Potential Energy Surface
Transition State
Making INPUT 1

- First lines are input of method and basis set
  - #P HF/STO-3G pop=reg

- Empty line

- Title of the calculation: Anything is OK

- Empty line

- Charge and spin multiplicity: usually we consider neutral molecule so charge 0, multiplicity is number of unpaired electrons +1, usually we consider filled electron so 1
Making INPUT 2

- Then define the molecule either using **XYZ** or **Z-matrix** input

<p>| | | | |</p>
<table>
<thead>
<tr>
<th></th>
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</tr>
</thead>
<tbody>
<tr>
<td>O1</td>
<td>0.000000</td>
<td>0.754227</td>
<td>-0.058812</td>
</tr>
<tr>
<td>O2</td>
<td>0.000000</td>
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<td>-0.058812</td>
</tr>
<tr>
<td>H3</td>
<td>-0.742068</td>
<td>-1.085986</td>
<td>0.470499</td>
</tr>
<tr>
<td>H4</td>
<td>0.742068</td>
<td>1.085986</td>
<td>0.470499</td>
</tr>
</tbody>
</table>

- Then end with one blank line

<p>| | | | |</p>
<table>
<thead>
<tr>
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<tr>
<td>O1</td>
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<td></td>
</tr>
<tr>
<td>O2</td>
<td>1,</td>
<td>RO1O2</td>
<td></td>
</tr>
<tr>
<td>H3</td>
<td>2,</td>
<td>RO2H3, 1, AO1O2H3</td>
<td></td>
</tr>
<tr>
<td>H4</td>
<td>1,</td>
<td>RO1H4, 2, AO2O1H4, 3, DH3O2O1H4</td>
<td></td>
</tr>
</tbody>
</table>

RO1O2=1.50845307
RO2H3=0.97
RO1H4=0.97
AO1O2H3=110.0
AO2O1H4=110.0
DH3O2O1H4=109.
Review

• Last week we did diatomic molecules with only one bond so we only have to think about forming a bond or breaking that bond
• Today we will consider something more complex molecules
• Then we will make and break a bond at the same time REACTION
Water Molecule
Potential Energy Curve

![Diagram of Water Molecule with Potential Energy Curves for ROH1 and theta]
Water Molecule: Stretch Stretch
Potential Energy Surface

ROH1

ROH2

ROH1

ROH2

ROH2

ROH1
Water Molecule: Stretch Bend Potential Energy Surface
Normal Mode Vibration

First we consider mass–weight Cartesian Coordinates

\[ q_1 = m_1^{1/2} \Delta X_1; q_2 = m_1^{1/2} \Delta Y_1; q_3 = m_1^{1/2} \Delta Z_1; q_4 = m_2^{1/2} \Delta x_2; \ldots q_{3N} = m_N^{1/2} \Delta Z_N \]

Next expand the potential energy to second term near equilibrium

\[ V = V(0) + \sum_{I}^{3N} K_I q_I + \frac{1}{2} \sum_{I}^{3N} \sum_{J}^{3N} K_{IJ} q_I q_J = \frac{1}{2} \sum_{I}^{3N} \sum_{J}^{3N} K_{IJ} q_I q_J \]

Total energy is given as

\[ E = \frac{1}{2} \sum_{I}^{3N} \dot{q}_I^2 + \frac{1}{2} \sum_{I}^{3N} \sum_{J}^{3N} K_{IJ} q_I q_J \]

If we diagonalize \( K_{IJ} \)

\[ E = \frac{1}{2} \sum_{I}^{3N-5/6} \dot{Q}_I^2 + \frac{1}{2} \sum_{I}^{3N-5/6} \lambda_I Q_I^2 \]

Motion described by \( 3N-6 \) terms (5 for linear molecule) \( \text{NORMAL MODES} \)

\[ Q_I = \sum_{J=1}^{3N} L_{IJ} q_J \quad I = 1, 3N - 5/6 \]

5/6 Modes that are ignored have zero \( \lambda_I \) \( \text{TRANSLATION/ROTATION} \)
Normal Modes of Water

- Symmetric stretch
- Antisymmetric stretch
- Bend
$F + HCl \rightarrow FH + Cl$ Potential Energy Surface

Hydrogen Abstraction Reaction, break a HCl bond form a HF bond
You need enough energy to go over the potential barrier to react! The minimum energy path that connect the barrier with reactant and product is called intrinsic reaction path. For F+HCl case you need about 5 kcal/mol of for reaction to occur.
How to quantify Barrier?

• At the barrier the first derivative is zero and the second derivative is negative for one degree of freedom and the rest are always positive. In Gaussian you can use the freq keyword to check if there is imaginary frequency.

Harmonic Oscillator approximation at barrier

\[ F = m \frac{d^2 x}{dt^2} = -kx \]

\[ k: \text{force constant} \quad \omega = \sqrt{\frac{k}{m}} \]

In the case of barrier the force constant \( k \) is negative so \( \omega \) is imaginary.
Find the potential Barrier

• Input a geometry that is close to the barrier and use the keyword Opt=(ts)
• Check if the optimized structure is a barrier by calculating the frequency by the freq keyword
• Use the IRC keyword to follow the reaction to the reactant and product keyword IRC(forward), IRC(backward)
Transition State Theory

• Once you have the barrier you can estimate the thermal rate constant of the reaction from the calculation results! (Assuming that the reaction proceeds along the IRC)

\[ A + B \rightarrow (AB)^+ \rightarrow \text{product} \]

\[ -\left( \frac{d[A]}{dt} \right) = \frac{k_B T}{h} K^+ [A][B] \]

\( K^+ \) is the thermal rate constant that depends on temperature.
Things Needed To Calculate Rate Constant

\[ K^+ = \frac{Q[(AB)^+]}{Q[A]Q[B]} \exp \left( -\frac{\Delta E}{k_B T} \right) \]

Q is the partition function of the respective molecules
\( \Delta E \) is the energy difference from the reactant to the barrier
Partition Function 1

\[ Q_{\text{trans}} = \left( \frac{2\pi mk_B T}{\hbar^2} \right)^{3/2} \]

\[ V = \left( \frac{2\pi m k_B T}{\hbar^2} \right)^{3/2} \frac{k_B T}{P} \]

Usually you consider 1atm pressure

\[ Q_{\text{electronic}} = D_0 \exp\left[ -\varepsilon_0 / k_B T \right] + D_1 \exp\left[ -\varepsilon_1 / k_B T \right] + D_2 \exp\left[ -\varepsilon_2 / k_B T \right] + \ldots \]

\[ = D_0 \]

D is the degeneracy of the electronic state, usually only consider ground electronic state
Partition Function 2

\[ Q_{\text{rot}} = \frac{\pi^{1/2}}{\sigma_r} \left( \frac{T^{3/2}}{(\theta_A \theta_B \theta_C)^{1/2}} \right) \]

\[ \theta_{A,B,C} = \frac{h^2}{8\pi^2 I_{A,B,C} k_B} \]

\( I \) is the moment of inertia around the respective axis

\[ Q_{\text{vib}} = \prod_{i}^{N_{\text{vib}}} \frac{1}{1 - \exp \left[ -\frac{h \nu_i}{k_B T} \right]} \]

\( \nu_i \) is the vibrational frequency of the i-th vibrational mode
Methanediol Dehydration

\[ \text{CH}_2(\text{OH})_2...\text{H}_2\text{O} \]  \hspace{1cm} \text{TS Complex} \hspace{1cm} \text{CH}_2\text{O}...\text{H}_2\text{O}...\text{H}_2\text{O} \]
Output of TS Optimization

-----

<table>
<thead>
<tr>
<th>Item</th>
<th>Value</th>
<th>Threshold</th>
<th>Converged?</th>
</tr>
</thead>
<tbody>
<tr>
<td>Maximum Force</td>
<td>0.00000</td>
<td>0.000450</td>
<td>YES</td>
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<tr>
<td>RMS Force</td>
<td>0.00000</td>
<td>0.000300</td>
<td>YES</td>
</tr>
<tr>
<td>Maximum Displacement</td>
<td>0.000017</td>
<td>0.001800</td>
<td>YES</td>
</tr>
<tr>
<td>RMS Displacement</td>
<td>0.000007</td>
<td>0.001200</td>
<td>YES</td>
</tr>
</tbody>
</table>

Predicted change in Energy = -3.389145D-12
Optimization completed.
  -- Stationary point found.

! Optimized Parameters !
! (Angstroms and Degrees) !

<table>
<thead>
<tr>
<th>Name</th>
<th>Definition</th>
<th>Value</th>
<th>Derivative Info.</th>
<th>!</th>
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<tbody>
<tr>
<td>R1</td>
<td>R(1,2)</td>
<td>1.2942</td>
<td>-DE/DX = 0.0</td>
<td>!</td>
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<tr>
<td>R2</td>
<td>R(1,3)</td>
<td>1.7415</td>
<td>-DE/DX = 0.0</td>
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<tr>
<td>R3</td>
<td>R(1,4)</td>
<td>1.0985</td>
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<td>!</td>
</tr>
<tr>
<td>R4</td>
<td>R(1,5)</td>
<td>1.0964</td>
<td>-DE/DX = 0.0</td>
<td>!</td>
</tr>
<tr>
<td>R5</td>
<td>R(2,9)</td>
<td>1.2826</td>
<td>-DE/DX = 0.0</td>
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<tr>
<td>R6</td>
<td>R(3,6)</td>
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<tr>
<td>R7</td>
<td>R(3,7)</td>
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<td>!</td>
</tr>
<tr>
<td>R8</td>
<td>R(6,8)</td>
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<td>-DE/DX = 0.0</td>
<td>!</td>
</tr>
<tr>
<td>R9</td>
<td>R(8,9)</td>
<td>1.1596</td>
<td>-DE/DX = 0.0</td>
<td>!</td>
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<tr>
<td>R10</td>
<td>R(8,10)</td>
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<td>-DE/DX = 0.0</td>
<td>!</td>
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<tr>
<td>A1</td>
<td>A(2,1,3)</td>
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<td>-DE/DX = 0.0</td>
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<td>A2</td>
<td>A(2,1,4)</td>
<td>118.899</td>
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<tr>
<td>A3</td>
<td>A(2,1,5)</td>
<td>117.0873</td>
<td>-DE/DX = 0.0</td>
<td>!</td>
</tr>
</tbody>
</table>
## Output of TS Optimization

### Thermochemistry

- Temperature: 298.150 Kelvin
- Pressure: 1.00000 Atm.
- Atom 1: Atomic number 6, Mass 12.00000
- Atom 2: Atomic number 8, Mass 15.99491
- Atom 3: Atomic number 8, Mass 15.99491
- Atom 4: Atomic number 1, Mass 1.00783
- Atom 5: Atomic number 1, Mass 1.00783
- Atom 6: Atomic number 1, Mass 1.00783
- Atom 7: Atomic number 1, Mass 1.00783
- Atom 8: Atomic number 8, Mass 15.99491
- Atom 9: Atomic number 1, Mass 1.00783
- Atom 10: Atomic number 1, Mass 1.00783
- Molecular mass: 66.03169 amu.

### Principal axes and moments of inertia in atomic units:

<table>
<thead>
<tr>
<th>Eigenvalues</th>
<th>1</th>
<th>2</th>
<th>3</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>208.97954</td>
<td>286.92164</td>
<td>456.13868</td>
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</table>

<table>
<thead>
<tr>
<th>X</th>
<th>0.69691</th>
<th>-0.60799</th>
<th>0.38035</th>
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</thead>
<tbody>
<tr>
<td>Y</td>
<td>-0.56629</td>
<td>-0.14111</td>
<td>0.81204</td>
</tr>
<tr>
<td>Z</td>
<td>0.44004</td>
<td>0.78131</td>
<td>0.44264</td>
</tr>
</tbody>
</table>

This molecule is an asymmetric top.
- Rotational symmetry number: 1
- Rotational temperatures (Kelvin): 0.41446, 0.30187, 0.18988
- Rotational constants (GHz): 8.63597, 6.29001, 3.95656

1 imaginary frequencies ignored.
- Zero-point vibrational energy: 198551.1 (Joules/Mol)
Output of TS Optimization

### Full mass-weighted force constant matrix:

Low frequencies: 1369.6748, -12.0457, -3.0710, 0.0008, 0.0014, 0.0015

Low frequencies: 15.2049, 164.8661, 367.0583

1 imaginary frequencies (negative Signs)

### Diagonal vibrational polarizability:

<p>| | | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>68.2855903</td>
<td>48.1711286</td>
<td>42.8890866</td>
</tr>
</tbody>
</table>

### Harmonic frequencies (cm**-1), IR intensities (KM/Mole), Raman scattering activities (A**4/AMU), depolarization ratios for plane and unpolarized incident light, reduced masses (AMU), force constants (mDyne/A), and normal coordinates:

<table>
<thead>
<tr>
<th>Atom</th>
<th>AN</th>
<th>X</th>
<th>Y</th>
<th>Z</th>
<th>X</th>
<th>Y</th>
<th>Z</th>
<th>X</th>
<th>Y</th>
<th>Z</th>
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<tbody>
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<td>-0.05</td>
<td>-0.02</td>
<td>0.21</td>
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<td>0.07</td>
<td>0.04</td>
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<tr>
<td>2</td>
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<td>0.02</td>
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<td>0.03</td>
<td>-0.06</td>
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<td>0.13</td>
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<td>0.06</td>
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<td>0.33</td>
<td>0.08</td>
<td>0.08</td>
<td>0.25</td>
<td>0.09</td>
</tr>
</tbody>
</table>

ts2.log lines 1508-1536/1913 79%
Hartree Fock Projects 2

- Vinyl alcohol H2C=CHOH, CH3CHO isomer energy and barrier energy (IRC check)
- \(R_1R_2C=O\) optimization effect of substituent on the C=O vibrational frequency and intensity
- CO2+H2O carbonic acid formation barrier
- \(R_1R_2R_3C-CR_4R_5R_6\) and \(R_1R_2C=CR_3R_4\) torsion barrier and potential curve