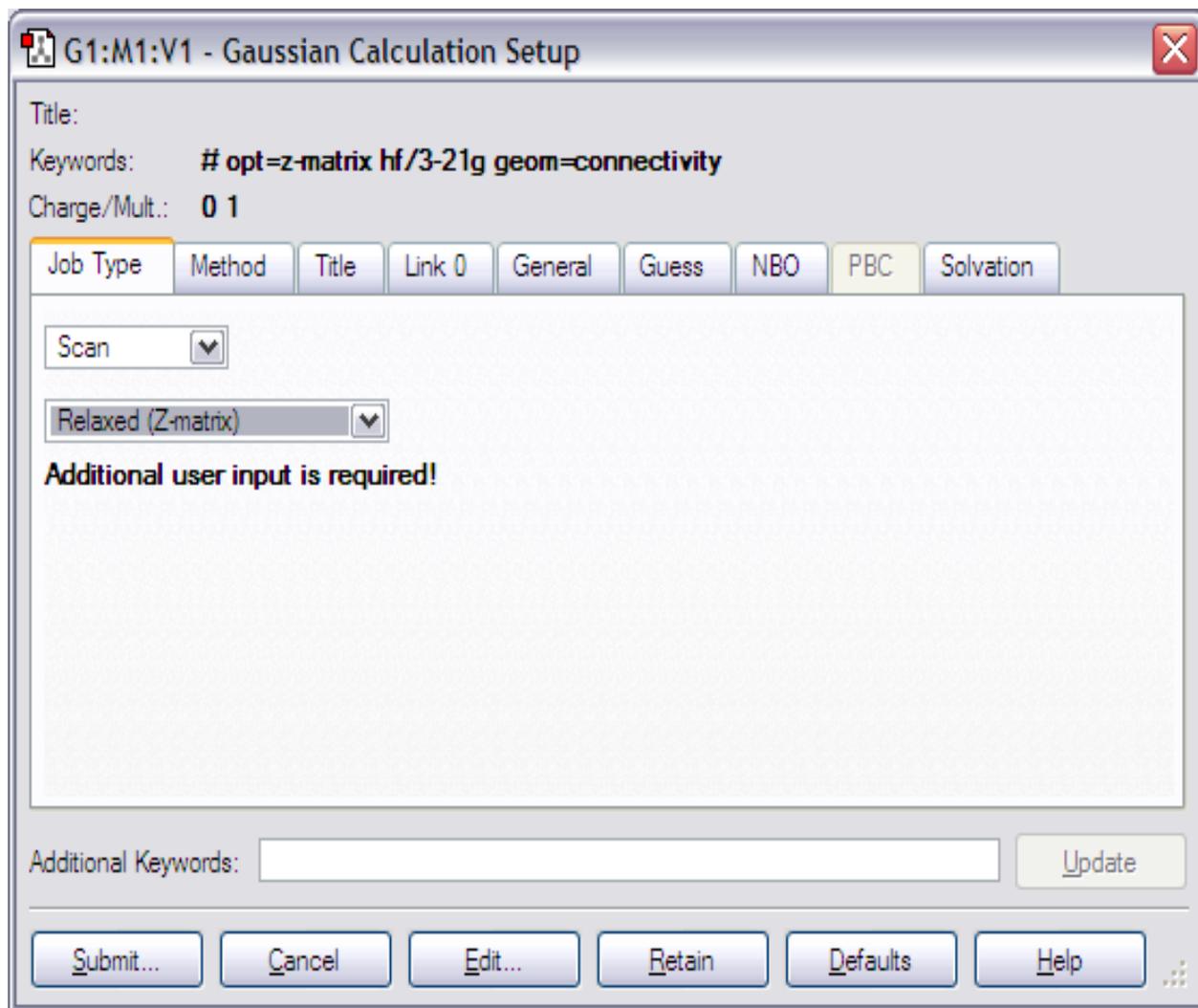
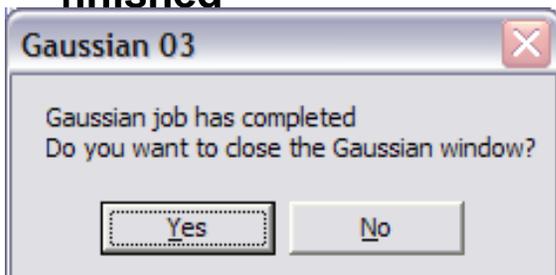
- click submit to run the calculation



- sometimes additional input is required



- notification when finished



Gaussview – Results

You can analyze the results with: Results → Option (depends on type of job)

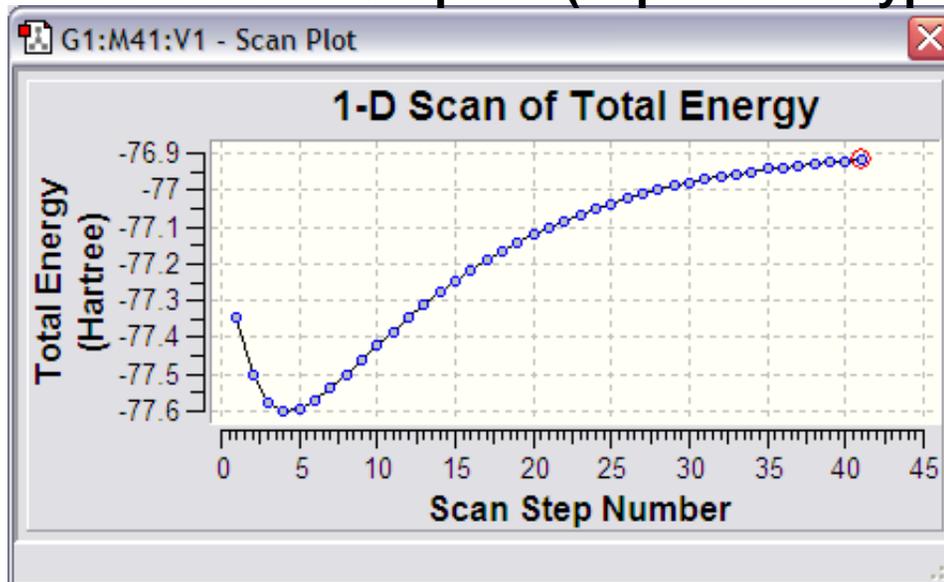
G1:M1:V1 - Calculation Summary

Title Card Required

File Type	.log	
Calculation Type	FREQ	
Calculation Method	RHF	
Basis Set	3-21G	
E(RHF)	-114.39801919	a.u.
RMS Gradient Norm	0.00007469	a.u.
Imaginary Freq	0	
Dipole Moment	2.1227	Debye
Point Group	C1	

Job cpu time: 0 days 0 hours 0 minutes 11.0 seconds.

Ok



G1:M1:V1 - Display Vibrations

# /	Freq	Infrared	Raman	Depolar-P	Depolar-U
1	360.694	172.728	6.0799	0.75	0.8571
2	1090.36	99.0305	7.4934	0.2913	0.4512
3	1152.73	19.0775	7.0726	0.5664	0.7232
4	1253.78	0.924	9.2184	0.75	0.8571
5	1480.79	30.4862	6.3543	0.7291	0.8434
6	1637.29	4.9074	6.5274	0.7111	0.8311
7	1685.37	3.1547	26.2697	0.75	0.8571
8	1697.91	3.3291	24.2007	0.7494	0.8568
9	3179.44	40.8931	111.586	0.0799	0.1479
10	3218.86	85.0498	62.2213	0.75	0.8571
11	3295.12	24.0426	73.9626	0.5224	0.6872

Frames / Cycle:

Displacement:

Show Displacement Vectors

Show Dipole Derivative Unit Vector

Close Cancel Start Spectrum Help

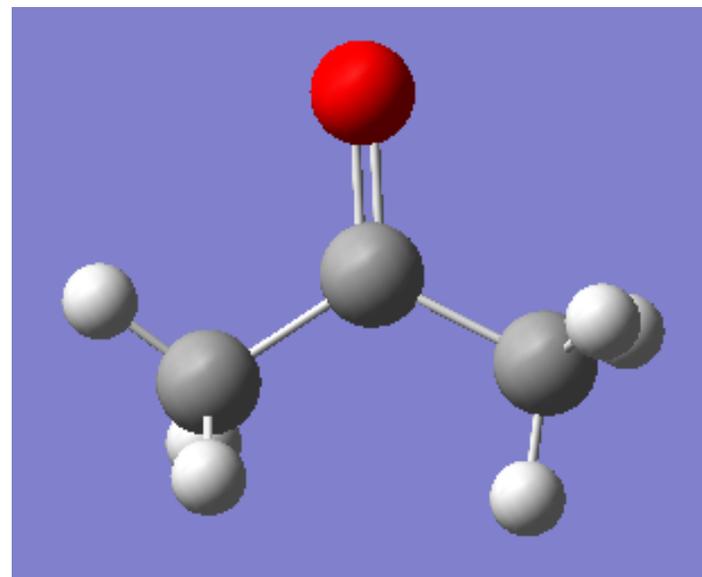
1. Geometry Optimization

Geometry Optimization:

- minimize the energy of a molecule by iteratively modifying its structure
- provides the energetically-preferred structure of a molecule
- the located structure will correspond to the local minimum nearest on the potential energy surface to the input structure
- suitable for determining the structures and energies of reactants and products

This example:

- optimize the geometry of $(\text{CH}_3)_2\text{CO}$ starting from a structure built with gaussview using standard bond lengths and angles
- geometry provided in Z-matrix format
- calculation performed at hf/3-21G level of theory (more on this in future lectures)



Geometry Optimization – Input

opt hf/3-21g nosymm ←

- keyword 'opt' requests a geometry optimization to a minimum energy structure

Title Card Required

```
0 1
C
H 1 B1
H 1 B2 2 A1
H 1 B3 3 A2 2 D1
C 1 B4 4 A3 3 D2
O 5 B5 1 A4 4 D3
C 5 B6 1 A5 6 D4
H 7 B7 5 A6 1 D5
H 7 B8 5 A7 1 D6
H 7 B9 5 A8 1 D7
```

- 'hf/3-21G' specifies level of theory for the calculation
- 'nosymm' tells the program to set the initial symmetry to C1
 - geometry optimizations sometimes change the symmetry of the system, causing the calculation to fail
 - the minimum energy structure may not have the same symmetry as the initial structure

```
B1 1.07000000
B2 1.07000000
B3 1.07000000
B4 1.54000000
B5 1.43000000
B6 1.54000000
B7 1.07000000
B8 1.07000000
B9 1.07000000
A1 109.47120255
A2 109.47121829
A3 109.47121829
A4 120.00000000
A5 120.00000000
A6 109.47122063
A7 109.47122063
A8 109.47122063
D1 120.00000060
D2 -120.00003407
D3 180.00000000
D4 -180.00000000
D5 166.53624326
D6 46.53624326
D7 -73.46375674
```

Geometry Optimization – Output

in a geometry optimization we may want to determine:

- a stationary point corresponding to a minimum energy structure
→ need to monitor whether the convergence criteria are met

first step:

Item	Value	Threshold	Converged?
Maximum Force	0.196220	0.000450	NO
RMS Force	0.033395	0.000300	NO
Maximum Displacement	0.253014	0.001800	NO
RMS Displacement	0.052569	0.001200	NO

intermediate step:

Item	Value	Threshold	Converged?
Maximum Force	0.001162	0.000450	NO
RMS Force	0.000252	0.000300	YES
Maximum Displacement	0.260013	0.001800	NO
RMS Displacement	0.096764	0.001200	NO

final step:

Item	Value	Threshold	Converged?
Maximum Force	0.000058	0.000450	YES
RMS Force	0.000018	0.000300	YES
Maximum Displacement	0.001554	0.001800	YES
RMS Displacement	0.000615	0.001200	YES

- a stationary point corresponding to a minimum energy structure
→ need to monitor whether the convergence criteria are met
- energy of the optimized structure
→ energy statement in step where convergence criteria are met
→ last energy statement in the output file

```
SCF Done: E(RHF) = -190.887221224 A.U. after 9 cycles  
          Conv = 0.57300-08 -V/T = 2.0019  
          S**2 = 0.0000
```

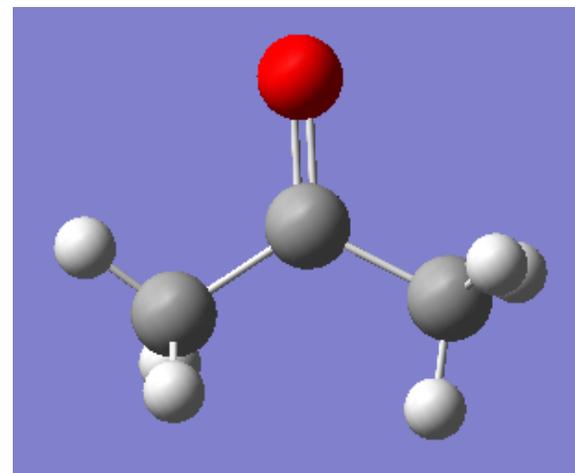
2. Frequency Calculation

Frequency Calculation:

- calculate the normal modes and associated vibrational frequencies for the input structure
- used to characterize stationary points as minima or transition states
- used to calculate zero-point vibrational energies
- used to calculate thermal corrections to the potential energy
- used to simulate IR/Raman spectra

This example:

- perform a frequency calculation of $(\text{CH}_3)_2\text{CO}$
- geometry provided in Z-matrix format
→ geometry obtained through a previous optimization
- calculation performed at hf/3-21G level of theory



Frequency Calculation - Input

```
# freq hf/3-21g
```

```
Title
```

```
0 1
```

```
C
```

```
H 1 B1
H 1 B2 2 A1
H 1 B3 3 A2 2 D1
C 1 B4 4 A3 3 D2
O 5 B5 1 A4 4 D3
C 5 B6 1 A5 6 D4
H 7 B7 5 A6 1 D5
H 7 B8 5 A7 1 D6
H 7 B9 5 A8 1 D7
```

```
B1 1.07000000
B2 1.07000000
B3 1.07000000
B4 1.54000000
B5 1.43000000
B6 1.54000000
B7 1.07000000
B8 1.07000000
B9 1.07000000
A1 109.47120255
A2 109.47121829
A3 109.47121829
A4 120.00000000
A5 120.00000000
A6 109.47122063
A7 109.47122063
A8 109.47122063
D1 120.00000060
D2 -120.00003407
D3 180.00000000
D4 -180.00000000
D5 166.53624326
D6 46.53624326
D7 -73.46375674
```

- keyword 'freq' requests a frequency calculation
- 'hf/3-21G' specifies level of theory for the calculation
- coordinates in Z-matrix format, but frequency calculations can also be performed with cartesian coordinates
- structure must correspond to a stationary point
- recall, frequency calculations in harmonic approximation are only valid at stationary points

Frequency Calculation - Output

in a frequency calculation we may want to determine:

- normal modes and vibrational frequencies

Harmonic frequencies (cm⁻¹), IR intensities (KM/Mole), Raman scattering activities (Å⁴/AMU), depolarization ratios for plane and unpolarized incident light, reduced masses (AMU), force constants (mDyne/Å), and normal coordinates:

	1	2	3	
	Å	Å	Å	
Frequencies --	85.8357	160.7480	405.9040	← mode
Red. masses --	1.0197	1.1162	2.2117	← frequencies in cm ⁻¹
Frc consts --	0.0044	0.0170	0.2147	
IR Inten --	0.0000	0.0462	1.1897	
Raman Activ --	0.0519	0.0007	0.2617	
Depolar (P) --	0.7500	0.7493	0.2558	
Depolar (U) --	0.8571	0.8567	0.4074	

Atom	AN	X	Y	Z	X	Y	Z	X	Y	Z
1	6	0.00	0.00	0.02	0.00	0.00	0.04	0.16	0.10	0.00
2	1	0.00	0.00	-0.35	0.00	0.00	0.41	-0.06	0.39	0.00
3	1	0.16	0.32	0.25	-0.17	-0.31	-0.19	0.36	0.12	0.01
4	1	-0.16	-0.32	0.25	0.17	0.31	-0.19	0.36	0.12	-0.01
5	6	0.00	0.00	0.00	0.00	0.00	0.02	0.00	-0.13	0.00
6	8	0.00	0.00	0.00	0.00	0.00	-0.07	0.00	-0.13	0.00
7	6	0.00	0.00	-0.02	0.00	0.00	0.04	-0.16	0.10	0.00
8	1	0.00	0.00	0.35	0.00	0.00	0.41	0.06	0.39	0.00
9	1	0.16	-0.32	-0.25	0.17	-0.31	-0.19	-0.36	0.12	0.01
10	1	-0.16	0.32	-0.25	-0.17	0.31	-0.19	-0.36	0.12	-0.01

← normal mode displacement s

Frequency Calculation - Output

in a frequency calculation we may want to determine:

- normal modes and vibrational frequencies
- zero-point vibrational energies

```
Zero-point vibrational energy      236075.8 (Joules/Mol)
                                   56.42347 (Kcal/Mol)
```

- thermal corrections to the potential energy

```
Zero-point correction=             0.089917 (Hartree/Particle)
Thermal correction to Energy=      0.095029
Thermal correction to Enthalpy=    0.095973
Thermal correction to Gibbs Free Energy= 0.062198
Sum of electronic and zero-point Energies= -190.797305
Sum of electronic and thermal Energies= -190.792192
Sum of electronic and thermal Enthalpies= -190.791248
Sum of electronic and thermal Free Energies= -190.825023
```

Lab activities

Optimize the following g molecules and report the properties according to the chart given below;

	Angle-VSEPR predicted (i.e. 109.5° , $<109.5^\circ$)	Angle after optimization	Angle-experimental	Bond length 'cleanup' optimization (A)	Bond length after optimization (A)	Change in Gibbs free energy (ΔG)
H ₂ O			104.5°			
NH ₃			107.3°			
CH ₄			109.5°			

The End