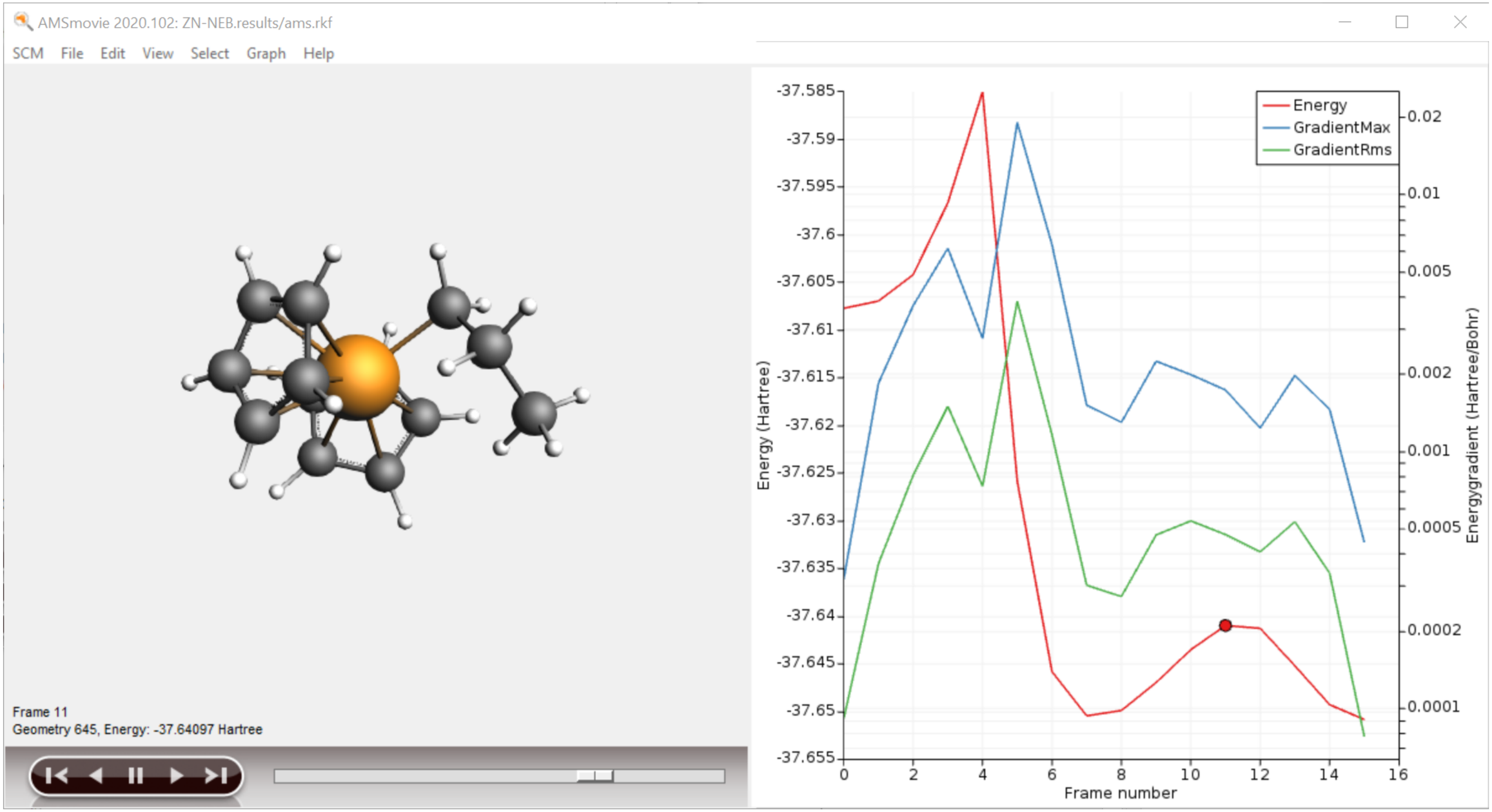
More transition state tips & tricks



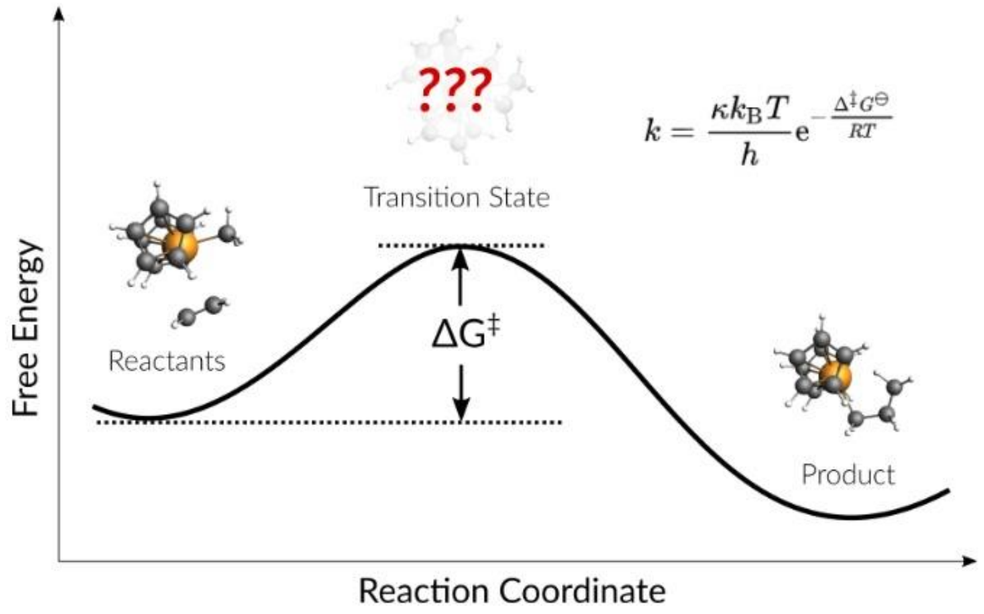
SCM
Software for Chemistry & Materials

Transition states 2, TU Delft, 22 January 2021

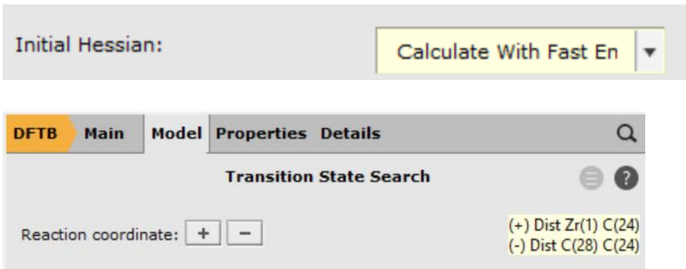
SCM support: support@scm.com

Pointers & ideas for TS search

1. Good starting point (**geometry** close to TS)
   - First explore reactant and product
   - (Initially) use low convergence criteria
   - Scan the PES with MOPAC or GFNx-TB
     - Sometimes scanning from product side is easier
     - Can use complex composite scan coordinates
   - Use CI-NEB (See TS 1 by Thomas)
     - Always a good idea to explore Reactants
   - Pass on coordinates (+Hessian) to ADF
   - Previous TS ‘similar’ system
   - Consider first doing constrained/partial optimization



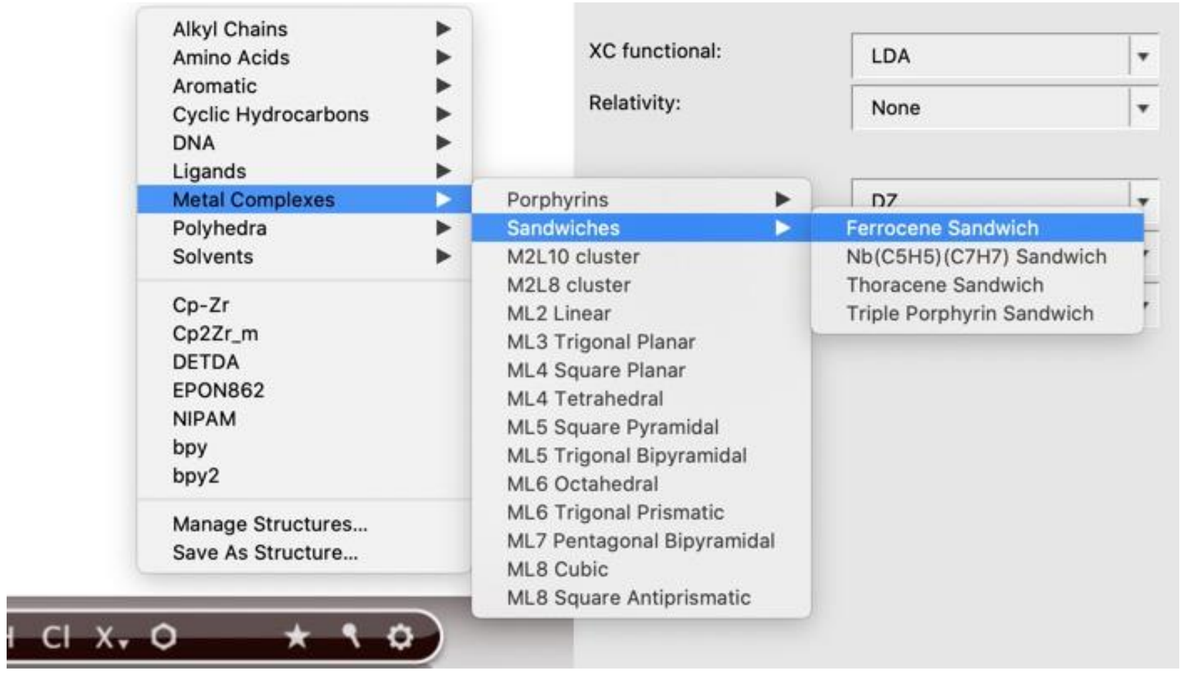
2. Good description of the **curvature**: lowest Hessian eigenmode(s)
   - Partial Hessian
   - **Low-level Hessian** from previous, of for ADF choose ‘Calculate With Fast Engine’
   - TSRC: define (complex) reaction coordinate
   - Consider ‘TS point characterization’ to check only 1 negative eigenmode

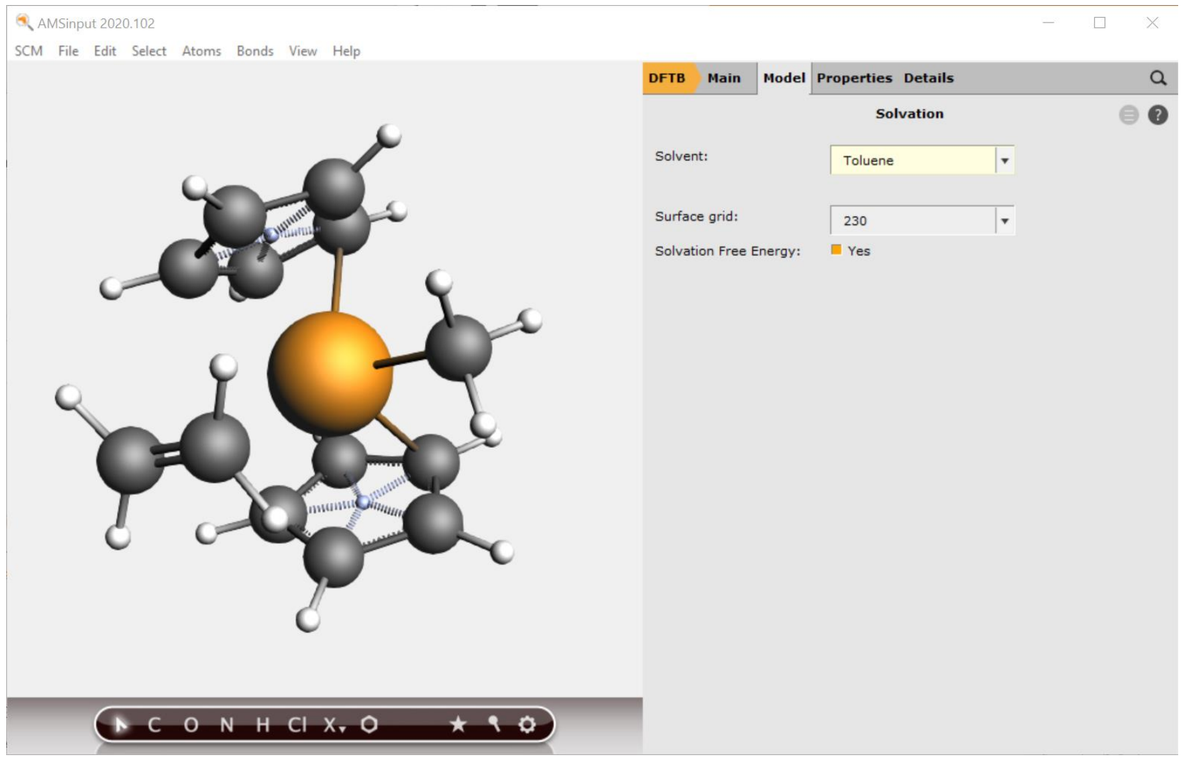


3. Accuracy?
   - Solvent effects: COSMO and/or SM12 (single point only)
   - metaGGA? TZP/DZP? Good numerical quality?
   - Double hybrids (single point)
   - Low-eigenmode corrections to frequencies
   - Sometime spurious 2nd imaginary modes are hard to get rid of -> ScanFreq

Transition State through PES scan

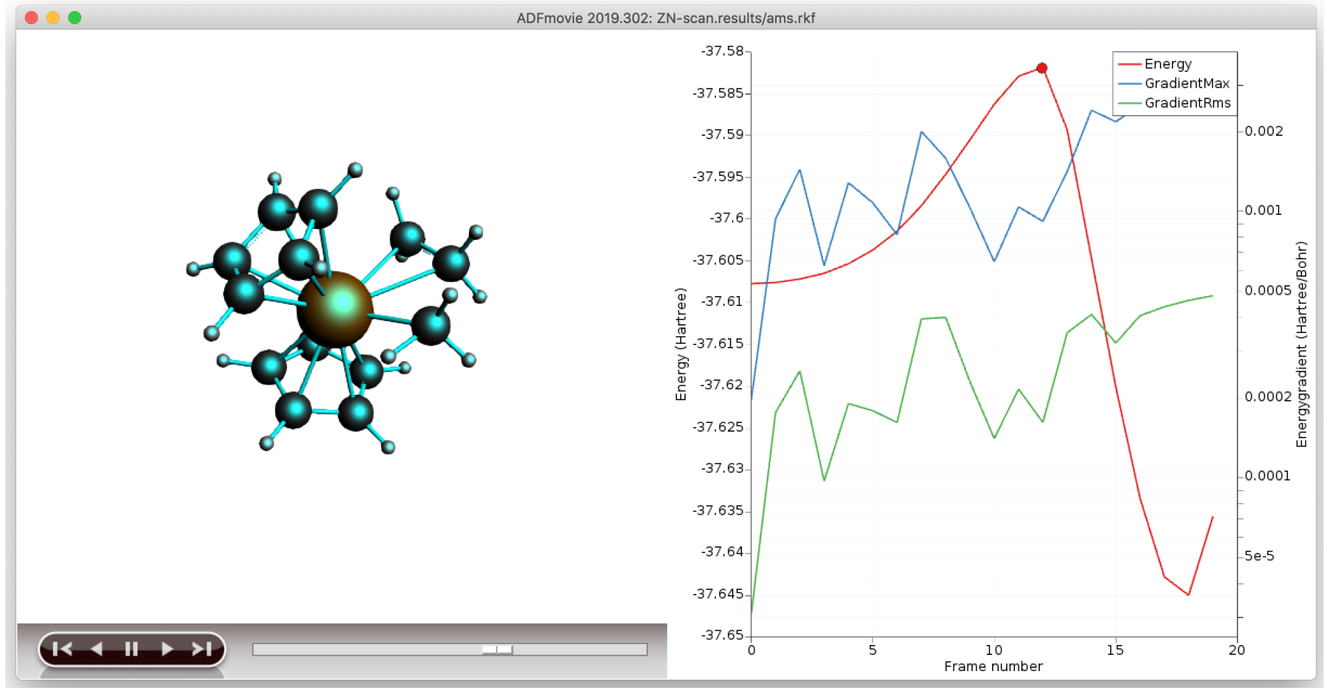
- Exercise (Ziegler-Natta tutorial):
  - New DFTB input
  - Build Cp_2ZrMe^+
    - structure tool ⬡ => ferrocene
    - Right-click Fe -> Element -> Zr
    - Add C and replace by methyl
    - (Use dummies to change CpMCp angle)
    - Model -> Solvent -> Toluene
    - Add charge and optimize
  - Add ethene (use the 🔍)
    - Manipulate it in position
    - Right-click + drag = translate
    - Left-click + drag = rotate
    - Ctrl+M = select molecule
    - Remove dummies
    - Optimize

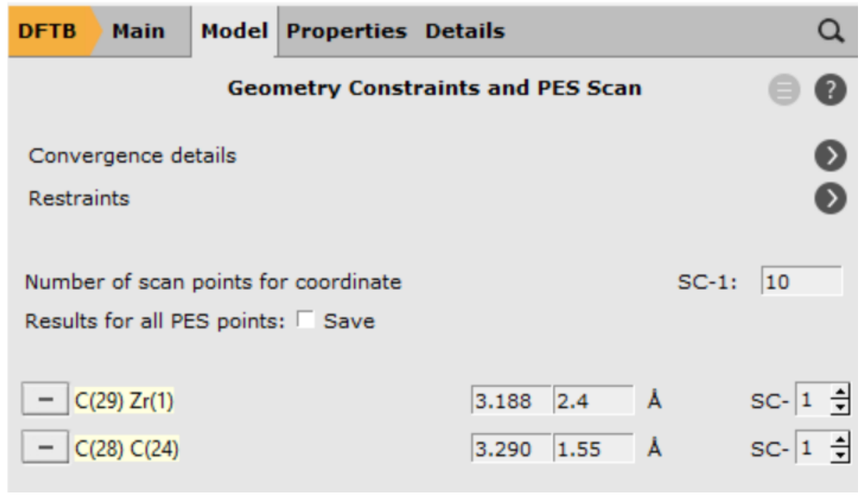


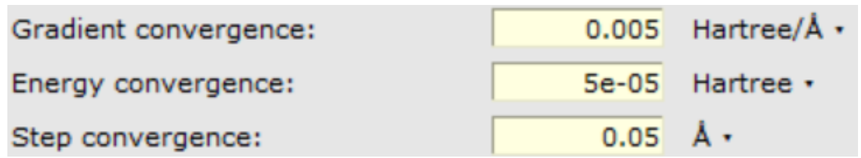


Transition State through PES scan

- Set up a PES scan, using **1 combined scan coordinate**
  - Zr-C to 2.4 & C-C to 1.55
- Details -> Geometry Optimization:
  - Loosen the Convergence criteria by a factor of 5
- Run, and when finished, open AMSMovie





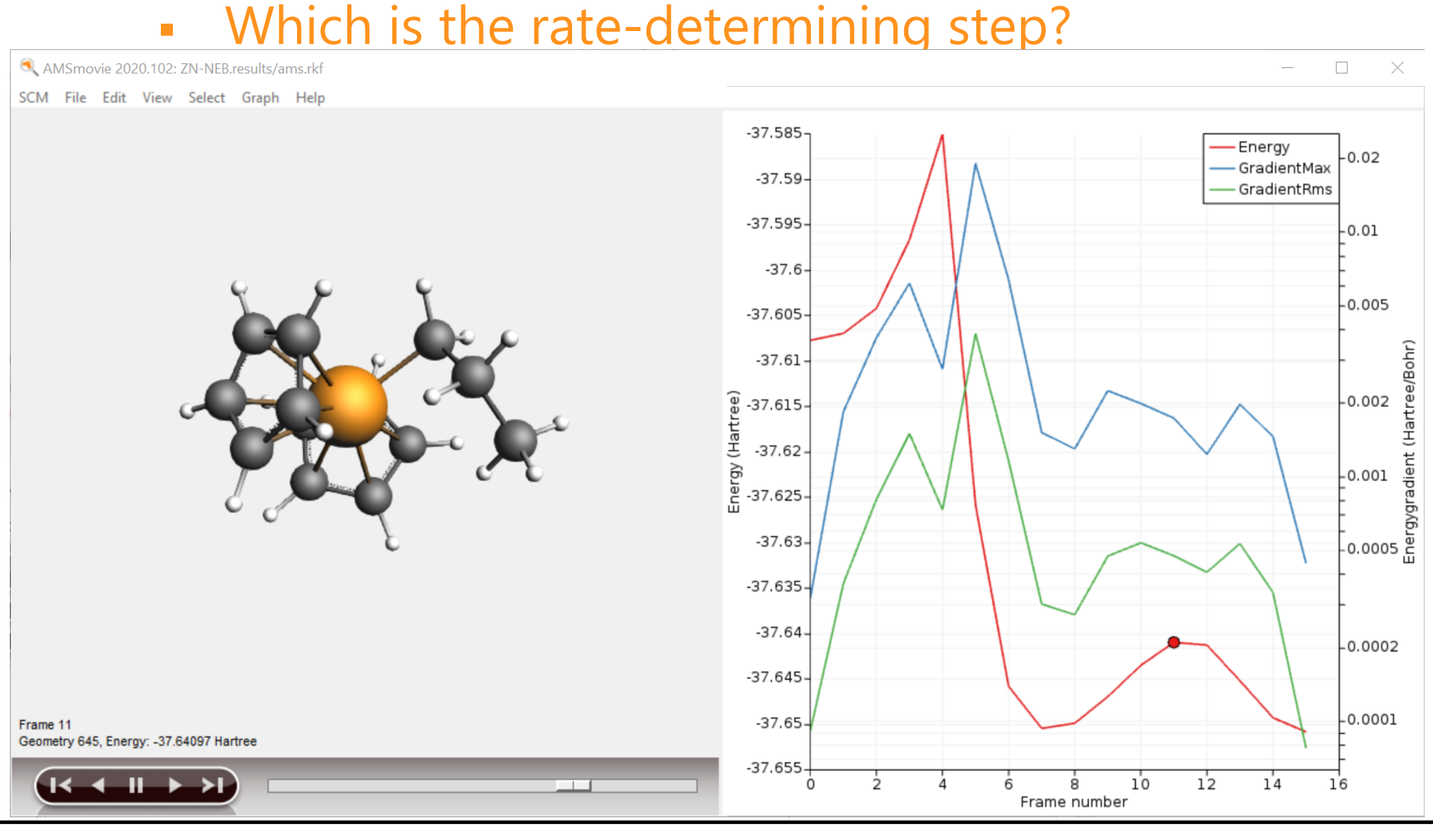


- Copy the highest energy structure (e.g. Ctrl+U), or save as structure
- Set up a TS run (ideally make a new input)
  - make sure there are no constraints, and regular convergence
  - use a calculate Hessian as initial guess and calculate frequencies

Transition State, start with NEB - Ziegler-Natta

- Exercise:
  - Optimize reactant & product from the last PES scan points
  - Rotate the Zr-C-C-H dihedral to ~0 (metallacycle Zr-C-C-H) & optimize => alpha-agostic
  - Set up a climbing nudged elastic band calculation Task: NEB
  - Choose this structure as final, the other product as intermediate, and R as initial (import structures from results/ams.rkf) and choose 14 points
  - Don't optimize R&P, relax convergence by factor 5
  - Open AMSMovie when finished
    - Which is the rate-determining step?

Tip: use CI-NEB to get close enough to TS, use Hessian-based optimization to find it




```
<Jan20-2021> <13:58:17>  Numerical nuclear derivatives calculation complete.
<Jan20-2021> <13:58:17>  Scanning mode: 7
<Jan20-2021> <13:58:18>  PES point character: Geometry corresponds to a transition state.
<Jan20-2021> <13:58:18>  TS barrier height from the left          0.02270445 Hartree
<Jan20-2021> <13:58:18>                                          14.247 kcal/mol
<Jan20-2021> <13:58:18>                                          59.611 kJ/mol
<Jan20-2021> <13:58:18>  TS barrier height from the right         0.06580135 Hartree
<Jan20-2021> <13:58:18>                                          41.291 kcal/mol
<Jan20-2021> <13:58:18>                                          172.761 kJ/mol
<Jan20-2021> <13:58:18>  NORMAL TERMINATION
Job ZN-NEB has finished
```

Transition States: Further considerations

- <u>Reaction rates</u>:
  - Calculate $\Delta G^{\#}$: include H_{vib}, S (AMSoutput -> Other Properties -> Statistical Thermal Analysis)

```
   Temp                                                  Transl      Rotat     Vibrat     Total
   ----                                                  ------      -----     ------     -----

   298.15   Entropy (cal/mol-K):                         42.601     31.288     52.371    126.261
            Nuclear Internal Energy (kcal/mol):           0.889      0.889    160.907    162.684
            Constant Volume Heat Capacity (cal/mol-K):    2.981      2.981     56.260     62.222
        (c) Constant Volume Heat Capacity (cal/mol-K):    2.981      2.981     52.800     58.761

     Summary of energy terms
                                          hartree            eV         kcal/mol          kJ/mol
                                    --------------------  ----------  ----------  ----------
    Energy from Engine:             -37.585024915182686  -1022.7406   -23584.96   -98679.47
    Nuclear Internal Energy:          0.259253970109237      7.0547      162.68      680.67
(c) Nuclear Internal Energy:          0.257445594179003      7.0055      161.55      675.92
    Internal Energy U:              -37.325770945073451  -1015.6859   -23422.28   -97998.80
    pV/n = RT:                        0.000944186013486      0.0257        0.59        2.48
    Enthalpy H:                     -37.324826759059967  -1015.6602   -23421.68   -97996.32
    -T*S:                            -0.059990510871653    -1.6324      -37.64      -157.51
(c) -T*S:                            -0.058176671371776    -1.5831      -36.51      -152.74
    Gibbs free energy:              -37.384817269931617  -1017.2926   -23459.33   -98153.82


(c) The properties marked with this symbol have been corrected using 'low vibrational frequency free rotor
    interpolation corrections'. For those terms all positive frequencies are used (also ones below 20 1/cm),
    but the contribution to the partition function of small vibrational frequencies is modified as described
    in the following paper:
    S. Grimme, 'Supramolecular Binding Thermodynamics by Dispersion-Corrected Density Functional Theory'
    (Chem. Eur. J. 2012, 18, 9955-9964)
    Configuration: Dampener Frequency         :   100.000 1/cm
                   Dampener Alpha             :     4.000
                   Averaging Moment of Inertia : 1.000E-44 kg m2
```

  - <u>hTST as first approximation</u>: k ~ exp (-$G^{\#}$/RT), Low-level frequencies: Grimme corrections
  - Could also try <u>mircokinetics</u>. More underway (<u>ReaxPro</u>)
- Suggestions & troubleshooting
  1. <u>get close to TS</u>: NEB, PES Scan, constrained opt, previous TS + change ligands (PLAMS script!), ….
  2. <u>get a good curvature</u> (Hessian): pre-calc with GFN-xTB, MOPAC; partial Hessian
  3. check final curvature / path: Frequency calculation, PES point characterization, <u>IRC</u>
  4. Spurious imag. Freq.: displace along that mode (AMSSpectra, Ctrl+8 *5) & retry

Periodic systems: surfaces & bulk

- How to get good TS geometry guess?
  - Literature or previous results:
    - similar TS + constrained optimization
  - Quick (?) NEB (you want to find R & P anyway)
  - PES scan (can you use ReaxFF, MOPAC, GFN-xTB? Otherwise: cheaper DFT?) (video)
  - Maybe you can get away with periodic DFT/DFTB (video) or DFT/MM ?

- How to get good guess for lowest few Hessian eigenmodes?
  - Could try MOPAC or DFTB Hessian
    - Inspect modes first?
  - Define reaction coordinate (TSRC)
  - Use a partial Hessian (‘active’ region)