Modeling Heterogeneous Catalysis on Surfaces and Nanomaterials

Tutorial 3: Vasp calculations for reaction pathways (NEB)

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Outline

1. Concepts for elementary reaction

2. Procedures for transition state search: nudged elastic band (NEB) method
   CH$_3$OH: O-H bond scission on 3-layer Pt(111) slab (slab model)

3. Hand-on practice:
   H$_2$O: O-H bond scission on Pt$_3$ cluster (cluster model)

4. Homework
   H$_2$O: O-H bond scission on 3-layer Pt(111) slab (slab model)

5. Final remarks

6. To do list
Concepts for an elementary reaction:
1. reaction energy; 2. reaction pathway; 3. activation energy.

H₂O: O-H bond scission on Pt₃ cluster

\[
\text{H}_2\text{O}^* + ^* \rightarrow \text{OH}^* + \text{H}^*
\]

\[\text{IS} (-22.98531506 \text{ eV})\]
\[\text{FS} (-23.43286216 \text{ eV})\]

\[\text{TS} (-22.222629 \text{ eV})\]

\[E_{\text{rxn}} = -0.45\text{eV}\]

\[E_a = 0.76\text{eV}\]
Complex catalyst surface at atomic scale

Example:

Possible active sites at (111) facet of fcc metal:

1. top site; 2. bridge site; 3. 3-fold hollow sites, \textit{fcc} and \textit{hcp}

When combined with the orientation of an molecule, even for a simple diatomic molecule H\textsubscript{2} on Cu(111), the possible configurations can be quite a lot!

\textbf{Rule of thumbs}: identify the lowest-energy structure

Landscape of potential energy surface for a catalytic reaction can be very complicated!!!
Surface calculations (Tutorial 1 &2)

1. Bulk calculation
2. FFT-meshes and k-points for surface calculation
3. Number of bulk and vacuum layers
Procedures for transition state search
1. Identify initial state and final state

Example: Optimized Pt fcc bulk and p(2×2) Pt(111) surface

Space group: FM-3M
Pt fcc unit cell
Lattice constant = $3.984 \, \text{Å}$
3.924Å
Procedures for transition state search

1. Identify initial state and final state

Example: O-H bond scission in methanol decomposition on p(3×3) Pt(111) surface

\[
\text{CH}_3\text{OH}^* + * \rightarrow \text{CH}_3\text{O}^* + \text{H}^*
\]
Procedures for transition state search: nudged elastic band (NEB) method

2. Generate intermediate images

Example: Methanol decomposition on $p(3\times3)$ Pt(111) surface

The simplest linear interpolation eq.

\[
\frac{y - y_0}{x - x_0} = \frac{y_1 - y_0}{x_1 - x_0}
\]
Procedures for transition state search

2. Generate intermediate images

Example: Methanol decomposition on p(3×3) Pt(111) surface

\[
\text{CH}_3\text{OH}^* + * \rightarrow \text{CH}_3\text{O}^* + \text{H}^*
\]
Procedures for transition state search

3. Optimize images

Example: Methanol decomposition on \( p(3\times3) \) Pt(111) surface

\[ \ce{CH3OH* + * -> CH3O* + H*} \]

- Refinement near saddle point might be needed!
- NEB method can be computationally very expensive!
Procedures for transition state search

4. Analyze data

Example: Methanol decomposition on p(3×3) Pt(111) surface

\[ \text{CH}_3\text{OH}^* + * \rightarrow \text{CH}_3\text{O}^* + \text{H}^* \]

\[ d(\text{O-H}) = 1.84 \]

\[ E_a = 0.73 \text{eV} \]

\[ E_{\text{rxn}} = 0.45 \text{eV} \]
O-H = 1.80 Å
T.S.

E* = 0.81 eV

ΔE_{rxn} = 0.62 eV

Greeley and Mavrikakis, J. AM. CHEM. SOC. 2002, 124, 7193-7201
Hand-on practice:
H$_2$O: O-H bond scission without catalyst

\[ \text{H}_2\text{O(g)} \rightarrow \text{OH(g)} + \text{H(g)} \]

Erxn = 5.6eV (cal.)
5.1eV (exp.)

Visualized using p4vasp
Hand-on practice:
H$_2$O: O-H bond scission on Pt$_3$ cluster using NEB vtst code
1. Initial state (IS); 2. Final state (FS); 3. number of image

\[ \text{H}_2\text{O}^* + \* \rightarrow \text{OH}^* + \text{H}^* \quad \text{E}_\text{rxn} = -0.45 \text{eV} \]

Again, correct IS and FS is critical!
Setup for NEB using vtst code

Henkelman Group, UT Austin
(http://theory.cm.utexas.edu/vtsttools/neb.html)

INCAR
KPOINTS
POSCAR
POTCAR
qsub script must be in the same directory (*Tutorial 1 &2*)
INCAR

```
# neb_vtst
IMAGES    =    5
SPRING    =   -5
LCLIMB    =  .TRUE.
ICHAIN    =    0
ENCUT     =   400
ISPIN     =    2
MAGMOM    =  3*2 1*2 2*1
NSW       =  1000
ISIF      =    0  stress and relaxation

#FORCE_BASED_OPTIMIZERS
IBRION    =    3
POTIM     =   0.0
IOPT      =    3
PREC      =  Accurate
EDIFF     =  1.0E-3
EDIFFFG   =  -0.1
ISMEAR    =    0
SIGMA     =   0.1
GGA       =   91
VOSKOWN   =    1
```

Invoke NEB_vtst code

Turn on the climbing image algorithm

Bond-breaking and –forming: using SP-DFT!

Γ–point only for cluster model

KPOINTS

```
1x1x1
0
Monkhorst
1 1 1
0 0 0
```
POSCAR (Tutorial 1 & 2)

```
OHH
1.
10.0000000000000000 0.0000000000000000 0.0000000000000000
0.0000000000000000 10.0000000000000000 0.0000000000000000
0.0000000000000000 0.0000000000000000 10.0000000000000000

Pt  O  H
3   1   2
Selective dynamics

Direct
0.35486999999999982 0.32103000000000004 0.54773000000000014 F F F F
0.48194999999999977 0.36654999999999966 0.300460000000000011 F F F F
0.636139999999999975 0.321629999999999990 0.531910000000000034 F F F F
0.1378039634263367 0.3253340562196527 0.5646722371919545 T T T T
0.1123025124768432 0.4194857099933090 0.5694509845710483 T T T T
0.104857624401898  0.2927451104489520 0.4786464421892127 T T T T
```

POTCAR
(order of element must be consistent with those in POSCAR)

```
PAW_GGA Pt 05Jan2001
10.0000000000000000
parameters from PSCTPR are:
  VRHFIN =Pt: s1d9
  LEXCH = 91
  EATOM =  730.0441 eV,  53.6567 Ry
TITEL = PAW_GGA Pt 05Jan2001

End of Dataset
PAW_GGA O 05Jan2001
6.0000000000000000
parameters from PSCTPR are:
  VRHFIN =O: s2p4
  LEXCH = 91
  EATOM =  433.0277 eV,  31.8266 Ry
```
Confirmation of TS: frequency run

INCAR setup for frequency run

IBRION = 7  7-vibrational frequencies (perturbation theory).
NFREE = 2  central differences (i.e. each ion is displaced)
POTIM = 0.015

OUTCAR

Eigenvalues and eigenvalues of the dynamical matrix

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<th>f/i</th>
<th>THz</th>
<th>2PiTHz</th>
<th>cm^-1</th>
<th>meV</th>
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<tr>
<td>8</td>
<td>8.999493</td>
<td>56.545482</td>
<td>300.190762</td>
<td>37.218924</td>
</tr>
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<td>X</td>
<td>Y</td>
<td>Z</td>
<td>dx</td>
<td>dy</td>
</tr>
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<td>3.548700</td>
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<td>0</td>
<td>0</td>
</tr>
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<td>0</td>
</tr>
<tr>
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<td>5.319100</td>
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<td>0</td>
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<tr>
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<tr>
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<td>2.192599</td>
<td>3.369512</td>
<td>4.628285</td>
<td>-0.052341</td>
<td>-0.879015</td>
</tr>
</tbody>
</table>
INCAR

# neb_vtst
IMAGES = 5
SPRING = -5
LCLIMB = .TRUE.
ICHAIN = 0
ENCUT = 400
**ISPIN** = 2
**MAGMOM** = 27*0 1*2 2*1
NSW = 1000
ISIF = 0  stress and relaxation

#FORCE BASED OPTIMIZERS
**IBRION** = 3  ionic relax: 0-MD 1-quasi-New 2-CG 3-Damped molecular dynamics
**POTIM** = 0.0
**IOPT** = 3

KPOINTS

K-points grid needed for slab model
H$_2$O: O-H bond scission on 3-layer Pt(111) slab
Computational cost (>1500 cpu hours)

H$_2$O* + * → OH* + H*
Final remarks

- Computationally very expensive (>1000 cpu hours)
- Test run
- IS and FS
- Setup consistency
- Experimental data support
To do list:

1. Find NEB vtst Code location:
   - Henkelman Group, UT Austin (http://theory.cm.utexas.edu/vtsttools/neb.html)
   - Code location on CFN cluster: /software/Workshop14/bin
   - Executable: vaspP_NEB
To do list:

2. Generate images:
   - Make your own directory;
     Copy files from:
     /software/Workshop14/Tutorials/Tutorial3/vtst/H2O_Pt3/H2O_Pt3_ts/Generate_Image
   - Add new line “export PATH=$PATH:/software/Workshop14/bin/vtstscripts” to file .bashrc
     type: source .bashrc
   - Create images:
     type: nebmake.pl POSCAR1 POSCAR2 5
     You can visualize the created images using p4vasp
To do list:

3. Submit the job and run NEB_vtst calculation
   - Copy directory:
     Note: all geometries in POSCAR are pre-converged!
   - submit the job:
     type: qsub job
To do list:

4. Examine the results after converged run, :

- Type: nebbarrier.pl
  output: energy, distance, and forces along the neb in file neb.dat

- Type: nebspline.pl
  output: spline.dat, exts.dat, mep.eps

- Type: convert mep.eps mep.png