Imperial College
London

Second Year Physical Chemistry Laboratory

DEPARTMENT OF CHEMISTRY

CP3:

Molecular Reaction Dynamics: Applications to Triatomic systems

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A template/guide to the write-up required and points for discussion are included at the end of the exercise. A (proforma)data sheet is attached. You might find it convenient to enter data and make sketches) in the data sheet at points indicated in the text by **==> data sheet**

Background reading: *Atkins and de Paula* Physical Chemistry, Chapter 25 (sections 25.5) and Chapter 27 Molecular Reaction Dynamic, sections 27.4, 27.5 and 27.6-27.8 are important , see also Chapter 28 in Physical Chemistry, A Molecular Approach, Mc Quarrie and Simon pub University Science Books

Information on trajectory computations: *F. Jensen* Introduction to Computational Chemistry (Wiley 1999) pp 383,

D.M.Hirst Potential Energy Surfaces (Taylor & Francis, 1985)

Objectives.

To use Molecular Dynamics to study the reactivity of triatomic systems. Effects that will be studied include

a) re-crossing the transition state region

b) isotope effects

c) special effects for heavy-light-heavy reactions (entropy locked intermediates)

and

d) vibrational energy release in an exothermic reaction.

Relevance to other courses: Molecular Interactions and Dynamics Course (First Year Alan Taylor) and the Statistical Thermodynamics Course (Second Year Fernando Bresme) and the Chemical Dynamics Course (David Klug Third Year).

Note : all distances and velocities are in atomic units for this exercise

1) Theory

The electrons in a molecular system move very rapidly compared with the speed of nuclear motion in most problems of chemical reactivity. Consequently it is possible to understand much of chemical reactivity using the classical Newtonian mechanics for the nuclei.

$$\mathbf{m}\,\ddot{\mathbf{r}} = -\frac{\mathbf{dV(r)}}{\mathbf{dx}}$$

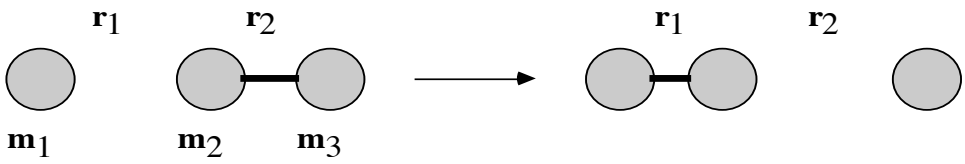
$\ddot{\mathbf{r}}$ = **acceleration a** $\qquad -\frac{\mathbf{dV(r)}}{\mathbf{dx}}$ = **force F**

The dots indicate time derivatives, **m** is a column vector that contains the masses of the nuclei, **r** is a position vector that contains the cartesian co-ordinates of the atoms and **V(r)** is the potential energy function. (for a diatomic molecule **V(r)** is just the usual 1 dimensional potential energy curve that expresses the change in the energy as the two nuclei are displaced from their equilibrium positions by changing the interatomic distance). Molecular Dynamics *simulation* of the system involves solving these equations expressing the changes in the atomic co-ordinates etc at a time increment Δt

$$\mathbf{r_i}(\mathbf{t} + \Delta\mathbf{t}) = \mathbf{r_i}(\mathbf{t}) + \dot{\mathbf{r}}_\mathbf{i}(\mathbf{t})\,\Delta\mathbf{t}$$
$$\dot{\mathbf{r}}_\mathbf{i}(\mathbf{t} + \Delta\mathbf{t}) = \dot{\mathbf{r}}_\mathbf{i}(\mathbf{t}) + \ddot{\mathbf{r}}_\mathbf{i}(\mathbf{t})\,\Delta\mathbf{t}$$

The time step used is typically .1 fs (femtosecond = 10^{-15} sec). In this way one obtains a *classical trajectory* **r(t)** that describes how the system evolves in time. Such simulations have many applications in chemistry and biology since by computing trajectories sufficiently long times one can obtain the time average of any property. In the computations we will perform, it is convenient to use internal co-ordinates (bond lengths and angles) rather than cartesian co-ordinates of the atoms. The form of the "F=ma" equation changes slightly but this is a detail that does not need to concern us.

In this exercise we will apply this method to study the reactivity of atom diatom collisions.



For a linear triatomic exchange reaction, the potential function **V** is a function of only two parameters $\mathbf{r_1}$ and $\mathbf{r_2}$. Thus we can plot the potential energy as a contour plot of $\mathbf{V}(\mathbf{r_1},\mathbf{r_2})$ versus $\mathbf{r_1}$ and $\mathbf{r_2}$. A trajectory $\{\mathbf{r_1}(t)\ \mathbf{r_2}(t)\}$ can then be drawn on this potential. One obtains a figure of the form shown below.

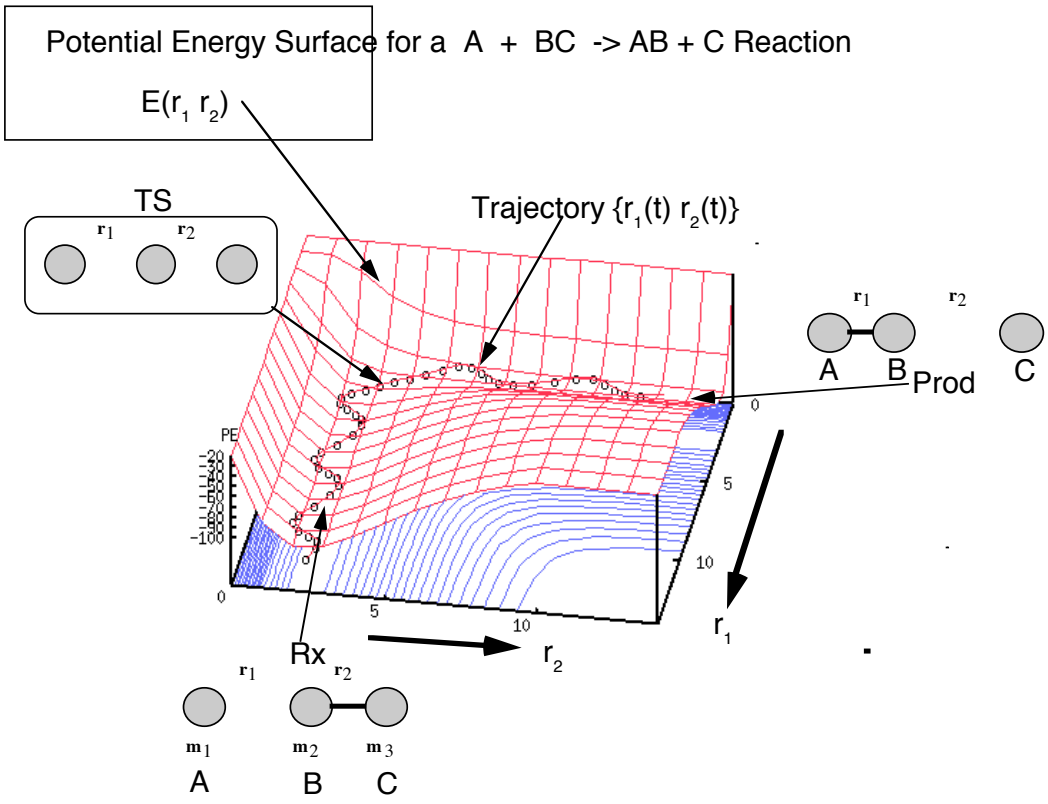


Figure 1 An example of a reactive trajectory for H + H2 potential surface

In this sketch, the reactants ($\mathbf{r_1}$ large $\mathbf{r_2}$ small), a transition structure where $\mathbf{r_1}$=$\mathbf{r_2}$ and the products ($\mathbf{r_1}$ small $\mathbf{r_2}$ large) are indicated in the boxes. A *reactive* trajectory that passes through the *transition structure* is shown as a wavy line. (The transition structure is a saddle point in the potential energy surface). Notice that the trajectory shown involves vibration in $\mathbf{r_2}$ as the interfragment distance $\mathbf{r_1}$ is *decreased* in the *entrance* channel (at the top left of the figure) and vibration in

$\mathbf{r_1}$ as the interfragment distance $\mathbf{r_2}$ is *increased* in the *exit* channel (at the bottom right of the figure). An unreactive trajectory would bounce off the barrier and regenerate the reactants.

For a given potential surface, The outcome of a dynamics simulation (i.e. the positions $\mathbf{r_1}(t)$ $\mathbf{r_2}(t)$ and the momenta $\mathbf{p_1}(t)$ $\mathbf{p_2}(t)$ $\mathbf{p_i} = m\mathbf{v_i}$) at some time t are determined by the initial conditions at time t=0 (i.e. $\mathbf{r_1}(0)$ $\mathbf{r_2}(0)$ and the momenta $\mathbf{p_1}(0)$ $\mathbf{p_2}(0)$. Only certain initial conditions will lead to a trajectory that passes via the transition structure to the products even if one has enough energy to surmount the barrier.

In the program you will use, you will run trajectories on several potential surfaces for a variety of input conditions. You will be able to *animate* the trajectory on the potential surface and examine the distribution of vibrational and translational energy in the products. As a demonstration you will study the potential surface for $H + H_2$ to illustrate the principles and to learn how to use the main features of the program. Then you will experiment with some more subtle examples.

EXERCISE 1 $H + H_2$ potential surface

This example is essentially a demonstration. Thus the instructions are rather verbose. The objective is to illustrate the various features of the program and to establish some important fundamentals.

TO START THE PROGRAM SEE THE ATTACHED INSTRUCTIONS

a) Viewing the potential surface

• Start up the program by typing **triatomics.** You will see the main menu on the screen. Various options and sub-menus are available by typing the corresponding menu number. The triatomic that is currently being studied will be shown at the bottom of the screen together with initial conditions for the current trajectory.

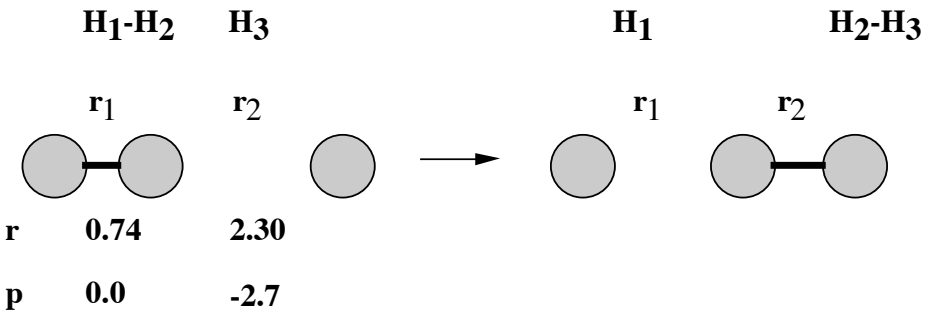
• View the $H + H_2$ surface by typing **1**. A new window will open up showing the potential surface as an *elevated* surface. You will also see that a new menu has appeared (**POTENTIAL ENERGY SURFACE** menu) that allows you to view the surface in many ways.

• **to change the view** a)**click** on the menu window b)type the **return** or enter key (the view of the potential surface will vanish) then c) type the menu entry for the new view desired. For example type **3** to view the surface from the exit channel. Type **7 Top View** to see a contour representation. Then enter **9** to return to the original view.

• enter **99** to return to the main menu when you are finished.

b)Run a reactive trajectory.

The default settings of the positions and momenta are initialised to produce a *reactive trajectory*.



To run this proceed as follows

• be sure you are in the main menu. Observe the initial conditions that are shown in the menu ($\mathbf{r_1}(0) = .74$ $\mathbf{r_2}(0) = 2.30$ and the momenta $\mathbf{p_1}(0)=0$ $\mathbf{p_2}(0) = -2.7$). A *negative* value of the momentum corresponds to a velocity that *decreases* the interatomic distance. Thus in this case we are starting the trajectory by giving the system some velocity in the direction that decreases $\mathbf{r_2}$.

• enter **2** to run the trajectory.

• enter **3** to select the menu (**ANALYSE TRAJECTORY RESULTS**). Various options can be selected to view various properties such as the energy and geometry as a function of time. It is suggested that you experiment with most of these and attempt to understand the results.

• To animate the trajectory on the potential energy surface enter **1**. (You will view the potential surface from whatever orientation was selected previously from the **POTENTIAL ENERGY SURFACE** menu) You should see that the system executes a few vibrations in the *entrance* channel before crossing the transition state. Notice that in the exit channel the system is vibrationally excited. The most important point to observe in conservation of energy: t*he system will always oscillate between energy contours with the same value. (see figure 1)*

• **to return to a menu at any time when a graphics window is displayed proceed as follows** a)**click** on the menu window (you may need to move the graphics window with the mouse) b)type the **return** or enter key (the graphics window will vanish) then c) type the next menu entry.

• return to the ANALYSE TRAJECTORY RESULTS menu.

• To animate the geometry enter 2. You will see that initially r_2 decreases as H_3 approaches H_1-H_2, then after the transition state, H_1 leaves and H_2-H_3 is formed in a vibrationally excited state.

•This same information can be displayed in a different form by selecting menu item 5. In this graphical display the values of $r_1(t)$ $r_2(t)$ are given (Y axis) against time t (X axis). Notice that r_2 decreases from the original value of 2.3. during the first .38 time units, then it has an oscillatory behaviour for the remainder of the trajectory corresponding to H_2-H_3 vibration. In contrast r_1 has a slight oscillatory behaviour initially, then after the transition state, it grows in value as H_1 leaves. Notice that $r_1(t) = r_2(t)$ at .= .38. This is effectively the transition state.

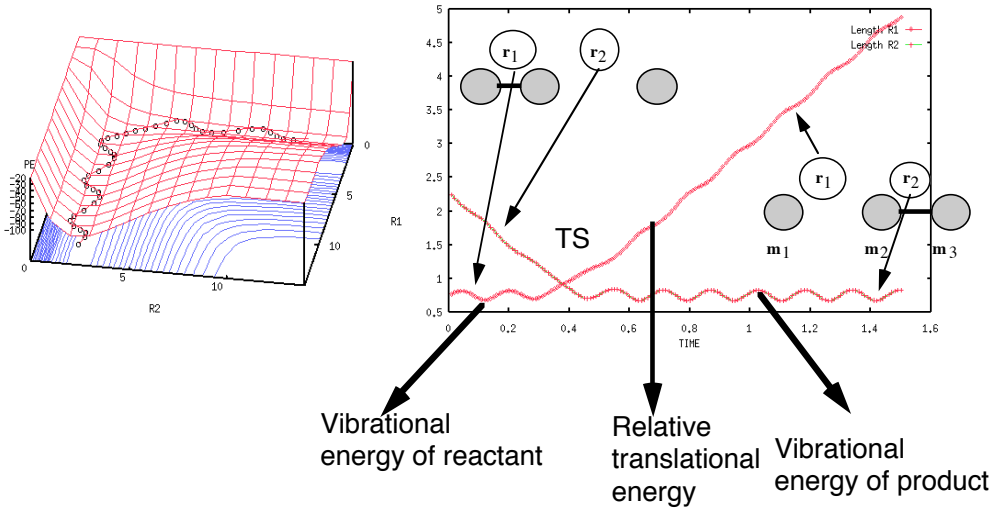
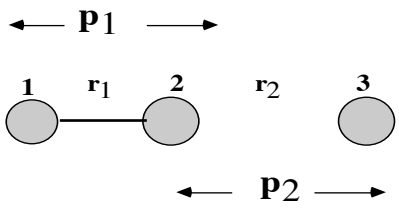


Figure 2 r1(t) r2(t) are given (Y axis) against time t (X axis)

• Menu item **3** will display the potential energy as a function of time. It will show an oscillatory behaviour rising in energy until the transition state is reached. The potential energy then falls as the trajectory moves into the exit channel. The energy is continually switching from potential energy to kinetic energy during the trajectory. At the turning point of a trajectory one is at the maxima of the oscillations. At the bottom of the trough of the oscillations the potential energy is low and the molecule is moving faster so the energy has gone into kinetic energy. You can see this using menu item **4** which displays the kinetic energy. In this case the kinetic energy reaches its minimum value at the transition state (i.e. the system is moving slowly)

• Finally the momenta $\mathbf{p_1}(t)$ $\mathbf{p_2}(t)$ ($\mathbf{p_i} = m\mathbf{v_i}$), can be displayed using menu item **6**. This result is not easy to interpret because the momenta correspond to bond stretching displacements $\mathbf{r_1}$ $\mathbf{r_2}$ as illustrated below.



Thus $\mathbf{p_1}$ is the momentum in the coordinate $\mathbf{r_1}$. Notice that the momentum in the atom 2 results from both momenta $\mathbf{p_1}$ and $\mathbf{p_2}$. Thus if we want to collide atom 3 with 1-2 (by giving some $\mathbf{p_2}$) in such a way that the diatom 1-2 does not vibrate,

then we must give some momentum in $\mathbf{p_1}$ as well. Following the momentum distribution from the transition state provides some insight as we now discuss.

The important observations are as follows. initially $\mathbf{p_1}(0)=0$ and $\mathbf{p_2}(0) = -2.7$. At the beginning of the trajectory $\mathbf{p_2}(t)$ decreases and $\mathbf{p_1}(t)$ takes on an oscillatory behaviour. $\mathbf{p_1}(t)$ oscillates because the initial momentum in $\mathbf{p_2}$ also forces $\mathbf{r_1}$ to change as is evident from the picture above. After the transition state at t=.38, $\mathbf{p_1}(t)$ rises rapidly and remains constant (corresponding to translation) as $\mathbf{r_1}$ becomes large as H_1 leaves. In contrast $\mathbf{p_2}$ initially corresponds to translation. After the transition state $\mathbf{p_2}$ oscillates (corresponding to vibration).

c) Dynamics from the transition state region

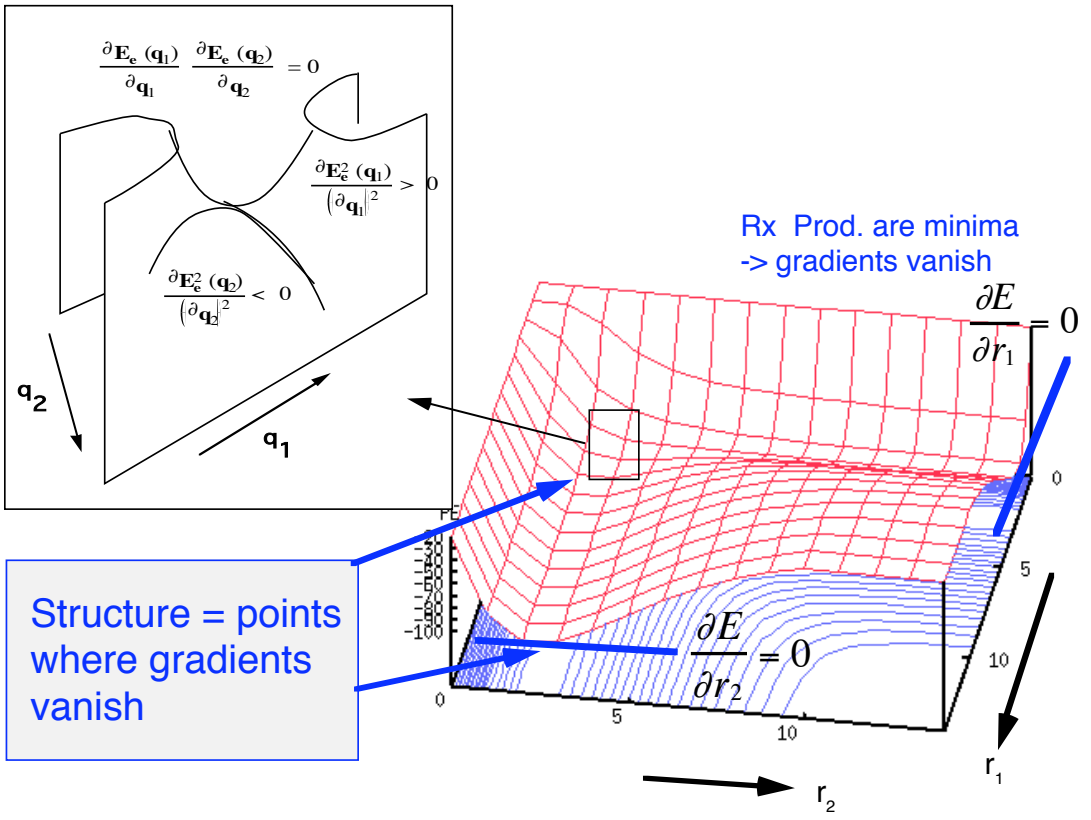


Figure 3 Gradients at the TS region

The *transition state* is defined *high point* on the l*owest energy path* between the reactants and the products. It has the special property that at this point $dV(\mathbf{r})/d\mathbf{r}$ is zero. Consequently, if one starts a trajectory exactly at the transition state with no initial momentum it will remain there for ever. If one changes the geometry by a

small amount in the direction of the products it will roll towards the products (and similarly for the reactants). One way of locating the transition state is to start trajectories near the transition state and see whether they "roll" towards the reactants or products. The *reaction path* (minimum energy path **mep**) is a very special trajectory that corresponds to infinitely slow motion (i.e. the velocity always zero). Once the transition state has been located one may run the very special trajectory that corresponds to the **mep**.

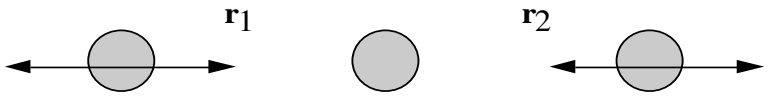
Since the $H + H_2$ surface is symmetric, the transition state must have $\mathbf{r_1} = \mathbf{r_2}$. If we start a trajectory on the ridge $\mathbf{r_1} = \mathbf{r_2}$ there is no gradient in the direction at right angles to the ridge, thus the trajectory will oscillate on the ridge and never fall off. As we will see, this fact can be use to locate the TS geometry. If we start a trajectory at $\mathbf{r_1} = \mathbf{r_{ts}}+\delta$ $\mathbf{r_2} = \mathbf{r_{ts}}$ the trajectory "falls off" $\mathbf{r_1} = \mathbf{r_2}$ ridge. We begin by running trajectories from near the TS geometry.

i) trajectories from $\mathbf{r_1} = \mathbf{r_2}$

• Be sure you are in the **main menu** then select menu item **4 (Change Parameters)**

•First set the momenta to exactly 0. Select item **2** (Change Initial Momentum). You will be prompted to type in values of the momenta corresponding to $\mathbf{r_1}$, $\mathbf{r_2}$. **You should supply exactly 0.0 here.**

• Then select item **1** (**Change Initial Geometry**). You will be prompted to type in values of $\mathbf{r_1}$, $\mathbf{r_2}$. You should supply one choice of values of $\mathbf{r_1}$ and $\mathbf{r_2}$ that are exactly equal in the region of .85 to .95. Then return to the main menu and run the trajectory (menu item **2**). Following this select **3** (**Analyse results of trajectory**). If you select **2** (**Animate Geometry**) you will see that the system undergoes a periodic symmetric vibration of the form:



• now select **5** (**Graph : Geometry versus Time**). You will see that the plots for $\mathbf{r_1}$ and $\mathbf{r_2}$ are superimposed (because they are oscillating exactly in phase. The geometry about which they are oscillating is the transition state geometry.

Determine this value of $\mathbf{r_1} = \mathbf{r_2}$ as accurately as you can from the graph. We shall refer to this value as $\mathbf{r_{ts}}$. ***==> data sheet***

• return to the **main** menu.

ii) trajectories from $\mathbf{r_1} = \mathbf{r_{ts}}+\delta$ $\mathbf{r_2} = \mathbf{r_{ts}}$

• Now we will run trajectories in the forward and reverse directions from $\mathbf{r_1} = \mathbf{r_2} = \mathbf{r_{ts}}$ with $\mathbf{p_1} = \mathbf{p_2} = 0$. This can be accomplished by running trajectories with $\mathbf{r_1} = \mathbf{r_{ts}}$ $\mathbf{r_2} = \mathbf{r_{ts}}+.01$ (this should terminate at $\mathbf{r_2} > 2.0$ with $\mathbf{r_1}$ oscillating i.e. at $\mathbf{H_1}$-$\mathbf{H_2}$ + $\mathbf{H_3}$). (You might convince yourself that a trajectory with $\mathbf{r_1} = \mathbf{r_{ts}}+.01$ $\mathbf{r_2} = \mathbf{r_{ts}}$ will give similar results terminating at $\mathbf{r_1} > 2.0$ with $\mathbf{r_2}$ oscillating ie at $\mathbf{H_1}$+ $\mathbf{H_2}$- $\mathbf{H_3}$). You will need to use the **4 Change Parameters option** (to change the geometry) from the main menu, then **2 Run Trajectory**, then **3 Analyse Results of Trajectory**. For the last operation, it is most instructive to use the **1 Animate Trajectory on PES** option.

• Finally, use **6 GRAPH: MOMENTA VS TIME** and **5 GEOMETRY VS TIME** and note the final values of the positions $\mathbf{r_1}(t)$ $\mathbf{r_2}(t)$ and the average momenta $\mathbf{p_1}(t)$ $\mathbf{p_2}(t)$ at large t for later use. ***==> data sheet***

Consider the results of the trajectory with $\mathbf{r_1} = \mathbf{r_{ts}}$ $\mathbf{r_2} = \mathbf{r_{ts}}+.01$ which terminated at $\mathbf{r_2} > 2.0$ with $\mathbf{r_1}$ oscillating i.e. at $\mathbf{H_1}$-$\mathbf{H_2}$ + $\mathbf{H_3}$ Thus asymptotically ,the $\mathbf{r_1}$ oscillates about the $\mathbf{H_1}$-$\mathbf{H_2}$ equilibrium bond length (.74) as $\mathbf{r_2}$ became large. The momentum $\mathbf{p_1}$ oscillates around 1.25 (i.e. between .8 and 1.5) while $\mathbf{p_2}$ becomes constant at around 2.5. By simply reversing the signs of the final momenta we can run the trajectory backwards to give a reactive trajectory. This data tells us that any trajectory will be reactive for $\mathbf{r_1} = .74$ $\mathbf{r_2} = \mathbf{2.0}$ $\mathbf{p_2 = -2.5}$. with $\mathbf{-1.0 < p_1 < -1.5.}$

iii) The **mep** from $\mathbf{r_1} = \mathbf{r_2}$

• the **mep** can be run as follows: a) leave the geometry and momenta as in the previous exercise (i.e. the positions $\mathbf{r_1} = \mathbf{r_{ts}}+.01$ $\mathbf{r_2} = \mathbf{r_{ts}}$ and the momenta $\mathbf{p_1}=0$ $\mathbf{p_2}=0$) b) select **3 Type of Computation: Dynamics** from the **Change Parameters** menu (it will change to **Type of Computation: MEP**). c) select **2 Run Trajectory** from the main menu and d) then select **1 Animate trajectory on PES** from the **ANALYSE TRAJECTORY** menu.

• You will see that the trajectory simply follows the valley floor to $\mathbf{H_1 + H_2 - H_3}$

d) Generating a reactive trajectories

How do we determine the conditions for a reactive trajectory that starts in the region of the reactants and passes near the TS region? As you will discover, simply adjusting the collision parameters so that the system has enough energy to reach the **TS** is not enough. The energy must be distributed correctly.

• change the mode of operation of the program back to dynamics by selecting **3 Type of Computation: MEP** from the **Change Parameters** menu (it will change back to **Type of Computation: Dynamics**).

From our computations that began at the transition state with $\mathbf{r_1}$ = $\mathbf{r_{ts}}$ $\mathbf{r_2}$ = $\mathbf{r_{ts}}$+.01 we know that a reactive trajectory will correspond to $\mathbf{r_1}$ = .74 $\mathbf{r_2}$ = **2.0** $\mathbf{p_2}$**= -2.5**. with **-.8 <**$\mathbf{p_1}$**<-1.5.**

• run several trajectories with $\mathbf{r_1}$ = .74 $\mathbf{r_2}$ = **2.0** $\mathbf{p_2}$**= -2.5**. with **-.8 <**$\mathbf{p_1}$**<-1.5.** They should all be reactive. ***==> data sheet***

• run the trajectory with $\mathbf{r_1}$ = .74 $\mathbf{r_2}$ = **2.0** $\mathbf{p_1}$**-1.25** $\mathbf{p_2}$**= -2.5**. Notice that the motion is purely linear in the input channel. ***==> data sheet***

•run a trajectory with $\mathbf{r_1}$ = .74 $\mathbf{r_2}$ = **2.0** $\mathbf{p_1}$ =**-1.5** $\mathbf{p_2}$**= -2.0**. WHY IS IT UNREACTIVE? ***==> data sheet***

•run a trajectory with $\mathbf{r_1}$ = .74 $\mathbf{r_2}$ = **2.0** $\mathbf{p_1}$= **1.5** $\mathbf{p_2}$**= -2.5** WHY IS IT UNREACTIVE? ***==> data sheet***

• run a trajectory with $\mathbf{r_1}$ = .74 $\mathbf{r_2}$ = **2.0** $\mathbf{p_1}$= **-2.5** $\mathbf{p_2}$**= -5.0** (i.e. similar to the trajectory where we force pure translation in the input channel but with the momenta twice as large). The result is quite remarkable: The trajectory actually crosses the transition state region but does not go on to products even though we

have given it more than twice the momentum needed to surmount the barrier. It is instructive to **Animate the Geometry** for this example. You should see the bond in the product actually forms but then the system reverts back to the reactants. ***==> data sheet***

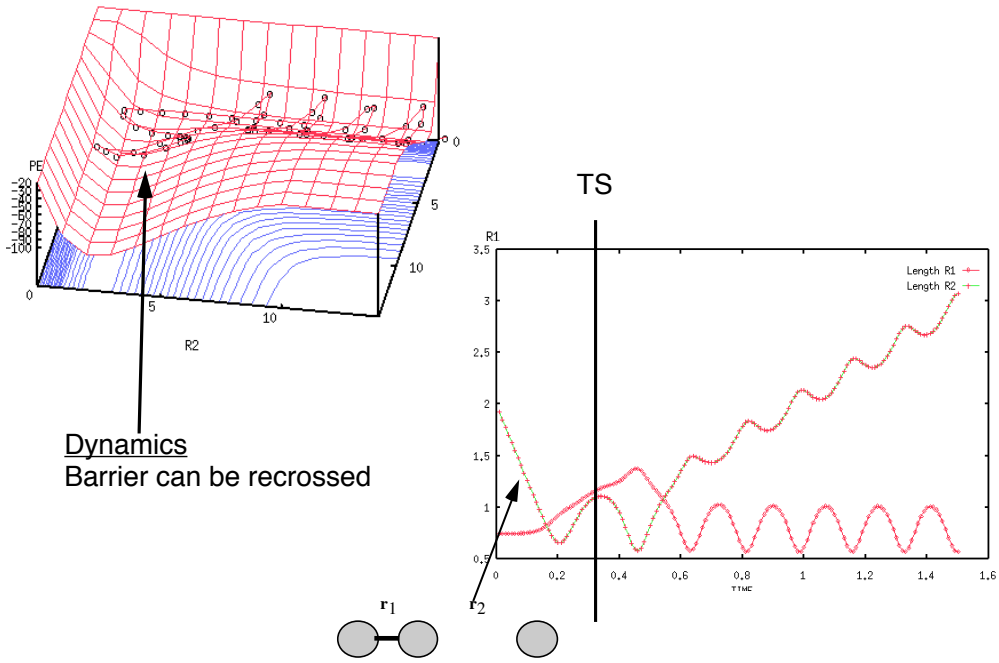


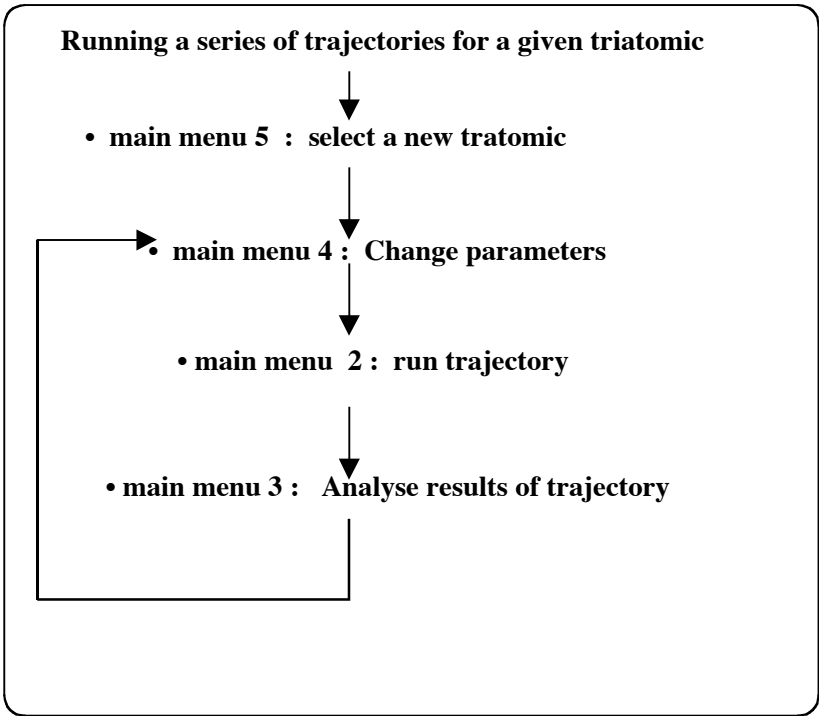
Figure 4 Trajectory that recrosses the TS region

- running a trajectory with $\mathbf{r_1}$ = .74 $\mathbf{r_2}$ = **2.0** $\mathbf{p_1}$= **-2.5** $\mathbf{p_2}$**= -5.2** produces an usual result. ***==> data sheet***

Discussion: In the transition state theory of reaction rates it is assumed once the system reaches the transition structure it goes on to produce products. However transition state theory usually overestimates the reaction rate. Why?

From this point we will abbreviate the instructions assuming that you have learned how to use the program.

For most computations that follow you will need to use the following sequences from the main menu:



EXERCISE 2 H + D_2 potential surface

The H + D_2 potential surface is identical to that for H + H_2 (i.e. the forces between the atoms are electronic in origin and are not affected by the masses). Thus the *energy differences* and the p*osition of the transition state* are unaffected by isotopic substitution. However one does observe significant differences in reaction rates upon isotopic substitution. In fact the barrier height effectively becomes higher and this is called the *kinetic isotope effect*.

• select **5 Select a New Triatomic** from the main menu, then **2** from the **TRIATOMICS** menu for the H + D_2 reaction. Now run the H + D_2 trajectory using the conditions that produce a reactive trajectory for H + H_2 ($\mathbf{r_1}$ = **2.0** $\mathbf{r_2}$ = **.74** $\mathbf{p_1}$=**-2.5** $\mathbf{p_2}$= **-1.25**). You will see that the trajectory is unreactive. ***==> data sheet***

• now run a series of trajectories gradually increasing the momentum $\mathbf{p_1}$ of the incoming H atom (with $\mathbf{r_1}$ = **2.0** $\mathbf{r_2}$ = **.74** $\mathbf{p_2}$= **-1.25**). Note the value of $\mathbf{p_1}$ that is required to cross the barrier. ***==> data sheet***

• now run a series of trajectories gradually increasing the momentum $\mathbf{p_2}$ of the D_2 molecule (with $\mathbf{r_1}$ = **2.0** $\mathbf{r_2}$ = **.74** $\mathbf{p_1}$= **-2.5**). Note the value of $\mathbf{p_2}$ that is required to cross the barrier. ***==> data sheet***

Background information:

From Quantum Mechanics we know that the energy of a harmonic oscillator is

$$\mathbf{E_n} = \left(\mathbf{n} + \frac{1}{2}\right)\mathbf{h}\,\boldsymbol{\nu} \qquad \boldsymbol{\nu} = \frac{1}{2\pi}\sqrt{\frac{\mathbf{k}}{\boldsymbol{\mu}}}$$

where the reduced mass is

$$\boldsymbol{\mu} = \frac{\mathbf{m}_1\,\mathbf{m}_2}{\mathbf{m}_1 + \mathbf{m}_2}$$

(μH_2 = .5 μD_2 = 1)

k is the force constant and is a property of the potential surface and is independent of isotopic substitution. Thus the fundamental vibration frequency for D_2 is smaller than for H_2. Thus the barrier appears higher on isotopic substitution because the zero point energy of D_2 is less than H_2 as shown in the following sketch.

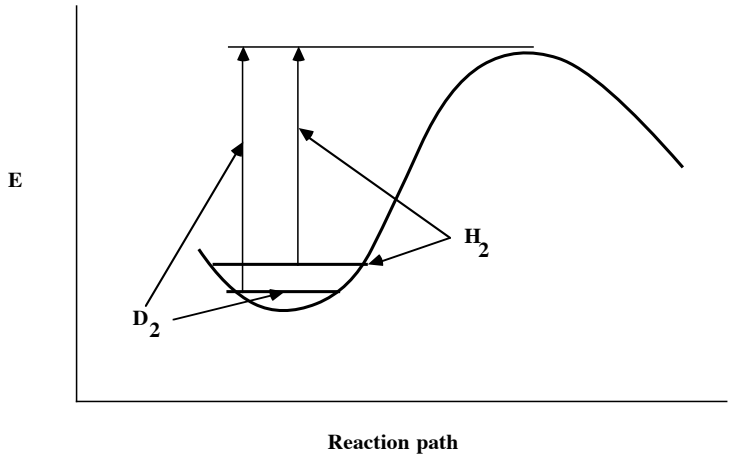


Figure 5 The effect of mass

Classically we use the velocities $\mathbf{v_i}$ ($\mathbf{p_i} = \mu\ \mathbf{v_i}$) in the co-ordinates $\mathbf{r_i}$ and the kinetic energy is

$$\mathbf{E} = \frac{1}{2}\,\mu\,\mathbf{v}^2 = \frac{\mathbf{p}^2}{2\,\mu}$$

Thus if the momenta for H_2 *and* D_2 *were the same, the kinetic energy of* D_2 *would be* 1/2 *that of* H_2. *Thus we should be able to generate a reactive trajectory either by increasing the magnitude of* $\mathbf{p_1}$ *(i.e. giving the H atom more translational energy as you have just done). Or by doubling the initial momentum of* D_2 ($\mathbf{p_2}$). *In either case the barrier appears higher than for* $H + H_2$ *because one requires a larger kinetic energy to surmount it.*

Exercise 3 I + HI potential surface

The I + HI surface is another example of a symmetric potential surface. The effects of putting a light atom between two very heavy atoms are interesting. Thus the translational energy of a heavy incoming I atom will set the HI diatomic vibrating wildly without causing a reaction. In this exercise the transition state

geometry has been located for you and the results of trajectories from this geometry (to determine initial conditions that are likely to lead to a reactive trajectory) are tabulated below. Your task is to discover the dynamics of the TS by varying the initial conditions in the same manner as in previous exercises. The results are more challenging to interpret.

i) Geometry of the TS and Trajectories from the TS

• The geom. of the TS here has $\mathbf{r_1} = \mathbf{r_2}$ with $\mathbf{r_1} = \mathbf{1.79}$

• trajectories from $\mathbf{r_1} = \mathbf{r_{ts}} + .01$ $\mathbf{r_2} = \mathbf{r_{ts}}$ with $\mathbf{p_1} = \mathbf{p_2} = 0$ give the following positions and average momenta at large t

r_1	r_2	p_1	p_2
~2.2	*~1.6*	*~9*	*~9*

ii) Reactive trajectories from the reactants

This problem is quite delicate because the system can oscillate in the transition state region. Thus small changes in the initial momenta will change from a reactive to an unreactive trajectory. You are encouraged to experiment with initial conditions.

• Check that a backwards trajectory is indeed reactive using the final values of the momenta and distances obtained from trajectories from the TS.

Use $\mathbf{r_1}$=**2.2152** and $\mathbf{r_2}$ = **1.6672** (the HI equilibrium bond distance) with $\mathbf{p_1}$ and $\mathbf{p_2}$ equal and slightly greater in magnitude (but negative!) than the final values obtained in trajectories from the TS above. ($\mathbf{p_1}$ = **9.2734** $\mathbf{p_2}$ = **9.2086**) You will also need to change the **number of steps** to **3000** from the **Change Parameters** menu. *You should see that this trajectory crosses the transition state region many times before going on the products.* You should experiment with small changes in the momenta in this region and you will see that at the threshold energy is very delicate whether or not the trajectory is reactive or not.***==> *data sheet***

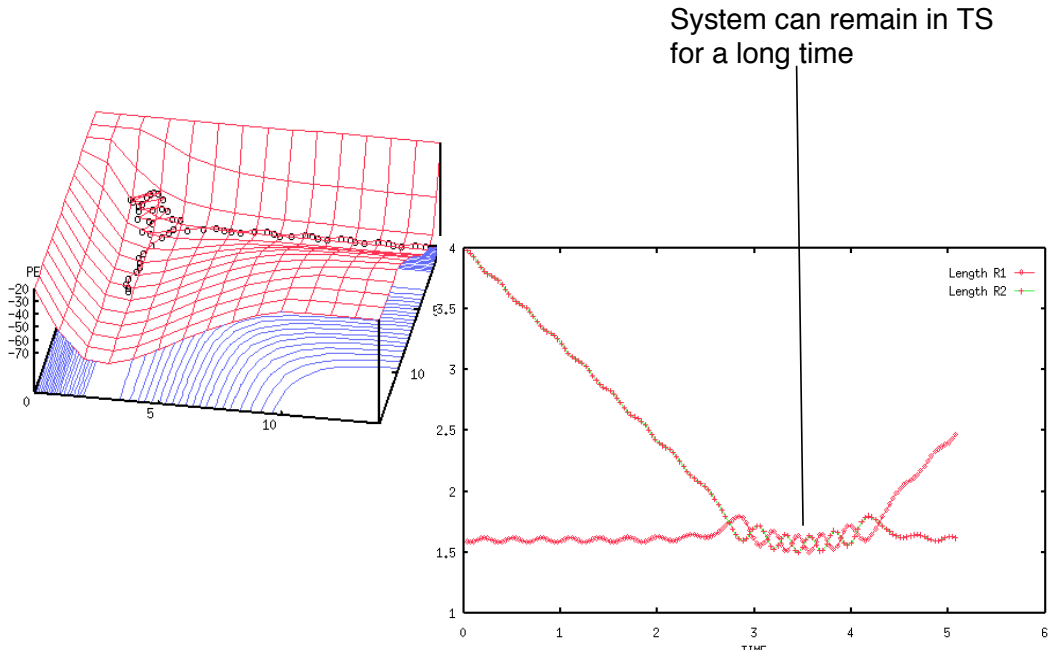


Figure 6 An example of a trajectory that "lives" in the TS region

- You can demonstrate the transition state recrossing more dramatically by using more energy. Use Use $\mathbf{r_1}$ = **1.6** (the HI equilibrium bond distance) $\mathbf{r_2}$ = **4.0** with $\mathbf{p_1}$ and $\mathbf{p_2}$ **= -50.0**. ***==> data sheet***

In the transition state theory of reaction rates, it is assumed that once the reaction has passed the transition state it goes on to produce products. In the present example we see that the reaction may oscillate many times in the transition state region before going on to products.

- experiment with trajectories where $\mathbf{p_1}$ and $\mathbf{p_2}$ have slightly different values.

Summarise your conclusions. *==> data sheet*

Exercise 4 F + H_2 potential surface

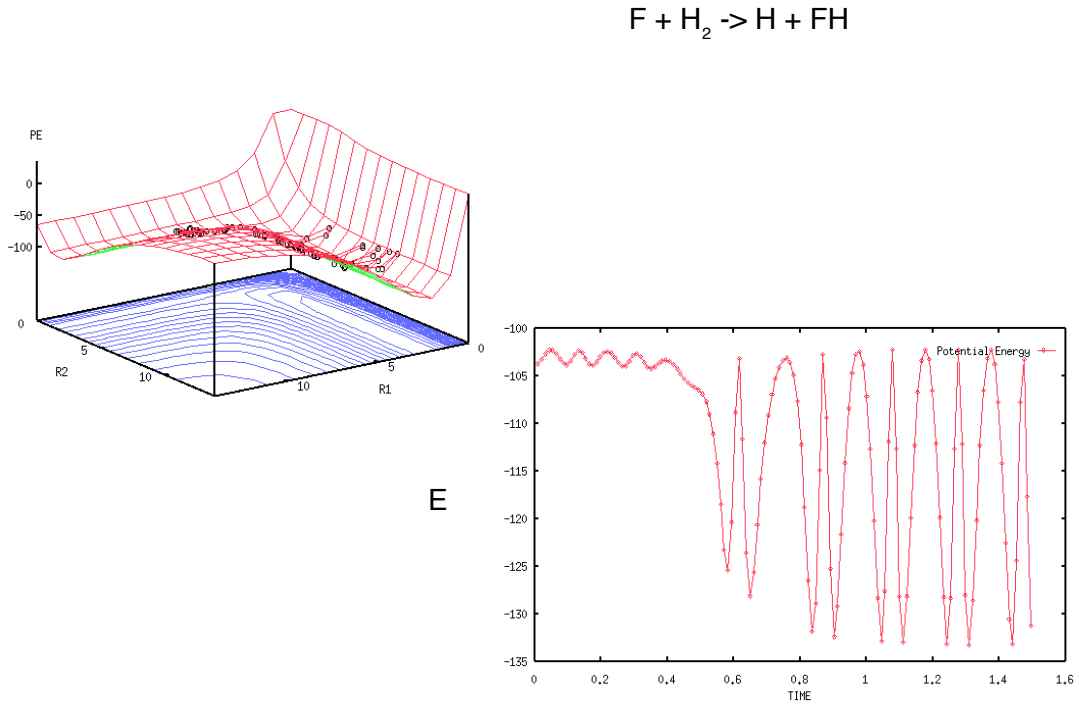


Figure 7 Vibrational Energy release in an exothermic reaction

For a discussion of the experimental background here see Chapter 28 pp 1156 in Physical Chemistry, A Molecular Approach, Mc Quarrie and Simon pub University Science Books

• Select the F + H_2 potential surface display the potential surface in the default view.

You will see that the reaction is highly exothermic (i.e. the exit channel is much lower in energy than the entrance channel since the HF bond is much stronger than the HH bond). Further there is no transition state.

• because the entrance and exit channels are so different you may find it convenient to select the **top view** for later work.

The **mep** has the form.

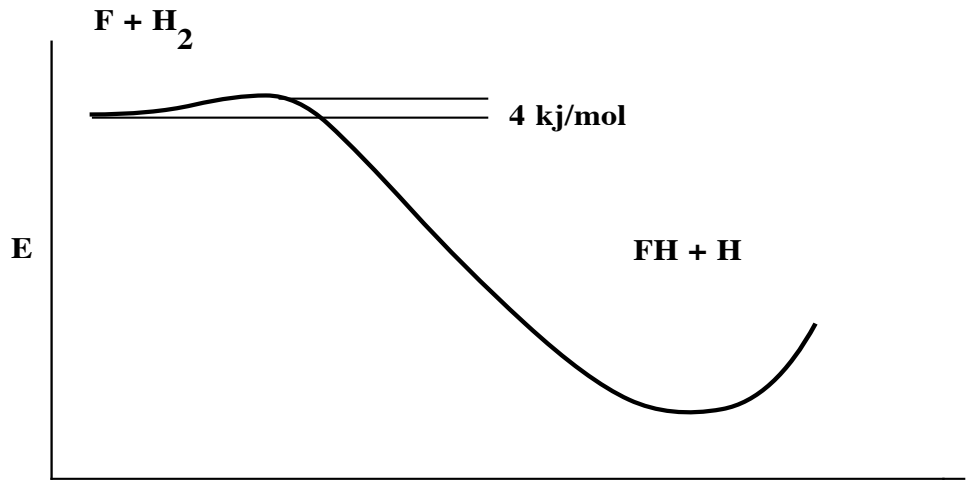


Figure 8 MEP for an exothermic reaction

In fact there is a barrier in the entrance channel (and consequently a transition state) but the barrier height is so small that it is not within the resolution of the program you are using. At the transition state $\mathbf{r_1}$ (F-H_2) = **1.33** and $\mathbf{r_2}$(FH-H) = **.85**. Thus because the reaction is exothermic the transition state is reactant-like and occurs in the entrance channel (an *early barrier*)

i) run an **mep** computation from the TS $\mathbf{r_1}$ = **1.33** and $\mathbf{r_2}$ = **.85**.

• from the **change parameters** menu, set the geometry and momenta to $\mathbf{r_1}$ = **1.33** $\mathbf{r_2}$ = **.85** $\mathbf{p_1}$=0 $\mathbf{p_2}$=0). Then select **3 Type of Computation: Dynamics** (it will change to **Type of Computation: MEP**). Then run the trajectory in the usual way. You will see that the trajectory simply follows the valley floor to **F-H + H.** ***==> data sheet***

ii) Dynamics computation from the TS: Release of the energy of exothermicity

• Now change from Type of Computation: MEP to Type of Computation: Dynamics

•run the trajectory again. Examine the results with Animate trajectory on PES, then Animate Geometry and GRAPH: MOMENTA VS TIME and GEOMETRY VS TIME.

What do you conclude about the release of the exothermicity of the reaction into translational and vibrational energy. ==> data sheet

DATA and Discussion Points

Exercise 1 H + H_2 potential energy surface

Determination of the TS geometry

r_{ts} = _____

Trajectories from TS

positions and average momenta at large t

r_1	r_2	p_1	p_2
____	____	____	____

Reactive and unreactive trajectories

Conditions	Reactive? Y/N	Description/discussion (notes or a sketch)

r_1 = .74 **r_2** = **2.0**
p_2= -2.5 -.8 <p_1<-1.5

a) p_1=____

b) p_1=____

c) p_1=____

---

r_1 = .74 **r_2** = **2.0**
p_1=-1.25 p_2= -2.5

$\mathbf{r_1}$ = .74 $\mathbf{r_2}$ = **2.0**
p_1=-1.5 p_2= -2.0

$\mathbf{r_1}$ = .74 $\mathbf{r_2}$ = **2.0**
p_1= 1.5 p_2= -2.5

$\mathbf{r_1}$ = .74 $\mathbf{r_2}$ = **2.0**
p_1=-2.5 p_2= -5.0

$\mathbf{r_1}$ = .74 $\mathbf{r_2}$ = **2.0**
p_1=-2.5 p_2= -5.2

For discussion: In the transition state theory of reaction rates it is assumed once the system reaches the transition structure it goes on to produce products. However transition state theory can overestimates the reaction rate. Why?

Exercise 2 H + D_2 trajectory computations

Describe the nature of the H + D_2 trajectory using the conditions that produce a reactive trajectory for H + H_2 ($\mathbf{r_1}$ = 2.0 $\mathbf{r_2}$ = **.74** $\mathbf{p_1}$=**-2.5** $\mathbf{p_2}$= **-1.25**).

trajectories gradually increasing the momentum $\mathbf{p_1}$ of the incoming H atom

Conditions	Reactive?(Y/N)	Description/discussion (notes or sketch)
r_1 = 2.0 r_2 = .74 **p_2= -1.25** **p_1** varies (give value used)		

trajectories gradually increasing the momentum $\mathbf{p_2}$ of the D_2 molecule

Conditions	Reactive? (Y/N)	Description/discussion (notes or sketch)
r_1 = 2.0 r_2 = .74 **p_1= -2.5** **p_2** varies (give value used)		

Exercise 3 I + HI potential energy surface

Determination of the TS geometry

$\mathbf{r_{ts}}$ = 1.79

Trajectories from TS

positions and average momenta at large t

$\mathbf{r_1}$	$\mathbf{r_2}$	$\mathbf{p_1}$	$\mathbf{p_2}$
2.2	1.6	9.0	9.0

Reactive trajectories from the reactants

Describe/sketch the backwards trajectory from $\mathbf{r_1}$=**2.2152** $\mathbf{r_2}$ = **1.6672** $\mathbf{p_1}$ = -**9.2734** $\mathbf{p_2}$ = **-9.2086**

Describe the trajectory from $\mathbf{r_1}$ = **1.6** $\mathbf{r_2}$ = **4.0** with $\mathbf{p_1}$ and $\mathbf{p_2}$ **= -50.0**.

Describe the trajectories where $\mathbf{p_1}$ and $\mathbf{p_2}$ have slightly different values

What is the significance of these results.

Exercise 4 $F + H_2$ potential energy surface

Describe the **mep** from the TS

Discuss the mechanism of release of the reaction energy of $F + H_2$. Indicate how it could be confirmed experimentally.

Molecular Reaction Dynamics: Applications to Triatomic systems

Suggested guide/template for write up 10-15 pages

Introduction

Theory

Briefly outline how chemical reactivity can be studied using classical trajectories computed from the gradient on the potential energy surface.

You should start by reading the discussions in Atkins and the handout itself. If you want to explore this subject in more depth you might read about how a potential surface for a triatomic system can be represented in the LEPS formalism and how the dynamics equations can be integrated. This information can be found in advanced physical chemistry and theoretical chemistry books. The ideas that have been used in this exercise are also used in dynamics computations on biomolecules. The only difference is that the potential surface is computed "on the fly" as the trajectory is computed.

General Observations

The central objectives of this exercise were to study triatomic reactivity. You should now understand a) re-crossing the transition state region, b)isotope effects, c)special effects for heavy-light-heavy reactions (entropy locked intermediates) and d)vibrational energy release in an exothermic reaction. You might introduce these ideas and discuss them in a general way as a prelude to the more specific discussion to follow

Discussion of the results of the 4 exercises

You should summarise the results and then discuss the 4 exercises

There are some discussion points indicated in the data sheet

Exercise 1 H + H_2 potential energy surface
Exercise 2 H + D_2 trajectory computations
Exercise 3 I + HI potential energy surface
Exercise 4 F + H_2 potential energy surface

Conclusions

Physical Chemistry
2nd Year Lab 2003
Mark Scheme for Computer Experiments.

Molecular Reaction Dynamics: Applications to Triatomic systems

Imperial College Department of Chemistry

Please note reports should NOT exceed 15 pages in length.

Student Name: ……

Marker: ……..

Presentation

- Legibility and Structure (is the report well laid out?)	/10
- Figures and Tables (are these well presented, labelled and clear?)	/10

Grammar

- Spelling (deduct marks for persistent errors)
- Grammatical construction (does it read well?)
- Proof reading (has the report been properly proof read?)

/10

Content

- Description of Aims and Theory	/5
- Trajectory computations (Have correct results been obtained)	/20
- Understanding of the theory involved (has the student shown a good overall grasp of theory being used?)	/5
- Discussion of each exercise 4 X 10	/40

Bonus Points

- Independent thought in interpretation.	/5
- Additional experiments / improvements to expt.	/5

TOTAL MARK /100

Triatomics Program Instructions
(For Hewlett Packard machines only)

To Start Program

1) If computer is in Windows (If computer is in Linux proceed to step 2)
    a. Log out of computer then press the power button (on front of machine).
    b. Press power button again to switch on machine and you will reach a prompt that asks you to select Windows or Linux. Select Red Hat Linux and press return.
2) At the login prompt type in your username and password (same as your Windows one).
3) Click on the Red Hat (bottom left hand corner of screen).
4) Select System Tools, then the application Terminal.
5) In the Terminal window type `/opt/chemistry/setup_triatomics` and press return. (Only need to run this once, the first time you log in).
6) To run the triatomics program, type ./`triatomics` in a Terminal window then return.

To print graphs or save them for use in documents

1) Open a new Terminal window
2) Type `ksnapshot &` and press enter
3) A window will come up with various options
4) Ensure "Only grab the window containing the pointer" is selected
5) Press "New Snapshot" button
6) Click on the window you wish to take a snapshot of and the snapshot will appear in the ksnapshot window
7) To save snapshot press "Save Snapshot" button then save it in your home directory as a `filename.png` file. The saved files will be on your networked L:\ drive under Windows – 'chemistry samba server (neon.ch.ic.ac.uk)' and can be printed from there or imported into word documents.
8) To print press "Print Snapshot" button then check that the print server used is CUPS (if not change it to CUPS), select the printer of your choice and then press print.