

# A Quasiclassical Trajectory Study of Atom Diatom Reactions

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**Summary.** The tutorial tackles the problem of calculating scattering properties of atom diatom reactions and analyzes the accuracy of integrated trajectories, their graphical representations and the agreement between measured and calculated quantities by making reference to the Li + HF reaction.

## 1. Introduction

The quasiclassical trajectory (QCT) method is a useful technique to study three-dimensional reactive collision dynamics. The QCT method assumes that the nuclei involved in a chemical reaction move according to the laws of Classical Mechanics on the potential energy surface of the system. The term “quasiclassical” denotes that the molecules are selected before the collision at discrete internal energy states corresponding to quantum states. After the collision, a “quantization” of the internal energy is also enforced on the product molecule.

The QCT method calculates the coordinates and momenta of all atoms of the considered system at any time during the collision and this can be used to obtain an animated representation of the reactive process. Another advantage of the method is that the QCT formulation can be easily generalized to systems involving a large number of atoms.

Although a rigorous treatment of molecular collisions should include quantum effects, in many cases the QCT method leads to sufficiently accurate estimates of the experimental observables provided that a proper sampling of initial conditions is selected. In this tutorial the foundations of the theoretical approach, the characteristics of some related computer codes and the application of these codes to the study of the Li + HF reaction are considered in detail.

## 2. Quasiclassical Trajectory Method

The first aim of the tutorial is to describe the guidelines of a quasiclassical approach to chemical reactivity and the general structure of related computational codes. In this section a short description of the QCT method is given (a complete description can be found in Ref. [1]).

In the QCT method, in order to avoid the integration of second order differential equations, the Hamilton's formalism (instead of the Newton's one) can be adopted. The classical Hamiltonian for a system of  $N_{nucl}$  atoms can be written as:

$$H(\{\mathbf{W}\}, \{\mathbf{P}_\mathbf{W}\}) = T(\{\mathbf{P}_\mathbf{W}\}) + V(\{\mathbf{W}\}) = \sum_{i=1}^{N_{nucl}} \frac{P_{Wx_i}^2 + P_{Wy_i}^2 + P_{Wz_i}^2}{2m_i} + V(\{\mathbf{W}\})$$

where  $\{\mathbf{W}\}$  and  $\{\mathbf{P}_\mathbf{W}\}$  represent the  $3N_{nucl}$  coordinates and  $3N_{nucl}$  momenta of the  $N_{nucl}$  atoms with mass  $m_i$ .  $P_{Wx_i}$ ,  $P_{Wy_i}$  and  $P_{Wz_i}$  are the cartesian components of the momentum for the atom  $i$ .  $T(\{\mathbf{P}_\mathbf{W}\})$  is the kinetic energy and  $V(\{\mathbf{W}\})$  is the potential energy. The Hamilton's equations of motion are then:

$$\dot{\mathbf{W}} \equiv \frac{d\mathbf{W}}{dt} = \frac{\partial H}{\partial \mathbf{P}_\mathbf{W}} = \frac{\partial T}{\partial \mathbf{P}_\mathbf{W}} \quad \dot{\mathbf{P}}_\mathbf{W} \equiv \frac{d\mathbf{P}_\mathbf{W}}{dt} = -\frac{\partial H}{\partial \mathbf{W}} = -\frac{\partial V}{\partial \mathbf{W}}$$

Since, in general, the potential energy is formulated as a function of the internuclear distances, the derivates are usually reconducted to its counterparts in the internuclear distances.

There are  $3N_{nucl}$  of such pairs of Hamilton's first order differential equations which have to be integrated to obtain the time evolution of the coordinates and momenta. To start the integration, initial values of the coordinates and momenta must be specified. These initial values are calculated from the collision parameters: collision energy, ro-vibrational states of the molecules, impact parameter, initial separation of the fragments, spatial orientation and vibrational phases of the molecules.

The time integration is carried out until the fragments produced by the collision are sufficiently separated. Then, the species produced are identified and the channel (non reactive, reactive or dissociative) is assigned. The result of the integration is a set of final values for coordinates and momenta of all the nuclei. By using this information, final properties of the system (like, for instance, the internal energies and rotational angular momenta of the molecules, the (approximate and continuous) rotational and vibrational "quantum numbers" of molecules, the orbital angular momentum, the relative velocity and translational energy, the scattering angle) are evaluated.

However, the outcome of a single trajectory is insufficient to describe the reaction characteristics. To this end, a statistically significant sample of trajectories has to be integrated and related outcomes averaged as follows to calculate the reaction cross section  $\sigma$ :

$$\sigma = \pi b_{max}^2 \langle \mathcal{P} \rangle$$

where  $b_{max}$  is the maximum impact parameter for which reaction occurs.  $\langle \mathcal{P} \rangle$  is the value of the reaction probability averaged over all possible values of the collision parameters.

The reaction probability function  $\mathcal{P}$  is a boolean function. It is zero when a specified trajectory is non reactive and the value of one when the trajectory is reactive. The average of the reaction probability can be expressed as a definite multidimensional integral over the collision parameters  $a_j$  ( $j=1$  to  $n$ ):

$$\langle \mathcal{P} \rangle = \int_0^1 \int_0^1 \dots \int_0^1 f(a_1, a_2, \dots, a_n) da_1 da_2 \dots da_n.$$

This integral is most often evaluated by using the Monte Carlo method:

$$\langle \mathcal{P} \rangle \approx \frac{1}{N} \sum_{i=1}^N f(a_1^{(i)}, a_2^{(i)}, \dots, a_n^{(i)})$$

In the Monte Carlo method one chooses  $N$  sets of random variables  $\{a_1^{(i)}, a_2^{(i)}, \dots, a_n^{(i)}\}$ , where  $i$  runs from 1 to  $N$ , calculates the function  $f(a_1^{(i)}, a_2^{(i)}, \dots, a_n^{(i)})$  for every set and averages the values of the calculated functions. In a QCT calculation the  $N$  sets correspond to the trajectories to be calculated, the random variables  $a_j^{(i)}$  are the collision parameters for each trajectory and the function  $f$  corresponds to the reaction probability function  $\mathcal{P}$  obtained at the end of each trajectory.

Accordingly, the QCT estimate of the reaction cross section is given by:

$$\sigma = \pi b_{max}^2 \frac{N_r}{N}$$

where  $N$  is the total number of trajectories integrated and  $N_r$  the number of reactive trajectories.

Similarly, an estimate of the thermal rate coefficient is given by:

$$k(T) = \left( \frac{8k_B T}{\pi \mu} \right)^{1/2} \pi b_{max}^2 \frac{N_r}{N}$$

where  $k_B$ ,  $T$  and  $\mu$  represent the Boltzmann's constant, the temperature and the reduced mass of the reactants respectively.

In the Monte Carlo method the error is proportional to  $N^{-1/2}$ . In other words, not too many trajectories are required to obtain a moderately accurate estimate of the cross section although a very large quantity of trajectories are required to obtain high accuracy.

### 3. Quasiclassical Trajectory Computational Codes

Several QCT programs are available from the Quantum Chemistry Program Exchange (QCPE) [2]. Some of them are:

Number	Authors	Name
229	J.T.Muckerman	CLASTR: Monte Carlo quasiclassical trajectory program
273	S.Chapman A.Gelb D.L.Bunker	A+BC: General trajectory program
453	W.L.Hase	MERCURY: A general Monte Carlo classical trajectory program
671	W.L.Hase <i>et al.</i>	VENUS96: A general chemical dynamics computer program

The first two programs are designed for atom-diatom systems whereas the other two can deal with larger systems.

The Hase's programs use a space fixed cartesian coordinate system. The differential equations to be solved are  $6N_{nucl}$  with  $N_{nucl}$  being the number of atoms of the system. The Muckerman's and the Chapman's programs separate the motion of the system center of masses. They use a center of mass relative coordinate system. The number of differential equations to be solved are  $6N_{Nucl} - 6$ . Despite these differences, the structure of the various QCT computer programs is similar and is sketched in the following scheme:

- Read data and Initializations
- LOOP on trajectories
  - Generate random numbers
  - Calculate collision parameters
  - Calculate initial coordinates and momenta
  - Write initial conditions
  - LOOP on time steps
    - LOOP on differential equations
      - ◊ Calculate the potential energy derivatives
      - END of differential equation loop
      - Check the end of the trajectory
    - END of time step loop
    - Evaluate final properties
    - Write final properties
  - END of trajectory loop
  - Calculate reactive properties

The fundamental structure of a QCT program is the loop over the trajectories having a given collision and internal energy as read from the input file. Remaining initial conditions are sampled statistically. The first step of the statistical sampling consists of the generation of a set of pseudorandom numbers using a suitable routine [3]. In a second step, collision parameters, such as the spatial orientation of the molecules, positions and velocities of the involved atoms (including the impact parameter) are worked out from a subset of the pseudorandom string. Finally, coordinates and momenta of the atoms involved in the reaction are calculated. Once the initial conditions are determined, the integration of the Hamilton's equations is carried out over time. The numerical integration is most often performed using an Adams-Moulton algorithm initiated by the necessary Runge-Kutta steps. Nested inside the time integration loop is the loop over differential equations of the conjugated position and momentum variables. Each pair of equations requires the calculation of the derivative of the potential. Inside the time integration loop the test of the end of the trajectory is performed. When the calculation of a trajectory is completed the final properties of the chemical system are evaluated. At first, the identification of the product channel is performed. Then, the internal properties of the product molecules and related scalar and vector features are calculated. After completing the trajectory

loop, the QCT program can calculate the reaction cross section and the reactivity functions (*i.e.* the variation of the reactive probability as a function of the initial collision parameters) and the final-state distributions giving information about spatial and energetic properties of the products.

The structure of the quasiclassical trajectory programs clearly shows that the integration of a given trajectory is an independent task. Therefore, QCT programs show a natural parallelism which can be exploited by modern parallel computer architectures. Accordingly, the speed-up that QCT programs can reach when properly implemented on parallel computers can be quite close to the number of processors of the machine [4].

It is important to know the distribution of cpu time spent in each subroutine of the QCT code. For this purpose a test run has been performed using the VENUS96 program [5] (results are similar for other codes). The distribution of time spent in a QCT calculation is shown in the following table:

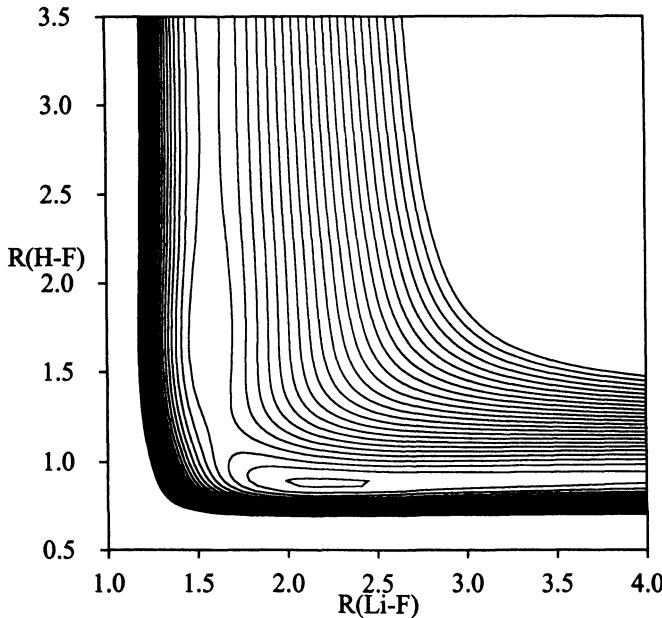
<i>Subroutine</i>	<i>Percentage</i>
DPOT	59.25 %
ADAMSM	14.80 %
DVDQ	8.00 %
TEST	7.30 %
SELECT	5.95 %
Others	4.70 %

The most time consuming routine of the program is the DPOT routine that evaluates the potential energy derivatives with respect to the internuclear distances. Also the DVDQ routine, which calculates the derivatives with respect to the cartesian coordinates, takes a significant time percentage. In total, the time for calculating the potential derivatives is 67.25 % of the total cpu time. Another routine which spends significant time is the ADAMSM routine. This routine performs an integration step of the sixth order Adams-Moulton integrator for the motion equations. Smaller time consuming routines are TEST and SELECT. The TEST routine is called at every step of the trajectory integration to calculate the separation between fragments and to check whether the end of the integration process has been reached. The SELECT routine sets up the initial conditions for coordinates and momenta.

#### 4. The $\text{Li} + \text{HF} \rightarrow \text{LiF} + \text{H}$ reaction

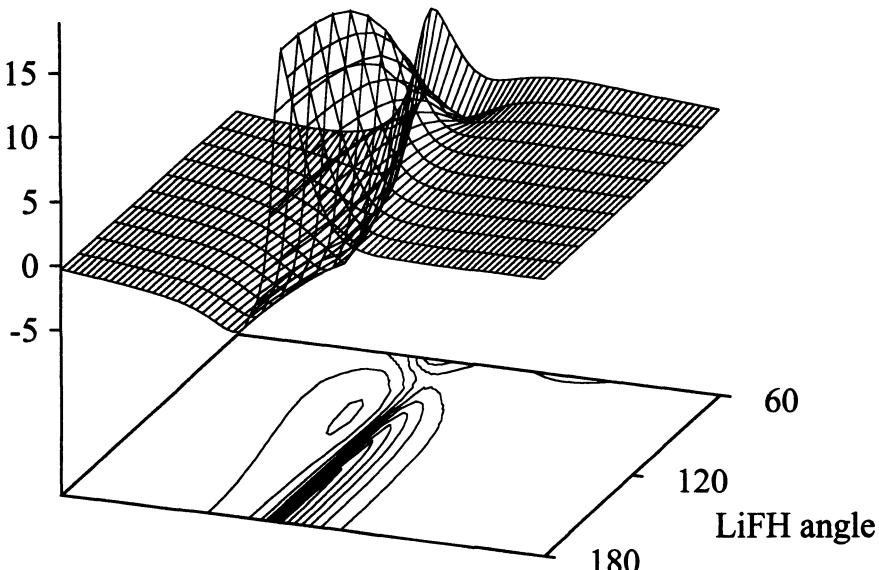
The tutorial focuses on the  $\text{Li} + \text{HF} \rightarrow \text{LiF} + \text{H}$  reaction using the potential energy surface built by Laganà [6] from *ab initio* electronic energies [7, 8].

In order to illustrate the main features of the surface, its isoenergetic contour maps at  $\widehat{\text{LiFH}} = 74^\circ$  (value corresponding to the transition state geometry) are shown in Figure 4.1 and the dependence of the minimum energy paths from the  $\widehat{\text{LiFH}}$  angle is illustrated in Figure 4.2. Figure 4.1 evidences that in the entrance channel there is a well 2.6 kcal/mol deep. The absolute minimum of the potential



**Fig. 4.1.**  $\text{Li} + \text{HF} \rightarrow \text{LiF} + \text{H}$  isoenergetic contours at  $\widehat{\text{LiFH}} = 74^\circ$ . Energies are given in kcal/mol from the  $\text{Li} + \text{HF}$  asymptote. Distances are given in Å. Contours are spaced of 2.5 kcal/mol.

Energy (kcal/mol)



**Fig. 4.2.**  $\text{Li} + \text{HF} \rightarrow \text{LiF} + \text{H}$  minimum energy paths plotted as a function of the angle  $\widehat{\text{LiFH}}$ . Isoenergetic contours are given in the underlying plane. Energies are given in kcal/mol from the  $\text{Li} + \text{HF}$  asymptote, values of the  $\widehat{\text{LiFH}}$  angle are given in degrees. Energy contours are spaced of 2.5 kcal/mol.

is of 6.9 kcal/mol below the reactant asymptote and is located at  $\widehat{\text{LiFH}} = 106^\circ$ . A sudden potential barrier located in the exit channel separates the reactant from the product valley. Its minimum of the barrier defining the transition state is 4.2 kcal/mol high. Another feature of the potential energy surface is a second well located in the exit channel and 2.3 kcal/mol deeper than the product asymptote.

## 5. Exercises

The tutorial on quasiclassical trajectories is articulated into three exercises. The first exercise is devoted to the evaluation of the accuracy of QCT results (in particular, the optimization of the integration time step). In the second exercise, the characteristics of typical reactive and non reactive trajectories are analyzed. In the third exercise, a statistically significant sample of trajectories is integrated to compare calculated values with results of a crossed molecular beam experiment.

To carry out the exercises use has been made of the VENUS96 program [5]. The input file used for this purpose is given in Table 5.1.

The output file contains the following information:

- a copy of input data.
- the (semiclassically calculated) ro-vibrational energy of the initial internal state of reactant molecules.
- the initial conditions of each trajectory: (1) the initial random number, (2) the orientation of the rotational angular momentum of the molecule, (3) the impact parameter and the orbital angular momentum, (4) the kinetic, potential and total energy, (5) the coordinates and momenta of all atoms and (6) the internuclear distances.
- the final properties of each trajectory: (1) the collision time, (2) the kinetic, potential and total energy, (3) the coordinates and momenta of all atoms, (4) the internuclear distances, (5) the channel reached by the collision, (6) the internal properties of the channel fragments, such as the total, vibrational and rotational energies, the rotational angular momentum, the (continuous) "quantum" vibrational and rotational numbers, (7) the relative properties between fragments, such as the translational energy and orbital angular momentum, (8) the scattering angles and (9) the final random number.

### 5.1 Accuracy of QCT calculations

The objective of the proposed exercise is to optimize the time step size for the trajectory study of the reaction  $\text{Li} + \text{HF}(v = 0, j = 2)$  with a collision energy  $E_{\text{tr}}$  of 10 kcal/mol.

The time step size for the integration of motion equations has an important influence on the accuracy and on the cpu time of a quasiclassical trajectory calculation. It must be optimized for every reaction and collision energy. The method used here to optimize the step size is to check the conservation of total energy and angular momentum for every trajectory calculated by using different

**Table 5.1.** Input file for the program VENUS96.

Li + HF	two lines of comments
Lagana's PES	
3	number of atoms
6.94,19.,1.008	masses of the atoms
15,40000,50	number of total trajectories to be calculated, maximum number of integration steps allowed, number of steps for intermediate printing
0.010	integration stepsize (units of $10^{-14}$ s)
1357997531	seed number to initiate the chain of random numbers
— characteristics of the initial fragments (Li + HF)	
1	number of atoms of the fragment A (Li)
0,0,0	equilibrium cartesianindexCoordinates!cartesian coordinates for fragment A (Li)
2	number of atoms of the fragment B (HF)
0,0,0,0.917,0,0	equilibrium cartesianindexCoordinates!cartesian coordinates for fragment B (HF)
0,2	vibrational and rotational numbers for molecule B (HF)
— internuclear parameters for reactants channel (Li + HF)	
1,2,12,0,0,0	indices of atoms of which internuclear distance is tested to stop a trajectory, distance to stop a trajectory in reactants channel, ergicity of the reactants channel
1,10,0,12,0	initial translational energy (option 1 means fixed energy) initial separation
0,2,1	maximum impact parameter (option 0 means random sampling)
— parameters for classifying channels	
2	number of reaction channels in addition to the reactants one
— parameters for channel 1 (H + LiF)	
12,0,1,2,3,61	distance to stop a trajectory in channel 1, number of atoms in fragments A (H) and B(LiF) in channel 1, ergicity for channel 1
2,3	indices of atoms which distance is tested to stop a trajectory
3	index for the atom of fragment A (H) in channel 1
0,0,0	equilibrium cartesian coordinates for fragment A (H)
1,2	indices for the atoms of fragment B (LiF) in channel 1
0,0,0,1.564,0,0	equilibrium cartesian coordinatesindexCoordinates!cartesian of fragment B (LiF)
— parameters for channel 2 (F + HLi)	
12,0,1,2,83,2	as above, for channel 2
2,3	
2	
0,0,0	
1,3	
0,0,0,1.5957,0,0	
— parameters for printing results	
1	option for printing the coordinates and momenta
1,3	option for printing the (three) internuclear distances
1,2	indices for atoms which internuclear distance is printed
1,3	idem
2,3	idem

step sizes. These quantities must be constant during the trajectory. Therefore, their conservation indicates the calculation accuracy.

The procedure of this exercise is the following:

- I Prepare the data file for the calculation of a representative number of trajectories at the mentioned conditions and select a time step size. Then, run the trajectory program and use the *time* command in order to obtain the cpu time.
- II Compare the initial and final total energy for all trajectories and calculate the maximum difference. Also, evaluate the conservation of the total angular momentum.
- III Recalculate the same trajectories with other step sizes. Write a table reporting the step size, the accuracy of the calculation and the cpu time.
- IV Select the optimum step size for a reasonably accuracy and a reasonably cpu time.

The obtained results for this exercise are summarized in the following table:

step size (s)	cpu time (s)	$N$	$N_r$	$\max( E_f - E_i )$ (kcal/mol)	$\max( J_f - J_i )$ ( $\hbar$ )
$0.050 \times 10^{-14}$	98.8	1000	101	131.3538997	0.10034725
$0.040 \times 10^{-14}$	120.2	1000	72	1.7784660	0.00303518
$0.030 \times 10^{-14}$	155.8	1000	70	0.0619055	0.00072160
$0.025 \times 10^{-14}$	184.4	1000	71	0.0610177	0.00017882
$0.020 \times 10^{-14}$	227.0	1000	72	0.0281331	0.00006146
$0.015 \times 10^{-14}$	297.7	1000	71	0.0048108	0.00001059
$0.010 \times 10^{-14}$	441.6	1000	71	0.0004947	0.00000094
$0.005 \times 10^{-14}$	865.1	1000	71	0.0000034	0.00000001
$0.002 \times 10^{-14}$	2146.6	1000	71	0.0000001	0.00000000

This table shows clearly the influence of the time step on the accuracy of the trajectory calculations. The number of the reactive trajectories varies on the time step used in the calculation. The cpu time increases (almost proportionally) as the time step decreases. The conservation of both the total energy and the total angular momentum improves significantly as the time step decreases. From the values reported in the Table one can conclude that a reasonable balance between accuracy (for the purpose of this tutorial) and cpu time can be achieved with a step size of  $0.010 \times 10^{-14}$  s. This value is used throughout the next exercises.

## 5.2 Properties of a trajectory

The objective of the proposed exercise is to study the initial and final properties of a reactive trajectory for the reaction  $\text{Li} + \text{HF}(v = 0, j = 2)$  with a collision energy  $E_{tr}$  of 10 kcal/mol.

The procedure of this exercise is the following:

- I Prepare the data file for the calculation of a small number of trajectories at the mentioned conditions, run the trajectory program and write the initial and final coordinates and momenta of all atoms for every trajectory.

II Check the output file and select a reactive trajectory. Calculate the properties specified in the following steps for the selected trajectory.

III Calculate the initial properties:

1. internuclear distances
2. relative distance Li-HF, i.e., between the Li atom and the center of mass of the HF molecule
3. relative velocity and translational energy Li-HF
4. impact parameter
5. orbital angular momentum
6. rotational angular momentum of the HF molecule
7. total angular momentum

IV Calculate the final properties:

1. internuclear distances:
2. relative distance H-LiF, i.e., between the H atom and the center of mass of the LiF molecule
3. relative velocity and translational energy H-LiF
4. orbital angular momentum
5. rotational angular momentum of the LiF molecule
6. total angular momentum
7. scattering angle, i.e., the angle between the initial velocity of the reactant atom and the final velocity of the product molecule

The results of this exercise are shown in the Table 5.2. The initial distances show that the atoms H and F are bound together while the Li atom is placed far away. The calculated relative distance between the atom Li and the center of mass of the molecule HF is 12 Å, i.e., the input data. Also, the calculated initial translational energy is equal to the input data. The initial relative velocity Li-HF has only Z component and the molecule HF is on the plane YZ. Therefore, the initial orbital angular momentum is parallel to the X axis. On the contrary, the initial rotational angular momentum of the molecule HF is randomly oriented. The trajectory stops when the distance between the atoms F and H is larger than 12 Å. The final distances show that the atoms Li and F are bound together, that is, this collision is a reactive collision (path=2). The final rotational quantum number of the molecule LiF is 16 and the final relative translational energy H-LiF is 9.5 kcal/mol. The components and the magnitude of the total angular momentum are conserved. Finally, the scattering angle is 27 degrees (forward collision).

A second objective of this exercise is to represent the evolution of the internuclear distances during the collision. The procedure of this exercise is the following:

- I Modify the data file in order to write the coordinates and momenta during the trajectories (for example, every 50 integration steps). Run the trajectory program.
- II Calculate and represent the internuclear distances of all atoms as a function of the time for one non reactive and one reactive trajectories.

**Table 5.2.** Initial and final properties of a reactive collision.**Initial and final coordinates and momenta:**

Li	0.000000	0.000000	0.000000	0.000000	0.000000	2.076575
F	-0.037788	0.791591	11.977542	0.640640	-0.223863	-1.929527
H	0.712284	0.309344	11.935906	-0.640640	0.223863	-0.147048
Li	0.259827	-0.608802	9.205008	0.130309	-0.354962	0.811932
F	-0.396090	0.930183	9.301076	-0.530617	0.309633	-0.033175
H	5.676765	1.889521	-1.005256	0.400307	0.045329	-0.778757

**Initial Properties**Distances ( $\text{\AA}$ ):  $R_{\text{LiF}}=12.004$ ,  $R_{\text{HF}}=0.893$ ,  $R_{\text{LiH}}=11.961$ Impact parameter: 0.767  $\text{\AA}$ 

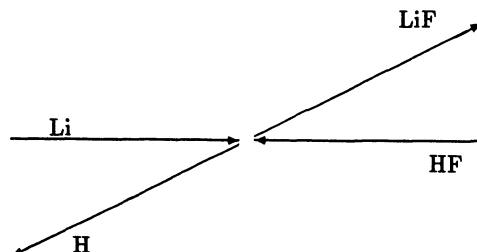
Relative Li-HF translational energy: 10.00 kcal/mol

Relative Li-HF velocity ( $\text{\AA}/10^{-14} \text{ s}$ ):  $v=0.403$ ,  $v_x=0.000$ ,  $v_y=0.000$ ,  $v_z=0.403$ Relative Li-HF position ( $\text{\AA}$ ):  $R=12.000$ ,  $R_x=0.000$ ,  $R_y=-0.767$ ,  $R_z=-11.975$ Li-HF orbital angular momentum ( $\hbar$ ):  $l=25.09$ ,  $l_x=-25.09$ ,  $l_y=0.00$ ,  $l_z=0.00$ HF rotational angular momentum ( $\hbar$ ):  $j=2.45$ ,  $j_x=0.47$ ,  $j_y=0.92$ ,  $j_z=-2.22$  $j(j+1)=6.00 \hbar^2$ , rotational quantum number: 2.00Total angular momentum ( $\hbar$ ):  $J=24.74$ ,  $J_x=-24.62$ ,  $J_y=0.92$ ,  $J_z=-2.22$ **Final Properties**Distances ( $\text{\AA}$ ):  $R_{\text{LiF}}=1.676$ ,  $R_{\text{HF}}=12.001$ ,  $R_{\text{LiH}}=11.825$ , Path: 2

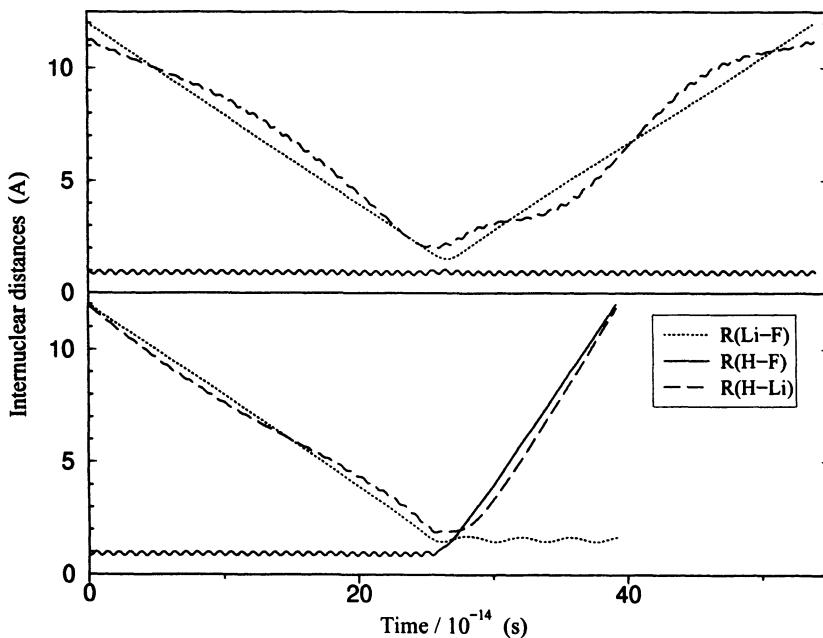
Relative H-LiF translational energy: 9.47 kcal/mol

Relative H-LiF velocity ( $\text{\AA}/10^{-14} \text{ s}$ ):  $v=0.904$ ,  $v_x=0.413$ ,  $v_y=0.047$ ,  $v_z=-0.803$ Relative H-LiF position ( $\text{\AA}$ ):  $R=11.931$ ,  $R_x=0.897$ ,  $R_y=1.371$ ,  $R_z=-10.281$ H-LiF orbital angular momentum ( $\hbar$ ):  $l=12.88$ ,  $l_x=-9.48$ ,  $l_y=7.51$ ,  $l_z=-4.43$ LiF rotational angular momentum ( $\hbar$ ):  $j=16.66$ ,  $j_x=-15.14$ ,  $j_y=-6.59$ ,  $j_z=2.21$  $j(j+1)=277.71 \hbar^2$ , rotational quantum number: 16.17Total angular momentum ( $\hbar$ ):  $J=24.74$ ,  $J_x=-24.62$ ,  $J_y=0.92$ ,  $J_z=-2.22$ 

Scattering angle: 27.35°



The result of this exercise is shown in Figure 5.1. In this figure, the distance LiF decreases as the collision time increases. The distance HF shows oscillations corresponding to the vibrational motion  $v=0$ . The distances LiH shows wide oscillations corresponding to the rotation of H atom around the F atom in the HF molecule. After a time, the three atoms are close and the rearrangement takes place. The upper panel shows an inelastic collision, the products of the collision are Li + HF. One can see that the vibrational motion of HF is not disturbed while the rotational motion is modified from  $j=0$  to  $j'=3.6$ . The lower panel shows a reactive collision, the products of the collision are H + LiF. The oscillations correspond to the classical vibrational number  $v=0.3$  of the LiF molecule.



**Fig. 5.1.** Evolution of the internuclear distances as a function of the collision time for a non-reactive trajectory (upper panel) and for a reactive trajectory (lower panel).

### 5.3 QCT estimates of reactive properties

The objective of the exercise proposed is to calculate some reactive properties for the reaction  $\text{Li} + \text{HF}(v = 0, j = 1) \rightarrow \text{LiF}(v', j') + \text{H}$  at the collision energies of  $E_{tr} = 8.7$  and  $3.0$  kcal/mol and to compare the calculated results with the experimental data [9].

In order to obtain both reactivity functions and the final-state distributions, a statistically significant sample of trajectories is calculated. These properties are studied using the histogrammic method. In this method the range of the

property is divided in bins and then the trajectory results are sorted in these bins.

The procedure of this exercise is the following:

- I Prepare the data file for the calculation of a large number of trajectories (for example, 1000000 trajectories) at the mentioned conditions. Run the trajectory program and write for all trajectories the product channel, the impact parameter, the product translational energy, the scattering angle and the vibrational and rotational (continuous) “quantum” numbers.

- II 1. Calculate the reactive cross sections and their errors:

$$\sigma = \pi b_{\max}^2 \frac{N_r}{N} \quad \Delta\sigma = \sigma \left( \frac{N - N_r}{NN_r} \right)^{1/2}$$

where  $N$  is the total number of trajectories calculated and  $N_r$  is the number of reactive trajectories.

2. Represent the calculated excitation function ( $\sigma$  vs  $E_{tr}$ ), including the experimental results:  $\sigma = 0.80^{+0.80}_{-0.40}$  and  $0.94^{+0.94}_{-0.47}$  Å<sup>2</sup> at  $E_{tr} = 3.0$  and 8.7 kcal/mol, respectively.

- III Calculate the opacity functions:

$$P(b_i) = \frac{N_r(b_i)}{N(b_i)}$$

with  $N(b_i)$  being the total number of trajectories with initial impact parameter falling in the bin  $i$  ( $b_i, b_i + \Delta b$ ) and  $N_r(b_i)$  the corresponding number of reactive trajectories. Represent the calculated opacity functions ( $P(b)$  vs  $b$ ) for the two translational energies.

- IV Calculate the differential cross sections:

$$\frac{d^2\gamma(\chi_i)}{d\Omega} \propto \frac{N_r(\gamma_i)}{\sin \bar{\gamma}_i}$$

with  $N_r(\gamma_i)$  being the number of trajectories leading to products scattered in the bin  $i$  ( $\gamma_i, \gamma_i + \Delta\gamma$ ) and  $\bar{\gamma}_i$  the value of the scattering angle  $\gamma$  at the center of bin  $i$ . Represent the calculated differential cross sections for the two translational energies and include the experimental results.

- V Calculate the product translational energy distributions:  $P(E'_{tr,i}) \propto N_r(E'_{tr,i})$ , where  $N_r(E'_{tr,i})$  is the number of reactive trajectories with product translational energy in the bin  $i$  ( $E'_{tr,i}, E'_{tr,i} + \Delta E'_{tr,i}$ ). Represent the calculated product translational energy distributions for the two initial translational energies and include the experimental results.
- VI Calculate the product vibrational quantum number distributions:  $P(v') \propto N_r(v')$ , where  $N_r(v')$  is the number of reactive trajectories with product vibrational quantum number in the range  $(v' - 0.5, v' + 0.5)$ . Represent the calculated product vibrational quantum number distributions for the two initial translational energies.
- VII As in item VI, for the product rotational quantum number distributions.

The results of this exercise can be summarized as follows:

- The calculated cross sections ( $0.513 \pm 0.008 \text{ \AA}^2$  at  $E_{tr}=3.0 \text{ kcal/mol}$ , and  $1.033 \pm 0.012 \text{ \AA}^2$  at  $E_{tr}=8.7 \text{ kcal/mol}$ ) are within the experimental error bars but the calculated slope is slightly larger than the measured one.
- The opacity function shows that the reaction probability has its maximum at small impact parameter and the probability decreases as the impact parameter increases.
- At the higher collision energy the calculated angular distribution well reproduces the structure of the experimental data (forward scattering). At the lower collision energy the experimental angular distribution is symmetric with a slight backward peak. On the contrary, the calculated distribution shows a forward bias.
- The calculated product translational energy reproduces the experimental result (very well at low collision energy; fairly well at high collision energy). At high energy, in fact, the maximum occurs at values higher than the experimental ones.
- There are not experimental vibrational and rotational distributions to compare with.

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