8.4 Recording a Potential Energy Profile: The Intrinsic Reaction Coordinate (IRC)

A transition state search merely guarantees that one reaches a first-order saddle point on the PES; there is, however, no guarantee that it is really linked to the reactant and product. (For instance, there may be further transition states lying in between.) Although the visualisation of the imaginary vibrational mode may give some hint as to whether one has found a reasonable saddle point, this information is not sufficient to guarantee a connection to the reactant and product well. Following the negative Hessian eigenvalues from the transition state to the next local minimum, on the other hand, will immediately reveal whether such a connection exists. This Hessian-following in mass-weighted coordinates is referred to as a search along the *Intrinsic Reaction Coordinate* (IRC). This search will create a potential energy profile for the reaction, as well as a trajectory that visualises the lowest energy path from reactant to TS to product. In this last exercise session, you will verify whether the transition state you computed in the last exercise is the proper state that connects your starting material to the product, and you will build the reaction profile and visualise the trajectory in VMD.

Finding Products and Reactants: IRC

Copy the Checkpoint file you saved from the transition state frequency calculation (section 8.3) to your working directory. Create the following input:

```
%NProcShared=2
%Mem=1GB
%OldChk=TSFreq
%Chk=For
#P B3PW91/6-31+G* IRC=(RCFC,Forward,Stepsize=10,Maxpoint=100,ReCorrect=Test)
   Guess=Read Geom=Checkpoint

IRC Forward

-1 1
```

Note that the route section `#` can be distributed over more than one line. `IRC` instructs Gaussian to perform an IRC Search, `Stepsize`, `Maxpoint` and `ReCorrect` are variables that are often specific to a reaction and that, in the worst case, have to be found by trial and error. For this run, you are provided with working variables. Again, we use both the `Guess` wavefunction, the Hessian `RCFC` and the `Geom` from the Checkpoint file to save computational time. `Forward` specifies the direction of the search. However, `Forward` does not imply that the search will proceed to the product, as the choice of the direction is based on the local curvature at the TS. Therefore, `Forward` may actually lead to the reactants, and the opposite keyword `Reverse` may lead to the product instead. Create a second input for the `Reverse` IRC search:

```
%NProcShared=2
%Mem=1GB
%OldChk=TSFreq
%Chk=Rev
#P B3PW91/6-31+G* IRC=(RCFC,Reverse,Stepsize=10,Maxpoint=100,ReCorrect=Test)
   Guess=Read Geom=Checkpoint

IRC Reverse

-1 1
```

Submit the jobs to Gaussian *one at a time*. (If you work in groups of two, split the tasks to save time.) Once the runs finish, verify whether they found a minimum on the PES (`PES minimum detected on this side of the pathway`). If this is the case, you may extract the coordinates using the script `g09_scan_trajectory.sh`:

```
bash g09_scan_trajectory.sh -i filename -n number_of_atoms -o output.xyz
```

Make sure that the `g09_scan_trajectory.sh` output has the extension `.xyz`. Do this for both the forward and reverse run, and open the xyz files you obtained in VMD (first one, then the other). You will see that both trajectories start from the transition state. In order to have a proper visualisation, you need to reverse one of them. Identify the trajectory that leads to the reactants (is it `Forward` or `Reverse`?) and note the number of frames this trajectory contains. This trajectory is the one that you need to reorder, such that the first frame is given by the reactants, rather than the TS. Use the script `reverse_trajectory.sh`:

```
bash reverse_trajectory.sh -i filename -n number_of_atoms \
-f number_of_frames -o output.xyz
```

Then, you can concatenate the reversed reactant trajectory and the trajectory that leads to the product to one single trajectory:

```
cat reversed_reactant_trajectory product_trajectory > reaction.xyz
```

Open the concatenated trajectory in VMD. As VMD is by default not able to redraw bonds during a trajectory, you will have to fiddle with the representation. Go to `Graphics` in the *VMD Main*, then to `Representations...` and change the `Drawing method` to `CPK`. Set the `Bond Radius` to 0.0. Click on `Create Rep` and, for the new representation, change the `Drawing method` to `Dynamic bonds`. Decrease the `Bond Radius` to 0.1 and increase the `Distance Cutoff` to 2.0. If you go through the trajectory now, you will see how bonds are being broken and formed as the reaction proceeds.

a) How do the C-Cl and the two relevant C-O bond lengths change during the trajectory? Does the C-C bond in the ring contract as the epoxide is formed? Show a graph depicting the evolution of these parameters as the reaction progresses. (Hit `2` to select bond lengths, and use `Graphics` (*VMD Main*), `Labels` and `Graph` (*Labels* Menu) to visualise the changes, just as you did in the PES scan of butane.)

b) What is happening to the methyl group as the reaction proceeds? Find a suitable parameter (angle, dihedral) to describe and characterise possible changes you observe. (Hit `3` to select angles, or `4` for dihedrals.)

c) Is the stereochemistry at the carbon at which the reaction takes place retained?

All the information on the reaction energy profile can be found at the end of the Gaussian output files after `Summary of reaction path following`. You can extract this information using grep:

```
grep -A number_of_steps+3 "Summary of reaction path" outputfile > energy_file
```

Do this for both IRC outputs, writing to different files. Make sure that you specify a number that exceeds the number of steps by 3. You can then use a plotting program, LibreOfficeCalc or Microsoft Excel to visualise this data (both LibreOfficeCalc and Excel have the ability to import plain text files). We recommend a quick approach. From the command line, invoke the plotting program gnuplot:

```
gnuplot
```

In the gnuplot interface, type the following:

```
set xlabel 'Reaction Coordinate'
set ylabel 'Energy [kcal/mol]'
plot './forward_energies' using 3:($2*627.5095) with lines title 'forward',\
'./reverse_energies' using 3:($2*627.5095) with lines title 'reverse'
```

After every line, hit enter. In the `plot` command, the first number after `using` specifies the x axis, which is the third column in your energy file (the reaction coordinate). The second number specifies the y axis, which corresponds to the second column in the energy file (the energy of the system). The multiplication by a factor of 627.5095 converts the y-values to kcal mol^{-1}. If the resulting graph shows a reaction that proceeds from right to left, rather than from left to right as requested by convention, you may replace the x-axis specification `3` by `-$3`, which will create a plot that takes the negative of the reaction coordinate as its x axis.

d) Take a screenshot of the graph of the potential energy profile you recorded. Make sure that the left half corresponds to the reactants, and that the product state can be found to the right.

e) Why is the barrier for the epoxide formation so low? Will this be the overall barrier for the reaction as depicted in section 8.1?