Excercise : Ammonia Flipping

Faculty of Physics, AG-CMP, University of Vienna

universität wien

CMS CENTER FOR COMPUTATIONAL MATERIALS SCIENCE

Transition State of NH_3 flipping

general remarks (1)

- this excercise consists of 4 steps which unfold if you untar the file ammonia_flipping.tgz
  `tar zxvf ammonia_flipping.tgz`
  1. $\longrightarrow$ scf: relaxed geometry of NH_3
  2. $\longrightarrow$ NEB: TS search using the Nudged Elastic Band method
  3. $\longrightarrow$ TS_vib: get the vibrational modes of the TS (planar NH_3) to find the mode of the decay direction, to be given in the improved-dimer calculation
  4. $\longrightarrow$ improved-dimer: TS search using the improved dimer method.
  5. compare the results and runtimes using NEB and the improved dimer method

Transition State of NH_3 flipping

general remarks (2)

- for all calculations of this excercise, use:
  - PAW-PBE pseudopotentials (`potpaw_PBE_54.tar.gz` data set)
  - an orthorhombic 6×7×8 unit cell
  - Γ-point only:
- `KPOINTS`

  `k-points`

  `0`

  `G`

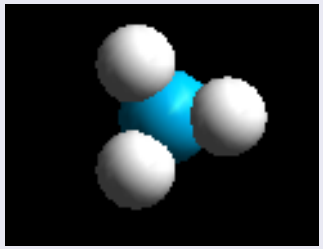
  `1 1 1`

Transition State of NH_3 flipping: 1. Relaxed Geometry

POSCAR

```
ammonia flipping
1.000000
6.000000 0.000000 0.000000
0.000000 7.000000 0.000000
0.000000 0.000000 8.000000
3 1
Selective dynamics
Direct
0.636429 0.567446 0.549205 T T T
0.500000 0.364896 0.549205 T T T
0.363571 0.567446 0.549205 T T T
0.500000 0.500000 0.500000 F F F
```

NH_3 Relaxed Geometry



- use Selective dynamics
- fix the position of N
  `F F F`
  to avoid that the molecule drifts through the cell

Transition State of NH_3 flipping

INCAR

```
SYSTEM = Ammonia flipping
IBRION = 2
NSW = 2
ALGO = N
POTIM = 0.5
EDIFF = 1e-6
EDIFFG = -0.01
NELMIN = 5
```

NH_3 Relaxed Geometry

- CG-algorithm for ionic relaxation
- blocked Davidson for el. relaxation
- at least 5 el. steps for each ionic step

$E^0 =$ -19.4955 eV: see `OUTCAR`

```
energy without entropy= -19.50322126 energy(sigma->0) =
-19.49549072
```

Transition State of NH_3 flipping

1. using the Nudged Elastic Band Method ...

G. Mills *et.al.* Surf. Sci. **324**,305 (1995)

1. generate the final state by applying σ_z (mirror plane through N at $z = \frac{1}{2}c$) to the relaxed (ground state) geometry
2. generate directories for the intermediate geometries along the reaction path: `00, 01, 02,.....07 (IMAGES+1)`
   `00:` `POSCAR` of the initial state,
   `07 (IMAGES+1):` `POSCAR` of the final state
3. concatenate the `POSCAR`s of the initial and final states:
   `cat POSCAR_in POSCAR_fin > POSCAR_if`
4. generate the `POSCAR` files of the intermediate steps (`IMAGES`) along the reaction path by using the script `interpolatePOSCAR`
   `interpolatePOSCAR POSCAR_if`

Transition State of NH_3 flipping

1. . . . using the Nudged Elastic Band Method

1. to obtain reasonable results `Selective` Dynamics has to be used, again fixing the position of N (like for the scf-run)
2. edit the `POSCAR` files in the sub-directories 00 . . . 07 to apply these changes:
   insert the keyword `Selective` above the line `Direct` (there must be NO space character at the beginning of this line)
   add `T T T` (`F F F`) at the end of the lines giving the positions of the atoms
3. run vasp: the number of cores for a NEB job must be an integer multiple of the number of `IMAGES`
4. the output of each `IMAGE` is written into the sub-directories 01 . . . 06, there is no output written to 00 and 07

Transition State of NH_3 flipping

INCAR

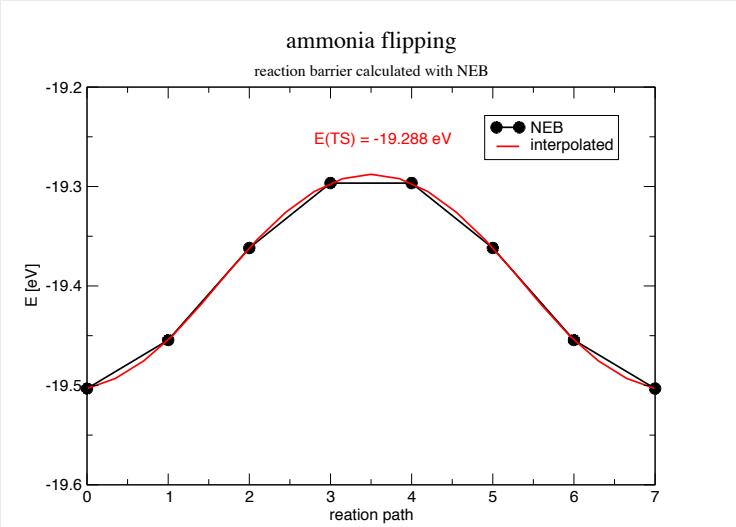
```
SYSTEM = Ammonia flipping
IMAGES = 6
SPRING = -5
IBRION = 2
NSW = 50
ALGO = N
POTIM = 1.0
EDIFF = 1e-6
```

NEB

- IMAGES defines the number of intermediate geometries along the reaction path
- SPRING: tangential springs to keep the images equidistant

Transition State of NH_3 flipping

E along the reaction path



post-processing

- after vasp has finished, collect the total energies of the `IMAGES` from the `OUTCAR` files in 01,...
- plot the calculated and interpolated energies eg. using the scripts `showbarrier_gnuplot` or `showbarrier_xmgrace`
- $E^{\ddagger}$ is obtained from the interpolated data
- $E^{\ddagger}$(NEB) = -19.2882 eV

Transition State of NH_3 flipping

Improved Dimer Method

A. Heyden *et.al.*, J.Chem.Phys.**123**, 224101 (2005)

- the Improved Dimer Method is a method to optimize transition sates, by maximizing the potential energy along the unstable mode.
- it speeds up the search of the transition state significantly, as compared to the NEB method
- the number or cores can be reduced.
- to direction of the unstable mode (decay direction, = dimer axis) has to be specified `POSCAR`
- this direction can be found from analyzing the vibration spectrum of the TS: it corresponds to the hardest mode of the vibrations with imaginary frequecies `(f/i)`
- $\Rightarrow$ as preliminary step, the vibration frequencies of the TS have to be calculated.

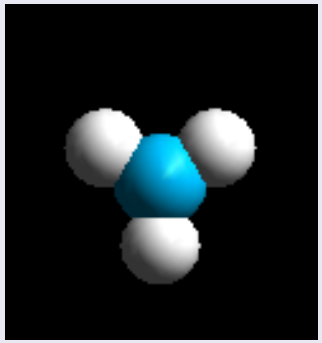
Transition State of NH_3 flipping

POSCAR

```
ammonia flipping
1.00000
6.00000 0.00000 0.00000
0.00000 7.00000 0.00000
0.00000 0.00000 8.00000
3 1
Direct
0.6462 0.5736 0.5000
0.5000 0.3547 0.5000
0.3538 0.5736 0.5000
0.5000 0.5000 0.5000
```

TS geometry

the TS of the NH_3 flipping reaction is a planar molecule:



Transition State of NH_3 flipping

INCAR

```
SYSTEM = Ammonia flipping
IBRION = 5
NSW = 1
ALGO = F
POTIM = 0.015
EDIFF = 1e-8
NWRITE = 3
```

vibration modes of the TS

- `IBRION = 5` calculate the vibration modes, using finite differences
- `POTIM`: has to be chosen small enough to stay in the harmonic regime of the oscillators
- `EDIFF`: tight convergence criterium for the energies to obtain accurate frequencies

Transition State of NH_3 flipping

extract the decay mode from OUTCAR

- altogether there are 12 DOFs, leading to 12 vibrational modes.
- 3 of these modes (those with the lowest energies) are related to translational modes of the molecule through the box
- the hardest imaginary mode corresponds to the decay path from the TS:
- the last 3 columns correspond to the eigenvectors of the modes:

```
12 f/i= 21.058633 THz 132.315291 2PiTHz 702.440353 cm^1
87.091535 meV
X Y Z dx dy dz
3.877200 4.015200 4.000000  0.000005 -0.000005 0.511988
3.000000 2.482900 4.000000  -0.000005 -0.000003 0.547857
2.122800 4.015200 4.000000  -0.000003 0.000002 0.511993
3.000000 3.500000 4.000000  0.000000 0.000000 -0.111986
```

Transition State of NH_3 flipping

POSCAR

```
ammonia flipping
1.00000
6.00000 0.00000 0.00000
0.00000 7.00000 0.00000
0.00000 0.00000 8.00000
3 1
Direct
0.6462 0.5736 0.5000
0.5000 0.3547 0.5000
0.3538 0.5736 0.5000
0.5000 0.5000 0.5000
!  decay direction
0.000004 -0.000001 0.511990
0.000000 -0.000003 0.547859
-0.000004 -0.000001 0.511988
0.000000 0.000000 -0.111986
```

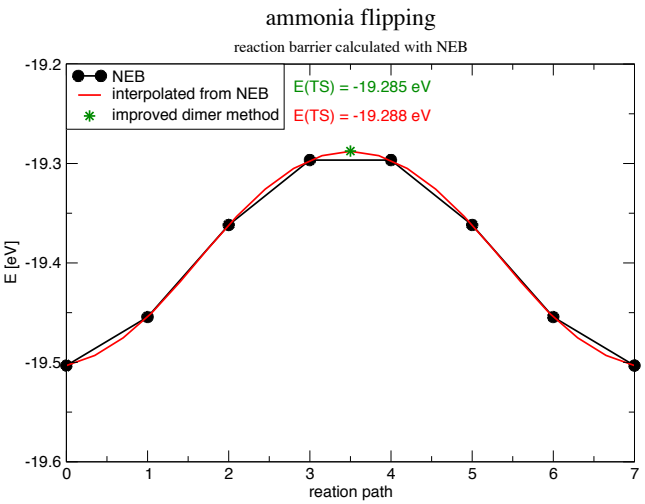
- the decay direction (dimer axis) as taken from the calculation of the vibration mode has to be added at the end of the file, separated from the atomic positions by a blank line

Transition State of NH_3 flipping

INCAR

```
SYSTEM = Ammonia flipping
IBRION = 44
NSW = 100
ALGO = F
EDIFF = 1e-6
EDIFFG = -0.01
```

- `IBRION = 44` activates the improved dimer method
- use the plot-script `showbarrier_gnuplot` to display the collected results
- $E^{\ddagger}$(i.d.) = -19.2875 eV



Transition State of NH_3 flipping

collecting the results

- (1) the E-barrier height (activation energy, ΔE) for the flipping process of NH_3 can be calculated from
  $\Delta E = E^{\ddagger} - E^0$
  the results of the methods agree within 1meV / molecule
- the 'computational cost' of both approaches can be compared by having a look at the number of cores and the CPU-time used for the calculations (both written on `OUTCAR`)
  - # cores: `grep 'running on ' OUTCAR`
  - CPU-time: `grep 'Total CPU time used ' OUTCAR`