Chemistry 4000/5000/7000 Fall 2021
Assignment 3 solutions

1. If you look over the entire assignment as well as the streamlined procedure for calculating the Wigner correction, you will realize that you need a relatively small number of calculations. You might as well use a reasonably sized basis set then. By the same token, we don't want to go nuts with a huge basis set. I chose the aug-cc-pVDZ basis set, a medium-sized basis set that includes diffuse functions. The latter may be important for the through-space interaction between atoms attached to the two carbon atoms (e.g. the interaction between the large Cl atom and the opposite H atom at the transition state). There are no true dispersion forces here, so I used the B3LYP functional, which tends to be a good general-purpose functional. Because this is a simple octet-rule molecule, I imposed restricted wavefunctions.

   Since I'm going to need partition functions to calculate rate constants, I ran `Opt+Freq` jobs for each of the structures right away. In the following, M1 denotes the lowest-energy conformer, M2 is the secondary minimum, and TS is the relevant transition state.

	ϵ/hartree	∠F-C-C-Cl/degrees	∠F-C-C/degrees	∠Cl-C-C/degrees	C-C length/Å
M1	$-638.702\,881$	180.00	107.77	108.89	1.52
M2	$-638.702\,091$	69.73	110.73	112.31	1.51
TS	$-638.697\,887$	121.64	109.14	112.40	1.53

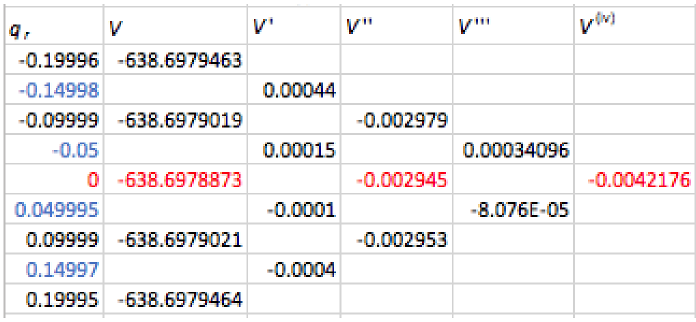
2. We have the energies in the table above. For this and the next question, we also need the partition functions, which Gaussian helpfully calculated for us:

	ϵ/hartree	$\hat{q}$
M1	$-638.702\,881$	5.337×10^{-15}
M2	$-638.702\,091$	6.143×10^{-15}
TS	$-638.697\,887$	3.203×10^{-15}

   The first rate constant to calculate is M1 → M2 passing through the TS.

$$\begin{aligned}
k_{12} &= \frac{k_BT}{h}\frac{\hat{q}^{\ddagger}}{\hat{q}_{\text{M1}}}e^{-\Delta^{\ddagger}\epsilon/k_BT}\\
\Delta^{\ddagger}\epsilon &= \epsilon_{\text{TS}} - \epsilon_{\text{M1}}\\
&= -638.697\,887 - (-638.702\,881)\,\text{hartree}\\
&= 0.004\,994\,\text{hartree}\\
&\equiv (0.004\,994\,\text{hartree})(4.359\,745\times10^{-18}\,\text{J})\\
&= 2.177\times10^{-20}\,\text{J}
\end{aligned}$$

Table 1: Energies along the IRC along with the derivatives calculated by central differences. Blue entries were obtained by averaging adjacent coordinates. The transition state is highlighted in red.



q_r	V	V'	V''	V'''	$V^{(iv)}$
-0.19996	-638.6979463				
-0.14998		0.00044			
-0.09999	-638.6979019		-0.002979		
-0.05		0.00015		0.00034096	
0	-638.6978873		-0.002945		-0.0042176
0.049995		-0.0001		-8.076E-05	
0.09999	-638.6979021		-0.002953		
0.14997		-0.0004			
0.19995	-638.6979464				

$$\begin{aligned}
\therefore k_{12} &= \frac{(1.380\,649\times10^{-23}\,\mathrm{J\,K^{-1}})(298.15\,\mathrm{K})}{6.626\,070\times10^{-34}\,\mathrm{J\,Hz^{-1}}}\,\frac{3.203\times10^{-15}}{5.337\times10^{-15}}\\
&\qquad\times\exp\left(\frac{-2.177\times10^{-20}\,\mathrm{J}}{(1.380\,649\times10^{-23}\,\mathrm{J\,K^{-1}})(298.15\,\mathrm{K})}\right)\\
&= 1.881\times10^{10}\,\mathrm{s^{-1}}.
\end{aligned}$$

3. For the reverse rate constant, we have

$$\begin{aligned}
k_{21} &= \frac{k_BT}{h}\,\frac{\hat{q}^\ddagger}{\hat{q}_{\mathrm{M2}}}e^{-\Delta^\ddagger\epsilon/k_BT}\\
\Delta^\ddagger\epsilon &= \epsilon_{\mathrm{TS}}-\epsilon_{\mathrm{M2}}\\
&= -638.697\,887-(-638.702\,091)\,\mathrm{hartree}\\
&= 0.004\,204\,\mathrm{hartree}\\
&\equiv (0.004\,204\,\mathrm{hartree})(4.359\,745\times10^{-18}\,\mathrm{J})\\
&= 1.833\times10^{-20}\,\mathrm{J}\\
\therefore k_{21} &= \frac{(1.380\,649\times10^{-23}\,\mathrm{J\,K^{-1}})(298.15\,\mathrm{K})}{6.626\,070\times10^{-34}\,\mathrm{J\,Hz^{-1}}}\,\frac{3.203\times10^{-15}}{6.143\times10^{-15}}\\
&\qquad\times\exp\left(\frac{-1.833\times10^{-20}\,\mathrm{J}}{(1.380\,649\times10^{-23}\,\mathrm{J\,K^{-1}})(298.15\,\mathrm{K})}\right)\\
&= 3.773\times10^{10}\,\mathrm{s^{-1}}.
\end{aligned}$$

4. $K = k_{12}/k_{21} = 0.499$

5. The results of my IRC scan are shown in figure 1. The calculated energies along the IRC and their derivatives are shown in table 1.

   We need to convert the data to SI units. The reduced mass was taken from the log file

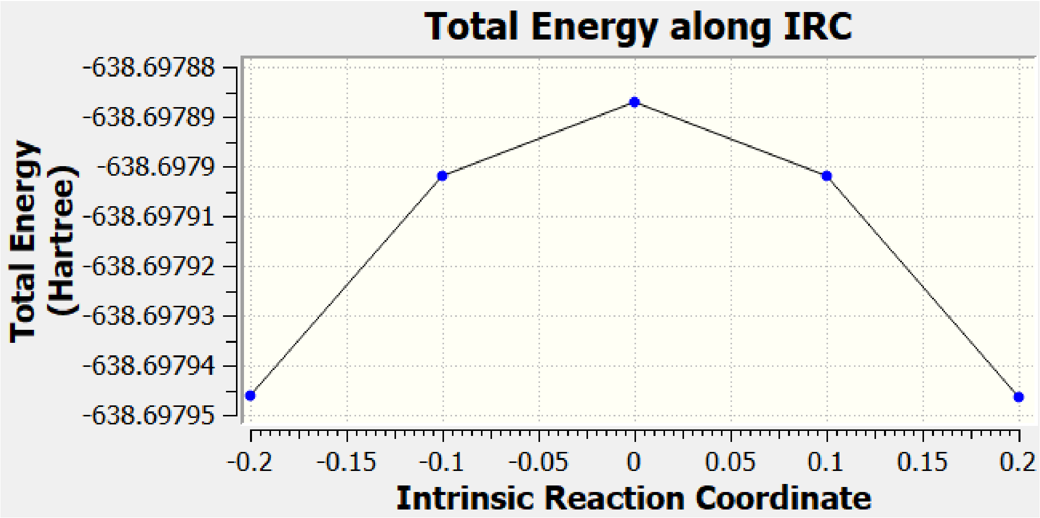


Figure 1: IRC scan about the M1 $\rightleftharpoons$ M2 transition state

of the transition-state calculation.

$$\begin{aligned}
V_2 &= \frac{(-0.002\,945\,\mathrm{hartree\ bohr^{-2}})(4.359\,745\times10^{-18}\,\mathrm{J\,hartree^{-1}})}{(5.291\,772\times10^{-11}\,\mathrm{m\ bohr^{-1}})^2}\\
&= -4.585\,\mathrm{J\,m^{-2}}\\
V_4 &= \frac{(-0.004\,218\,\mathrm{hartree\ bohr^{-4}})(4.359\,745\times10^{-18}\,\mathrm{J\,hartree^{-1}})}{(5.291\,772\times10^{-11}\,\mathrm{m\ bohr^{-1}})^4}\\
&= -2.345\times10^{21}\,\mathrm{J\,m^{-4}}.
\end{aligned}$$

As well,

$$\begin{aligned}
\mu_r &= (3.2953\,\mathrm{amu})(1.660\,539\times10^{-27}\,\mathrm{kg\,amu^{-1}})\\
&\equiv 5.4720\times10^{-27}\,\mathrm{kg}.\\
\kappa_{\text{tunnel}} &= 1-\frac{1}{24}\left(\frac{h}{k_BT}\right)^2 V_2-\frac{h^2}{96\mu_r k_BT}\frac{V_4}{V_2}\\
&= 1-\frac{1}{24}\left(\frac{6.626\,070\times10^{-34}\,\mathrm{J\,Hz^{-1}}}{(1.380\,649\times10^{-23}\,\mathrm{J\,K^{-1}})(298.15\,\mathrm{K})}\right)^2(-4.585\,\mathrm{J\,m^{-2}})\\
&\quad-\frac{(6.626\,070\times10^{-34}\,\mathrm{J\,Hz^{-1}})^2}{96(5.4720\times10^{-27}\,\mathrm{kg})(1.380\,649\times10^{-23}\,\mathrm{J\,K^{-1}})(298.15\,\mathrm{K})}\\
&\qquad\times\frac{-2.345\times10^{21}\,\mathrm{J\,m^{-4}}}{-4.585\,\mathrm{J\,m^{-2}}}\\
&= 1+4.950\times10^{-27}-0.1038=0.8962
\end{aligned}$$

6. Using the computational methods I used, I get a nonsensical result due to the sign of V_4. (κ_{tunnel} should be larger than 1.) The relatively small deviation from 1 does

suggest that tunneling is not particularly important for this system, but a much better set of calculations would have to be performed in order to verify this.

Bonus: If you think about writing the rate equation for (e.g.) the most stable conformation, you get

$$\frac{d[\mathrm{M1}]}{dt} = -k_{12}[\mathrm{M1}] - k_{12}[\mathrm{M1}] + k_{21}[\mathrm{M2}] + k_{21}[\mathrm{M3}].$$

There are *two* k_{12} terms, one for going from M1 to M2, and the other for going from M1 to M3. Defining the lumped variable [M23] = [M2] + [M3], we get

$$\begin{aligned}\frac{d[\mathrm{M1}]}{dt} &= -2k_{12}[\mathrm{M1}] + k_{21}\left([\mathrm{M2}] + [\mathrm{M3}]\right) \\ &= -k_{123}[\mathrm{M1}] + k_{21}[\mathrm{M23}],\end{aligned}$$

where $k_{123} = 2k_{12}$. Thus, k_{21} is unchanged, but the rate constant for going from M1 to the secondary minima is doubled.

You can also approach this from the TST formulae, but it's tricky. Take k_{12} for example:

$$k_{12} = \frac{k_B T}{h} \frac{\hat{q}^{\ddagger}}{\hat{q}_{\mathrm{M1}}} e^{-\Delta^{\ddagger}\epsilon/k_B T}.$$

When we lump together the two secondary minima, the two transition states also have to be lumped together. Thus, $q^{\ddagger}$ would double, and k_{12} would therefore also double. By a similar argument, k_{21} remains unchanged since both $q^{\ddagger}$ and q_{M2} double.