

Problem 1: Finite Difference Approximation

Derive a finite difference approximation to the Schrödinger equation for a particle moving in a potential $V(x)$

$$-\frac{\hbar^2}{2m} \frac{d^2}{dx^2} \psi(x) + V(x)\psi(x) = E\psi(x)$$

that can be used to calculate iteratively the wavefunction over all space if the value of the energy is known as well as the value of the wave function at two adjacent discretization points on the x-axis.

Problem 2: Vibrational (normal) modes

Find the vibrational frequency and atomic displacement vectors for the stretching modes of the CO_2 molecule by doing an eigenvalue calculation of the motion of the atoms along the molecular axis (i.e. a 1-dimensional approximation which does not include the bends). The interaction between each of the O-atoms and the central C-atom can be approximated by a Morse potential function

$$V(r) = D \left(e^{-2\beta(r-r_b)} - 2e^{-\beta(r-r_b)} \right)$$

with parameters taken to represent a C-O bond. A rough approximation for the well depth and bond length can be obtained from the properties of the CO molecule, which is found to have a bond energy of 11 eV and bond length of 1.1 Ångström. Adjust the value of the parameter β to get a best fit of the measured vibrational frequencies of CO_2 which are: 2349 cm^{-1} , 1333 cm^{-1} and 667 cm^{-1} . Note that one of these values refers to the two bending modes (which one?) and is not relevant for this discussion.

Problem 3: Classical trajectories on a 2-dimensional PES

Use the contour plot of the LEPS potential energy surface for a tri-atomic molecule in one-dimension shown below. Assume r_{AB} is on the y-axis and r_{BC} on the x-axis, and the unit length of the axes is one Ångström. (Compare with figure 9.25 in the text book by Laidler et al. and the relevant text in section 9.11).

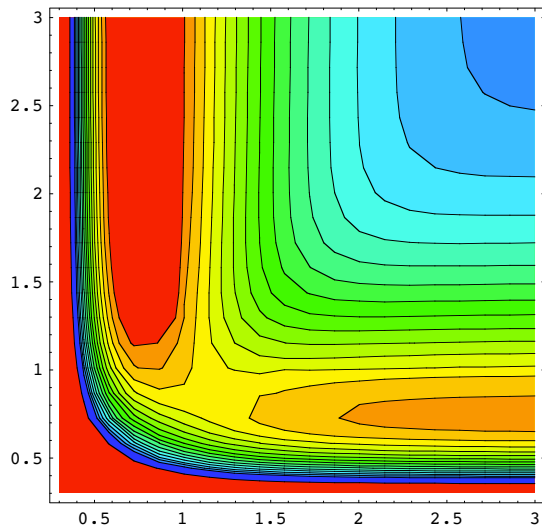


Figure 1: *Contour plot of a LEPS potential surface for three atoms placed along a line where each atom can only form one bond.*

Sketch classical trajectories for the following situations (assuming the total energy of the molecule is constant, i.e. no connection with a heat bath):

- (a) Atom A is initially 3 Å away from the center of a BC molecule and is moving towards the molecule, collides with it, and an exchange reaction occurs. The BC molecule is initially vibrating with an amplitude of 0.1 Å.
- (b) Same as part (a) except that an exchange reaction does NOT occur.
- (c) Which degree of freedom is more efficient in promoting an exchange reaction, the translational energy of the A-atom or the vibrational energy of the BC-molecule?

Problem 4: Transition state theory (TST)

- (a) What are the four basic assumptions of TST? What should the shape of the potential energy surface be like in order for TST to give a good approximation to the rate constant of a transition?
- (b) A hydrogen atom adsorbed on the surface of a metal crystal can diffuse by hopping from one binding site to another. The atom can be considered to be a particle moving on a periodic potential surface (PES) while the metal atoms can be taken to be stationary.

This is a good first approximation because the metal atoms are so much heavier than the hydrogen atom. For a hydrogen atom on the (001) surface of an FCC metal, the potential energy of the hydrogen atom can be approximated by the function

$$V(x, y, z) = V_s \left(e^{-\cos(2\pi x/b) - \cos(2\pi y/b) - 2\alpha z} - 2e^{-\alpha z} \right)$$

where V_s is 0.2 eV, b is 3 Å and $\alpha = 2 \text{ Å}^{-1}$. The normal to the crystal surface lies along the z-axis.

(Note on units: It is convenient to use the following, approximate relationship $\sqrt{eV/(amu \text{ Å}^2)} = 1.0 \times 10^{14} \text{ sec}^{-1}$).

Evaluate the rate constant for diffusion hops using the harmonic approximation to TST. Here are the steps you need to take in order to do that (see lecture notes):

(1) Identify the minima and saddle points on the potential energy surface. You should do this first of all by making a contour plot of the potential surface in the plane of the surface (x,y), using for example Matlab. By inspecting the plot, you can get the x and y coordinates of the minima and the saddle points. Then, you need to minimize the energy with respect to z given these values of x and y.

(2) Differentiate the potential function with respect to x, y and z and show that each one of the derivatives is zero at a minimum and at a saddle point. This verifies that you have found the right coordinates. The activation energy is obtained from the difference in the potential energy at the saddle point and at the minimum.

(3) In order to evaluate the prefactor of the rate constant, do a Taylor expansion of the potential energy function up to second order at a minimum and at a saddle point. You can use Matlab to do that. Get the frequency of each vibrational mode. Note that one of the modes at the saddle point corresponds to negative curvature (imaginary frequency). The ratio of products of the vibrational frequencies gives the prefactor (see lecture notes).

(c) What is the average length of time in between diffusion hops at room temperature, at 400 K and at 500 K? Notice the dramatic change as the temperature is increased.