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Classical trajectories

C: Triatomic reaction dynamics with LEPS potential

When modeling systems with covalent bonds, a more complex potential function than a sum of pair potentials (such as L-J) must be employed. For example, to model the collision dynamics when a *F* atom strikes a H_2 molecule, it is important to build into the potential function the constraint that only one covalent bond is formed in the stable configurations of the three atoms. A sum of L-J potentials for each pair would lead to aglomeration of the three atoms into a trimer. A quite successful potential function for modeling covalent bond breaking and bond formation was constructed by studying the energetics of three H atoms in the ground (singlet) and first excited (triplet) states. The potential is called LEPS after the names of the four scientists that contributed most to its development, London, Eyring, Polanyi and Sato. The functional form is quite complex. The parameters will be chosen here to be those used by Polanyi and Wang in their famous article published in J. Chem. Phys. vol. 51, page 1439 in 1969. They picked values representtive of H-H interaction (bond energy of 4.746 eV and bond length of 0.742 A), but then adjusted the parameters to get asymmetry between the reactants and products of an exchange reaction. With the unit of energy chosen to be eV, the unit of length chosen to be Angstrom, and the unit of mass being amu, the unit of time becomes close to 10 fsec. The LEPS potential energy surface for the triatomic system with atoms A, B, and C, is defined by the following m files:

```
-----------------------------------------------------------------------------------------
% par.m

d=[4.746,4.746,3.445];
% The well depths in eV of the [AB,BC,AC] interactions

r0=[0.742,0.742,0.742];
% The bond distances in Angstroms for the [AB,BC,AC] dimers

alfa=[1.942,1.942,1.942];
% The exponential decay lengths of the [AB,BC,AC] interactions

p1=[1.05,1.30,1.05];
% This is written as [(1+a),(1+b),(1+c)] in the lecture notes
-----------------------------------------------------------------------------------------

-----------------------------------------------------------------------------------------
function y=q(r,int)
par
y=d(int)/4*(3*exp(-2*alfa(int)*(r-r0(int)))-2*exp(-alfa(int)*(r-r0(int))));
-----------------------------------------------------------------------------------------

-----------------------------------------------------------------------------------------
function y=jod(r,int)
par
y=d(int)/4*(exp(-2*alfa(int)*(r-r0(int)))-6*exp(-alfa(int)*(r-r0(int))));
-----------------------------------------------------------------------------------------

-----------------------------------------------------------------------------------------------------------------------------------------
function y=potentid(r1,r2)
par
```

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y=q(r1,1)/p1(1)+q(r2,2)/p1(2)+q(r1+r2,3)/p1(3)-sqrt((jod(r1,1)/p1(1)).^2+(jod(r2,2)/p1(2)).^2+(jod(r1+r2,3)/
p1(3)).^2-jod(r1,1).*jod(r2,2)/(p1(1)*p1(2))-jod(r2,2).*jod(r1+r2,3)/(p1(2)*p1(3))-jod(r1,1).*jod(r1+r2,3)/
(p1(1)*p1(3)));
```

Q1: Make a contour plot of this potential surface and compare with the sum of L-J potentials (in part B). You will need to modify the plot range. Try {0.3, 3.0}. Also, you should modify the values defining the contours. Try every 0.5 eV between -4.5 eV to 1.0 eV. What is the essential difference between the shape of the LEPS potential surface and the L-J potential surface?

Q2: Define a Matlab function that gives the derivative of the potential with respect to the A-B distance and another function that gives the derivative with respect to the B-C distance (see the L-J expressions in part B). It is very convenient to be able to use Matlab here to find the derivatives, and then to define the expressions yourself to save on processing time.

Q3: Calculate trajectories for the collision of an A atom with a B-C molecule and try to find initial conditions leading to an

A + BC -> AB + C

exchange reaction. Copy the Matlab expressions from part B for doing the velocity Verlet calculations. Check the energy conservation along the trajectories calculated and make sure the time step size is not too large. Try for example initial conditions where, xA = -3.0, vA = 1.0, xB = 0.0, vB = 0.0, xC = 0.8 and vC = 0.0.

Q4: Address the question: Which is more effective in increasing the reaction probability, an increase in the translational energy of the A atom, or an increase in the vibrational energy of the BC molecule? Start with the initial conditions specified in the previous question. Then, increase the translational energy of the A atom by increasing the initial velocity to vA = 1.5. Then, go back to vA = 1.0 but now increase the vibrational energy of the BC molecule by the same amount as you increased the translational energy of A before. These are two different ways of increasing the energy of the system by the same amount. The question is which is more likely to result in increased reaction probability. The shape of the potential surface determines whether increased translational energy or increased vibrational energy is more effective. The important feature of the potential surface is the location of the saddle point, whether it is early or late along the minimum energy path going from reactants to products. In order to answer this question rigorously, many trajectories would need to be calculated and a proper average over initial conditions carried out (the phase of the B-C vibration as A hits the molecule is very important for determining the outcome of the collision). This is too tedious for this exercise, but could be the topic of a special project in the last two weeks of the course.

Q5: Repeat the previous study for the reverse reaction

AB + C -> A + BC

Now, the location of the saddle point along the minimum energy path is different. Which is now more effective in increasing the reaction probability, translational or vibrational energy?