Hands-on Transition State Search

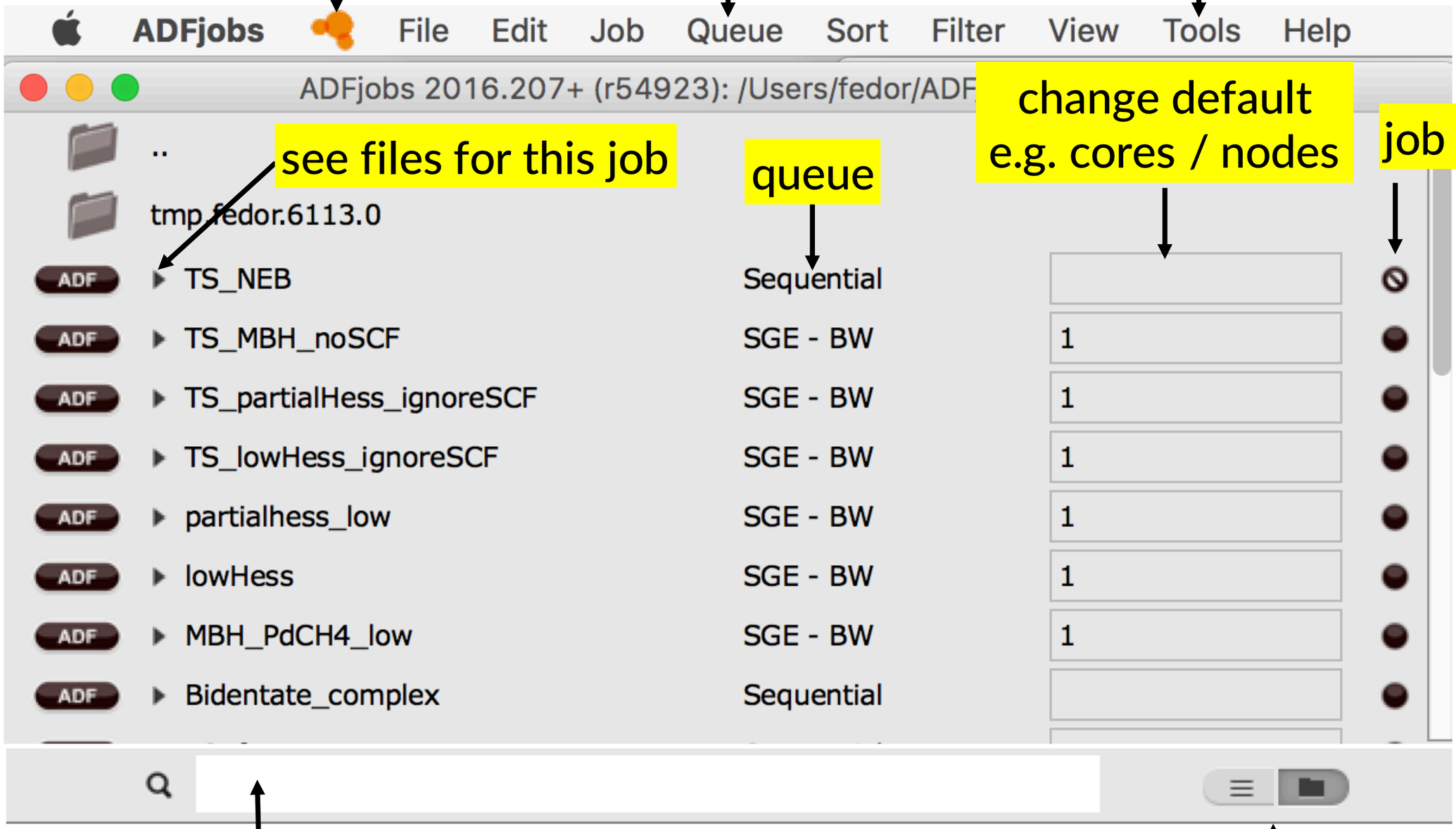
- Getting started – building molecules
- Running basic calculations & settings
- Transition states (TSs)
  - Finding & characterizing TSs
  - Activation strain model & EDA
  - ETS-NOCV
- Best practices & recommendations
- Properties demo: IR, NMR, EPR, UV/VIS?

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

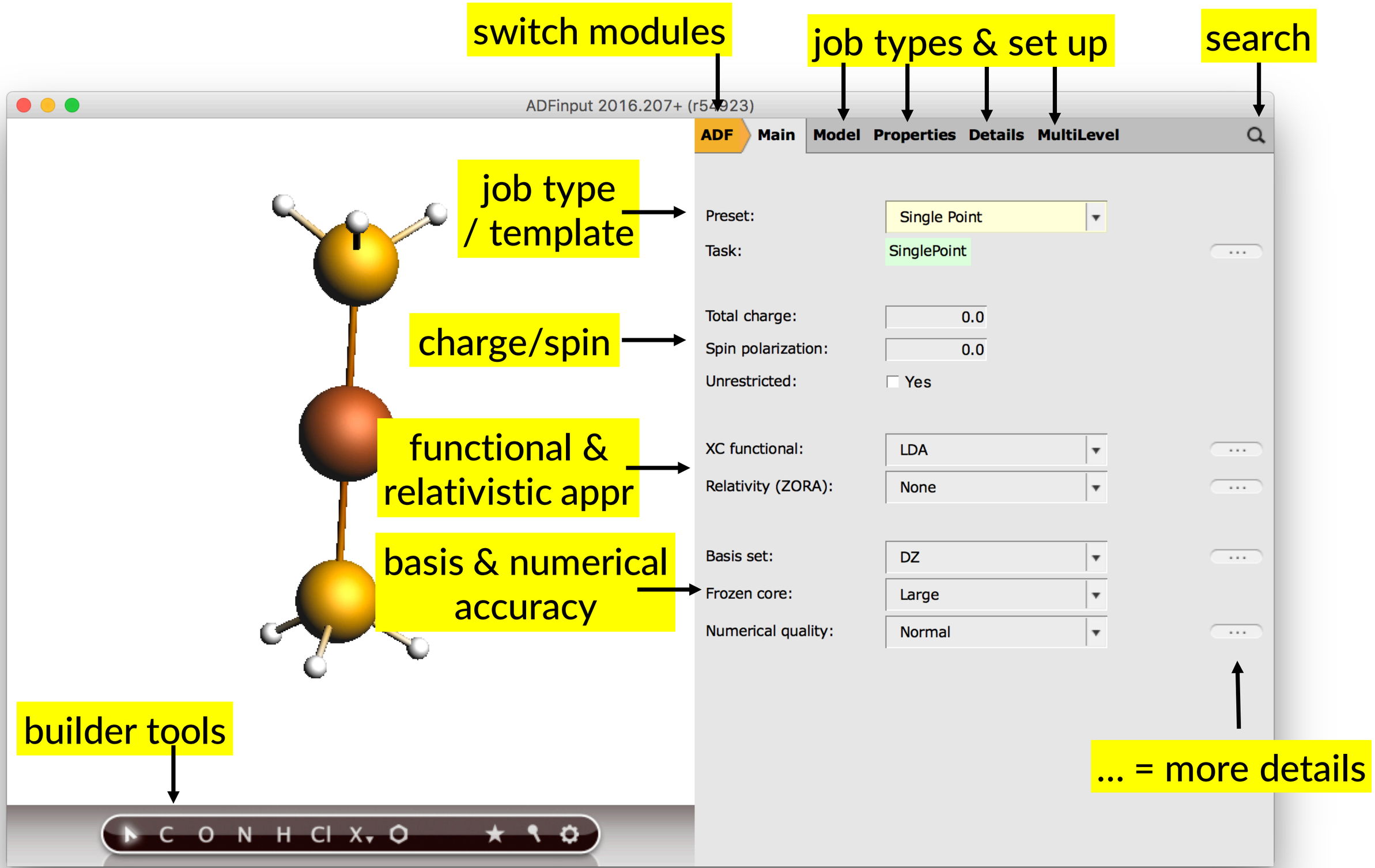
all jobs / folder view

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
- **Excercise:** Build a small molecule of choice and optimize (default settings)

Basic calculations & settings



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?

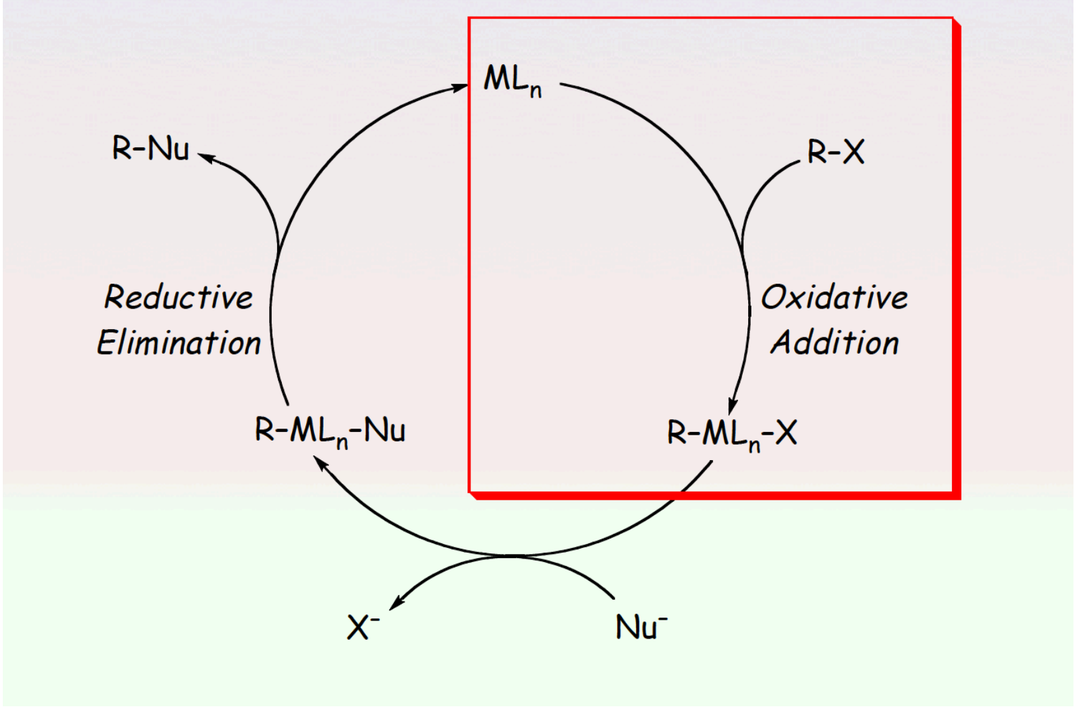
Remember: a TS has 1 and only 1 negative Hessian eigenvalue

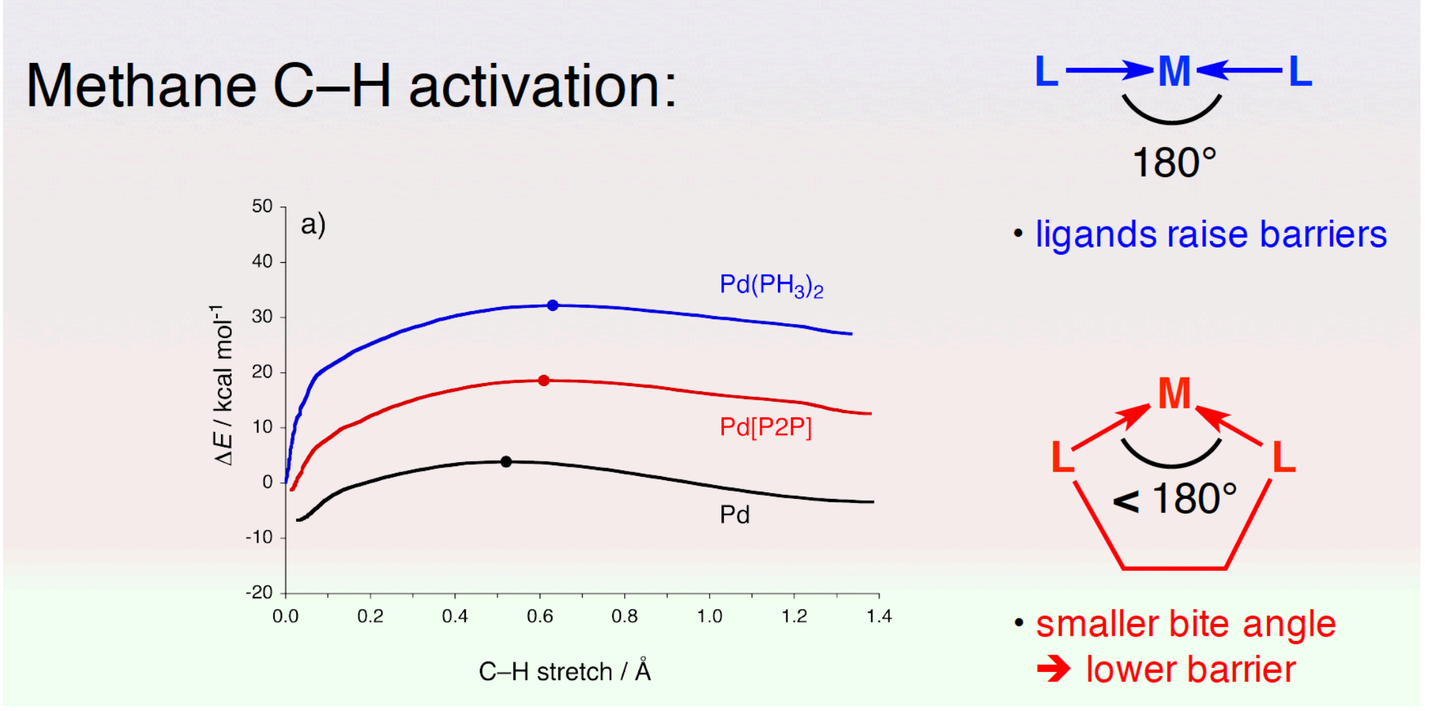
Example: Pd-catalysed oxidative addition

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

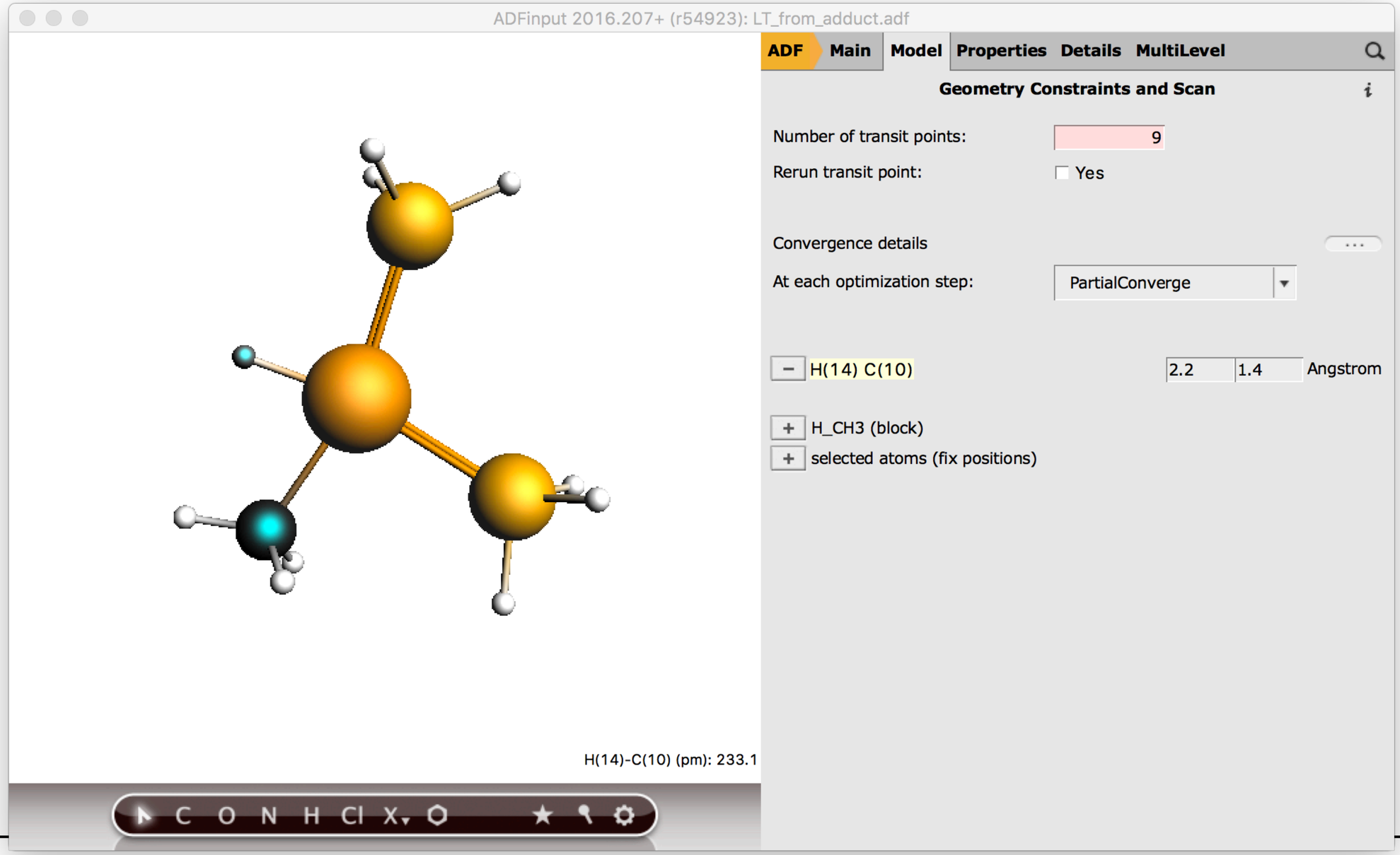




Chem. Eur. J. **15**, 6112 (2009)

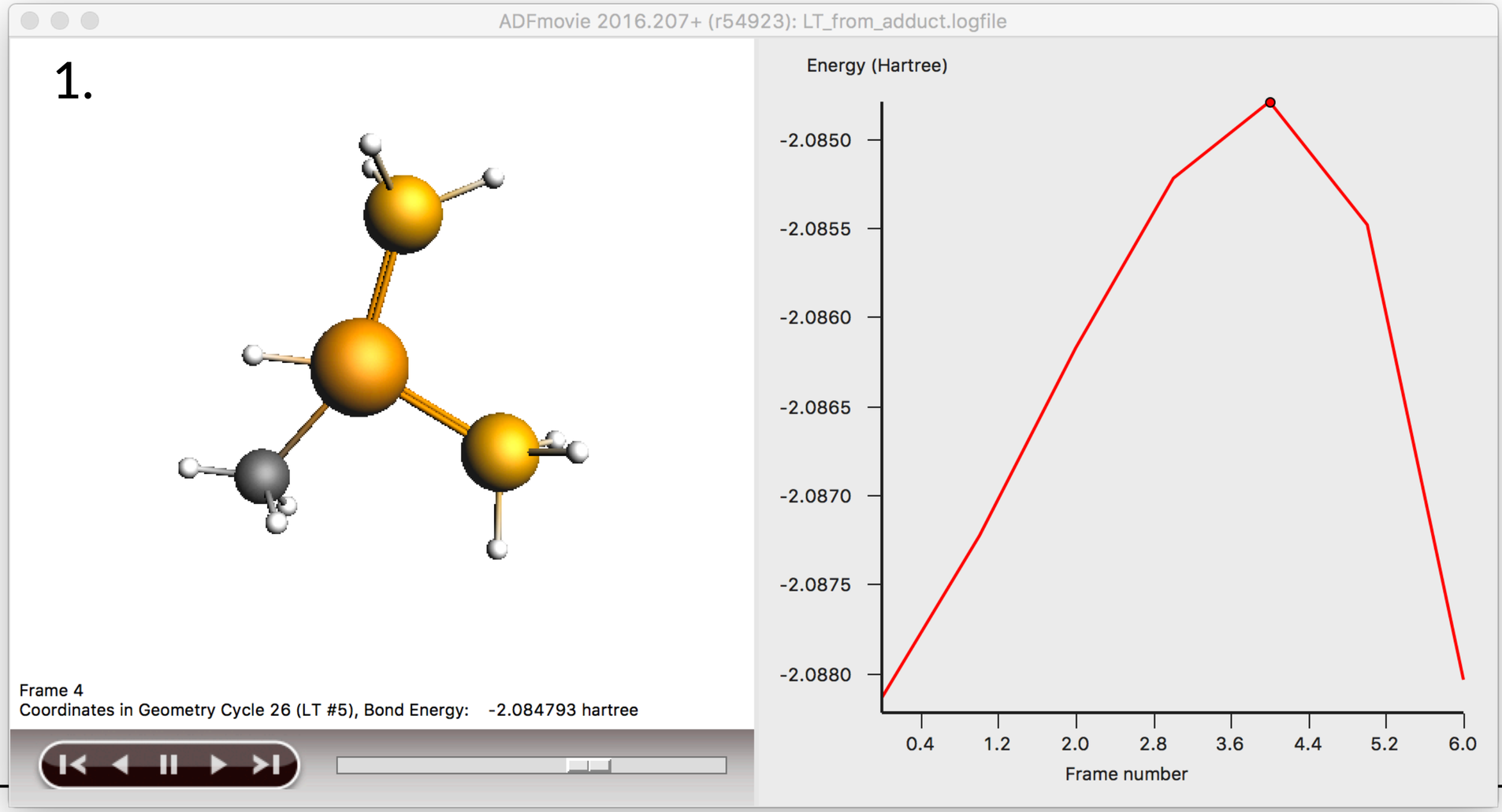
Good geometry guess: 1. LT

1. Build $(CH_3)(H)Pd(PH_3)_2$ - start with ML_4 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

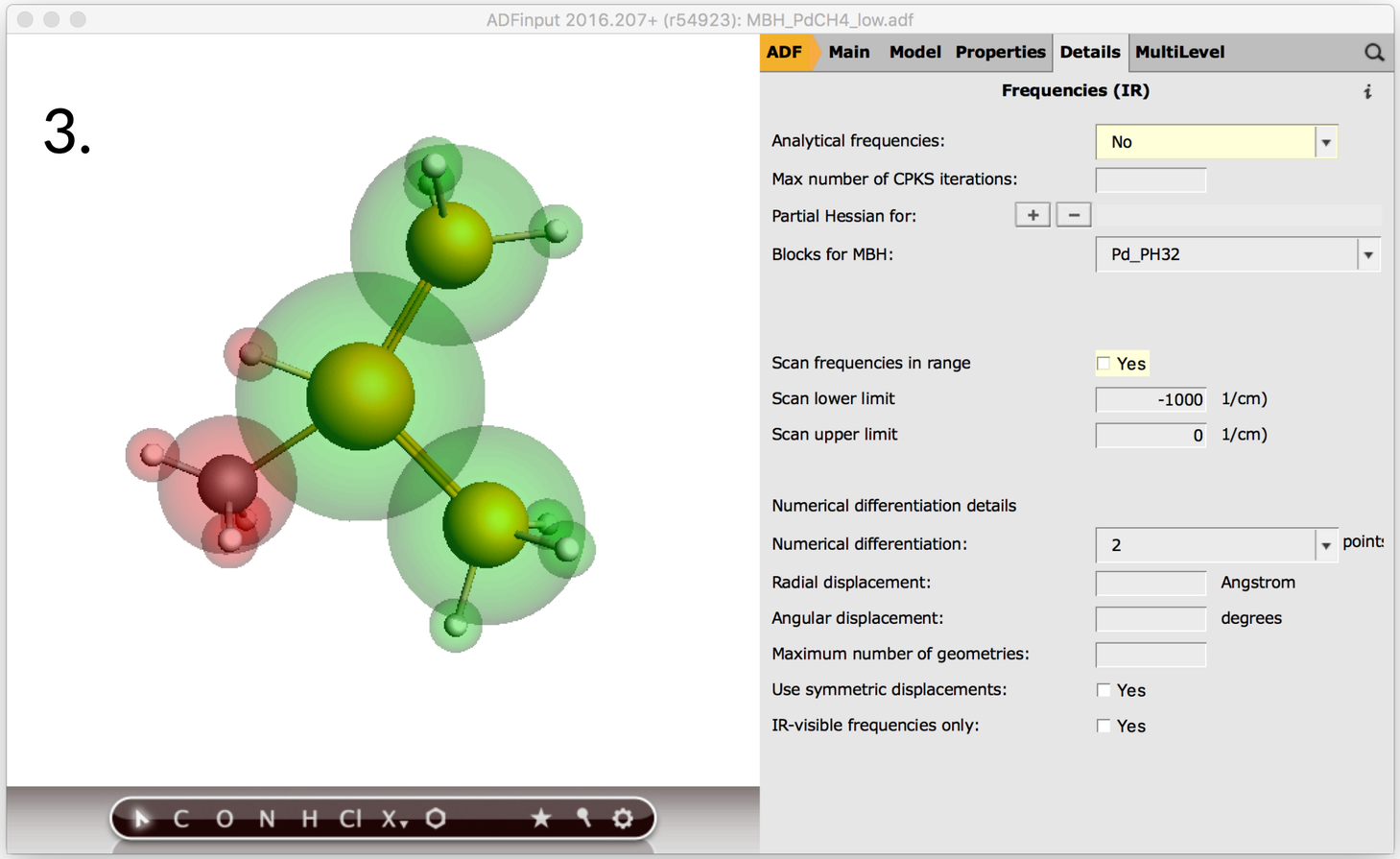
1. View linear transit result: ADFmovie -> view conv. geom. only
2. Click highest point; File => Update geometry in input
3. Change number of transition points to 0, remove constraint
4. Change preset to Transition State Search, click details (…)
5. Select C + H to add to TSRC (TSsearch_1LT.adf)



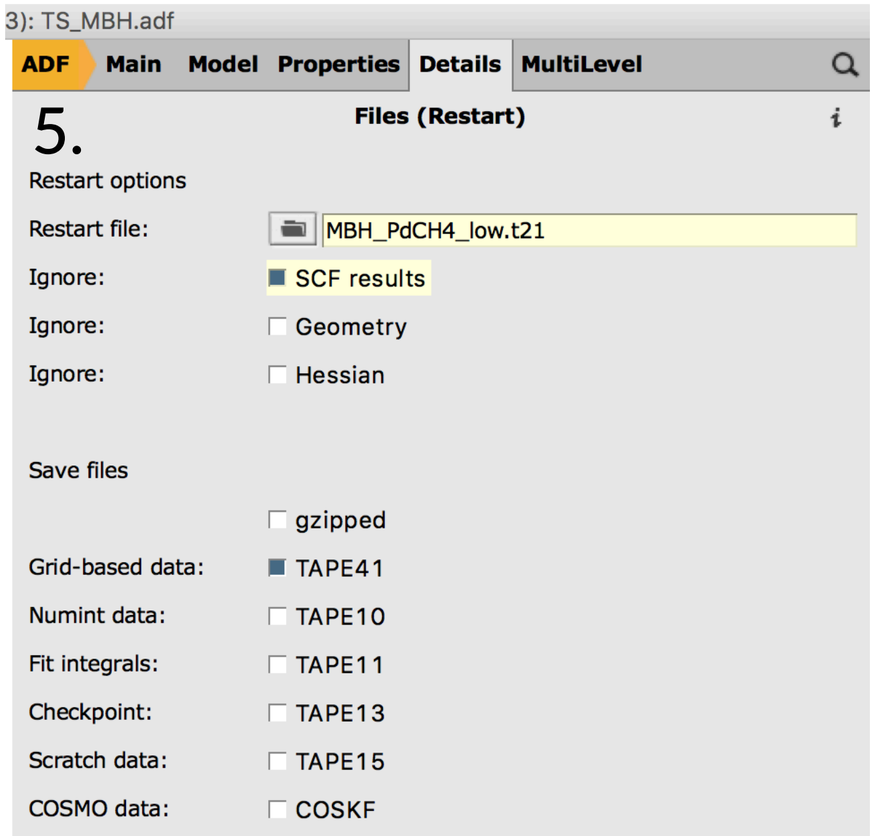
Get a guess Hessian: 2.-4.

2. Partial Hessian (partialhess_low.adf) – e.g. H, C, Pd
3. Mobile Block Hessian (MBH_$PdCH_4$_low.adf)
   - define regions first. E.g. treat $Pd(PH_3)_2$ as mobile block
4. Less accurate xc, basis set, numerical settings (lowHess.adf)
   - Can be combined with 1. & 2.
5. Restart with Hessian (TS_MBH.adf, TS_pHess.adf, TS_lowHess.adf)

3.

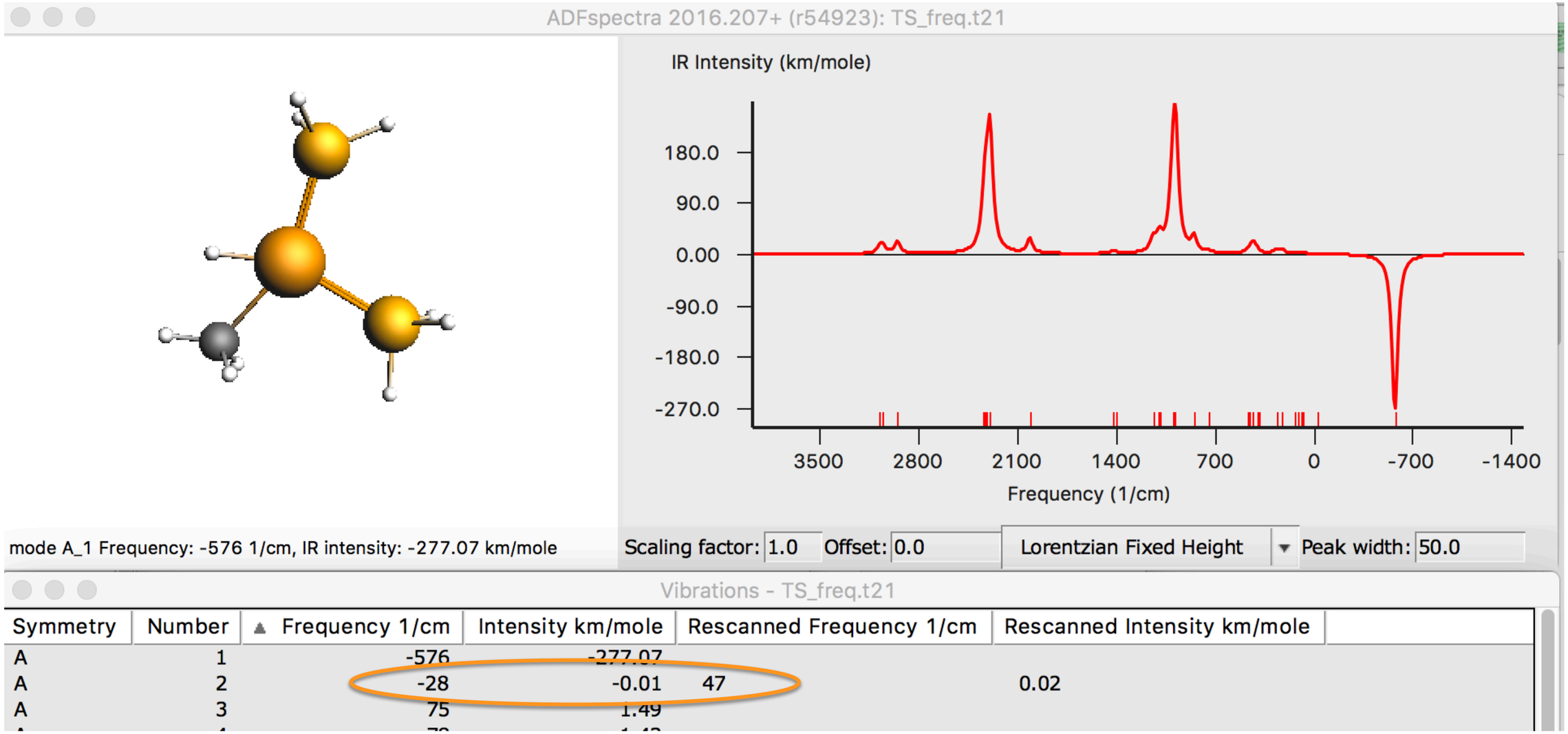


5.



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



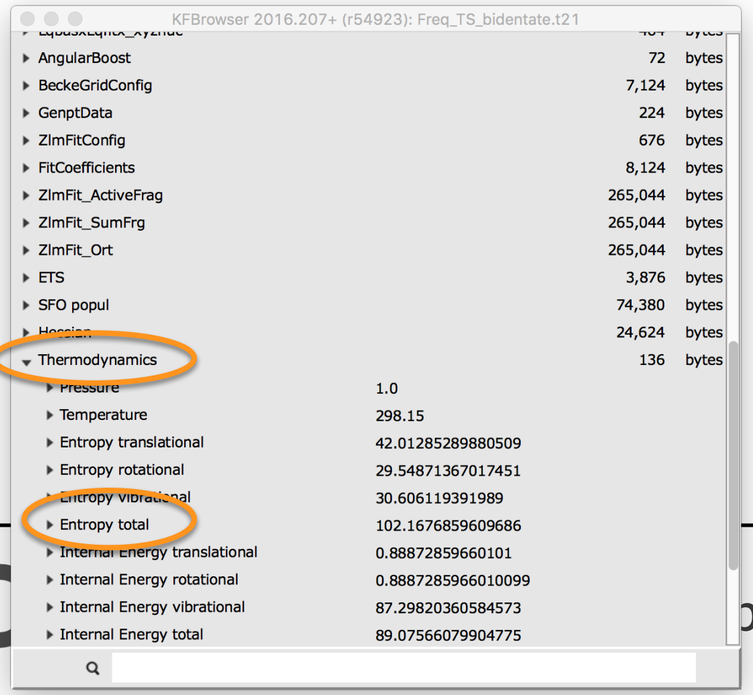
Calculate $\Delta E^{\#}$, $\Delta H^{\#}$, $\Delta G^{\#}$

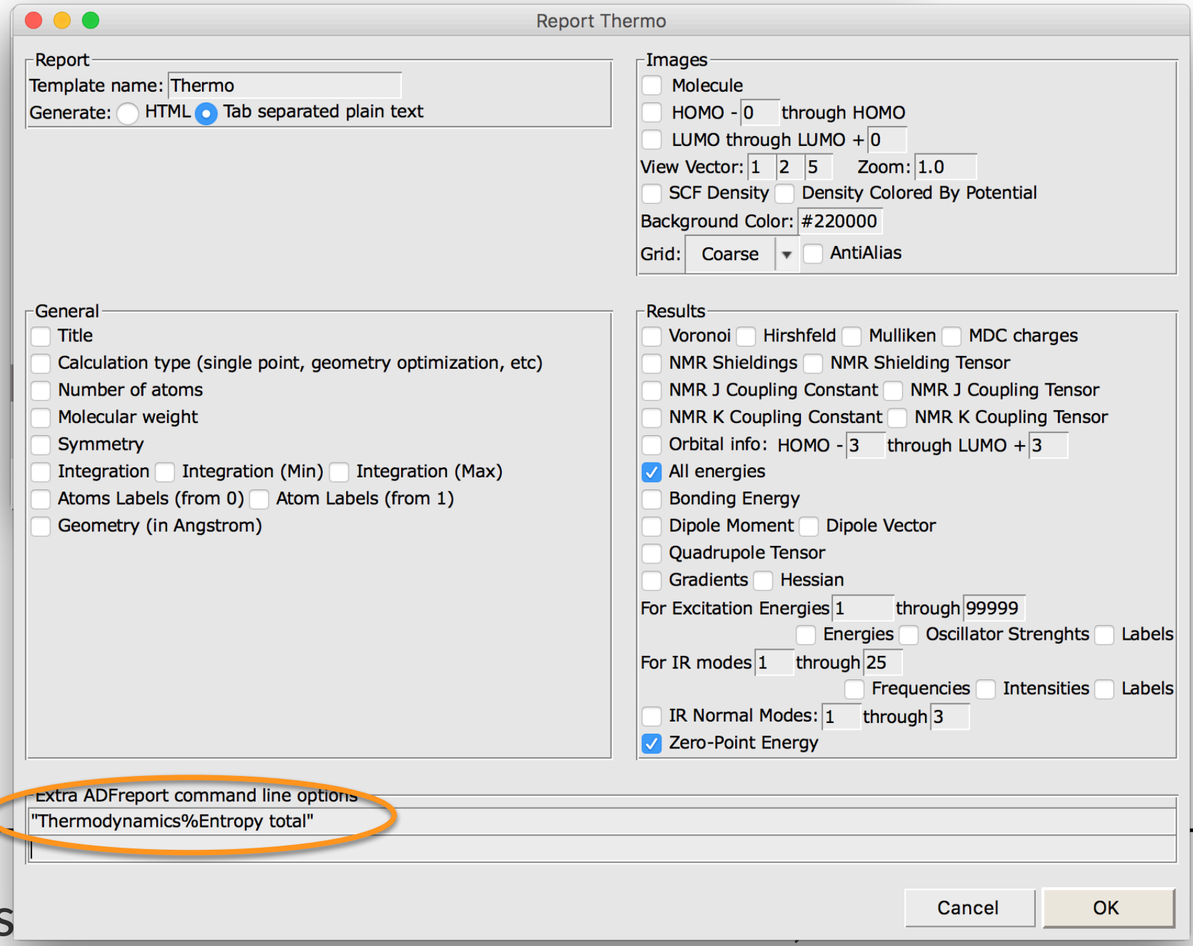
- Get the binding energy for reactants CH_4 + $Pd(PH_3)_2$
  - First optimize reactants separately, run frequencies for ZPE
  - Read from logfile, outputfile, use PLAMS / adfreport, or use report tool in GUI

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

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

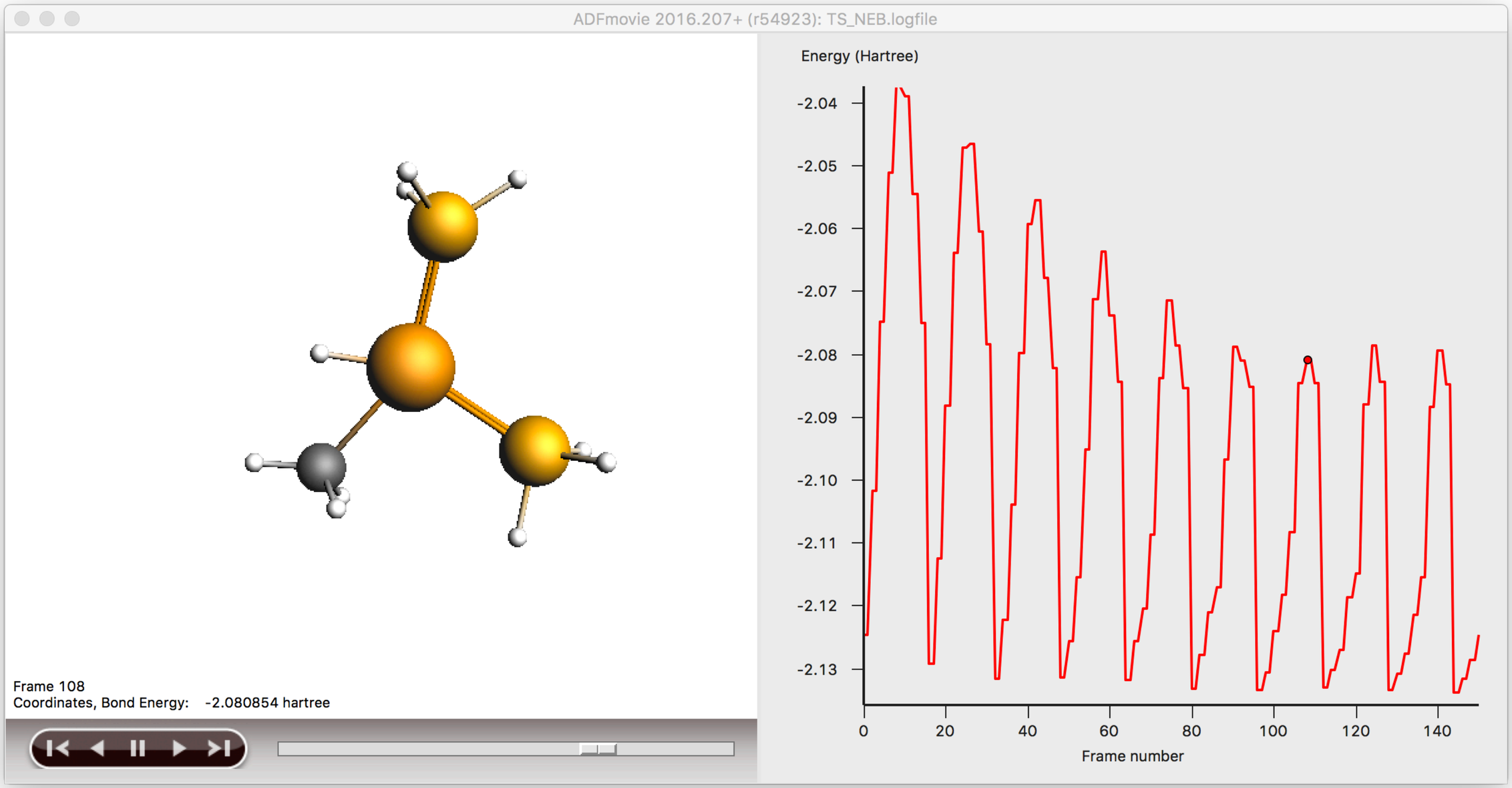
- Find relevant results on t21?
  - KFBrowser => expert mode
  - (adfreport –h result.t21 non-exhaustive)





Good geometry guess: 2. NEB

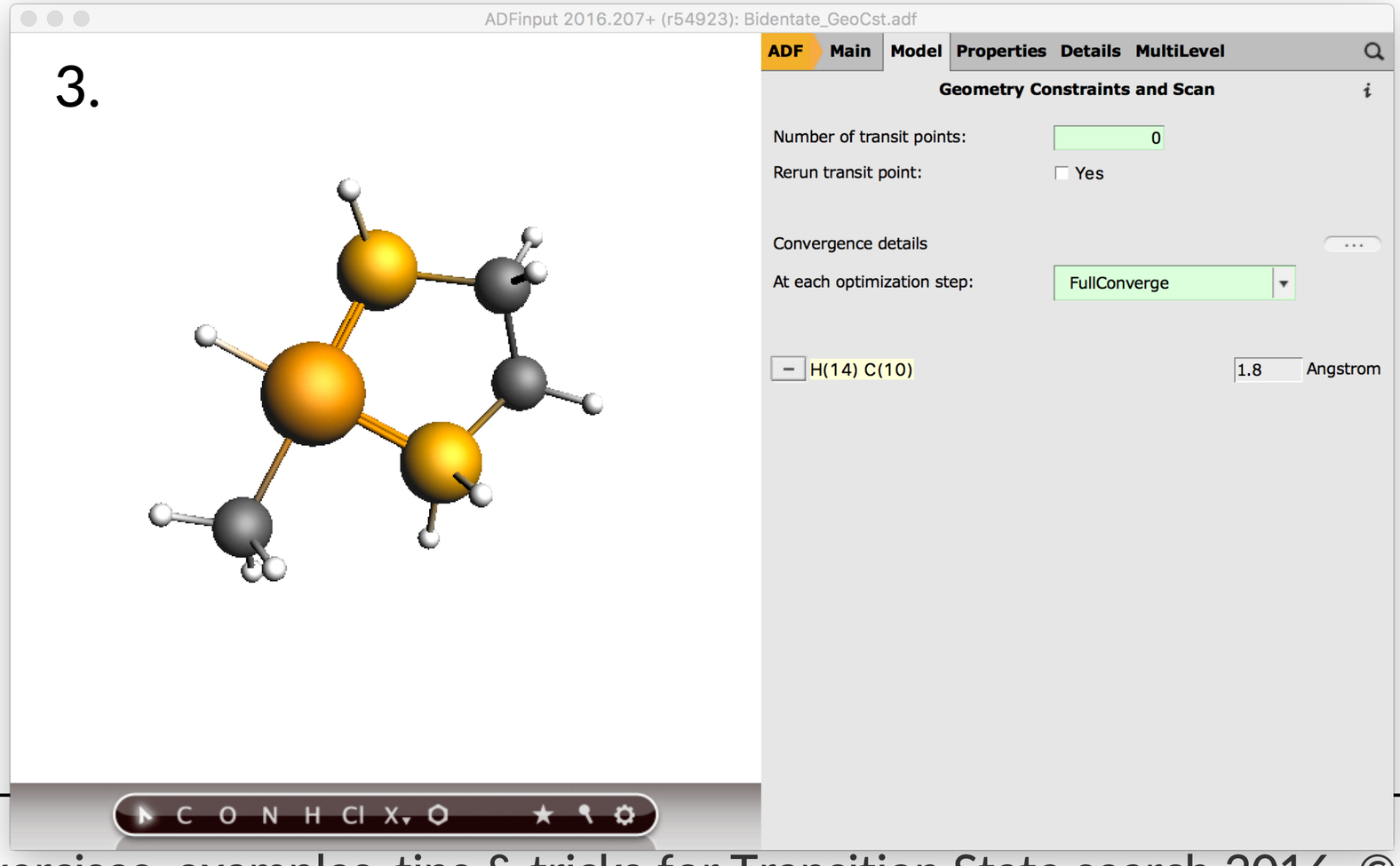
1. Optimize reactant state complex CH_4….$Pd(PH_3)_2$
2. Set up a NEB via ASE from reactant to product (TS_NEB.adf)
3. Don’t run through to the end. Stop and update geometry (highest point)



Geometry guess: 3. intuition

- Start from a TS from a comparable reaction (e.g. change ligands)

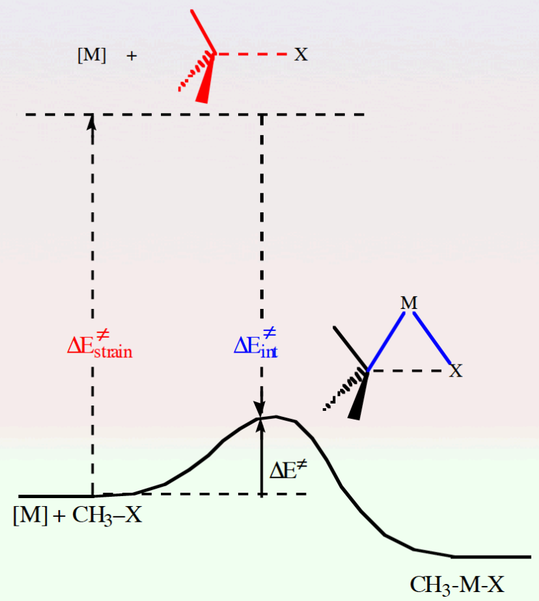
1. Take TS or product from $Pd(PH_3)_2$
2. Make a bidentate ligand (diphosphinoethane, dpe)
3. Run with a **constraint**: C-H distance ~1.8A (Bidentate_GeoCst.adf)
   (may use sloppy accuracy as well, or get xyz from literature)
4. Run your TS with TSRC or other Hessian (Bidentate_TS.adf)



Bonding analysis: ASM, EDA, NOCV

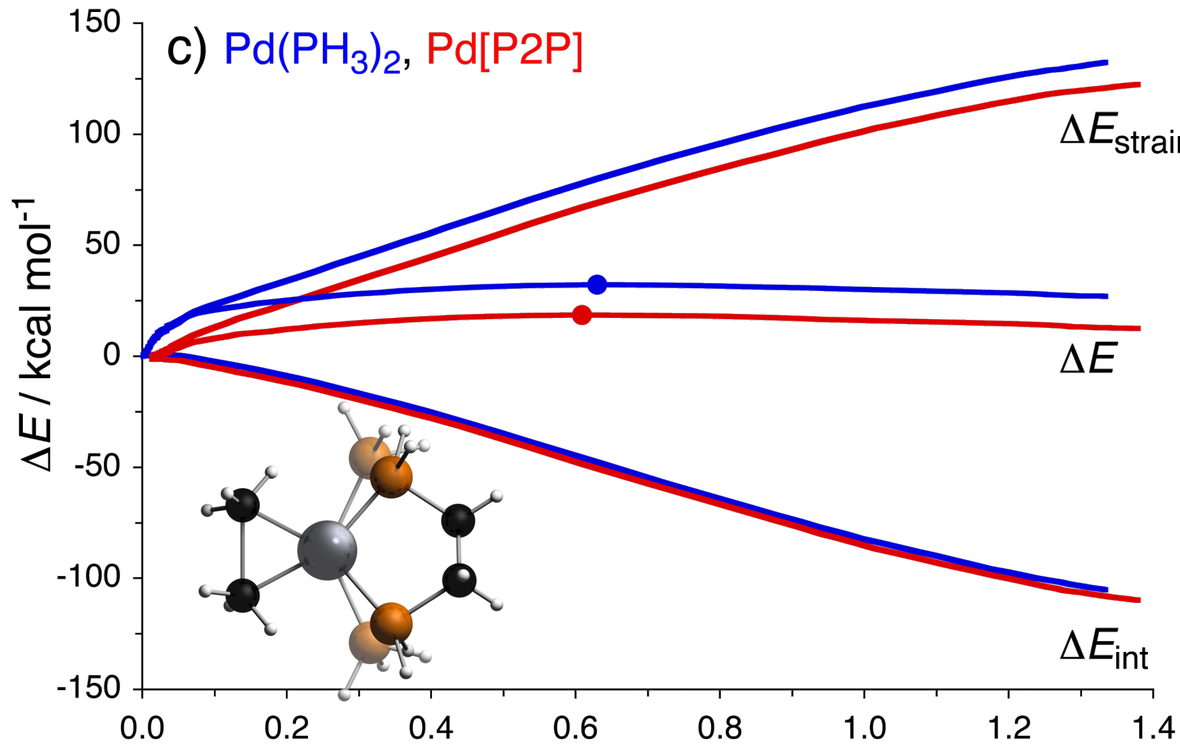
Activation Strain Model Bickelhaupt & co. based on Fragment MOs

- Decompose barrier:



$$\Delta E^{\neq} = \Delta E^{\neq}_{strain} + \Delta E^{\neq}_{int}$$

J. Comput. Chem. **1999**, *20*, 114; *Chem. Soc. Rev.* **2014**, *43*, 4953



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

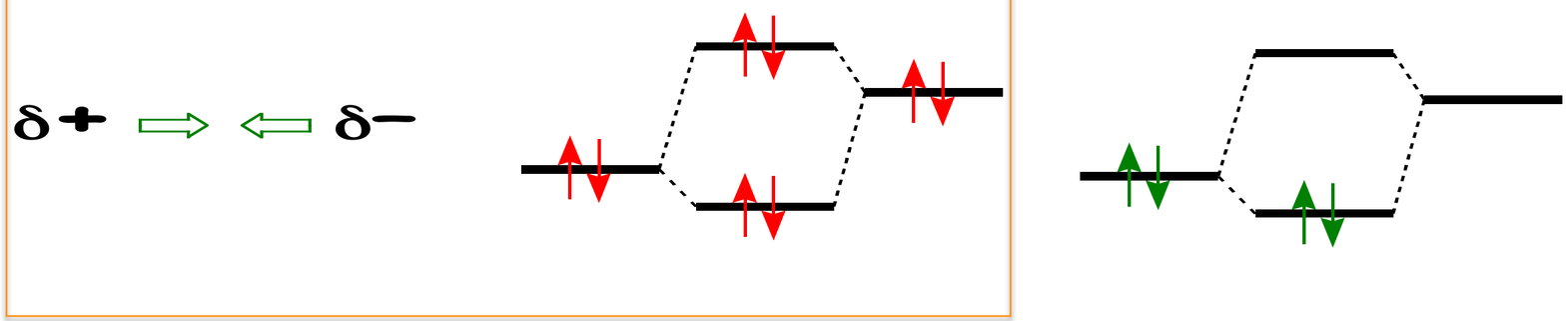
Rev. Comput. Chem. 2000, **15**, 1; Chem. Soc. Rev. 2014, **43**, 4953; WIRES Comput. Mol. Sci. 2015, **5**, 324

Energy decomposition analysis

$$\Delta E = \Delta E_{prep} + \Delta E_{int}$$

Rev. Comput. Chem. 2000, 15, 1

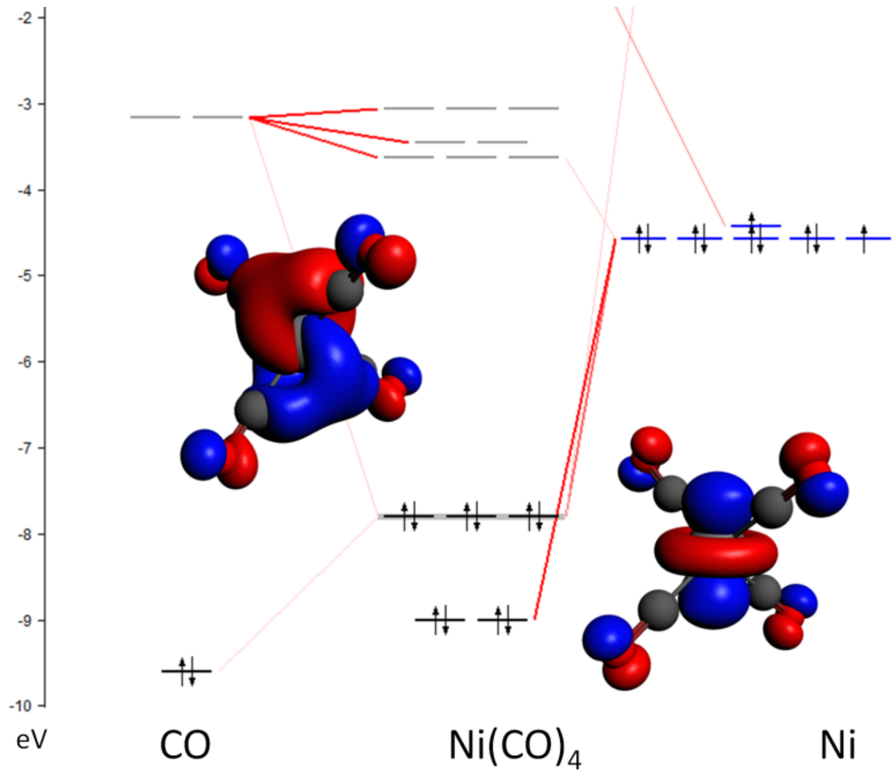
$$\Delta V_{elstat} + \Delta E_{Pauli} + \Delta E_{oi} + \Delta E_{disp}$$



- $\Delta E_{steric} = \Delta V_{elstat} + \Delta E_{pauli}$
- ΔE_{oi} = decomposed in irreps.

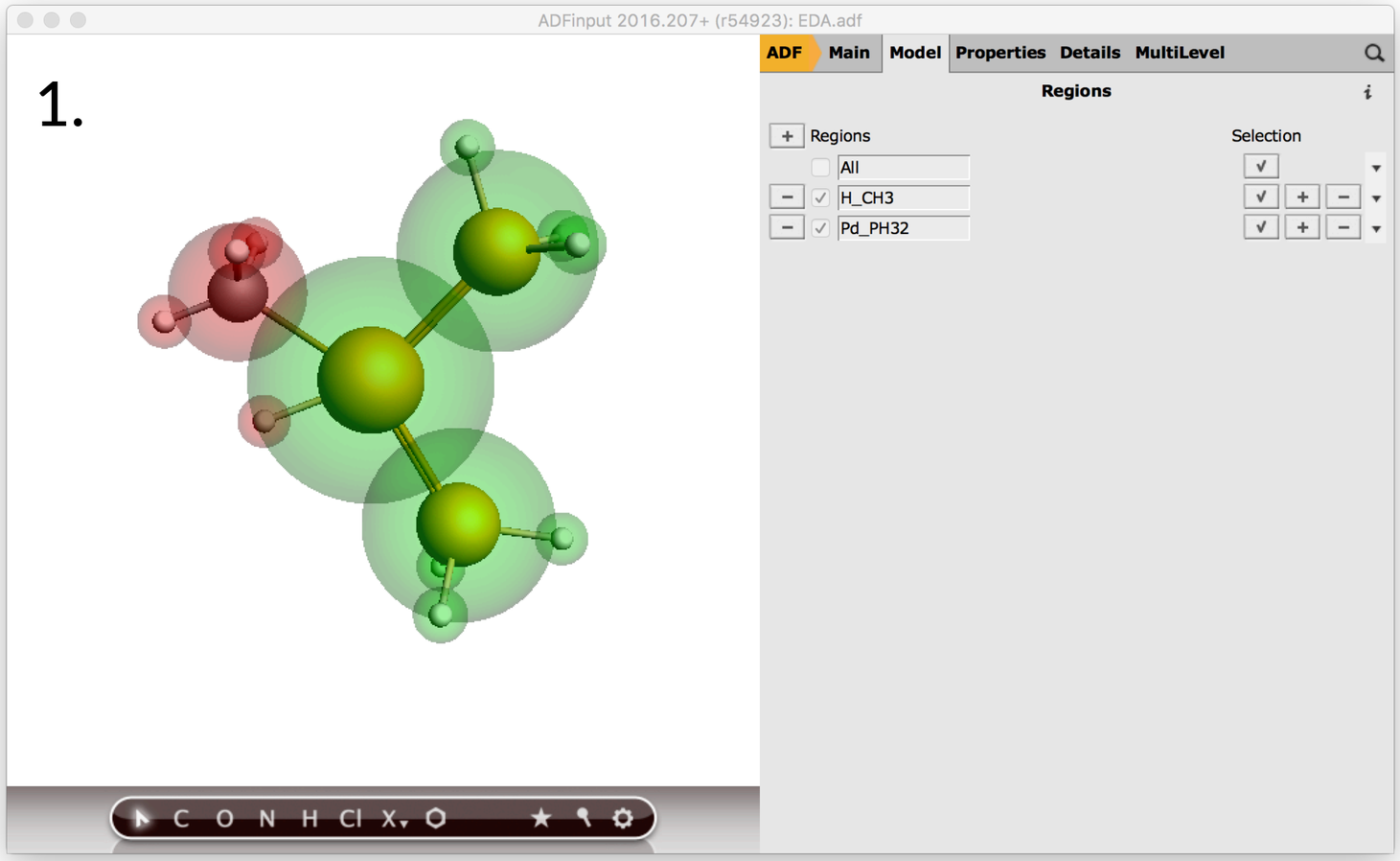
Extensions:

- ETS-NOCV: orbital interactions + deformation density M. Mitoraj et al., J. Chem. Theor. Comput. 5, 962 (2009)
- Periodic EDA: M. Raupach & R. Tonner, J. Chem. Phys. 142, 194105 (2015)): molecule-surface interactions



Energy decomposition analysis

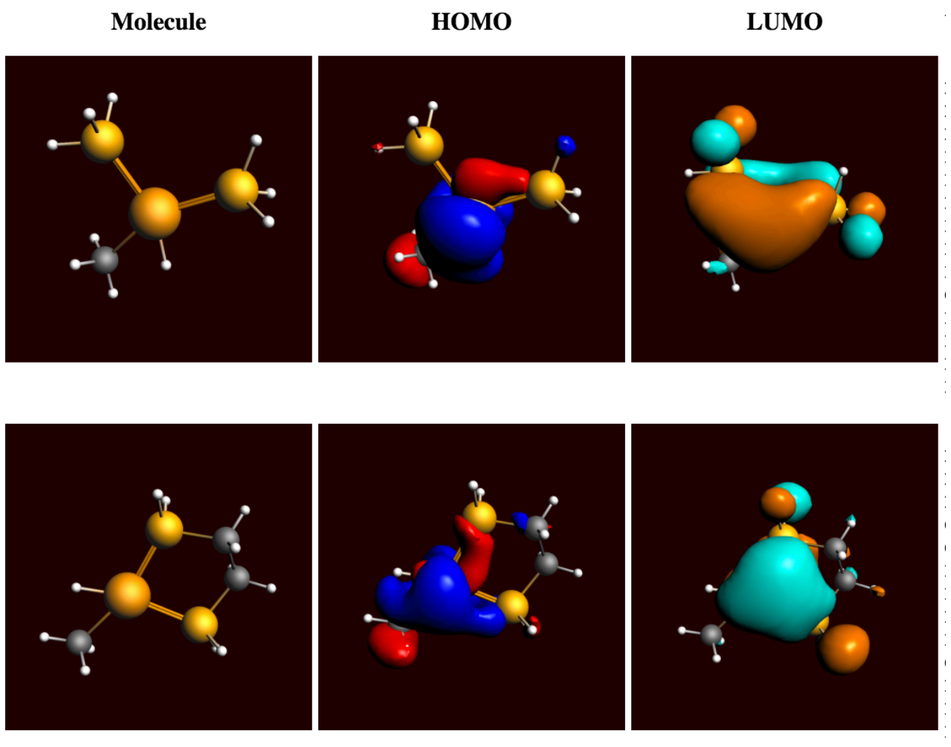
1. Define your fragments (**regions**)
2. Run your EDA or ETS-NOCV calculation
   - Single point calculation; check ‘Use fragments’ in MultiLevel tab
   - (Select ETS-NOCV type calculation in Properties => ETS-NOCV)
   - Results: ADFouput => Properties => Bonding Energy Decomposition
3. Optimize fragments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

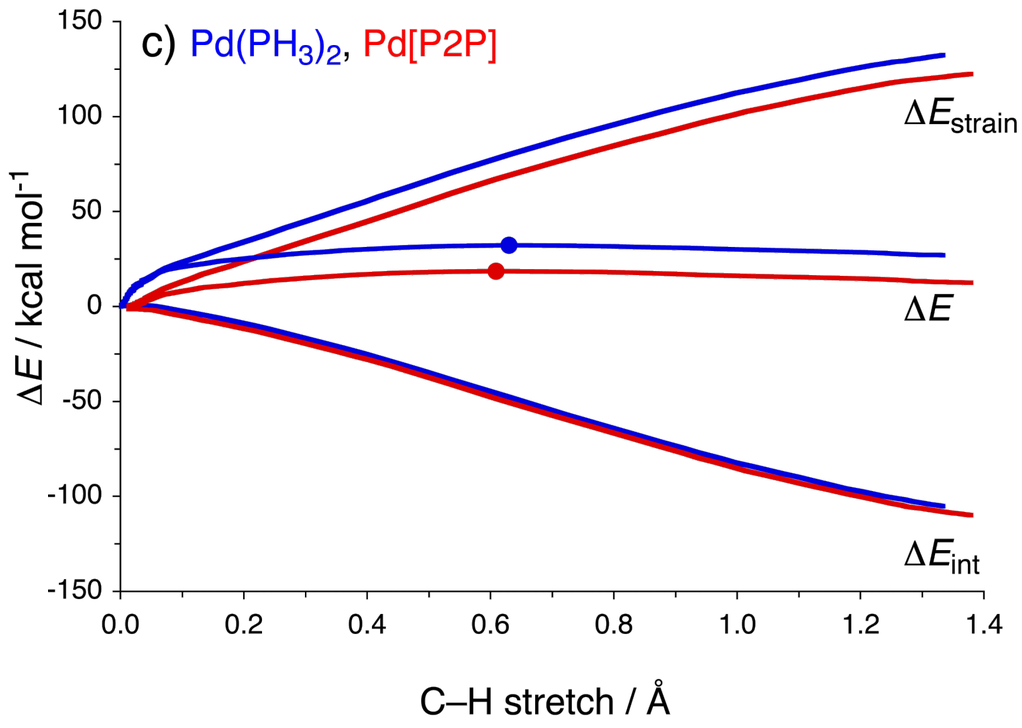


Energy decomposition analysis

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

	Pd(PH3)2	Pd(dpe)
Bonding Energy	-59.16	-59.62
Pauli Repulsion	186.41	178.66
Electrostatic Interaction	-155.27	-150.37
Steric Interaction	31.14	28.29
Orbital Interaction	-89.16	-86.90
C(10)-H(14)	1.804	1.786



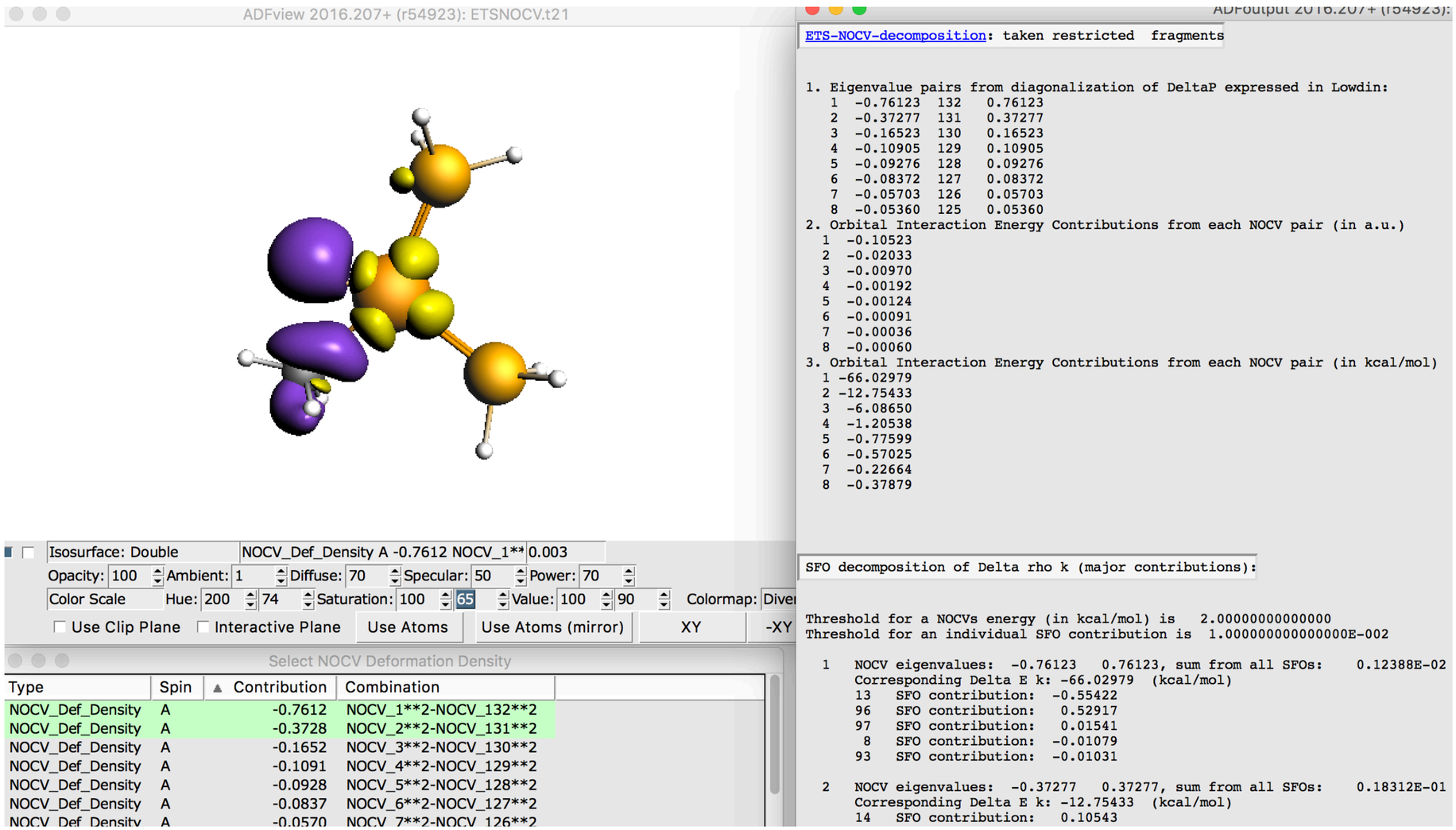


Strain built into bidentate

- Reduces *activation strain*
- Earlier TS
- Lower $\Delta E^{\#}$

ETS-NOCV

- Select closed-shell ETS-NOCV & run (ETSNOCV.adf)
- Visualize deformation densities in ADFview – play with settings



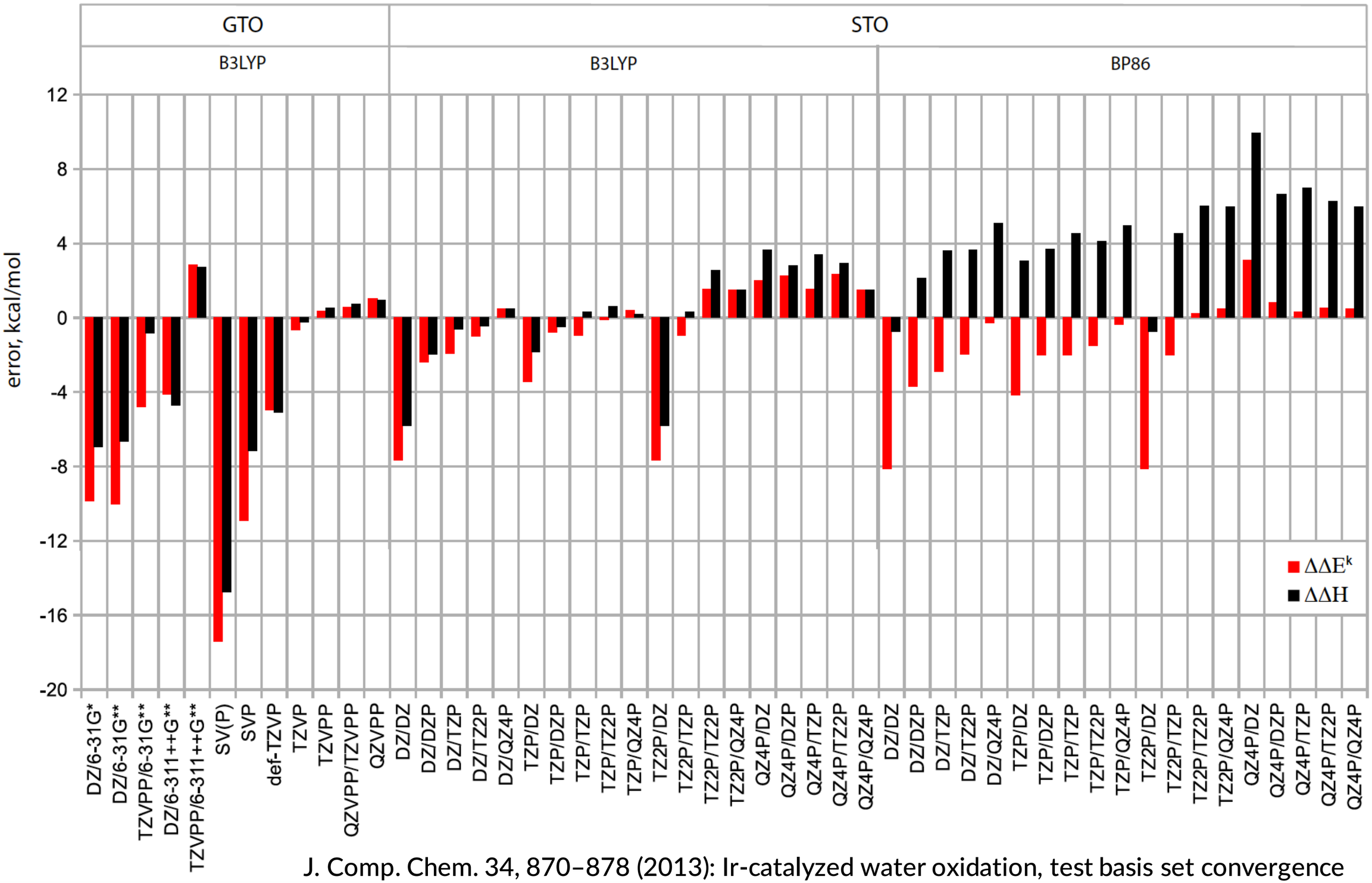
More (workshop) materials:
https://www.scm.com/adf-modeling-suite/wizard/teaching/adf-teaching-materials/
https://www.scm.com/adf-modeling-suite/adf-hands-on-workshops/

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 < 1kcal/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



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

Some more tips

- QUILD has more options for initial Hessians (ihopt) + updates (ihupd)
  - Uses a Hessian check by default (check a 2nd 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
  - Convergence tests http://www.scm.com/doc/Tutorials/ADF/Generating_a_batch_of_jobs.html
- Use ADFreport to get your results (GUI or cmd line scripting)
  - Commandline ADFreport allows further python / shell scripting
  - PLAMS: python workflows
  - See the scripting materials on: https://www.scm.com/adf-modeling-suite/wizard/teaching/adf-teaching-materials/

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