Computational Chemistry Course Lab Report 10

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Q1: Write an expression for the effective NEB force acting on an image and explain why it is important to have a good estimate of the tangent to the path.

The NEB force will be:

$$F^{NEB} = -\nabla V(x_i)|_{\perp} + (F_i^s \cdot \hat{\tau}_{\|})\,\hat{\tau}_{\|} \tag{1}$$

NEB depends on the perpendicular force to the path and the spring force parallel to the path. It is important to have a good estimate due to a poor estimate, that mixes the perpendicular and parallel components, will not find the proper MEP. Moreover, if the tangent is badly calculated, the images tend to cut corners, therefore the path does not follow the MEP valley and it will yield an incorrect MEP. ✓

Q2: If two MEPs exist connecting a given pair of reactant and product energy minima, to which one will the NEB converge?

The NEB will converge to the minimum energy path that is nearest to the initial guess path. ✓

Q3: Often, saddle points are referred to as transition states. Why is that strictly not correct? Due to the transition state~~ strictly is a first order saddle point. Not all the saddle points are TS, but all the TS are first order single points~~

Q4: How large is the energy barrier for the isomerization reaction of hydrogen cyanide? How does the barrier height compare to the thermal energy available at room temperature?

The energy barrier of the reaction is 1.36 eV. Compared with the thermal energy at room temperature (k_BT ≈ 0.025 eV), the barrier is really large. ✓

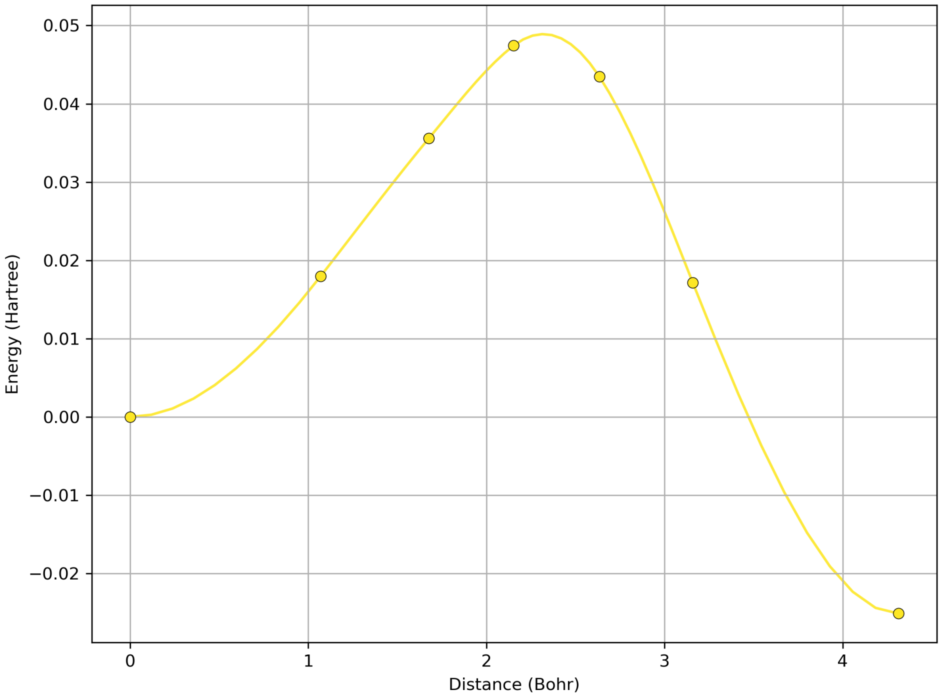
Q5: How do the two NEB calculations started from the two initial paths compare in computational efficiency, i.e. in number of optimisation steps and the number of times the energy and gradient of energy need to be evaluated? Explain the difference.

Normal NEB, 44 optimization steps, 292 times the energy and gradient have been evaluated and lasted 146.736 sec. NEB-CI 50 optimization steps, 322 times the energy and gradient have ✓

been evaluated and lasted 161.529 sec.

The NEB-CI needs more steps owing to the climbing image process. However, the difference in time is only 15 seconds and the TS is better defined with this method.

Q6: Make a graph of the minimum energy path (show the relative energy as a function of displacement along the MEP).



✓

Figure 1: MEP using NEB method.

Q7: How does the energy barrier obtained from the CI-NEB calculation compare with the one obtained from the regular NEB? Include a picture of the CI-NEB saddle point geometry in your report (stored in the file orca NEB-CI converged.xyz).

Observing the Figures 1 and 2, we observe that the NEB-CI method provides a slightly higher energy barrier compared with the NEB method. Moreover, the TS is better described in NEB-CI than regular NEB. ✓

A more accurate estimate of the activation energy is obtained from the CI-NEB results.

Q8: Describe the reaction coordinate at the transition state, i.e. the atomic motion involved in traversing the saddle point along the unstable mode.

The negative frequency of the TS is the displacement of the H atom toward the nitrogen. The reaction coordinate can be the distance between carbon and hydrogen or between nitrogen and hydrogen. ✓

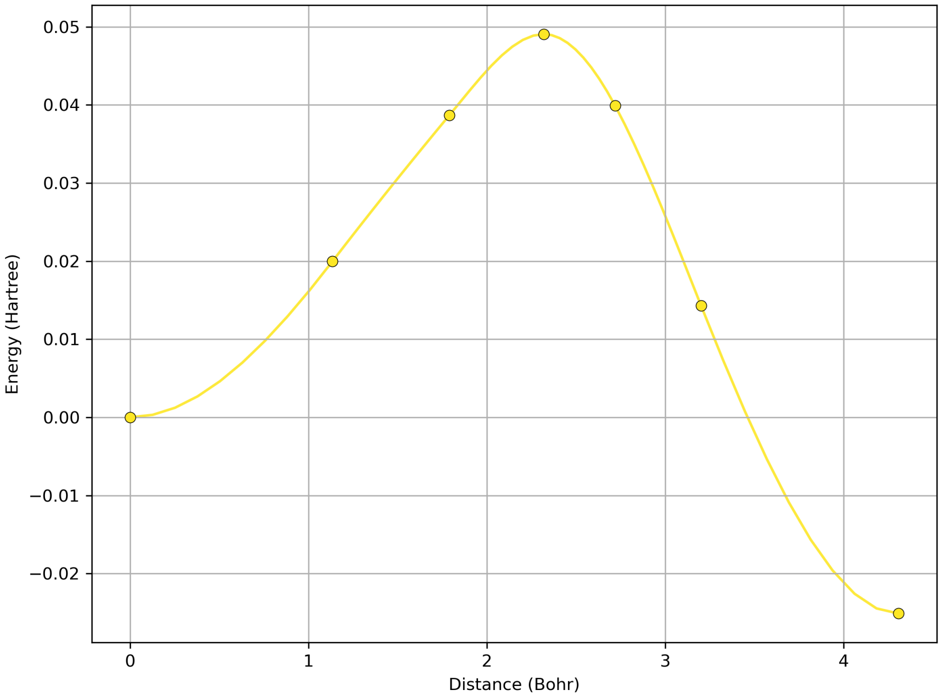


Figure 2: MEP using NEB-CI method.

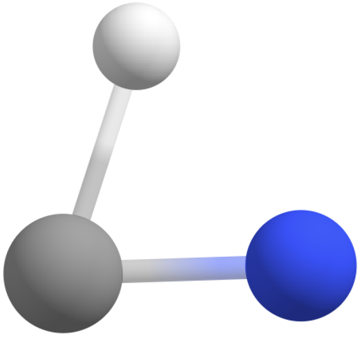


Figure 3: Structure of the saddle point geometry found by NEB-CI method.

Q9: Describe the reaction coordinate at the transition state, i.e. which atoms are moving mostly and in what way.

The negative frequency of the TS is the displacement of the H atom toward an oxygen atom. The reaction coordinate can be the distance between carbon and hydrogen or between oxygen and hydrogen. ✓

Q10: Make a graph of the energy along the MEP. Show the atomic configurations at reactant, product and saddle point as insets in the figure.

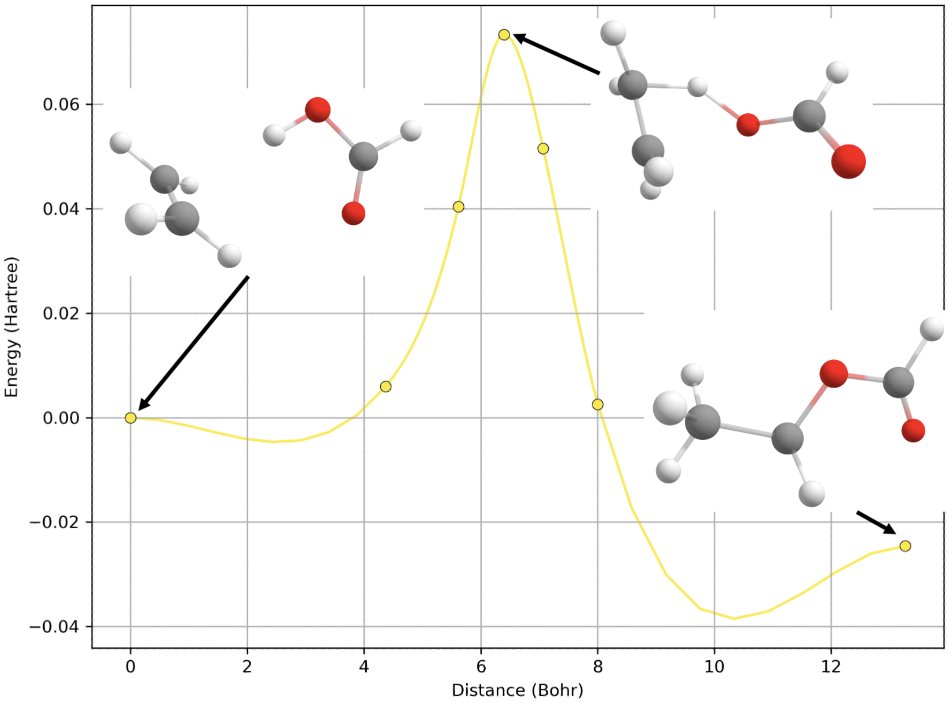


Figure 4: MEP of the pyrolysis of ethyl formate.

Q11: Briefly discuss/explain transition state theory (TST). What are the four basic assumptions of TST? What are some of the challenges of applying TST to molecular reactions?

Transition state theory is a method used for estimating the reaction rate of slow transitions between states owing to the thermal energy. The four basic assumptions of TST are: we rely on Born-Oppenheimer approximation, in other words, adiabatic potential energy curves of the system; we apply classical mechanics to the nuclei; in the initial state we assume Boltzmann distribution; and we assume no recrossing of TS, if the reaction reach the TS, the system will always finish in the products. The challenges of TST are: we neglect the re-crossings, so the estimated rate will be higher to the real one; then, we are not taking into account quantum effects as tunnelling; that may affect in the rate.

✓

Q12: What is the harmonic approximation to TST (HTST)? When is it a good approximation and when does it not apply?

Harmonic approximation to TST assumes that the PES between the reactant and the TS can be approximated with an harmonic approximation. The HTST works well when the energy difference between saddle points is higher than k_BT; and the potential is smooth enough to use second order terms of the Taylor expansion to describe the reactant region. HTST breaks down when the anharmonicity effect is too strong, where the temperature is too high and the energy differences between saddle points is lower than thermal energy. ✓

Q13: Calculate the rate constant of the pyrolysis reaction using HTST assuming (a) room temperature and (b) a temperature of 1000 K.

From our calculations we obtain a energy barrier of 2.00 eV a pre-exponential factor of 3.31 x 10^{11}. Then, the rate constant at room temperature (300 K) is 1.007x10^{-22} s^{-1} and at 1000 K, the rate constant is 29.133 s^{-1}. Comparing with the literature [1], who obtains a activation energy of 2.17 eV and a pre-exponential factor of 2.55 x 10^{14}, our calculations provide similar results compared to the bibliography. The differences between both results can be produced due to the different level of theory.

References

[1] B. Lowe, A. L. Cardona, J. Salas, A. Bodi, P. M. Mayer, M. A. Burgos Paci, “Probing the pyrolysis of ethyl formate in the dilute gas phase by synchrotron radiation and theory”, *J. Mass Spectrom.* **2023**, *58*, e4901.