

A Brief Guide to Intrinsic Reaction Coordinate Calculations

The following instructions for generating the intrinsic reaction coordinate (IRC) for an elementary chemical reaction assume that you have already identified the transition state (TS) for the reaction. The forces on all atoms should be negligible (converged) and the geometry should exhibit one imaginary vibrational frequency. The IRC is the minimum energy pathway (MEP) that connects the reactant molecule to the product through the TS. The IRC is represented by a series of points (geometries) along the MEP.

Let's assume that the Gaussian input for your frequencies calculation for the TS is in the file `myts.gau`.

1. Copy the TS input file, set up the forward IRC calculation, and run it.

```
cp myts.gau myts-ircf.gau
```

Edit `myts-ircf.gau` and change the route section to read:

```
# b3lyp/cc-pVDZ irc=(maxpoints=400,calcfc,recalc=5,tight,forward,lqa)
```

The keyword `irc` tells Gaussian to perform an IRC calculation. The options that follow do the following:

`maxpoints=400` – calculate up to 400 points (the maximum possible) along the IRC
`calcfc` – begin the calculation by calculating the force constants (curvatures)
`recalc=5` – recalculate force constants every five steps along the energy pathway
`tight` – use tight convergence thresholds for geometry optimizations
`forward` – move in the forward direction
`lqa` – use the local quadratic approximation

Submit this Gaussian calculation. Gaussian will calculate the MEP in the forward direction starting with the TS geometry and moving downward on the potential energy surface.

2. Copy the IRC input file, set up the reverse IRC calculation, and run it.

```
cp myts-ircf.gau myts-ircr.gau
```

Edit `myts-ircr.gau` and change the route section to read:

```
# b3lyp/cc-pVDZ irc=(maxpoints=400,calcfc,recalc=5,tight,reverse,lqa)
```

The only change to the Gaussian input file is to switch from `forward` to `reverse`.

Submit this Gaussian calculation. Gaussian will calculate the MEP in the reverse direction starting with the TS geometry and moving downward on the potential energy surface.

Note that the “forward” direction along the potential energy surface is rather arbitrary. Gaussian may determine that the forward direction is toward geometry that you would consider the product. But Gaussian may equally well determine that the forward direction is toward the reactant.

If the “forward” IRC calculation maps the TS to the *product*, then the “reverse” IRC will map from TS to *reactant*.

If the “forward” IRC calculation maps the TS to the *reactant*, then the “reverse” IRC will map from TS to *product*. In this case, we will fix the reaction direction later.

3. Gather the geometries along the forward IRC.

```
irc myts-ircf.log
```

The `irc` program reads the Gaussian `myts-ircf.log` output file and picks out the converged geometries that describe the forward IRC. These geometries are written to an external `.irc` file, in this case `myts-ircf.irc`.

Edit `myts-ircf.irc` and inspect its contents (but do not modify the file). Geometries are written in XYZ format of the following form

line 1: number of atoms (N) in geometry
line 2: brief title that lists the current point number, the IRC coordinate value, and the energy at this point of the IRC
next N lines: atomic symbols and Cartesian coordinates for each atom

Note that the first geometry is that of point 0 (IRC=0.00000), which corresponds to the TS. The last geometry in the file is the one that is closest to the product (or reactant, depending on what Gaussian chooses to call the forward direction).

4. Gather the geometries along the reverse IRC.

```
ircr myts-ircr.log
```

The `ircr` program reads the Gaussian `myts-ircr.log` output file and picks out the converged geometries that describe the forward IRC. These geometries are written in reverse order to an external `.irc` file, in this case `myts-ircr.irc`.

Edit `myts-ircr.irc` and inspect its contents. The first geometry in this file will be the one nearest the reactant (or product) along the IRC.

5. Concatenate the reverse and forward `.irc` files to make a composite `.irc` file.

```
cat myts-ircr.irc myts-ircf.irc > myts.irc
```

This command prints the contents of the two files `myts-ircr.irc` and `myts-ircf.irc`, one after the other, to the terminal screen. However, the “>” redirect command redirects the output from the screen to the file `myts.irc`.

At this point you will have an XYZ-formatted file `myts.irc` that lists all of the geometries along the IRC. This file is readable by `molden`. So `molden` the file

```
molden myts.irc
```

and run the “Movie” to see an animation of your reaction.

If your reaction runs “backwards”, from products to reactants, you can easily reverse the order of geometries in your `.irc` file using the following command:

```
irctoirc myts -1
```

The `irctoirc` program reads a `.irc` file (`myts.irc` in this case) and then writes a new `.irc` file of the same name (`myts.irc`). The “-1” tells `irctoirc` to write every geometry of the original file to the new file, but in reverse order.

Then `molden` the new `myts.irc` file and ensure that the animation runs in the desired direction.

6. Parse the composite `.irc` file for energies.

```
grep Energy myts.irc > myts.txt
```

Note that the “E” must be capitalized in this command.

The `grep` command will write every line that contains the character string “Energy” to the file `myts.txt`. These lines happen to be all of the titles for the XYZ-formatted geometries. Thus, all of the title lines `myts.irc` will be written to `myts.txt`.

Edit `myts.txt` and ensure that the title lines appear in the file.

7. Transfer `myts.txt` to your laptop and open the file in Excel. The columns of `myts.txt` are space-delimited. Convert the raw energy values to relative energies in kcal/mol (using the reactant energy as reference). Prepare a plot of the reaction profile, that is a plot of relative energy vs IRC value. Below is an example for formamide-formimidic acid tautomerism.

