

Foundations of Chemical Kinetics

Lecture 7: Introduction to potential energy surfaces

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Born-Oppenheimer revisited

- In an earlier lecture, we discussed the Born-Oppenheimer approximation which allows us to compute an effective potential (from which we get effective forces) acting on the nuclei as a function of nuclear positions.
- Types of interactions:
 - Bonded strong, roughly parabolic potentials, at least near the bottom of a potential well
 - Nonbonded \Rightarrow intermolecular forces
 - A variety of functional forms
 - May depend on both the distance and relative orientations of the molecules

Internal degrees of freedom

- A molecule with N atoms has $3N$ degrees of freedom.
 - 3 translational modes
 - 3 rotational modes for a nonlinear molecule
 - 2 rotational modes for a linear molecule
- The number of internal (vibrational) degrees of freedom is therefore
 - $3N - 6$ for a nonlinear molecule
 - $3N - 5$ for a linear molecule
- Once a linear molecule bends, it is no longer linear, so even a linear molecule can have its internal coordinates described by $3N - 6$ coordinates.

Potential energy surfaces for chemical reactions

- Consider a three-atom $A + BC \rightarrow AB + C$ reaction.
- The potential energy surface (PES) is a function of $3N - 6 = 3$ coordinates, which can be taken to be R_{AB} , R_{BC} and the A-B-C angle.
- This is hard to visualize.
- Solution: Vary (e.g.) R_{AB} and R_{BC} at fixed angle.
- Commonly, we look at a collinear collision, but other angles are possible.

The $\text{H} + \text{H}_2$ reaction

Computing the PES for a collinear reaction

- Computationally, the simplest $\text{A} + \text{BC}$ reaction is $\text{H} + \text{H}_2$.
- We can compute the PES of this reaction at fixed angle relatively easily in Gaussian.
We start with a collinear reaction.
- In GaussView, select a simple H atom in the Element fragment tool. Place three H atoms roughly in a line.
- Use the Builder to create an initial geometry with a “bond angle” of 180° and the atoms 0.6 \AA apart.

The $\text{H} + \text{H}_2$ reaction

Computing the PES for a collinear reaction

- We're going to use a slightly different technique to set up a scan due to problems with the Redundant Coordinates tool for linear structures. Click on `Tools`→`Atom List`.
- If you don't see columns with titles `Opt 1`, `2` and `3`, click on the `'0'` (`Show Optimization Flag Column`) button.
- Rows `2` and `3` should show the “bond lengths” in your initial structure. For each of these, select `Rxn/Scan` from the `Opt 1` column.
- Row `3` should additionally show a bond angle of 180° . Set `Opt 2` to `No`. This will keep this angle fixed during the optimization.

The $\text{H} + \text{H}_2$ reaction

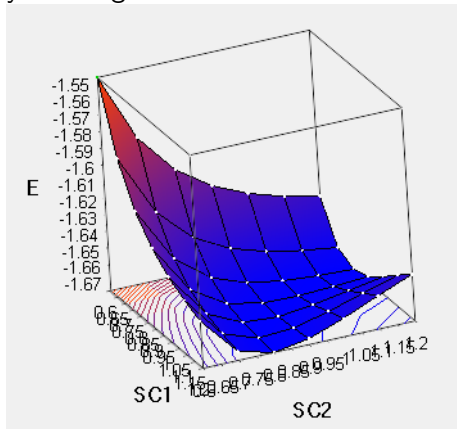
Computing the PES for a collinear reaction (continued)

- Now click on Calculate→Gaussian Calculation Setup.
- In the Job Type tab, select Scan and Rigid.
- We will start with a coarse scan, starting each atomic coordinate at 0.6 \AA and taking 6 steps of 0.1 \AA each. For Scan Coordinate 1, set the number of steps, step size and start value accordingly. Repeat for Scan Coordinate 2.
- Choose DFT, Unrestricted, B3LYP and a 6-31G++(d,p) basis set.
 - The 'd' doesn't do anything, but Gaussian gets confused if you don't put it in. (Why doesn't 'd' have any effect here?)
- Submit the job.

The $\text{H} + \text{H}_2$ reaction

Computing the PES for a collinear reaction (continued)

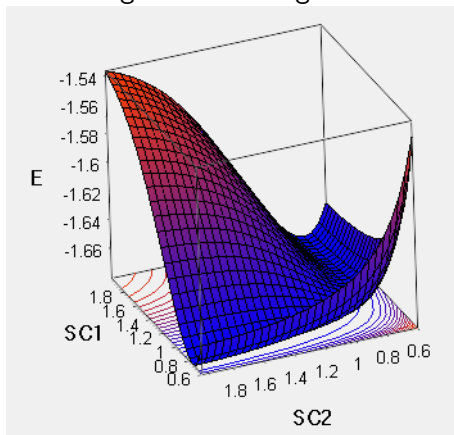
- Open the .log file (not the .chk file).
- Click and drag to rotate the image. Right-click and drag lets you straighten it out. Here's what we find:



The $\text{H} + \text{H}_2$ reaction

Computing the PES for a collinear reaction (continued)

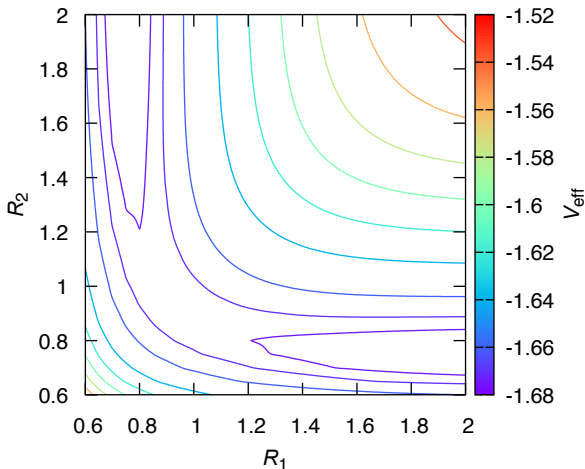
- And here is a version calculated with many more points and a wider range of bond lengths:



The $\text{H} + \text{H}_2$ reaction

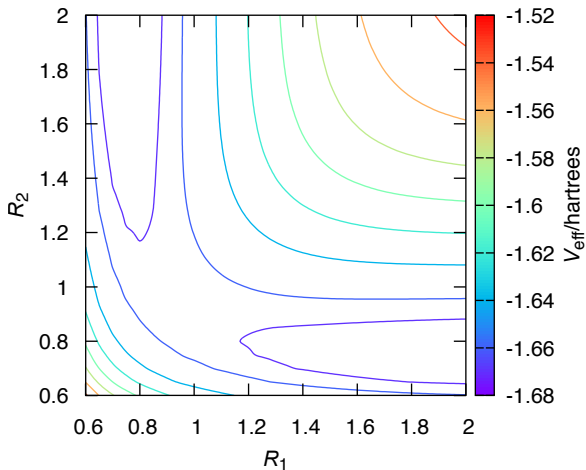
Computing the PES for a collinear reaction (continued)

- The PES is often more easily visualized as a contour plot:



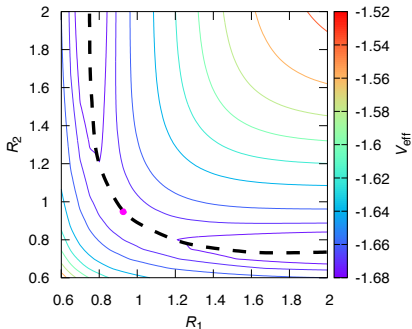
The $\text{H} + \text{H}_2$ reaction

PES at 135°



Reaction coordinate

- We can construct a **reaction coordinate** that measures the progress along the lowest-energy reaction path from reactants to products.
- The maximum point along this path is a saddle point on the PES (downhill in either direction along the reaction coordinate, uphill in all other directions).



Reaction coordinate (continued)

- The classical sketches of reaction profiles correspond to a path following the reaction coordinate.
- But the reaction coordinate **is not in general a simple Cartesian coordinate.**

Reaction coordinate (continued)

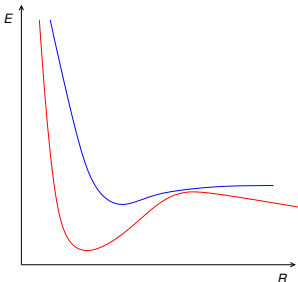
- We have $3N - 6$ internal coordinates, of which one is the reaction coordinate, so there are $3N - 7$ vibrational modes.
- For the vibrational modes, roughly speaking, $k_i = \partial^2 V / \partial q_i^2 > 0$, where q_i is the corresponding normal-mode coordinate, and $\omega_i = \sqrt{k_i / \mu_i}$, where μ_i is the generalized reduced mass associated with a mode.
- For the reaction coordinate at the transition state, $\partial^2 V / \partial q_i^2 < 0$ so the corresponding frequency is imaginary.

Why do we care about the PES?

- Shows us the lowest energy (most probable) path from reactants to products, including the transition state
- Can calculate classical or quantum trajectories on PES
 - Understanding changes in geometry and/or bonding during reaction
 - Can get a rate constant by collecting statistics from a very large number of trajectories
 - ⇒ direct computational counterpart of reactive scattering theory

Avoided crossings

- In diatomics, potential energy curves for electronic states with the same orbital symmetry and spin do not cross.



- In polyatomics, the potential energy curves can touch, but not cross.
- In the region of these avoided crossings, systems can cross from one electronic state to another.
Reactions in systems with avoided crossings can involve multiple PESs.