

Trajectory Calculations by the Rolling Ball Model

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One of the most important problems in chemistry is understanding chemical reaction rates. To this end, one of the main objectives in chemical kinetics is to make calculations of the rate of a reaction from first principles. Current experimental and theoretical methods of molecular dynamics allow us to understand at a microscopic level the mechanism of an elementary chemical process and make possible the interpretation of macroscopic kinetics in molecular terms.

A chemical reaction is a process in which the interactions among the reactants determine the formation of the products. The nature of these interactions is reflected by the potential energy surface for the system. Thus, all the geometrical rearrangements and energy variations that a supermolecule undergoes in a reactive collision can be represented by a trajectory on this potential surface.

The theoretical methods of molecular dynamics allow us to study these movements of systems on potential surfaces (1–5). One of the procedures for dealing with this problem is to choose a set of initial conditions and solve the classical equations of motion for the nuclei of the colliding system. For each initial condition one trajectory on the potential surface is obtained. The analysis of these classical trajectories allows us to interpret and discuss energy disposal in exoergic reactions, the relative importance of translational and internal energy in overcoming a potential barrier, and collision details. In addition, by averaging trajectories over the initial conditions, quantities such as cross sections and rates can be obtained.

The objective of this paper is to propose as an exercise in chemical kinetics the construction of a set of programs that perform the calculation and graphical representation of classical trajectories for a triatomic colinear system on a LEPS surface (6, 7) by using the model of the rolling ball. According to this model, for a colinear collision one can simulate exactly the actual trajectory by the process of rolling a ball on the corresponding potential energy surface (1). This model represents, for the student, a relatively simple access to the subject of molecular trajectories.

The Classical Equations of Motion and the Analogy of the Rolling Ball

For a colinear triatomic system ABC, in which only the relative motion is considered, the Hamiltonian is a function of only four variables—two coordinates and two momenta (8). Under these conditions, the motion of the nuclei is governed by a set of four differential equations

$$\frac{\partial H}{\partial p_i} = \dot{q}_i \quad (1)$$

$$\frac{\partial H}{\partial q_i} = -\dot{p}_i \quad (2)$$

where $i = 1, 2$, the q_i are the generalized coordinates, the p_i are conjugate momenta, and \dot{q}_i and \dot{p}_i are their time derivatives. Trajectories for the system are determined by integrating numerically these four simultaneous differential equations (9).

An alternative approach to this problem is to simulate the actual trajectory by a ball rolling on the potential energy surface (1). In order to carry out this analogy it is necessary to transform the coordinates of the actual system so that the

Hamiltonian is formally identical to a monoparticle Hamiltonian

$$H = \frac{1}{2} m(\dot{x}^2 + \dot{y}^2) + V(x, y) \quad (3)$$

In this way, solving the classical equations of motion for the actual system is identical to solving the equation for the motion of a particle on the potential surface.

The Hamiltonian for the triatomic system may be written (10):

$$T = \frac{1}{2} \frac{m_A m_B}{m_A + m_B} \dot{r}_{AB}^2 + \frac{1}{2} \frac{(m_A + m_B)m_C}{m_A + m_B + m_C} \left(\dot{r}_{BC} + \frac{m_C}{m_A + m_B} \dot{r}_{AB} \right)^2 \quad (4)$$

$$V = V(r_{AB}, r_{BC}) \quad (5)$$

$$H = T + V = H(r_{AB}, r_{BC}, \dot{r}_{AB}, \dot{r}_{BC}) \quad (6)$$

where m_A , m_B , and m_C are the masses of atoms A, B, and C; r_{AB} and r_{BC} the distances between atoms A and B, and B and C; and \dot{r}_{AB} and \dot{r}_{BC} the corresponding time derivatives. In order to get T in the form of eqn. (3) the new coordinates x and y are defined:

$$y = \frac{r_{BC}}{C} \cos \theta \quad (7)$$

$$x = r_{AB} + y \tan \theta \quad (8)$$

where

$$\sin \theta = \frac{C m_C}{m_A + m_B} \quad (9)$$

and

$$C = \sqrt{\frac{m_A(m_B + m_C)}{m_C(m_A + m_B)}} \quad (10)$$

From $V = V(x, y)$ and substitution of eqns. (7) and (8) into eqn. (4) we have

$$T = \frac{1}{2} m(\dot{x}^2 + \dot{y}^2) \quad (11)$$

where

$$m = \frac{m_A(m_B + m_C)}{m_A + m_B + m_C} \quad (12)$$

Now we have $\dot{x} = p_x/m$ and $\dot{y} = p_y/m$, thus the only differential equations to solve are

$$\frac{\partial H}{\partial x} = -\dot{p}_x \quad (13)$$

$$\frac{\partial H}{\partial y} = -\dot{p}_y \quad (14)$$

In this paper, given the initial position and momentum, the numerical integration of eqns. (13) and (14) has been carried out over small time increments, δt , using the equations

$$p_x(t + \delta t) = p_x(t) + \dot{p}_x(t)\delta t = p_x(t) - \left(\frac{\partial H}{\partial x}(t) \right) \delta t \quad (15)$$

$$p_y(t + \delta t) = p_y(t) + \dot{p}_y(t)\delta t = p_y(t) - \left(\frac{\partial H}{\partial y}(t) \right) \delta t \quad (16)$$

The trajectory is given by the equations

$$x(t + \delta t) = x(t) + \frac{p_x(t)}{m} \delta t \quad (17)$$

$$y(t + \delta t) = y(t) + \frac{p_y(t)}{m} \delta t \quad (18)$$

Trajectories on a LEPS Surface

For a triatomic system ABC the LEPS potential energy expression is (6)

$$V = \frac{1}{(1+K)} (Q_{AB} + Q_{BC} + Q_{AC} - \sqrt{0.5} \{(J_{AB} - J_{BC})^2 + (J_{BC} - J_{AC})^2 + (J_{AC} - J_{AB})^2\}^{1/2}) \quad (19)$$

where K is an adjustable constant, the Sato constant. The expressions for Q_{MN} and J_{MN} result (7)

$$Q_{MN} = \frac{3+K}{4} D_{MN} \exp(-2\beta_{MN}(r_{MN} - r_{MN}^0)) - \frac{1+3K}{2} D_{MN} \exp(-\beta_{MN}(r_{MN} - r_{MN}^0)) \quad (20)$$

$$J_{MN} = \frac{1+3K}{4} D_{MN} \exp(-2\beta_{MN}(r_{MN} - r_{MN}^0)) - \frac{3+K}{2} D_{MN} \exp(-\beta_{MN}(r_{MN} - r_{MN}^0)) \quad (21)$$

where D_{MN} is the classical dissociation energy, r_{MN}^0 is the equilibrium bond length and β_{MN} is a constant for the molecule MN.

According to eqns. (7) and (8), Q_{MN} and J_{MN} can be expressed as functions of x and y , and so, $V = V(x, y)$. Then, the derivative $\partial H/\partial x$ in eqn. (15) and $\partial H/\partial y$ in eqn. (16) take the form

$$\begin{aligned} \frac{\partial H}{\partial q} = \frac{\partial V(x, y)}{\partial q} &= \frac{1}{(1+K)} \left\{ \frac{\partial Q_{AB}}{\partial q} + \frac{\partial Q_{BC}}{\partial q} + \frac{\partial Q_{AC}}{\partial q} \right. \\ &- \sqrt{0.5} \left\{ (J_{AB} - J_{BC}) \left(\frac{\partial J_{AB}}{\partial q} - \frac{\partial J_{BC}}{\partial q} \right) \right. \\ &+ (J_{BC} - J_{AC}) \left(\frac{\partial J_{BC}}{\partial q} - \frac{\partial J_{AC}}{\partial q} \right) \\ &\left. \left. + (J_{AC} - J_{AB}) \left(\frac{\partial J_{AC}}{\partial q} - \frac{\partial J_{AB}}{\partial q} \right) \right\} \right\} / \\ &\{(J_{AB} - J_{BC})^2 + (J_{BC} - J_{AC})^2 + (J_{AC} - J_{AB})^2\}^{1/2} \quad (22) \end{aligned}$$

where $q = x, y$. Substituting into eqn. (22) the derivatives of (20) and (21)

$$\begin{aligned} \frac{\partial Q_{AB}}{\partial x} &= -\frac{3+K}{2} D_{AB} \beta_{AB} \exp(-2\beta_{AB}(x - y \operatorname{tg}\theta - r_{AB}^0)) \\ &+ \frac{1+3K}{2} D_{AB} \beta_{AB} \exp(-\beta_{AB}(x - y \operatorname{tg}\theta - r_{AB}^0)) \quad (23) \end{aligned}$$

$$\begin{aligned} \frac{\partial J_{AB}}{\partial x} &= -\frac{1+3K}{2} D_{AB} \beta_{AB} \exp(-2\beta_{AB}(x - y \operatorname{tg}\theta - r_{AB}^0)) \\ &+ \frac{3+K}{2} D_{AB} \beta_{AB} \exp(-\beta_{AB}(x - y \operatorname{tg}\theta - r_{AB}^0)) \quad (24) \end{aligned}$$

$$\frac{\partial Q_{AB}}{\partial y} = -\operatorname{tg}\theta \frac{\partial Q_{AB}}{\partial x} \quad (25)$$

$$\frac{\partial J_{AB}}{\partial y} = -\operatorname{tg}\theta \frac{\partial J_{AB}}{\partial x} \quad (26)$$

$$\frac{\partial Q_{BC}}{\partial x} = \frac{\partial J_{BC}}{\partial x} = 0 \quad (27)$$

$$\frac{\partial Q_{BC}}{\partial y} = -\frac{3+K}{2} D_{BC} \beta_{BC} \frac{C}{\cos\theta} \exp\left(-2\beta_{BC} \left(\frac{Cy}{\cos\theta} - r_{BC}^0\right)\right)$$

$$+ \frac{1+3K}{2} D_{BC} \beta_{BC} \frac{C}{\cos\theta} \exp\left(-\beta_{BC} \left(\frac{Cy}{\cos\theta} - r_{BC}^0\right)\right) \quad (28)$$

$$\begin{aligned} \frac{\partial J_{BC}}{\partial y} &= -\frac{1+3K}{2} D_{BC} \beta_{BC} \frac{C}{\cos\theta} \exp\left(-2\beta_{BC} \left(\frac{Cy}{\cos\theta} - r_{BC}^0\right)\right) \\ &+ \frac{3+K}{2} D_{BC} \beta_{BC} \frac{C}{\cos\theta} \exp\left(-\beta_{BC} \left(\frac{Cy}{\cos\theta} - r_{BC}^0\right)\right) \quad (29) \end{aligned}$$

$$\begin{aligned} \frac{\partial Q_{AC}}{\partial x} &= -\frac{3+K}{2} D_{AC} \beta_{AC} \exp\left(-\beta_{AC} \left(x - y \left(\operatorname{tg}\theta - \frac{C}{\cos\theta}\right) - r_{AC}^0\right)\right) \\ &+ \frac{1+3K}{2} D_{AC} \beta_{AC} \exp\left(-\beta_{AC} \left(x - y \left(\operatorname{tg}\theta - \frac{C}{\cos\theta}\right) - r_{AC}^0\right)\right) \quad (30) \end{aligned}$$

$$\begin{aligned} \frac{\partial J_{AC}}{\partial x} &= -\frac{1+3K}{2} D_{AC} \beta_{AC} \exp\left(-2\beta_{AC} \left(x - y \left(\operatorname{tg}\theta - \frac{C}{\cos\theta}\right) - r_{AC}^0\right)\right) \\ &+ \frac{3+K}{2} D_{AC} \beta_{AC} \exp\left(-\beta_{AC} \left(x - y \left(\operatorname{tg}\theta - \frac{C}{\cos\theta}\right) - r_{AC}^0\right)\right) \quad (31) \end{aligned}$$

$$\frac{\partial Q_{AC}}{\partial y} = -\left(\operatorname{tg}\theta - \frac{C}{\cos\theta}\right) \frac{\partial Q_{AC}}{\partial x} \quad (32)$$

$$\frac{\partial J_{AC}}{\partial y} = -\left(\operatorname{tg}\theta - \frac{C}{\cos\theta}\right) \frac{\partial J_{AC}}{\partial x} \quad (33)$$

we can evaluate eqns. (14) and (15) and, finally, obtain through eqns. (16) and (17) the trajectory on the LEPS surface.

Trajectories for the H₃ System

As an illustration of the capabilities of the set of programs mentioned in this paper we now present some trajectories for the H₃ system on a LEPS surface, calculated by the procedure described in the previous sections.

The LEPS surface has been calculated by the program LEPS for a value $K = 0.15$ (7), $D_{HH} = 109.4$ kcal/mol, $r_{HH}^0 = 0.74$ Å, and $\beta_{HH} = 1.94$ Å⁻¹ (11). Trajectories are calculated by the program TRAJE and represented on the energy surface $V = V(r_{AB}, r_{BC})$ by the program REPRE in the way shown in Figures 1, 2, and 3. Table 1 shows the energy intervals associated with each symbol displayed in this graphical representation of the trajectories. A time interval $\delta t = 0.5 \times 10^{-18}$ s has been taken determining a maximum oscillation in the total energy along the trajectories which is always less than 5×10^{-3} eV. The TRAJE program performs graphical representations of the values of r_{AB} , r_{BC} , and r_{AC} versus t as well, as shown in Figures 4 and 5.

Trajectories have been chosen for different experimentally accessible ranges of energy (9, 12). The range of vibrational energy runs from 0.25 to 1.5 eV, corresponding to the first few vibrational levels of H₂. The initial relative velocity has been selected from the range 0.5×10^4 to 2.0×10^4 m·s⁻¹ (~ 0.09 –1.38 eV). For all the trajectories calculated, the starting position of the ball is the bottom of the entrance or reactive valley.

In Figures 1–5 we present a selection of the most interesting trajectories. For the trajectory in Figure 1 the relative velocities are $\dot{r}_{AB} = -10,254$ m·s⁻¹ and $\dot{r}_{BC} = 0$ m·s⁻¹ (total energy = 0.363 eV). As can be observed, under these conditions the collision between H_A and H_B–H_C is nonreactive and inelastic. The ball has not translational energy enough to roll over the saddle-point and returns to the starting position with a transfer between translational and vibrational energy.

A reactive trajectory results from $\dot{r}_{AB} = -3775$ m·s⁻¹ and $\dot{r}_{BC} = -8815$ m·s⁻¹, this last value corresponding to the zero-point vibrational energy of H₂ (total energy = 0.433 eV) (Fig. 2). This shows plainly the importance of vibrational energy in overcoming a potential barrier. Figure 3 shows the studied reactive trajectory of minimum pure translational energy without vibration of H_B–H_C. For this trajectory $\dot{r}_{AB} = -10,255$ m·s⁻¹ and $\dot{r}_{BC} = 0$ m·s⁻¹ (total energy = 0.363 eV).

In Figures 4 and 5 the values of r_{AB} , r_{BC} , and r_{AC} versus time are represented. The trajectory corresponding to Figure 4 has been achieved with $\dot{r}_{AB} = -7500 \text{ m-s}^{-1}$ and $\dot{r}_{BC} = -8815 \text{ m-s}^{-1}$ (total energy = 0.692 eV). It is clearly a reactive collision by a direct mechanism, the lifetime of the collision complex being

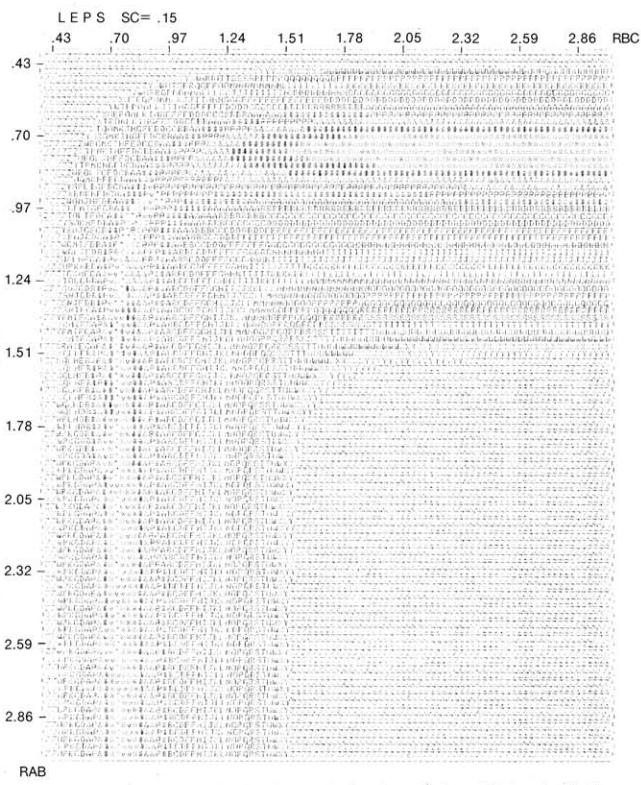


Figure 1. Trajectory for a nonreactive inelastic collision obtained with $\dot{r}_{AB} = -10254 \text{ m-s}^{-1}$ and $\dot{r}_{BC} = 0 \text{ m-s}^{-1}$.

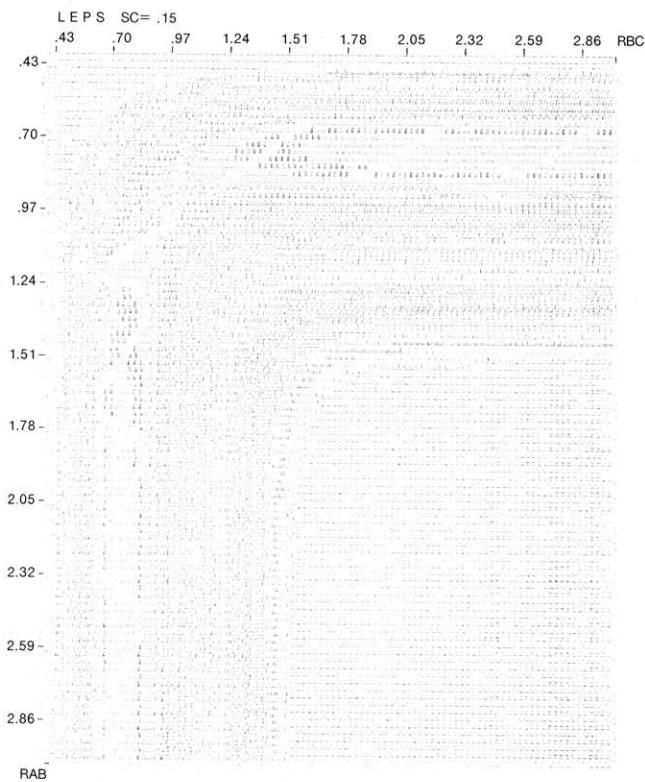


Figure 2. Trajectory for a reactive collision obtained with $\dot{r}_{AB} = -3775 \text{ m-s}^{-1}$ and $\dot{r}_{BC} = -8815 \text{ m-s}^{-1}$.

about $0.2 \times 10^{-14} \text{ s}$. Note that the collision is inelastic—the product H_A-H_B molecule has less vibrational energy than the reactant H_B-H_C molecule. In this same figure we can see

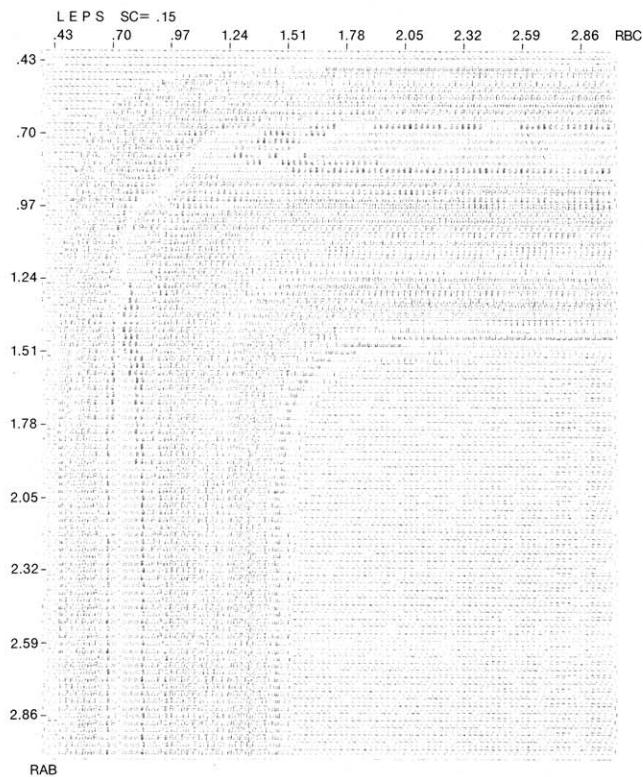


Figure 3. Trajectory for a reactive collision obtained with $\dot{r}_{AB} = -10255 \text{ m-s}^{-1}$ and $\dot{r}_{BC} = 0 \text{ m-s}^{-1}$.

Table 1. Symbols Used in the Trajectory Representation and Energy Intervals Associated with Them.

SYMBOL	lower E	upper E(eV)
*	0.000104	0.100211
#	0.100211	0.200319
&	0.200319	0.300427
@	0.300427	0.400535
\$	0.400535	0.500643
A	0.500643	0.600751
B	0.600751	0.700858
C	0.700858	0.800966
D	0.800966	0.901074
E	0.901074	1.001182
F	1.001182	1.101290
G	1.101290	1.201398
H	1.201398	1.301505
I	1.301505	1.401613
J	1.401613	1.501721
K	1.501721	1.601829
L	1.601829	1.701937
M	1.701937	1.802045
N	1.802045	1.902153
O	1.902153	2.002260
P	2.002260	2.102368
Q	2.102368	2.202476
R	2.202476	2.302584
S	2.302584	2.402692
T	2.402692	2.502800
U	2.502800	2.602907
W	2.602907	2.703015
X	2.703015	2.803123
Y	2.803123	2.903231
Z	GREATER THAN	2.903231

The zero of energy is taken to be the limiting energy for $\text{H}_2 + \text{H}$. ($-109.4 \text{ Kcal-mol}^{-1}$ = -4.744 eV)

RAR= * RBC= 0 RAC= +

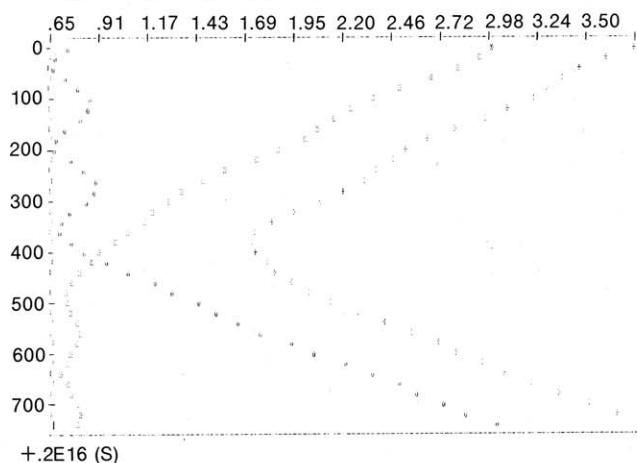


Figure 4. Reactive inelastic trajectory obtained with $\dot{r}_{AB} = -7500 \text{ m-s}^{-1}$ and $\dot{r}_{BC} = -8815 \text{ m-s}^{-1}$.

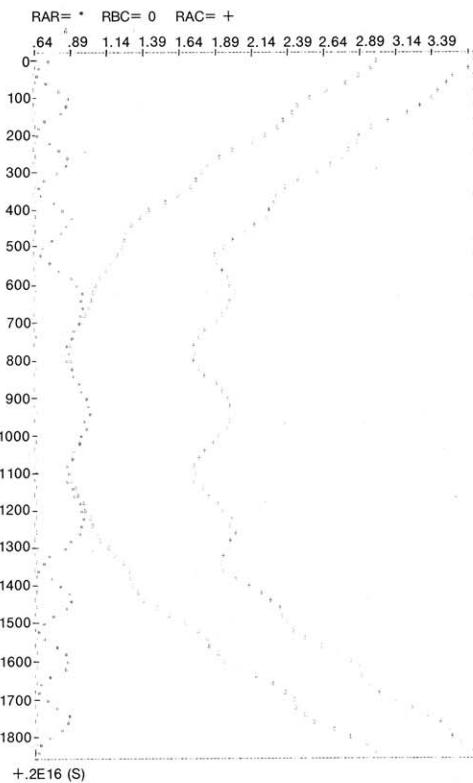


Figure 5. Nonreactive trajectory obtained with $\dot{r}_{AB} = -3774 \text{ m-s}^{-1}$ and $\dot{r}_{BC} = -8815 \text{ m-s}^{-1}$.

that the vibration period of H_2 is, according to our calculations, about $0.8 \times 10^{-14} \text{ s}$, in good agreement with Karplus et al. (13). Again in agreement with these authors, we have not found trajectories with collision complexes of large lifetimes. The longest interaction time found by us is about $2.7 \times 10^{-14} \text{ s}$ and corresponds to the trajectory in Figure 5 which has been achieved with $\dot{r}_{AB} = -3774 \text{ m-s}^{-1}$ and $\dot{r}_{BC} = -8815 \text{ m-s}^{-1}$ (total energy = 0.433 eV).

In Table 2 are listed some of the trajectories studied by us. These results show again the role of translational and vibrational energies in achieving a reactive collision. The first tra-

Table 2. Initial Velocities for Some Trajectories

$\dot{r}_{AB}(\text{m-s}^{-1})$	$\dot{r}_{BC}(\text{m-s}^{-1})$	Total Energy (eV)	Reactive ?
-10255	0	0.363	yes
-10254	0	0.363	no
-12024	-8503	1.104	yes
-19012	-8503	2.059	yes
-20827	-8503	2.363	no
-19012	-12024	2.541	no
-17005	-12024	2.207	yes
-12024	-12024	1.500	yes
-19673	0	1.337	yes
-19674	0	1.337	no
-20827	0	1.500	no

The starting point for all of them is the bottom of the reactive valley.

jectory in Table 2 shows the minimum translational energy required to obtain the products. This energy is about $3.1 \times 10^{-3} \text{ eV}$ greater than the potential barrier (0.360 eV). The last trajectory in Table 2 shows clearly that, for high-energy collisions, nonreactive trajectories are possible.

All these calculations and graphical representations have been carried out on an HP 9835B desk computer and a 2631A printer with the above-mentioned programs written in Basic language. A Fortran 77 version of these programs for a HP 1000 computer is also available from the authors. The LEPS surface used has been constructed with a 97×97 grid and took about 35 min on the HP 9835B and about 3 min on the HP 1000. The calculation and printout of each trajectory takes about 15 min on the HP 9835B and 2 min on the HP 1000.

Conclusions

This paper reports a very simple alternative for trajectory calculations. All types of mathematical complexities have been avoided trying to concentrate attention on chemical features. The construction of these programs is, then, a good exercise in physical chemistry yielding a considerable physical insight into the dynamics of a chemical process. In addition, these programs could be used in freshman chemistry courses to get the student acquainted with very important concepts in chemistry: the subjacent collision mechanism and the main collision features, the order of molecular velocities, potential surfaces and potential barriers, etc. Further, this procedure introduces students to the possibility of theoretical simulation and experimentation. Moreover, all those serious things can be achieved by simply playing a kind of "chemical golf."

Listings of the programs and a selection of the most interesting results are available for a postage-and-handling charge of \$10.

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