Computational Materials Science

Department of Applied Chemistry & Department of Bionano Technology, Hanyang University

Sang Uck Lee
Computational Materials Science
Computational Materials Science

• Overall Goal: Use mathematical and computer models to understand and predict chemical structure, properties, and reactivity

• Methods:
  – Gaussian09: Most popular research-level computer program for computing electronic structure and properties of molecules
  – WebMO: Web-based interface for preparing, submitting, and visualizing computational chemistry jobs
Computational Chemistry

- Computer-based calculation of chemical structure, properties, and reactivity

- Usefulness
  - Complements and explains experimental results
  - Makes predictions and can guide experiments
Computational Chemistry Approaches

• Molecular Mechanics (Force-field based simulation)
  – Classical mechanics
  
  \[ E = \sum_{\text{bonds}} \frac{1}{2} k_r (r - r_0)^2 + \sum_{\text{angles}} \frac{1}{2} k_\theta (\theta - \theta_0)^2 + \ldots \]
  
  – Parameters \( k_r, r_0, k_\theta, \theta_0, \ldots \) chosen to fit observed data
  – No explicit treatment of electrons
  – Very fast

\[ -\frac{dV}{dr} = m \frac{d^2r}{dt^2} \]
Computational Chemistry Approaches (con’t)

- Electronic Structure Methods
  - Quantum Mechanics
  - $\hat{H}\Psi = E\Psi$
  - Electrons (molecular orbitals) explicitly calculated
  - Much slower, but more general
Electronic Structure Methods

• Semi-empirical (MOPAC, AMPAC, HyperChem)
  – use parameters to evaluate integrals
  – relatively fast

• \textit{ab initio} (Gaussian, Spartan, GAMESS)
  – evaluate integrals from first principles
  – slow
  – scales poorly with size
Electronic Structure Methods (con’t)

• Density Functional Theory (Gaussian, GAMESS)
  – similar to \textit{ab initio}
  – includes electron correlation
  – electron density calculated, not orbitals
  – not as slow
Modeling & Simulation

- **Modeling & Simulation**
  - Should be unbiased, well-defined, uniformly applicable
  - Modeling: Generate coordinate of molecules
  - Simulation: Calculate properties
- **Methods**
  - Hartree-Fock (HF), Möller-Plesset (MP2), B3LYP
- **Basis Set**
  - Functions that approximate atomic orbitals
  - STO-3G, 3-21G, 6-31G(d), ...
- **Open vs. Closed Shell**
  - unrestricted (U) if unpaired electrons exist
  - restricted (default) when all electrons are paired
- **Compound Methods**
  - geometry at lower theory; energy at higher theory
  - Ex: MP4/6-311+G(2d,p)//HF/6-31G(d)
<table>
<thead>
<tr>
<th>Method/Basis Set</th>
<th>HF Limit</th>
<th>MP2</th>
<th>MP3</th>
<th>MP4</th>
<th>QCISD(T)</th>
<th>Full CI</th>
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<tr>
<td>Type</td>
<td></td>
<td></td>
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</tr>
</tbody>
</table>
Energy Calculations
WebMO Quick Start

– Login: Username=guest#, Password = guest#

– Job Manager: Create New Job
– Build Molecule: Open Editor, Build Model, Close Editor
– Choose Engine: Gaussian09
– Job Options: Single Point, Hartree-Fock, Basic, Preview
– Input File
– Preview Gaussian Input File: Submit Job
– Job Manager: View
Running Calculations

• WebMO User Interface
  – Build molecule
  – Choose engine
  – Select job options
  – Submit job
  – Monitor progress
  – View results

• WebMO behind-the-scenes actions
  – Create input file
  – Queue and run job
  – Format output file
# Gaussian Input File

```
#N HF/3-21G SP

HFCO

0 1

C
O 1 1.50
F 1 1.49 2 120.0
H 1 1.09 2 120.0 3 180.0
```

Route (job options)
Title
Charge and Multiplicity(2S+1)
Geometry Specification
# Z-Matrix

<table>
<thead>
<tr>
<th>Atom</th>
<th>Index</th>
<th>Atom Distance</th>
<th>Bond Angle</th>
<th>Dihedral Angle</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>1</td>
<td>1.50</td>
<td></td>
<td></td>
</tr>
<tr>
<td>O</td>
<td>2</td>
<td>1.49</td>
<td>120.0</td>
<td></td>
</tr>
<tr>
<td>F</td>
<td>3</td>
<td>1.09</td>
<td>120.0</td>
<td>180.0</td>
</tr>
</tbody>
</table>

At:  
- Atom distance ($r$)  
- Bond angle ($\theta$)  
- Dihedral angle ($\phi$)
Z-Matrix (con’t)

- Z-Matrix is chemically intuitive (atom distance, bond angle, dihedral angle)
- Z-Matrix is efficient because it has only 3N-6 coordinates (vs. 3N for Cartesian coordinates)
- Many possible Z-matrices due to different ordering of atoms
- Near linear molecules have poorly defined dihedral angles
Gaussian Output File

• Geometry
  Standard orientation:

• Energy
  SCF Done:  \( E(\text{RHF}) = \)

• Molecular Orbitals and Energies
  Molecular Orbital Coefficients
  EIGENVALUES
Gaussian Output File (con’t)

• Atomic Charges
  Total atomic charges:

• Dipole Moment
  Dipole moment (Debye): Tot =

• NMR Shifts
  GIAO Magnetic shielding tensor (ppm): C Isotopic =
Modeling

WebMO

CORINA

Avogadro
Simulation

CMSLab @ Hanyang Univ.
Web based Quantum Mechanical Simulations
Version: 10.0.007p

WebMO Job Manager

Configure Gaussian Job Options

Build Molecule

Import Molecule

Job Name
Calculation
Theory
Basis Set
Charge
Multiplicity
Web based CMS

- Lecture Notes -
  1. Lecture Note / 2. Lecture Note & Practice
  3. Web based 2D/3D structure modeling
  4. Download "Avogadro Simulator"

Build Molecule

Status
- guest10
- Students
- 10:00
- unlimited
- 0 jobs

Progress
- Job manager
- Build molecule

Build a new molecule using the Avogadro builder, or import an existing molecule from a file. Additionally, you can export the molecule to a variety of file formats.

Choose engine
- Job options
- Submit job

Editor help

http://cmctschem.hanyang.ac.kr/cp-hm3/webmg/napm.cgi
http://cmctschem.hanyang.ac.kr/cp-hm3/webmg/napm.cgi

Total strain energy: 0.004 kcal/mol
Web based CMS

Lecture Notes
1. Lecture Note 2. Lecture Note & Practice
3. Web based 2D/3D structure modeling
3. Download "Avogadro Simulator"

Calculated Quantities

http://cmshome.hanyang.ac.kr/cp-bin/3/webmo/logincgi
http://cmshome.hanyang.ac.kr/cp-bin/3/webmo/login.cgi
이 개발물
## Atoms & Coordinates

C
C
C
C
C
C
H
H
H
H
H
H
H

### Z-matrix

<table>
<thead>
<tr>
<th>C</th>
<th>B1</th>
<th>A1</th>
<th>D1</th>
<th>0</th>
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<tbody>
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<td>B10</td>
<td>A10</td>
<td>D10</td>
<td>0</td>
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</table>

### Variables:

- B1: 1.38679
- B2: 1.38679
- B3: 1.38679
- B4: 1.38679
- B5: 1.38679
- B6: 1.08294
- B7: 1.08294
- B8: 1.08295
- B9: 1.08294
- B10: 1.08295
- B11: 1.08295
- A1: 119.99998
- A2: 119.99998
- A3: 120.00005
- A4: 120.00005
- A5: 120.00005
- A6: 119.99997
- A7: 119.99998
- A8: 120.00005
- A9: 120.00005
- A10: 119.99998
- D1: 0.
- D2: 0.
- D3: 0.
- D4: 180.
- D5: 180.
- D6: 180.
- D7: 180.
- D8: 180.
- D9: 180.

### Cartesian

<table>
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<th>Atom</th>
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<th>Y</th>
<th>Z</th>
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</thead>
<tbody>
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<tr>
<td>10</td>
<td>0</td>
<td>-0.937858</td>
<td>0.000000</td>
</tr>
</tbody>
</table>

%mem=2Gb
%chk=./BZ.chk

#P HF/STO-3G OPT FREQ

Benzene OPT-Freq

0 1
Basis & LCMO-MO & Methode (HF,DFT,Semi-empirical)

HF/STO-3G

H : 1s 1-AO
1st row: 1s, 2s, 2p 5-AOs
2nd row: 1s, 2s, 3s, 2p, 3p 9-AOs

36 basis functions, 108 primitive gaussians, 36 cartesian basis functions
21 alpha electrons 21 beta electrons

One-electron integrals, $M^2$
Two-electron integrals, $M^4$
Computed at the start; do not change

\[ \phi_i = \sum_{\alpha} c_{\alpha i} \chi_{\alpha} \]

Hartree-Fock (HF) Approximation

\[ \hat{H}\psi = E\psi \quad \text{→} \quad \hat{F}_i \phi_i = \varepsilon_i \phi_i \]

Variational Principle

\[ E = \frac{\int \Psi^* \hat{H} \Psi d\tau}{\int \Psi^* \Psi d\tau} \]

\[ E = \sum_{i=1}^{N} \sum_{\alpha\beta} c_{\alpha i} c_{\beta i} \langle \chi_{\alpha} | \hat{h}_i | \chi_{\beta} \rangle + \frac{1}{2} \sum_{i,j}^{N} \sum_{\alpha\beta\gamma\delta} c_{\alpha i} c_{\beta j} c_{\beta i} c_{\delta j} \left( \langle \chi_{\alpha} \chi_{\gamma} | \hat{g} | \chi_{\beta} \chi_{\delta} \rangle - \langle \chi_{\alpha} \chi_{\gamma} | \hat{g} | \chi_{\delta} \chi_{\beta} \rangle \right) + V_{nn} \]
Molecular Orbitals

HF/STO-3G

H : 1s
1st row: 1s, 2s, 2p
2nd row: 1s, 2s, 3s, 2p, 3p

Alpha occ. eigenvalues
-11.02925
-11.02925
-11.02925
-11.02885
-11.02885

Alpha occ. eigenvalues
-11.02869
-1.09565
-0.95809
-0.95809
-0.76891

Alpha occ. eigenvalues
-0.76891
-0.66561
-0.59350
-0.55725
-0.53600

Alpha occ. eigenvalues
-0.53600
-0.46090
-0.43371
-0.43371
-0.28264

Alpha virt. eigenvalues
0.27077
0.27077
0.50913
0.57885
0.64961

Alpha virt. eigenvalues
0.64961
0.72878
0.74339
0.74339
0.88993

Alpha virt. eigenvalues
0.88993
0.90623
0.90623
1.09947
1.16378

36 basis functions, 108 primitive gaussians, 36 cartesian basis functions
21 alpha electrons, 21 beta electron

Canonical MO

Natural MO

HOMO
LUMO
Analysis

- Energy
- IR
- UV
- H-NMR
- C-NMR
Problem 1

Use WebMO Editor to build the following molecules.

A. Propene, CH₃CH=CH₂

B. Aspirin, C₉H₈O₄

Problem 2

Use the Fragment Library (Build: Fragment...) in the WebMO Editor to create the following molecules.

C. Trans-stilbene, C₆H₅CH=CHC₆H₅

D. Equatorial methylcyclohexane (chair conformation), CH₃C₆H₁₁

When working with two fragments, it is often useful to select one fragment, and then rotate or translate just the selected fragment with Adjust: Rotate Selection or Adjust: Translate Selection. It is also useful to cleanup just a portion of the molecule by selecting the atoms for cleanup, choosing Clean-Up: Selection Only and the choosing Clean-Up Comprehensive.
Problem 3

Import the following molecule from Avogadro. Perform a single point Hartree-Fock 3-21G calculation on it.

E. Buckminsterfullerene, $C_{60}$

Problem 4

Build formaldehyde, $H_2CO$. Perform a single point Hartree-Fock 3-21G calculation on it. Perform a molecular orbital using the 3-21G basis set.

Characterize the following sets of orbitals:
- the two lowest energy orbitals
- the remaining occupied orbitals
- the unoccupied orbitals

- View the HOMO and LUMO, and describe each orbital
- What atomic orbitals are used for row 2 atoms (O and C) in each basis set? For H atoms?
### Problem 4

**C13 NMR shifts of butane, butene and butyne.**

Build butane, butene and butyne. Adjust the dihedral angles to result in planar, staggered conformations. Perform an NMR Hartree-Fock 3-21G calculation on each.

Gaussian computes absolute chemical shifts.

Make a table with columns for compound, C atom (outer or inner)

<table>
<thead>
<tr>
<th>Compound</th>
<th>C Atom</th>
<th>Formula</th>
</tr>
</thead>
<tbody>
<tr>
<td>Butane</td>
<td>Outer</td>
<td>(-C-C-C-C)</td>
</tr>
<tr>
<td>Butene</td>
<td>Outer</td>
<td>(-C-C=)</td>
</tr>
<tr>
<td>Butyne</td>
<td>Outer</td>
<td>(-C-C=)</td>
</tr>
</tbody>
</table>
Geometry Optimizations
Potential Energy Surfaces
Slices through a 2D potential energy surface give 1D surfaces.
Optimization

For a **minimum**

\[ \frac{\partial^2 E}{\partial q^2} > 0 \]

for all \( q \).

For a **transition state**

\[ \frac{\partial^2 E}{\partial q^2} > 0 \]

for all \( q \), except along the reaction coordinate, and

\[ \frac{\partial^2 E}{\partial q^2} < 0 \]

along the reaction coordinate.

Some PES’s have points where the **second derivative of energy with respect to more than one coordinate is negative**; these are **higher-order saddle points or hilltops**: for example, a **second-order saddle point** is a point on the PES which is a maximum along two paths connecting stationary points.
PES Extrema (Stationary Points)

- **Minima**
  - 1st deriv (gradient) equals zero in all directions
  - 2nd deriv positive in all directions
  - Global vs. local

- **Saddle Point**
  - “Transition state”
  - 2nd deriv negative in one direction, positive in others

- **Hilltop**
  - 2nd deriv negative in more than one direction
Locating PES Extrema

- **Algorithms**
  - Minimize energy (local minima)
  - Minimize gradient (transition state)
  - Specialized methods

- **Convergence criteria**
  - Force \((\Delta E/\Delta r) \approx 0\)
  - Displacement \((\Delta r) \approx 0\)

- Indicated in output file
Geometry Optimization
Quick Start

- WebMO
- Build fluoroethene, C$_2$H$_3$F
- Gaussian
- Geometry Optimization, Hartree-Fock, 3-21G, Preview Input File
- Note bond angles; Submit Job
- View; Note bond angles
- Raw Output
General Strategies

• A good starting geometry is essential
• For large molecules, pre-optimize using a lower level of theory
• When a job fails
  – Read the output file to determine why
  – Look at the final geometry (Restart from Job Manager)
• Although every molecule is different, past experience will help guide your calculations
Locating Transition States

- Very difficult! Finding 1 point in $10^{3N-6}$
- Opt = (TS, CalcFC, NoEigenTest)
  - Minimize gradient
  - Must have a good starting point
- Opt = QST2
  - “Morph” reactants and products
  - Must provide both structures
  - Atoms must have same numbering!
Advanced Features

• Opt=CalcFC or Opt=CalcAll
  – Better computation of force constants

• Opt=(MaxCyc=n)
  – Increase maximum number of iterations

• Use checkpoint files (built into WebMO)
  – %Chk=output.chk to produce a checkpoint file
  – Geom=(Check,Step=n) to read checkpoint file

• Multiple options can be specified by
  Opt=(TS,CalcFC,MaxCyc=100)
Perform a Geometry Optimization, Hartree-Fock 3-21G calculation on each. Make a table with columns for molecule, number of optimization steps, energy (Hartree), relative energy (kcal/mol). The relative energy should be calculated relative to the global minimum.

**Transition State of Vinyl Alcohol.**

Build an approximate transition state for the isomerization of vinyl alcohol-0° and vinyl alcohol-180° as follows. View a geometry optimized vinyl alcohol job that successfully ran, and choose New Job Using This Geometry. Adjust the H-O-C=C dihedral angle to 90°. Perform a Transition State Optimization, Hartree-Fock 3-21G calculation.

Make a table with columns for conformation and relative energy (kcal/mol). Include the two stable conformations and the transition state in the table.
Frequency Calculations
Molecular Vibrations

- A molecule has $3N-6$ vibrational degrees of freedom
  
  $E = \frac{1}{2} k x^2$  where  $k = \frac{\partial^2 E}{\partial x^2}$

- Vibrations arises from a parabolic potential energy surface

- Transition states have imaginary (negative) frequencies
Vibrational Quantum States

- Vibrational states are quantized

\[ E = h\nu (n + 1/2) \]

- The fundamental transition occurs from 0 → 1
- Zero point energy (ZPE) is always present
Infrared Spectroscopy

- **FREQ** outputs vibrational frequencies and IR, Raman intensities
- Frequency calculation must be done at stationary point
- Frequency calculation must use same model and basis set as optimization
- *Ab initio* systematically overestimates frequencies by ~10% due to electron correlation and anharmonicity
Normal Modes

- **FREQ** outputs atomic displacement for each normal mode
- Gaussian output yields Cartesian displacements
- WebMO displays these displacements as 3-D vectors
Vibrational Spectroscopy Quick Start

– WebMO
– Build $\text{H}_2\text{CO}$
– Gaussian
– Optimize + Vib Freq, Hartree-Fock, 3-21G
– View results
– View vibrational modes
– View vibrational spectrum
Characterizing Stationary Points

- Minimum: all positive eigenvalues
- Saddle Point: one imaginary (negative) eigenvalue
- Hilltop: more than one imaginary (negative) eigenvalue
Transition State Quick Start

- Job Manager: View vinyl alcohol transition state from last week
- Note route for model chemistry (HF) and basis set (6-31G)
- New job with this geometry
- Gaussian
- Vibrational Frequencies calculation at same level of theory
- View negative frequency vibrational mode to visualize reaction coordinate
Thermochemistry

- **FREQ** also outputs
  - Zero Point Energy
  - Thermal energy correction (includes ZPE)
  - Constant Volume Heat Capacity
  - Entropy

- These are added to the electronic energy for
  - Internal Energy \( E = E_{\text{elec}} + ZPE + E_{\text{trans}} + E_{\text{rot}} + E_{\text{vib}} \)
  - Enthalpy \( H = E + RT \)
  - Free Energy \( G = H - TS \)

- Thermochemistry results are absolute (not \( \Delta_f H \))

- Results reported in Hartree for STP (298K, 1 atm)
Gaussian Output

• Zero Point Energy
  Zero-point correction

• Conditions
  Temperature 298.150 Kelvin. Pressure 1.00000 Atm.

• Internal Energy, Enthalpy, Free Energy
  Sum of electronic and thermal Energies
  Sum of electronic and thermal Enthalpies
  Sum of electronic and thermal Free Energies

• Heat Capacity and Entropy
  $C_V$ $S$
**Problem 6**

Build formaldehyde, $\text{H}_2\text{CO}$, and perform a Geometry Optimization PM3 calculation on it. View the result, click on New Job Using This Geometry, and perform a Vibrational Frequencies PM3 calculation. View the result, and view each vibrational mode. Fill in the following table of vibrational frequencies by visually identifying the description of each normal mode.

<table>
<thead>
<tr>
<th>Mode</th>
<th>Description</th>
<th>PM3 Frequency (cm$^{-1}$)</th>
<th>Literature Frequency (cm$^{-1}$)</th>
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</thead>
<tbody>
<tr>
<td>n1</td>
<td>Sym CH Stretch</td>
<td>2811</td>
<td></td>
</tr>
<tr>
<td>n2</td>
<td>CO stretch</td>
<td>1756</td>
<td></td>
</tr>
<tr>
<td>n3</td>
<td>CH$_2$ bend</td>
<td>1500</td>
<td></td>
</tr>
<tr>
<td>n4</td>
<td>out-of-plane bend</td>
<td>1170</td>
<td></td>
</tr>
<tr>
<td>n5</td>
<td>antisym CH stretch</td>
<td>2861</td>
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<tr>
<td>n6</td>
<td>CH$_2$ rock</td>
<td>1251</td>
<td></td>
</tr>
</tbody>
</table>
Problem 7

Stretching Frequencies of Carbonyl Groups.

Calculate the C=O stretching frequency of formamide, acetaldehyde and acetyl chloride.

Perform Optimize Geometry and Vibrational Frequencies (or Optimize+Vib Freq) Hartree-Fock 3-21G calculations for each molecule. Computed vibrational frequencies are systematically high and are routinely scaled need to be scaled frequencies. The scaling factor for HF/3-21G calculations is 0.9085. Make a table with columns for molecule, calculated CO stretch frequency, scaled CO stretch frequency, and experimental frequency (indicated above).
Problem 8

Transition State for 1,3 Hydrogen Shift of Fluoropropene.

Build the transition state for the 1,3 hydrogen shift of fluoropropene.

\[
\text{H} \quad \text{H} \\
| \quad | \\
\text{H}_{2} \quad \text{C} \quad \text{C} \quad \text{C} \quad \text{C} \\
| \quad | \\
\text{H} \quad \text{H} \quad \text{F} \\
\]

Do not do a comprehensive cleanup, as the Add Hydrogens function uses rules that are applicable to stable molecules, not transition states. Instead, manually add the hydrogens, including a hydrogen that is bonded to both C1 and C3. Adjust the hybridization of C2 to sp\(^2\), and clean up the geometry only.

Adjust the H-C2 bond angle appropriately so it is symmetric with respect to the ring. Perform an Optimize Transition State PM3 (or Hartree-Fock 3-21G) calculation on the molecule. If the job was successful, view the result to see if the molecule looks as expected. If the job failed, rebuild the transition state but try adjusting the C-C-C bond angle to approximately 100° while maintaining the symmetry of the ring (i.e., increase C1-C2-C3 by 15°, and then increase C3-C2-C1 by 15°).

Create a new job using the optimized transition state geometry. Perform a Frequency PM3 calculation on the previously optimized geometry. View the transition state.

Insert a picture of the transition state and reaction coordinate. How do you know that it is a transition state?

Build and optimize the geometries of the reactant and product for this reaction. Make a table with columns for species and energy, and include the energies of the reactant, transition state, and product. What is the reaction barrier for 1,3 hydrogen shift of fluoropropene?
Problem 9

Thermochemistry of CH$_3$CHO $\rightarrow$ CO + CH$_4$ in the gas phase.

Build and perform Optimize+Vib Freq Hartree-Fock, 6–31G(d) calculations on acetaldehyde, carbon monoxide, and methane. To speed up your calculation, start your acetaldehyde calculation from the same geometry as a previous lower level optimization.

Make a table of calculated values with columns for molecule, C$_v$, S, E$_{298}$, H$_{298}$, and G$_{298}$.

Visit the NIST webbook (http://webbook.nist.gov/chemistry) and make a table of experimental values with columns for molecule, C$_p$, S, and $\Delta_f$H (kcal/mol).

Compute C$_p$ from your calculations for each species by using the relationship that C$_p$ = C$_v$ + R for an ideal gas.

Compute $\Delta_{rxn}$H from your calculations by appropriately combining H$_{298}$ values and converting to kcal/mol. 1 Hartree = 627.5095 kcal/mol. Compute $\Delta_{rxn}$H from the experimental data by appropriately combining $\Delta_f$H.

Comment on the agreement between calculation and experiment by comparing C$_p$, S, and $\Delta_{rxn}$H values in a table.
Partial Charges and Potential Energy Surface Scans
Previous Applications

- Geometry optimization
- Conformation stability
- Transition states
- IR and NMR spectra
- Thermochemistry ($ZPE, C_V, S, H, G$)
- Enthalpies of reaction $\Delta_{\text{rxn}}H$
Partial Charges

- Mulliken populations: derived from AO coefficients and overlap integrals

\[ \int | \phi_j|^2 dV_j = 1 = c_{1j}^2 + c_{2j}^2 + \ldots + c_{bj}^2 + \sum_{r<s} 2c_{rij}c_{sij}S_{rs} \]

- Natural Bonding Orbitals: derived by assigning electrons to core, valence, and lone pair orbitals

- Electrostatic potential-derived charges: derived to match electrostatic potential at a given distance
Rigid Potential Energy Surface Scan

- **SCAN** keyword
- Series of Single Point calculations that systematically vary one (or more) coordinate
- Non-stepped coordinates are fixed, not optimized
- Relatively fast, but of limited utility
Relaxed Potential Energy Surface Scan

- **Opt=Z-matrix** or **Opt=AddRedundant** keyword
- A series of Optimize Geometry calculations that systematically vary one (or more) coordinate
- Stepped coordinate must be carefully chosen to represent chemical feature of interest
- Available in Z-matrix (easier input file) or redundant coordinates (more robust method)
Rotation & C-C bond variation

CB is free to rotate! Rotational quenching is intrinsic feature of CB.

**Rotational Energy Barrier**

- **4-MeCBIr [IO]**
- **5-MeCBIr [IO]**
- **CB1 [Out]**
- **CB2 [In]**

**Distance (Å)**

**Rotation Angle [deg]**

**ΔE (eV)**

- **4-MeCBIr_S0**
- **4-MeCBIr_T1**
- **5-MeCBIr_S0**
- **5-MeCBIr_T1**

- **4-MeCBIr_Avg.**
- **5-MeCBIr_Avg.**
1. Optimized 구조를 이용
2. Z-Matrix 선택
3. Scan 할 variable을 S로 선택 (S: scan, O: opt, F: fix)
4. Scan range 설정
5. Yellow line으로 표시됨
6. Fixed Scan 혹은 Relaxed Scan 선택
7. cartesian coordinate을 uncheck함.
8. Preview에서 Input 생성
9. Input 수정 후 submit
### Calculated Quantities

<table>
<thead>
<tr>
<th>Quantity</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Route</td>
<td>IN B3LYP/6-311+G(d,p) OPT=Z-matrix NOSYMMETRY</td>
</tr>
<tr>
<td>Stoichiometry</td>
<td>CH₄</td>
</tr>
<tr>
<td>Symmetry</td>
<td>C1</td>
</tr>
<tr>
<td>Basis</td>
<td>6-311+G(d,p)</td>
</tr>
<tr>
<td>RB3LYP Energy</td>
<td>-40.3434115216 Hartree</td>
</tr>
</tbody>
</table>

#### Rotational Constants

<table>
<thead>
<tr>
<th>Constant</th>
<th>Frequency (GHz)</th>
<th>Frequency (cm⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
<td>143.9344973</td>
<td>4.80113803597</td>
</tr>
<tr>
<td>b</td>
<td>57.9406775</td>
<td>1.93270297347</td>
</tr>
<tr>
<td>c</td>
<td>57.937582</td>
<td>1.93258955195</td>
</tr>
</tbody>
</table>

#### Dipole Moment

- 2.1722 Debye

#### Coordinate Scan

<table>
<thead>
<tr>
<th>Coordinate</th>
<th>Energy</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.70000</td>
<td>-40.31335</td>
</tr>
<tr>
<td>0.80000</td>
<td>-40.43874</td>
</tr>
<tr>
<td>0.90000</td>
<td>-40.50132</td>
</tr>
<tr>
<td>1.00000</td>
<td>-40.52795</td>
</tr>
<tr>
<td>1.10000</td>
<td>-40.53388</td>
</tr>
<tr>
<td>1.20000</td>
<td>-40.52808</td>
</tr>
<tr>
<td>1.30000</td>
<td>-40.51591</td>
</tr>
</tbody>
</table>

- **Relaxed Scan** 인 경우만 Scan에 따른 구조 변화 확인 가능
- **Fixed & Relaxed Scan** 모두 에너지 변화 plot 확인 가능
Problem 10

Partial Charge Analysis of Electrophilic Aromatic Substitution Reactions

1. Build nitrobenzene such that the nitro group lies in the molecular plane and has equal NO bond lengths. Optimize the geometry of nitrobenzene at the HF/3-21G level, also disabling symmetry for the calculation. If using Gaussian, disable symmetry using the Advanced Job Options. The reported partial charges are Mulliken partial charges.

2. If using Gaussian, use the New Job Using This Geometry button to perform a Single Point calculation (Molecular Energy) at same level of theory with the additional keyword “Pop=NBO”. [The Pop=NBO or Pop=NPA keywords request that Gaussian perform a Natural Bonding Orbital analysis of the molecule, in which electrons are assigned to “organic chemistry” orbitals as core electron pairs, single bonds, double bonds, lone pairs, etc.]

3. Finally, use the New Job Using This Geometry button to perform a Single Point calculation at same level of theory with the additional keyword “Pop=CHelpG”. [The CHelpG keyword requests that Gaussian calculate an electrostatic potential-derived potential in which atoms are assigned partial charges to match the electrostatic potential at the van der Waals surface.] View the Raw Output of each of these jobs and locate the respective partial charges.

4. Construct a table with columns for isomer (ortho, meta, para), Mulliken partial charge, NBO partial charge, ChelpG partial charge, and observed nitration product distribution percentage. Use these results to explain the preferred site of electrophilic attack by NO₂⁺.

5. Repeat the above calculations and construct a similar table for chlorobenzene.
Summary of Natural Population Analysis:

<table>
<thead>
<tr>
<th>Atom No</th>
<th>Natural Charge</th>
<th>Core</th>
<th>Valence</th>
<th>Rydberg</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>C 1</td>
<td>2</td>
<td>1.99865</td>
<td>4.23998</td>
<td>0.01513</td>
<td>6.25275</td>
</tr>
<tr>
<td>C 2</td>
<td>-0.19131</td>
<td>1.99865</td>
<td>4.23998</td>
<td>0.01513</td>
<td>6.25275</td>
</tr>
<tr>
<td>C 3</td>
<td>0.0078</td>
<td>1.99836</td>
<td>3.92257</td>
<td>0.01829</td>
<td>5.93922</td>
</tr>
<tr>
<td>C 4</td>
<td>-0.19125</td>
<td>1.99857</td>
<td>4.17661</td>
<td>0.01607</td>
<td>6.19131</td>
</tr>
<tr>
<td>C 5</td>
<td>0.02527</td>
<td>1.99865</td>
<td>4.23900</td>
<td>0.01513</td>
<td>6.25277</td>
</tr>
<tr>
<td>C 6</td>
<td>-0.19069</td>
<td>1.99864</td>
<td>4.17758</td>
<td>0.01448</td>
<td>6.19069</td>
</tr>
<tr>
<td>H 7</td>
<td>0.25065</td>
<td>0.00000</td>
<td>0.74076</td>
<td>0.00580</td>
<td>0.74635</td>
</tr>
<tr>
<td>H 8</td>
<td>0.25593</td>
<td>0.00000</td>
<td>0.74599</td>
<td>0.00557</td>
<td>0.74617</td>
</tr>
<tr>
<td>H 9</td>
<td>0.25290</td>
<td>0.00000</td>
<td>0.74197</td>
<td>0.00503</td>
<td>0.74702</td>
</tr>
<tr>
<td>H 10</td>
<td>0.25052</td>
<td>1.99904</td>
<td>4.47753</td>
<td>0.02291</td>
<td>6.49948</td>
</tr>
<tr>
<td>H 11</td>
<td>-0.40035</td>
<td>1.99973</td>
<td>6.39541</td>
<td>0.00521</td>
<td>8.40035</td>
</tr>
<tr>
<td>H 12</td>
<td>-0.40041</td>
<td>1.99973</td>
<td>6.39541</td>
<td>0.00521</td>
<td>8.40035</td>
</tr>
<tr>
<td>H 13</td>
<td>0.27978</td>
<td>0.00000</td>
<td>0.71819</td>
<td>0.00523</td>
<td>0.72042</td>
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<tr>
<td>H 14</td>
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<td>0.00000</td>
<td>0.74560</td>
<td>0.00587</td>
<td>0.74717</td>
</tr>
</tbody>
</table>

* Total * | 0.00000 | 17.98994 | 45.87579 | 0.13427 | 64.00000

Sum of ESP charges = 0.00000

NBO or ESP 계산

ESP charges:

1 C -0.148899
2 C -0.093212
3 C 0.030984
4 C 0.025553
5 C -0.147877
6 C -0.048389
7 H 0.123229
8 H 0.140724
9 H 0.157516
10 H 0.763126
11 O -0.455417
12 O -0.455378
13 N 0.157631
14 N 0.140395

* Total * | 0.00000 | 17.98994 | 45.87579 | 0.13427 | 64.00000

NBO or ESP 계산

ESP charges:

1 C -0.148899
2 C -0.093212
3 C 0.030984
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7 H 0.123229
8 H 0.140724
9 H 0.157516
10 H 0.763126
11 O -0.455417
12 O -0.455378
13 N 0.157631
14 N 0.140395

* Total * | 0.00000 | 17.98994 | 45.87579 | 0.13427 | 64.00000
Problem 11

Mechanism for the Nitration of Benzene

1. Intuitively explain the computed partial charges by drawing resonance structures for nitrobenzene that withdraw p-electron density from the ring and by drawing resonance structures for chlorobenzene that donate p-electron density into the ring.
Problem 12

Carbocation Intermediate Analysis of Electrophilic Aromatic Substitution Reactions

1. Aromatic substitution reactions proceed via a carbocation intermediate. The product distribution of an aromatic substitution reaction may be determined by the relative stabilities of the carbocation intermediates. The aldehyde group is meta-directing for aromatic substitution reactions.

2. Build planar benzaldehyde and optimize the geometry with a HF/3-21G calculation. View the partial charges of the ortho, meta, and para carbons (on the side of the ring closest to the H atom of the aldehyde group).

3. Click New Job Using This Geometry, and open the molecule in the WebMO editor. Add a chlorine atom to the ortho carbon (on the H atom side of the aldehyde group). Adjust the double bond to the ortho carbon to a single bond. Select the CHCl group, choose Clean-Up: Selection Only, and choose Clean-Up: Comprehensive so that only the new change is cleaned up. Optimize the geometry of this intermediate structure with a HF/3-21G calculation, setting the charge appropriately for a carbocation. Repeat this to compute the HF/3-21G energies of the meta and para intermediates.

4. Construct a table with columns for isomer (ortho, meta, para), partial charge, intermediate energy, and observed chlorination percentage.

<table>
<thead>
<tr>
<th>Product</th>
<th>ortho</th>
<th>meta</th>
<th>para</th>
</tr>
</thead>
<tbody>
<tr>
<td>C₆H₅CHOCl</td>
<td>19%</td>
<td>72%</td>
<td>9%</td>
</tr>
</tbody>
</table>
Problem 13

Fixed Potential Energy Scans of NH$_3$ and H$_2$O Inversion

1. Build NH$_3$ with the WebMO editor. Use Tools: Z-Matrix to scan the H4-N1-H2-H3 dihedral angle from 90 to 270 in 18 steps. Perform a Coordinate Scan calculation at the PM3 level. From the results page, view the Coordinate Scan and determine the barrier height for ammonia inversion in kcal/mol.

2. Repeat the calculation for H$_2$O, scanning the H3-O1-H2 bond angle from 90 to 270 in 18 steps. View the Coordinate Scan and determine the barrier for water linearization in kcal/mol.

3. Speculate on the reason for difference in barrier heights.
Problem 14

Relaxed Potential Energy Scan of CH Bond Dissociation

1. Build CH\textsubscript{4} and clean up only its geometry. Use Tools: Z-Matrix and Fix All coordinates. C1-H5 bond length from 0.7 to 2.7 in 20 steps. Perform a Coordinate Scan calculation at the HF/3-21G level.

2. Repeat the coordinate scan with B3LYP/6-311+G(p,d).

3. Download the coordinate scans and use Excel to plot these potential functions in the same figure. Comment generally on the differences among these plots.

4. Calculate the CH bond dissociation energy in kcal/mol by taking the difference between the minimum and separated energies. Compare your results to an experimental value from a general or organic chemistry textbook.
Bond Orders, Isodesmic Reactions, IRC Scans
Bond Orders

- No unique definition of assigning electrons to bonds
- **Density matrix analysis**: Mulliken density analysis allows crude calculation of bond orders
- **Atoms In Molecules (AIM) theory**: electrons are assigned to atoms based on the gradient of the electron density
- **Natural Bonding Orbitals (NBO)**: single and double bonds, lone pairs
Build the planar allyl radical $\text{C}_3\text{H}_5$ and perform a Geometry Optimization at the Hartree-Fock 3–21G level. Note that allyl has an odd number of electrons and is therefore a doublet.

View the output and run a New Job Using This Geometry.

Run a Gaussian Bond Order calculation at the same level of theory, which performs a NBO (Natural Bonding Orbital) analysis of the Bond Order.

If time permits, run a Gaussian Calculation “AIM=BondOrders” job at the same level of theory. Be patient since AIM jobs take a relatively long time! View the Raw Output to obtain the AIM bond orders.
Isodesmic Reaction

• No change in number of each bond type between reactants and products
  Ex: \( \text{CO}_2 + \text{CH}_4 \rightarrow 2 \text{H}_2\text{CO} \)
  (2 C=O and 4 C-H bonds on each side)

• Good results at low theory levels because of cancellation of errors

• Can use isodesmic reaction results plus other experimental data to calculate energetics of non-isodesmic reactions
Problem 16

Isodesmic Reaction Analysis of CO$_2$ Heat of Formation

Build and perform Optimize + Vib Freq calculations on carbon dioxide (CO$_2$), formaldehyde (H$_2$CO), and methane (CH$_4$) at the HF/6-31G(d) level. Tabulate the energy (0 K) and enthalpy (298 K) for each.

Use these results to calculate $\Delta_{\text{rxn}}H$ for

$$\text{CO}_2 + \text{CH}_4 \rightarrow 2\text{H}_2\text{CO}$$

|        | CO$_2$   | CH$_4$   | H$_2$CO   | $\Delta_{\text{rxn}}H$
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>E (0K)</td>
<td>-187.6342</td>
<td>-40.1952</td>
<td>-113.8663</td>
<td>0.0967</td>
</tr>
<tr>
<td>H (298K)</td>
<td>-187.6179</td>
<td>-40.1436</td>
<td>-113.8333</td>
<td>0.0949</td>
</tr>
</tbody>
</table>
Intrinsic Reaction Coordinate Scans

- Follows a reaction coordinate “downhill” (shedding kinetic energy or “momentum”)
- Starting from a transition state, forward and reverse IRC calculations go forward and backward along the reaction coordinate
- Calculation stops before equilibrium is reached; default is 6 steps
Problem 17

Intrinsic Reaction Coordinate Verification of the $\text{H}_2\text{CO} \rightarrow \text{H}_2 + \text{CO}$ Transition State

Compute the $\text{H}_2\text{CO} \rightarrow \text{H}_2 + \text{CO}$ transition state by building the following planar structure:

![Planar structure of $\text{H}_2\text{CO}$](image)

Perform a Transition State Optimization of the structure at the Hartree-Fock 3-21G level. View the Results, and then perform a Vibrational Frequencies job with the same geometry and theory. Report the value of any negative (imaginary) frequencies. Note the energy and H–H bond length.

Using the transition state geometry, perform a Forward & Reverse IRC calculation at the same theory. View the result and note the energy and H–H bond length.

Report all numerical values for energy and H–H bond length in a table. Also, include a sketch of the Potential Energy Surface for the $\text{H}_2\text{CO} \rightarrow \text{H}_2 + \text{CO}$ reaction coordinate, along with pictures of the reactant, transition state, and products.
Verifying Transition States

• Obtain starting point from literature, symmetry, or “morph” (QST2) calculation; minimize gradient (Opt=TS)
• Calculate vibrational spectrum (Freq); look for single negative (imaginary) frequency
• Perform forward and reverse IRC calculations; look for reactants and products