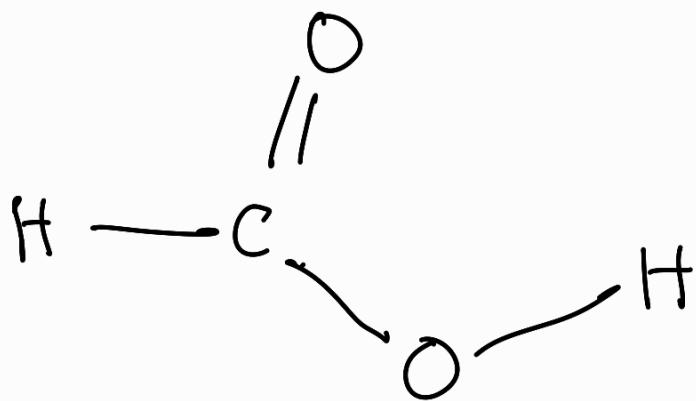


## Computational Work

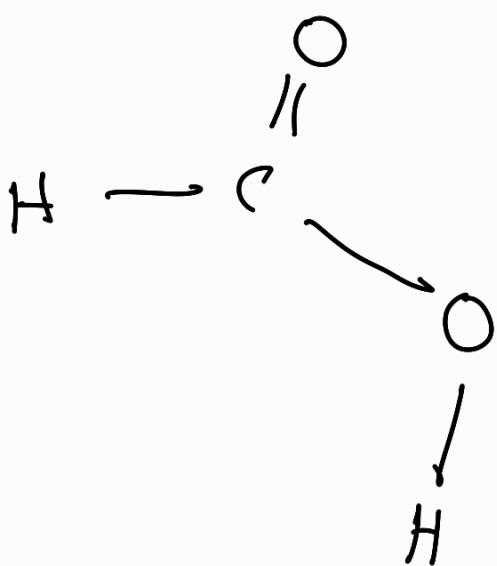
Note: This covers almost all topics discussed on Geometry Optimizations. The work has weightage of 2 times regular works.

In this work, we will consider optimizations involving formic acid  $\text{HCOOH}$ . The molecule is expected to have equilib geometry structures as follows.

(A)



(B)



$$R_{C=O} \approx 1.2 \text{ \AA}$$

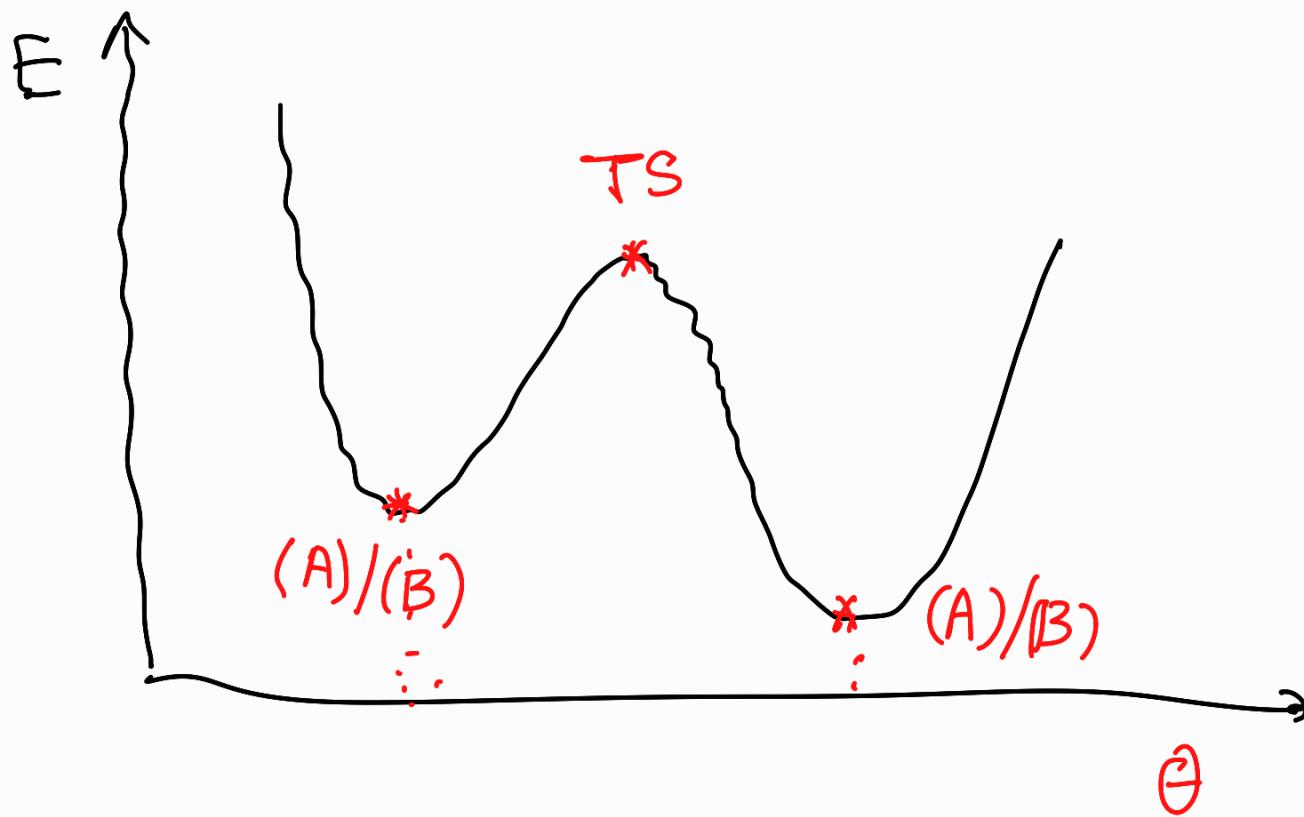
$$R_{C-O} \approx 1.01 \text{ \AA}$$

$$R_{C-H} \approx 1.0 \text{ \AA}$$

$$R_{O-H} \approx 1.0 \text{ \AA}$$

Both (A) & (B) are planar and they are not equivalent - meaning that one of them is lower in energy. This results in the

following schematic PES where  
 these two structures are connected  
 by a rotation of OH bond  
 around C=O bond.



$\theta$ : dihedral angle of  $C=O$

& O-H along C=O bond.

TS: Transition state connecting

(A) & (B)

Q1. Setup a suitable Z-matrix which describes both (A) & (B) structures connected by  $\Theta$  as one of Z-matrix parameters.

Optimize geometry of these structures using HF/6-31G\*.  
Carry out frequency calculations to confirm that they are minima, and explain how it is confirmed.

(6 Marks)

Q2. From the above calculations,

find out which structure is lower in energy & by how much (in kcal/mol units)

Further, using frequency values

compute "zero-point energy"

corrected energy difference as

follows.

$$E(\text{ZPE}, A/B) = \frac{1}{2} \sum_{\nu \in A/B} h\nu_i$$

$$\Delta E(\text{ZPE}) = E(\text{ZPE}, A) - E(\text{ZPE}, B)$$

$$\Delta E = \Delta E(\text{opt}) + \Delta E(\text{ZPE})$$

List out all frequencies and convert zero-point energy of each freq to kcal/mol units.

(4 Marks)

Q3. Setup an appropriate guess

structure for the transition state

connecting (A) & (B). Compute

gradient & hessian at this

guess structure and remark

whether hessian has correct

structure for transition state

optimization to be successful.

(4 Marks)

Q4. Perform geometry optimization for the transition state using Newton-Raphson method, and starting optimization using CalcFC option. Perform optimization using Z-matrix as well as Cartesian coords and verify that same final transition state is obtained in both methods. Write down the transition state geometry and comment how much it is different from initial guess.

(4 Marks)

Q5. Use frequency calculations and confirm that it is indeed a transition state. Also find the energy barrier for transition state,  $\Delta E(TS) = E(TS) - E(A)$  or  $E(B)$  in kcal/mol units. Also compute "zero-point energy corrected"  $\Delta E(TS)$  value. (4 Marks)

Q6. Perform IRC calculations

Starting from TS geometry & confirm if the TS connects

the structures (A) & (B).

(4 Marks)