Hands-on Transition State Search

- Getting started – building molecules

- Running basic calculations & settings

- Transition states (TSs)
  - Finding & characterizing TSs
  - Activation strain model & EDA
  - ETS-NOCV

- Best practices & recommendations

- Properties demo: IR, NMR, EPR, UV/VIS?
ADFjobs: job bookkeeping

- switch GUI functionality
- define & switch queues
- reports & templates
- see files for this job
- queue
- change default e.g. cores / nodes
- job status
- search
- all jobs / folder view
Building molecules

www.scm.com/doc/Tutorials/GUI_overview/Building_Molecules.html

- Import: SMILES, xyz, cif, pdb, ...

- Included library + building tools (step 7 tutorial = TM complexes)

- Nanoparticles: start from periodic => cut a cluster

- **Exercise:** Build a small molecule of choice and optimize (default settings)
Basic calculations & settings

- switch modules
- job types & set up
- search
- job type / template
- charge/spin
- functional & relativistic appr
- basis & numerical accuracy
- builder tools

... = more details
Transition states

1. Get close to the transition state
2. Good guess for the transition mode

How to get a good guess geometry?
- Intuition* + constrained optimization
- Linear transit
- Nudged elastic band
  * e.g. from literature, geometry from a previous TS

How to get a good guess for the transition mode?
- Transition State Reaction Coordinate (TSRC)
- Hessian: full, partial, or mobile-block, maybe smaller basis & lower accuracy?

Remember: a TS has 1 and only 1 negative Hessian eigenvalue
Example: Pd-catalysed oxidative addition

**Goal:** find reactant and transition states, understand
- Get a good geometry: LT, previous geometry, NEB
- Good Hessian: TSRC, partial Hessian
- Bonding analysis: Activation Strain Model (ASM)

- Example: Pd catalyzed oxidative addition: Wolters & Bickelhaupt

Methane C–H activation:

- ligands raise barriers
- smaller bite angle → lower barrier

Good geometry guess: 1. LT

1. Build (CH₃)(H)Pd(PH₃)₂ - start with ML₄ complex
2. Optimize product (Oxaddproduct_PdPH32.adf)
3. Set up a linear transit to reduce C-H (LT_from_adduct.adf)
Good Hessian: 1. TSRC

1. View linear transit result: ADFmovie -> view conv. geom. only
2. Click highest point; File => Update geometry in input
3. Change number of transition points to 0, remove constraint
4. Change preset to Transition State Search, click details (...)
5. Select C + H to add to TSRC (TSsearch_1LT.adf)
Get a guess Hessian: 2.-4.

2. Partial Hessian (partialhess_low.adf) – e.g. H, C, Pd
3. Mobile Block Hessian (MBH_PdCH₄_low.adf)
   - define regions first. E.g. treat Pd(PH₃)₂ as mobile block
4. Less accurate xc, basis set, numerical settings (lowHess.adf)
   o Can be combined with 1. & 2.
5. Restart with Hessian (TS_MBH.adf, TS_pHess.adf, TS_lowHess.adf)
Calculate frequencies

- Update geometry from TS run
- Change preset to frequency, click (...) for details
- In the Scan frequency range, set the lower limit to -100 or -50
  - This will rescan low-lying imaginary modes numerically
Calculate $\Delta E^\#$, $\Delta H^\#$, $\Delta G^\#$

- Get the binding energy for reactants $\text{CH}_4 + \text{Pd(PH}_3)_2$
  - First optimize reactants separately, run frequencies for ZPE
  - Read from logfile, outputfile, use PLAMS / adfreport, or use report tool in GUI

Note: ADF uses a fragment-based approach: binding energies are with respect to (atomic) fragments

- $\Delta E^\# = E(\text{TS}) - E(\text{reactants})$, same for $H$, $G$ (add ZPEs, pV term, S)

- Find relevant results on t21?
  - KFBrowser => expert mode
  - (adfreport -h result.t21 non-exhaustive)
Good geometry guess: 2. NEB

1. Optimize reactant state complex CH₄...Pd(PH₃)₂
2. Set up a NEB via ASE from reactant to product (TS_NEB.adf)
3. Don’t run through to the end. Stop and update geometry (highest point)
Geometry guess: 3. intuition

- Start from a TS from a comparable reaction (e.g. change ligands)
  1. Take TS or product from Pd(PH$_3$)$_2$
  2. Make a bidentate ligand (diphosphinoethane, dpe)
  3. Run with a **constraint**: C-H distance $\sim$1.8Å (Bidentate_GeoCst.adf) (may use sloppy accuracy as well, or get xyz from literature)
  4. Run your TS with TSRC or other Hessian (Bidentate_TS.adf)
Bonding analysis: ASM, EDA, NOCV

Activation Strain Model Bickelhaupt & co. based on Fragment MOs

- Decompose barrier:
  \[ \Delta E^\neq = \Delta E^\neq_{\text{strain}} + \Delta E^\neq_{\text{int}} \]

EDA along the reaction path
Bite-Angle Effect: Activation Strain analyses:
  - HOMO–LUMO interaction marginally improved
  - But: strain reduced by building it into catalyst

**Exercise:** check Pd(PH\(_3\))\(_2\) vs Pd(diphosphinoethane) TSs: C-H distance, EDA

Energy decomposition analysis

\[ \Delta E = \Delta E_{\text{prep}} + \Delta E_{\text{int}} \]

- \( \Delta V_{\text{elstat}} + \Delta E_{\text{Pauli}} + \Delta E_{\text{oi}} + \Delta E_{\text{disp}} \)

- \( \Delta E_{\text{steric}} = \Delta V_{\text{elstat}} + \Delta E_{\text{Pauli}} \)
- \( \Delta E_{\text{oi}} = \) decomposed in irreps.

Extensions:
Energy decomposition analysis

1. Define your fragments (regions)
2. Run your EDA or ETS-NOCV calculation
   - Single point calculation; check ‘Use fragments’ in MultiLevel tab
   - (Select ETS-NOCV type calculation in Properties => ETS-NOCV)
   - Results: ADFoutput => Properties => Bonding Energy Decomposition
3. Optimize fragments to get $\Delta E_{\text{prep}} = E_{\text{(fragments, relaxed)}} - E_{\text{(fragments in complex)}}$
Energy decomposition analysis

ADF report to get EDA results (EDA.adf) (add distance#labels#10#14)

<table>
<thead>
<tr>
<th></th>
<th>Pd(PH3)2</th>
<th>Pd(dpe)</th>
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</thead>
<tbody>
<tr>
<td>Bonding Energy</td>
<td>-59.16</td>
<td>-59.62</td>
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<tr>
<td>Pauli Repulsion</td>
<td>186.41</td>
<td>178.66</td>
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<tr>
<td>Electrostatic Interaction</td>
<td>-155.27</td>
<td>-150.37</td>
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<td>Steric Interaction</td>
<td>31.14</td>
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<td>Orbital Interaction</td>
<td>-89.16</td>
<td>-86.90</td>
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<tr>
<td>C(10)-H(14)</td>
<td>1.804</td>
<td>1.786</td>
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</table>

Strain built into bidentate
- Reduces activation strain
- Earlier TS
- Lower ΔE#
• Select closed-shell ETS-NOCV & run (ETSNOCV.adf)
• Visualize deformation densities in ADFview – play with settings

More (workshop) materials:
https://www.scm.com/adf-modeling-suite/adf-hands-on-workshops/
Exercises, examples, tips & tricks for Transition State search 2016, © SCM

Accuracy Recommendations

- **Relativity:** always use ZORA
  - For most systems + properties scalar relativistic (SR) suffices
  - Spin-orbit coupling (SOC) may be necessary for
    - Spectroscopy 4d, 5d elements (energy 5d? Ir < 1 kcal/mol)(*)
    - Geometries 6s, 6p elements (and beyond)

- **xc functional:** check experiments & literature(*)
  - Dispersion corrections: D3, or D3(BJ) good pragmatic options (may not affect $\Delta E$)
  - GGAs are faster in ADF than hybrids, and most have analytical frequencies
  - GGAs are usually as good or better than hybrids for geometries
  - Hybrids *may* give better (TS) energies, for TM catalysis GGAs usually OK
  - Good options: **PBE-D3, BPD3**(*). mGGAs: MN15L, S12g, M06L

- **Basis sets:** STOs converge faster than GTOs(*)
  - Geometries: DZP (=TZP for TM), or TZP. DZ not good enough
  - Energies: TZP or TZ2P, small or no core. *Large core not good enough for TM* energies.
  - Core spectroscopy: QZ4P

- **Numerical accuracy:** normal or good (higher for mGGAs, spectroscopy?)

(*) J. Comp. Chem. 34, 870–878 (2013): Ir-catalyzed water oxidation, test basis set convergence
### Basis set convergence

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<tr>
<th>Basis Set</th>
<th>GTO B3LYP</th>
<th>STO B3LYP</th>
<th>STO BP86</th>
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<tbody>
<tr>
<td>DZ/6-31G*</td>
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<tr>
<td>DZ/6-31+G(P)</td>
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<td>DZ/6-311++G*</td>
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Some more tips

- **QUILD** has more options for initial Hessians (ihopt) + updates (ihupd)
  - Uses a Hessian check by default (check a 2\textsuperscript{nd} small negative => freq + scan?)

- Solvent effects?
  - COSMO, SM12 (single point), COSMO-RS
  - Advanced: multi-layer (QM/MM, QUILD), embedding – SCRF, FDE

- Save your settings (xc, basis set, etc.) + job type as template in ADFinput

- Use ADFprepare to make multiple jobs

- Use ADFreport to get your results (GUI or cmd line scripting)
  - Commandline ADFreport allows further python / shell scripting
  - PLAMS: python workflows

Contact us at **support@scm.com** with any questions or problems