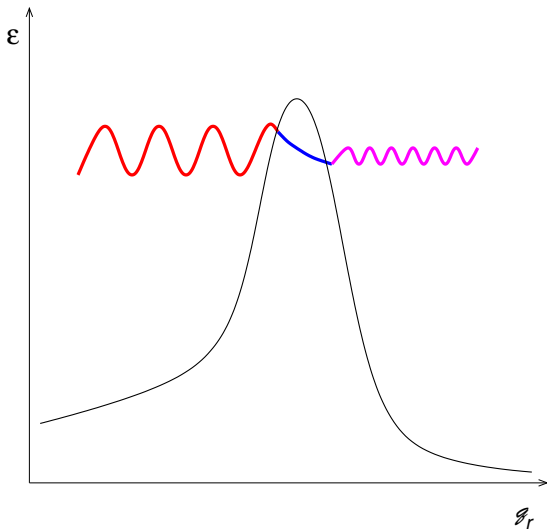


# Foundations of Chemical Kinetics Lecture 13: Tunneling corrections

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October 27, 2021

# Tunneling



# Tunneling

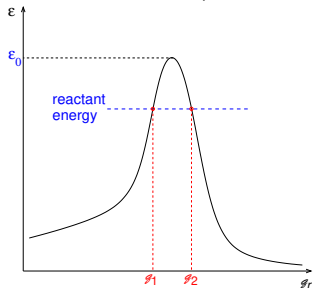
- Because we get extra crossings from reactant to product through the barrier, tunneling increases rate constants relative to values calculated without taking it into account.
- Tunneling probability:

$$P_{\text{tunnel}}(\epsilon) = \exp\left(-\frac{4\pi\sqrt{\mu}}{h} \int_{q_1}^{q_2} dq_r \sqrt{V_{\text{eff}}(q_r) - \epsilon}\right)$$

$(q_1, q_2)$  are the points where  $V_{\text{eff}}(q_r) = \epsilon$ .

# Tunneling

$$P_{\text{tunnel}}(\epsilon) = \exp\left(-\frac{4\pi\sqrt{\mu}}{h} \int_{q_1}^{q_2} dq_r \sqrt{V_{\text{eff}}(q_r) - \epsilon}\right)$$



## ■ $P_{\text{tunnel}}(\epsilon)$

- decreases with increasing difference between the height of the barrier and the energy of the reactants;
- decreases with increasing barrier width;
- decreases with increasing reduced mass (i.e. with the mass of whatever has to move to make the reaction happen).

## Tunneling correction

- The tunneling correction at temperature  $T$  is obtained by Boltzmann averaging  $P_{\text{tunnel}}(\epsilon)$ :

$$\kappa_{\text{tunnel}} = \int_0^{\infty} P_{\text{tunnel}}(\epsilon) \frac{\exp\left(-\frac{\epsilon - \epsilon_0}{k_B T}\right)}{k_B T} d\epsilon$$

where  $\epsilon_0$  is the energy at the top of the barrier.

- This factor multiplies a rate constant calculated without considering tunneling (e.g. in standard TST):

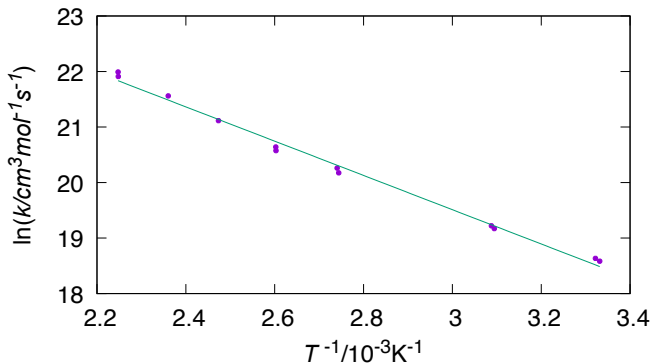
$$k = \kappa_{\text{tunnel}} k_{\text{TST}}$$

## Tunneling and Arrhenius plots

- At sufficiently low temperatures, only tunneling from the ground state occurs. (Why?)
- The rate constant therefore becomes independent of  $T$ .
- This results in curved Arrhenius plots.
- For reactions where tunneling is particularly important, curvature may show up at moderate temperatures because of the different temperature dependences of tunneling vs over-the-barrier events.

# Tunneling and Arrhenius plots

H + H<sub>2</sub> reaction



Data from Schulz and Le Roy, *J. Chem. Phys.* **42**, 3869 (1965)

## Wigner's formula

- In general, the tunneling correction has to be calculated numerically.
- Wigner has given an approximate formula valid for barriers that are neither too high nor too wide:

$$\kappa_{\text{tunnel}} = 1 - \frac{1}{24} \left( \frac{h}{k_B T} \right)^2 V_2 - \frac{h^2}{96 \mu_r k_B T} \frac{V_4}{V_2}$$

where  $V_i = \left. \frac{d^i V_{\text{eff}}(q_r)}{dq_r^i} \right|_{q_r(\text{TS})}$ ; usually, the coordinate system will be such that  $q_r(\text{TS}) = 0$ .

Note: at a saddle point,  $V_2 < 0$ .

- In order to evaluate the derivatives we need the potential energy along the reaction coordinate.



## Calculating the potential energy along the reaction coordinate in Gaussian

- The reaction coordinate is not uniquely defined.
- Gaussian can calculate Fukui's Intrinsic Reaction Coordinate (IRC), which is the steepest descent path, by default in mass-weighted coordinates, from the transition state to the reactants on one side, and to the products on the other.
- Gaussian needs to start this calculation from a transition state for which a frequency analysis has been done.
- We are going to return to our calculation for the  $\text{H} + \text{H}_2$  system.

# Calculating the potential energy along the IRC in Gaussian Preparation

- Open the .chk file for the transition state in GaussView.
- Open the Gaussian Calculation Setup dialog.
- In the Job Type tab, choose an IRC calculation, then enter the following:

Follow IRC: Both directions

Force Constants: Calculate Once

Check the Recalculate Force Constants  
Every nth Point box and choose  $n = 3$ .

# Calculating the potential energy along the IRC in Gaussian Preparation

- To speed things up, I used a modest basis set.
- Method:  $\omega$ B97X-D, unrestricted spin, aug-cc-pVTZ basis set

# Calculating the potential energy along the IRC in Gaussian Preparation

- We need to add an option to the Gaussian job that GaussView doesn't know about.

Because we need spatial derivatives, we need to use a Cartesian coordinate system.

Click on the `Edit` button at the bottom of the screen. In the editing session that opens up, you should see `irc=(calcfc,recalc=3)`. Change it to

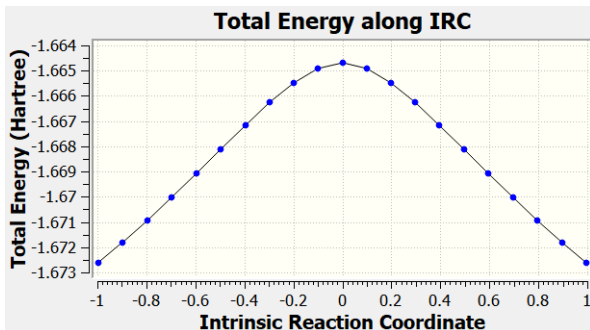
```
irc=(calcfc,recalc=3,Cartesian)
```

- Run the job. Spend a bit of time working on the essay for your Sociology class.

# Calculating the potential energy along the IRC in Gaussian

## Getting the data

- Once the job is done, open the .log file for your IRC calculation. Click on Results→IRC/Path.
- For the  $\text{H} + \text{H}_2$  calculation, I got something like this:



# Calculating the potential energy along the IRC in Gaussian

## Getting the data (continued)

- Save the data from this calculation to a text file.
- Now open the .log file **from your original transition state frequency calculation**. Write down the reduced mass corresponding to the negative frequency (i.e. the frequency associated with the reactive coordinate).

# Calculating the potential energy along the IRC in Gaussian

Getting the data (continued)

- The relevant part of the .log file looks like this in my calculation:

```

          1
        B2
Frequencies -- -1091.8084
Red. masses  --   1.0078
Frc consts   --   0.7078
IR Inten     --  193.0580
  Atom  AN      X      Y      Z
    1    1    0.00  0.00  0.82
    2    1    0.00  0.00 -0.41
    3    1    0.00  0.00 -0.41
```

# Calculating the tunneling correction

## Calculating the derivatives

- We need the 2nd and 4th derivatives of  $V_{\text{eff}}$  evaluated at the transition state along the IRC.
- Derivatives can be evaluated by central differences:

$$\left. \frac{df(x)}{dx} \right|_{x=x_i} \approx \frac{f_{i+1} - f_{i-1}}{x_{i+1} - x_{i-1}}$$

- If we use this same differencing scheme to take derivatives of the derivatives, we get second derivatives.
- Iterate for higher derivatives.



# Calculating the tunneling correction

## Calculating the derivatives

- The easiest way to calculate the derivatives is to import the energies along the IRC into a spreadsheet.
- Here are my results, with the columns renamed appropriately:

q	V <sub>eff</sub> /hartree	dV/dq	d <sup>2</sup> V/dq <sup>2</sup>	d <sup>3</sup> V/dq <sup>3</sup>	d <sup>4</sup> V/dq <sup>4</sup>
-0.99636	-1.672609441				
-0.89638	-1.671812427	0.0082884			
-0.7964	-1.670952092	0.008863593	0.00514158		
-0.69643	-1.670040151	0.009316459	0.003989112	-0.017133224	
-0.59645	-1.669089266	0.009661216	0.001715792	-0.029208193	-0.108620031
-0.49649	-1.668108488	0.009659514	-0.001850774	-0.038850713	-0.12206963
-0.39663	-1.667159102	0.009291394	-0.006047357	-0.053600147	-0.221288515
-0.29666	-1.666251788	0.008451071	-0.012561691	-0.083070797	-0.283845895
-0.19712	-1.665473029	0.006785211	-0.022620812	-0.110230242	-0.033960882
-0.09843	-1.664906756	0.003966947	-0.034412632	-0.089802862	0.558235978
0	-1.664691065	1.79305E-06	-0.040322752	-0.000190766	0.913170253
0.09833	-1.664906403	-0.003966958	-0.034450167	0.089872517	0.56155729
0.19699	-1.665472516	-0.006784545	-0.022618765	0.110430405	-0.034488053
0.29653	-1.6662511	-0.008449997	-0.012562861	0.083036985	-0.284901292
0.3965	-1.667158375	-0.009290962	-0.006052056	0.053589748	-0.221057079
0.49636	-1.668107713	-0.009659379	-0.001854022	0.038863148	-0.121961155
0.59632	-1.669088512	-0.009661432	0.001713578	0.02921947	-0.108647362
0.6963	-1.67003942	-0.009316767	0.003988119	0.017140195	
0.79627	-1.670951399	-0.008864008	0.00514076		
0.89625	-1.671811778	-0.008288872			
0.99623	-1.672608842				

## Calculating the tunneling correction

### Values and units

- Internally, Gaussian uses bohr for lengths and hartree for energies.
- It usually converts to more convenient length units, but not in an IRC calculation.
- $V_2 = -0.040\,323 \text{ hartree bohr}^{-2}$ 
  - Conversion factor from hartree to joules:  $4.359\,745 \times 10^{-18}$
  - Conversion factor from bohr to m:  $5.291\,772 \times 10^{-11}$
- 

$$\begin{aligned}
 V_2 &= \frac{(-0.040\,323 \text{ hartree bohr}^{-2})(4.359\,745 \times 10^{-18} \text{ J hartree}^{-1})}{(5.291\,772 \times 10^{-11} \text{ m bohr}^{-1})^2} \\
 &= -62.779 \text{ J m}^{-2}
 \end{aligned}$$

- Similarly,  $V_4 = 0.913\,17 \text{ hartree bohr}^{-4} \equiv 5.0770 \times 10^{23} \text{ J m}^{-4}$ .
- $\mu_r = 1.0078 \text{ amu} \equiv 1.6735 \times 10^{-27} \text{ kg}$

## Calculating the tunneling correction

Now to calculate the tunneling correction at 1000 K:

$$\begin{aligned}
 \kappa_{\text{tunnel}} &= 1 - \frac{1}{24} \left( \frac{h}{k_B T} \right)^2 V_2 - \frac{h^2}{96 \mu_r k_B T} \frac{V_4}{V_2} \\
 &= 1 - \frac{1}{24} \left( \frac{6.626\,070 \times 10^{-34} \text{ J Hz}^{-1}}{(1.380\,649 \times 10^{-23} \text{ J K}^{-1})(1000 \text{ K})} \right)^2 (-62.779 \text{ J m}^{-2}) \\
 &\quad - \frac{(6.626\,070 \times 10^{-34} \text{ J Hz}^{-1})^2}{96(1.6735 \times 10^{-27} \text{ kg})(1.380\,649 \times 10^{-23} \text{ J K}^{-1})(1000 \text{ K})} \\
 &\quad \times \frac{5.0770 \times 10^{23} \text{ J m}^{-4}}{-62.779 \text{ J m}^{-2}} \\
 &= 1 + 6.0248 \times 10^{-27} + 1.6008 = 2.6.
 \end{aligned}$$

## Calculating the tunneling correction (continued)

We had previously calculated (using a better basis set)

$k_{\text{TST}} = 1.11 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ , so

$$k = \kappa_{\text{tunnel}} k_{\text{TST}} \approx 2.9 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

which is reasonably close to the experimental value of  $(2.1 \pm 0.6) \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ .