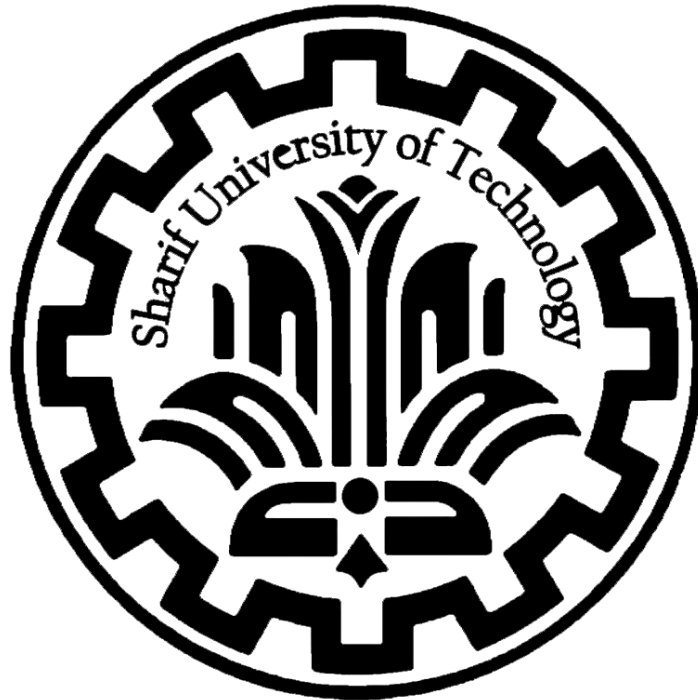4th Winter School of Computational Chemistry
Sharif University of Technology

Exercise Manual

Transition State

Transition State

There are three steps that we would take to find the right Transition State of a reaction:
1. Scan
2. Opt
3. IRC

In scanning, we wish to find a structure which has the greatest similarity to the final transition state. We can do it in ORCA using *ScanTS* keyword combined with *scan* sunblock in *geom* block. These are some recommended tips to take these steps:

- First take a look at your initial and final geometry. Find the bond(s) which will break or created during the reaction. Scan the PES using scan sunblock along that breaking bond.
- You can make an optimization before the PES Scan. It ensures that you are starting from a reasonable point.
- You can also ignore the ScanTS keyword and look carefully along the scan energies to find the non-optimized TS by yourself, and then run a separate job with *OptTS* keyword to find the optimized TS.
- The job will be terminated after the ScanTS finds a TS. You can force the ORCA to run even after finding the TS with:

```
%geom

    fullScan true # do not abort the scan with !ScanTS

end
```

The TS guess you made with PES Scan could have more than one imaginary mode (which its frequency is negative). We then should optimize the structure to have just one imaginary mode. In order to do that we can use the *OptTS* keyword. You can select the imaginary mode you would want to retain in the molecule using *TS_MODE* sunblock of *geom* block or you can give an internal coordinate that should be strongly involved in this mode:

```
%geom
    # Specify the exact mode index(the default is the one with
    #lowest eigenvalue):

    TS_Mode {M 1} # {M 1} mode with second lowest eigenvalue
            end   # (default: {M 0}, mode with lowest eigenvalue)



    # Alternatively giving the internal coord. that should be
    #involved in TS:

    TS_Mode {B 1 5} # bond between atoms 1 and 5,
```

```
    end                 # you can also choose an angle: {A N1 N2 N1}
                        # or a dihedral: {D N1 N2 N3 N4}
end
```

Also in order to improve the performance of converging we can specify the active atoms in TS:

```
%geom
    TS_Active_Atoms { 1 2 3 } # atoms that are involved in TS, e.g.
                              # for proton
    end     # transfer the proton, its acceptor and its donor
    TS_Active_Atoms_Factor 1.5 # factor by which the cutoff for
                              # bonds is increased for
                              # the above defined atoms.
                              # (Default 1.5, i.e. increased by 50%)
end
```

In the scan step you do not move along the right coordination of the reaction. So if you plot your energy along the path (written at the end of the output), you may not get a familiar hill-containing profile for the energy. In order to find the right trajectory you should run a job with *IRC* keyword. This keyword will take you from the optimized TS to the neighbour minima in the PES along the path imaginary mode of the TS would imply.

Let's take a deep look at these steps with the example shown in the above picture (proton abstraction from methane using OH radical):

- First run an scan using the following input file:

```
!PBE SV(P) TightSCF SlowConv
!Opt


%PAL nprocs 4 end


%geom
  scan
     B 0 1 = 1.5, 1.0, 20
  end
end

* xyz 0 2
  C    -0.21824606843760   -0.00083135856797    -0.00083081562683
  H     1.67779524187113   -0.04094917559541    -0.03267827046994
  H    -0.37057761122775    1.09123735886526    -0.00138668234101
  H    -0.24857594464979   -0.54750800753334    -0.95841634773405
  H    -0.29840228169862   -0.56000325630623    0.94623837749198
```

```
   O    2.62667873842690    0.25010374723712    0.07265217421081
   H    2.54131924529169    1.10814159314566    0.54071832533855
*
```

- You could alternatively run the PES Scan using an automatic black-box pathway used in ORCA to automatically find the reaction path between the reactants and products:

```
! PBE SV(P) TightSCF SlowConv
! IRC

%PAL nprocs 4 end


* xyz 0 2
  C    0.05558697688603    -0.01408092659732    0.00585563804212
  H    1.27376725114725    -0.05102984922335    0.08687711812722
  H   -0.27027466909650     1.04357254347761    0.07306313124187
  H   -0.18609983867210    -0.46383020579680   -0.97848602426769
  H   -0.31562091096290    -0.62100598743590    0.85639806418932
  O    2.59119607768573     0.21163738118097    0.20347666749510
  H    2.56143643258844     1.19492794563988    0.31911216604157
*
```

- Plot the energy vs distance between C and H to find a place having nearly zero first derivative.
- Take that geometry to Optimize the TS (replace your geometry in this block):

```
! PBE SV(P) TightSCF SlowConv
! OptTS Freq

%PAL nprocs 4 end

%geom
     Calc_Hess true  # calculation of the exact Hessian
                     # before the first optimization step

     # Optionally you can set the atoms for which you wish to find
     # the exact Hessian:

     # Hybrid_Hess {0 1 5 6} end
                     # this calculates a Hybrid Hessian with
                     # exact calculation for atoms 0, 1, 5 and 6
end
```

```
* xyz 0 2
  C    0.05456461987052    -0.00691469386863    -0.00293238546444
  H    1.29132559363955    -0.01083909918736    -0.01654437844809
  H   -0.28591192944162     1.04791673600096    -0.00764524470132
  H   -0.22280360927147    -0.54295486793244    -0.93322869650955
  H   -0.24709783876561    -0.55098104866324     0.91458212632522
  O    2.57280695967251     0.25501230945751     0.05582518390121
  H    2.54710752387207     1.10895156543829     0.55624015576647
*
```

- Check that the last Frequency Block in the output must contains only one imaginary mode:

```
-----------------------
VIBRATIONAL FREQUENCIES
-----------------------

Scaling factor for frequencies =  1.000000000  (already applied!)

     0:         0.00 cm**-1
     1:         0.00 cm**-1
     2:         0.00 cm**-1
     3:         0.00 cm**-1
     4:         0.00 cm**-1
     5:         0.00 cm**-1
     6:      -285.89 cm**-1 ***imaginary mode***
     7:        36.17 cm**-1
     8:       211.77 cm**-1
     9:       353.88 cm**-1
    10:       805.81 cm**-1
    11:      1051.92 cm**-1
    12:      1084.17 cm**-1
    13:      1290.04 cm**-1
    14:      1371.67 cm**-1
    15:      1384.34 cm**-1
    16:      1425.25 cm**-1
    17:      2982.57 cm**-1
    18:      3115.14 cm**-1
    19:      3117.53 cm**-1
    20:      3486.03 cm**-1
```

- Checkout to see whether the imaginary mode is the desired mode which leads us to products. This can be checked from the last column of the following table which indicates contributions of different internal coordinates in the optimized TS imaginary mode (or you can alternatively visualize the mode using ChemCraft or Avogadro to see whether this mode is valid or not):

5

```
-----------------------------------------------------------------------
                    Redundant Internal Coordinates

                    --- Optimized Parameters ---
                      (Angstroem and degrees)

    Definition                    OldVal   dE/dq    Step    FinalVal  comp.(TS mode)
-----------------------------------------------------------------------
 1. B(H    1,C   0)                1.2216 -0.000022 -0.0002   1.2214          0.47
 2. B(H    2,C   0)                1.1088 -0.000000  0.0000   1.1088
 3. B(H    3,C   0)                1.1089 -0.000002  0.0000   1.1089
 4. B(H    4,C   0)                1.1089  0.000001 -0.0000   1.1089
 5. B(O    5,H   1)                1.3479 -0.000002  0.0005   1.3484          0.86
 6. B(H    6,O   5)                0.9905  0.000000  0.0000   0.9905
 7. A(H    1,C   0,H   2)         108.54   0.000006  -0.00   108.54
 8. A(H    1,C   0,H   4)         105.41  -0.000024   0.04   105.45
 9. A(H    1,C   0,H   3)         105.34   0.000021  -0.03   105.31
10. A(H    2,C   0,H   4)         112.16  -0.000001   0.01   112.16
11. A(H    3,C   0,H   4)         112.71   0.000001  -0.00   112.70
12. A(H    2,C   0,H   3)         112.14  -0.000003  -0.01   112.13
13. A(C    0,H   1,O   5)         166.97  -0.000001  -0.00   166.97
14. A(H    1,O   5,H   6)         100.03  -0.000001  -0.00   100.03
15. D(O    5,H   1,C   0,H   2)     0.15  -0.000012   0.47     0.62
16. D(O    5,H   1,C   0,H   4)  -120.18  -0.000000   0.44  -119.75
17. D(O    5,H   1,C   0,H   3)   120.43   0.000000   0.44   120.86
18. D(H    6,O   5,H   1,C   0)     0.99  -0.000011   0.38     1.37
-----------------------------------------------------------------------
```

- Now you can run the IRC from the optimized structure to get your reactants and products (replace the structure with the optimized TS structure obtained in the last step):

```
! PBE SV(P) TightSCF SlowConv
! IRC

%PAL nprocs 4 end


* xyz 0 2
  C    0.05558697688603   -0.01408092659732    0.00585563804212
  H    1.27376725114725   -0.05102984922335    0.08687711812722
  H   -0.27027466909650    1.04357254347761    0.07306313124187
  H   -0.18609983867210   -0.46383020579680   -0.97848602426769
  H   -0.31562091096290   -0.62100598743590    0.85639806418932
  O    2.59119607768573    0.21163738118097    0.20347666749510
  H    2.56143643258844    1.19492794563988    0.31911216604157
*
```