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

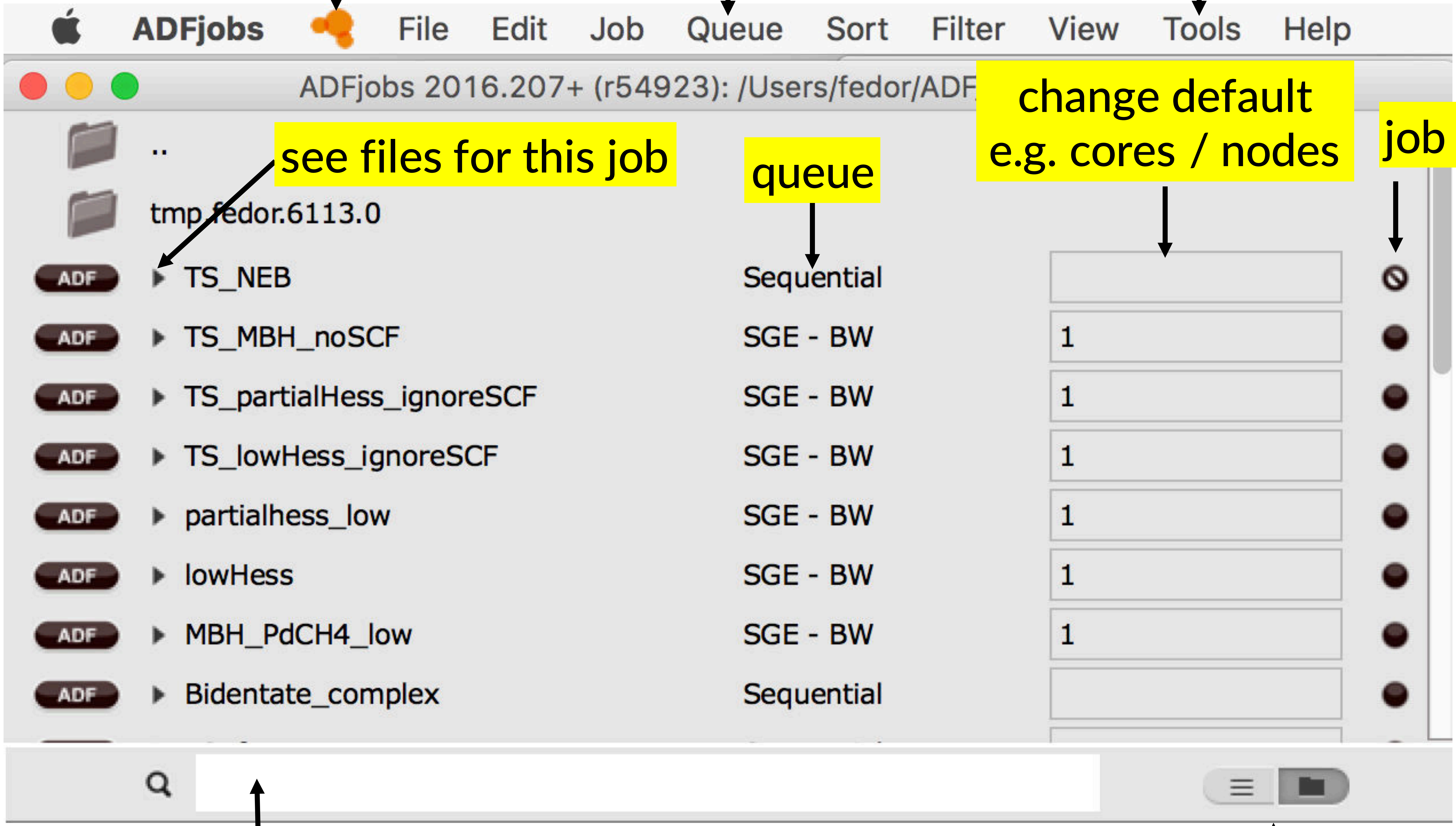
- Properties demo: IR, NMR, EPR, UV/VIS?

ADFjobs: job bookkeeping

switch GUI functionality

define & switch queues

reports & templates



ADFjobs 2016.207+ (r54923): /Users/fedor/ADF

..

tmp.fedor.6113.0

ADF	TS_NEB	Sequential		⊘
ADF	TS_MBH_noSCF	SGE - BW	1	●
ADF	TS_partialHess_ignoreSCF	SGE - BW	1	●
ADF	TS_lowHess_ignoreSCF	SGE - BW	1	●
ADF	partialhess_low	SGE - BW	1	●
ADF	lowHess	SGE - BW	1	●
ADF	MBH_PdCH4_low	SGE - BW	1	●
ADF	Bidentate_complex	Sequential		●

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

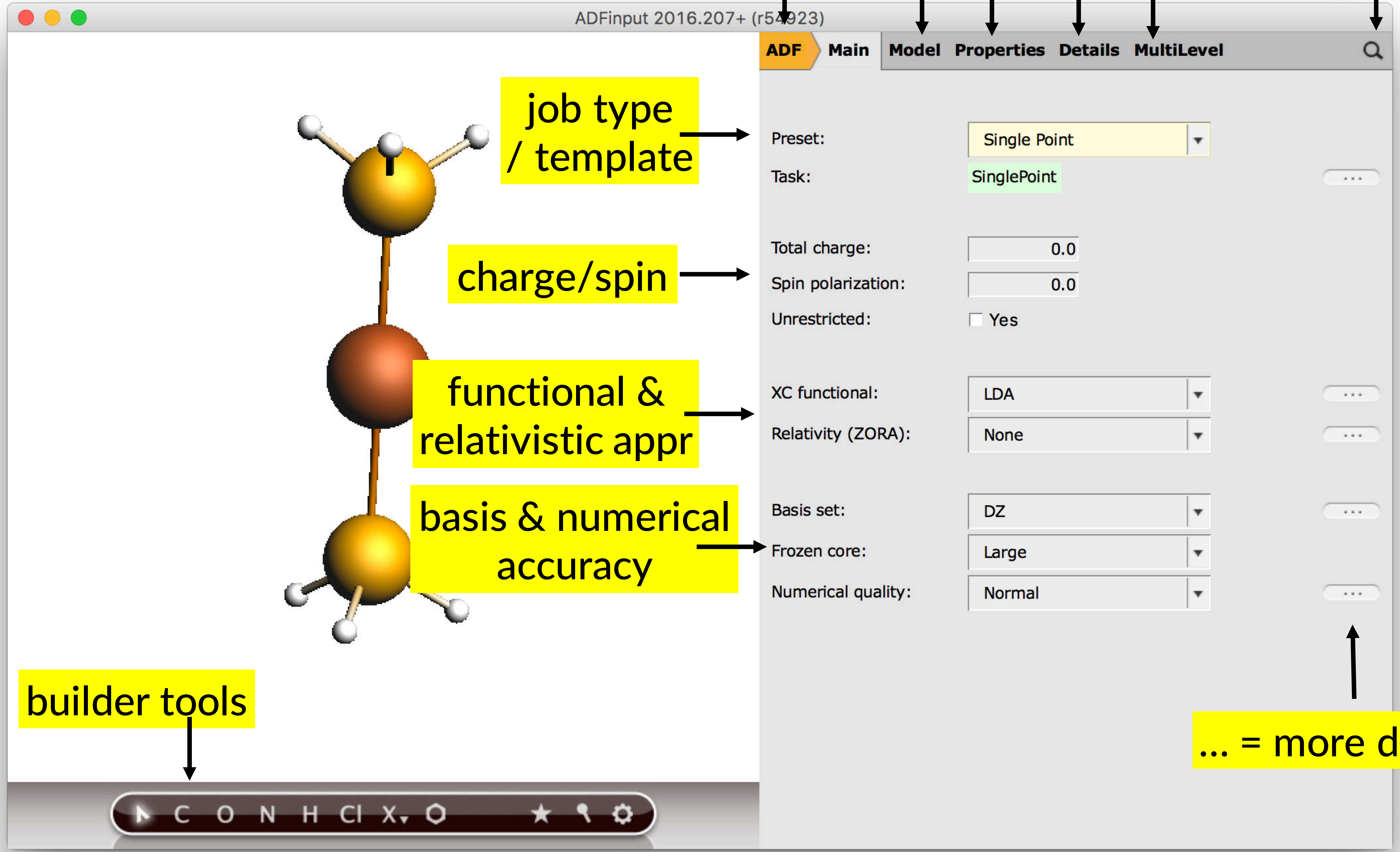
- **Excercise:** Build a small molecule of choice and optimize (default settings)

Basic calculations & settings

switch modules

job types & set up

search



Preset: Single Point

Task: SinglePoint

Total charge: 0.0

Spin polarization: 0.0

Unrestricted: ☐ Yes

XC functional: LDA

Relativity (ZORA): None

Basis set: DZ

Frozen core: Large

Numerical quality: Normal

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?

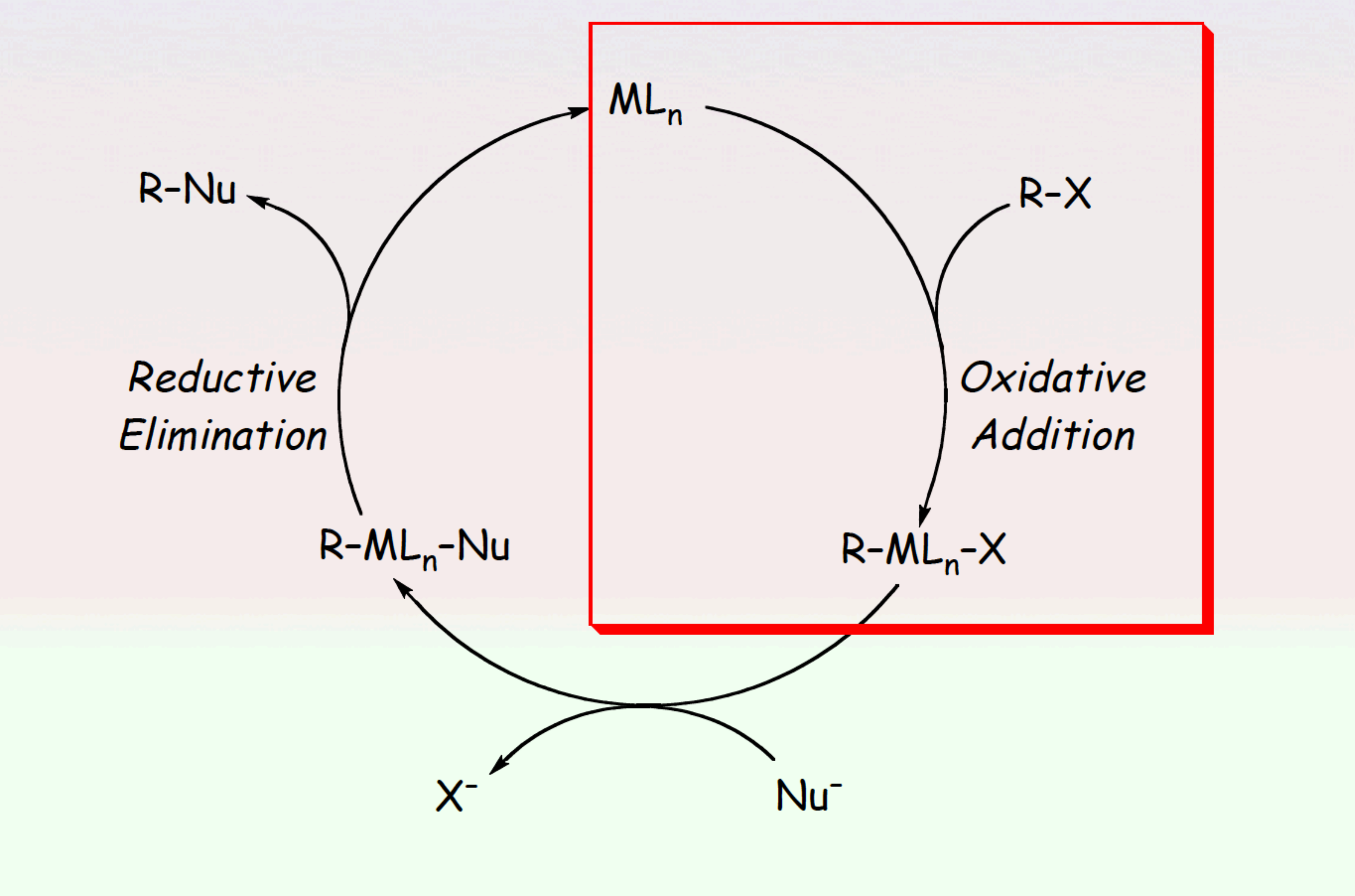
Remember: a TS has 1 and only 1 negative Hessian eigenvalue

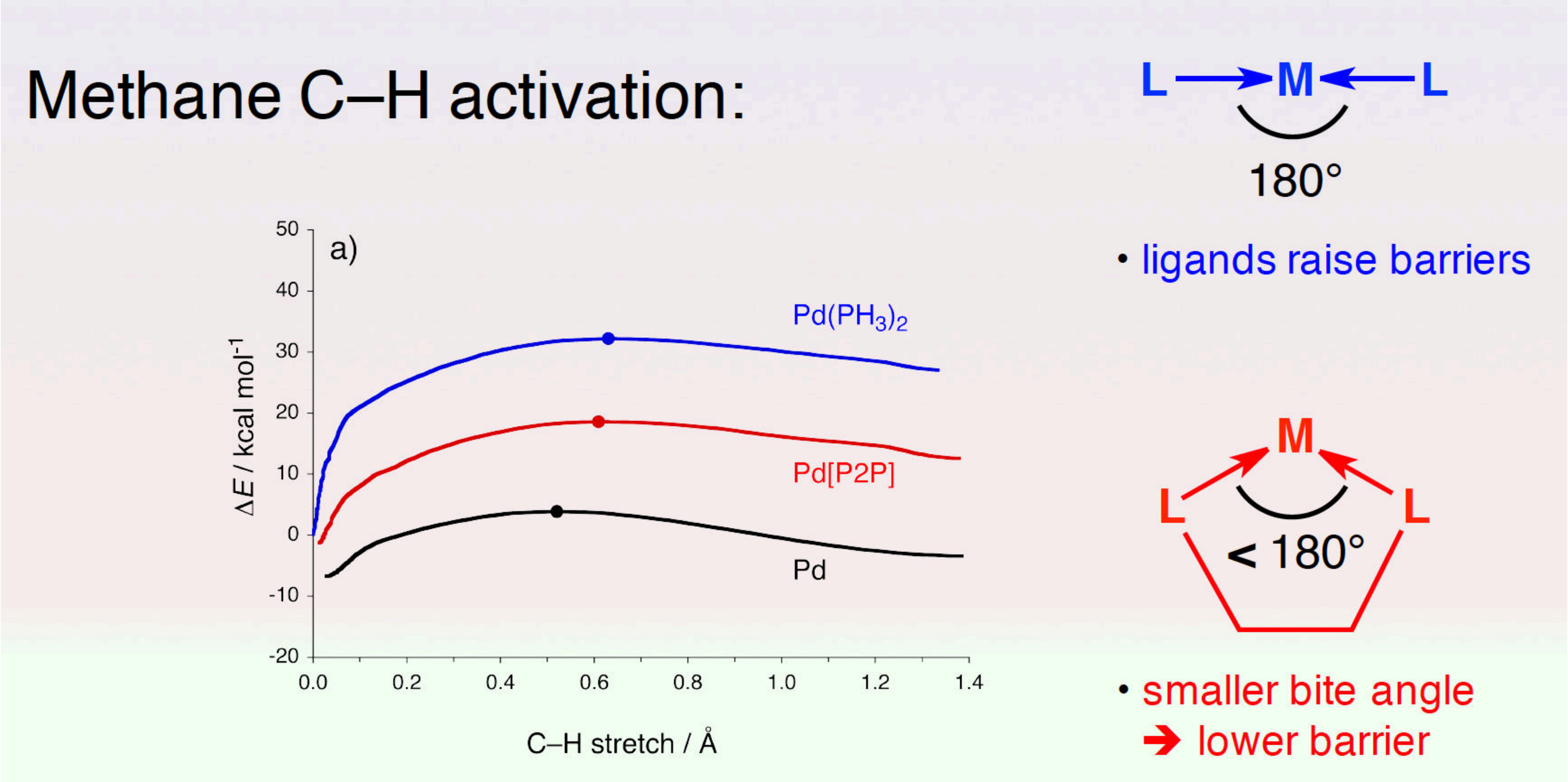
Example: Pd-catalysed oxidative addition

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



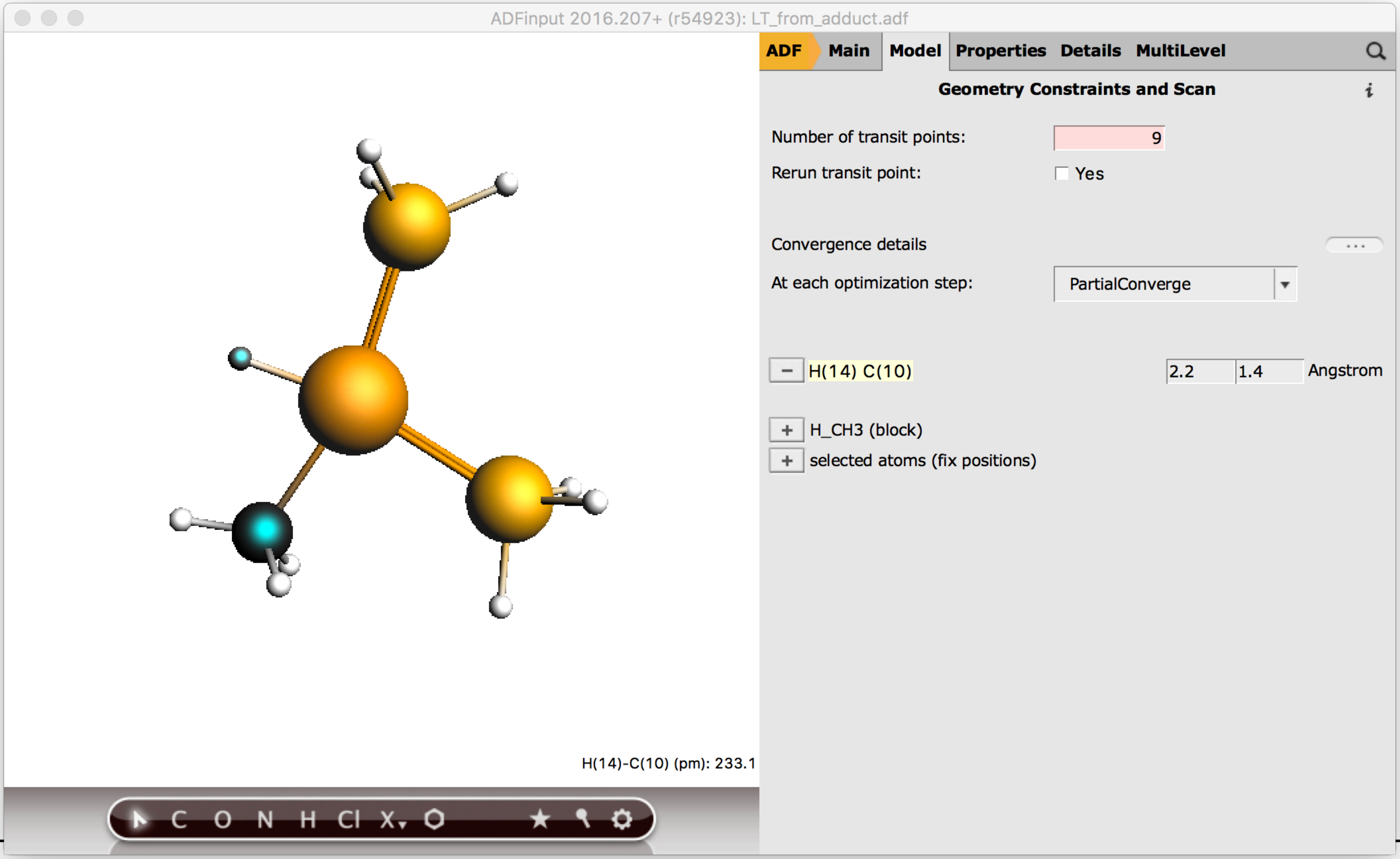


- ligands raise barriers
- smaller bite angle ➔ lower barrier

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)



ADFinput 2016.207+ (r54923): LT_from_adduct.adf

Geometry Constraints and Scan

Number of transit points: 9

Rerun transit point: ☐ Yes

Convergence details

At each optimization step: PartialConverge

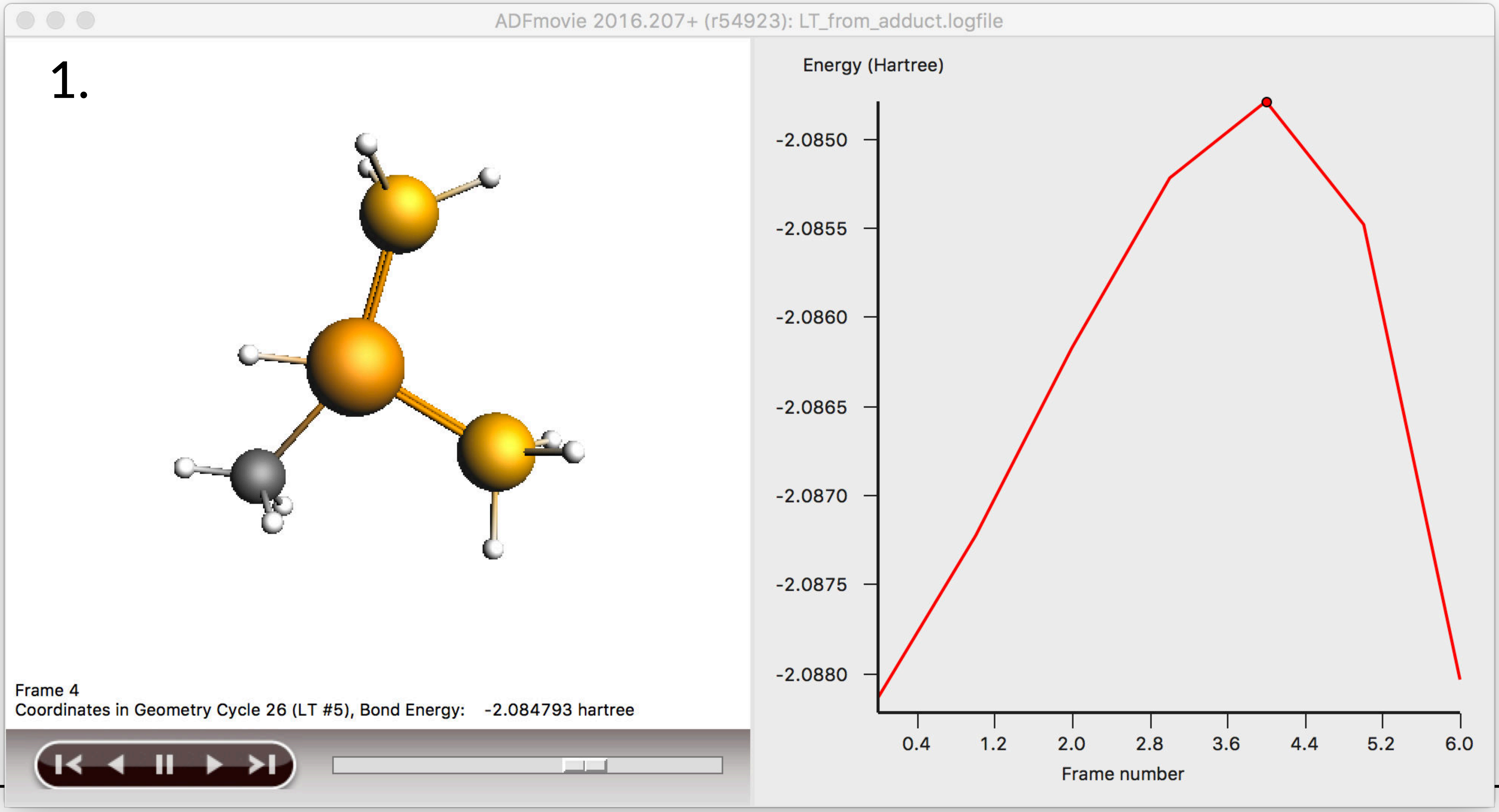
− H(14) C(10) 2.2 1.4 Angstrom

+ H_CH3 (block)

+ selected atoms (fix positions)

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)

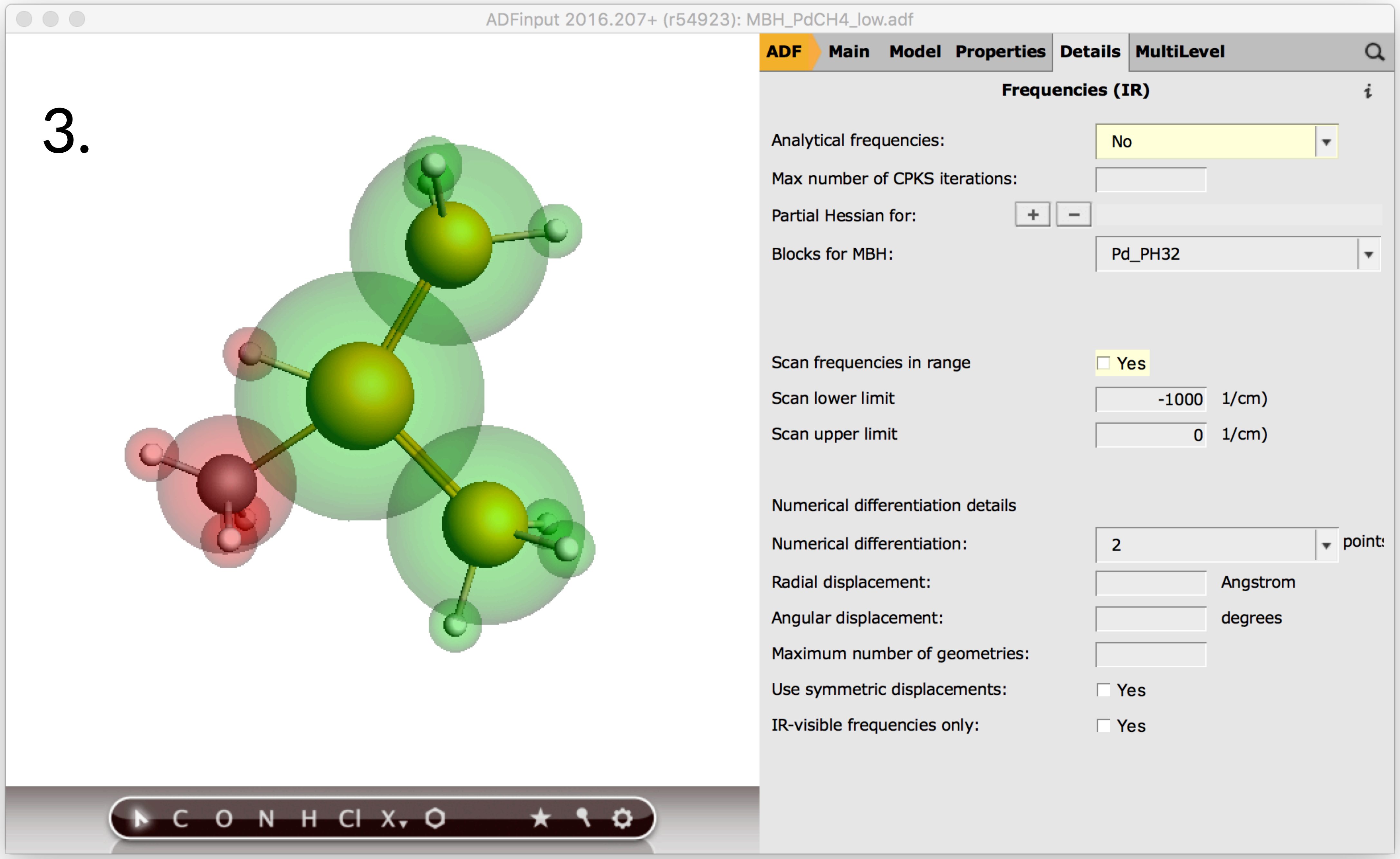


ADFmovie 2016.207+ (r54923): LT_from_adduct.logfile

Frame 4
Coordinates in Geometry Cycle 26 (LT #5), Bond Energy: -2.084793 hartree

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)



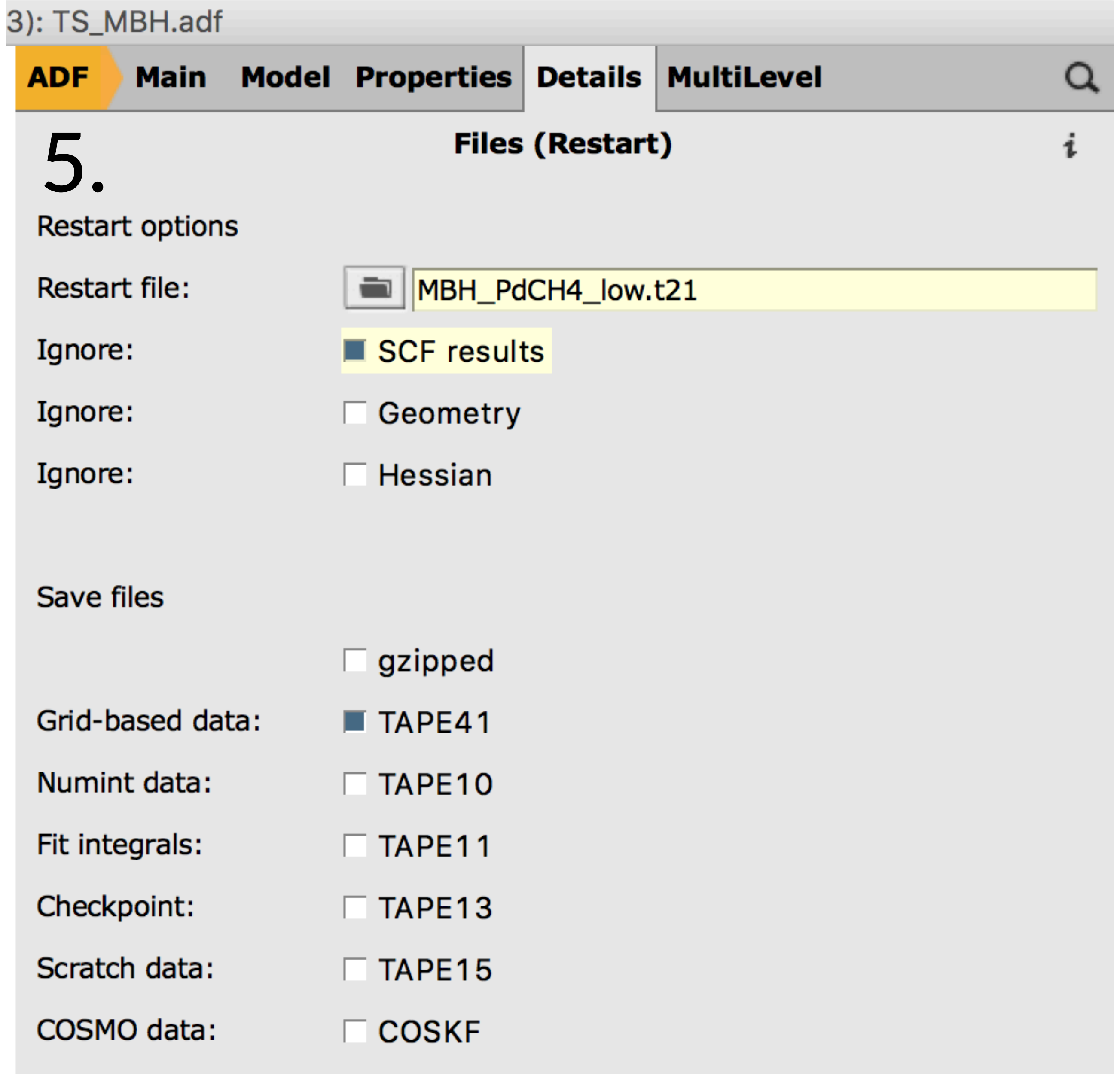
ADFinput 2016.207+ (r54923): MBH_PdCH4_low.adf

Frequencies (IR)

Analytical frequencies: No
Max number of CPKS iterations:
Partial Hessian for:
Blocks for MBH: Pd_PH32

Scan frequencies in range ☐ Yes
Scan lower limit -1000 1/cm)
Scan upper limit 0 1/cm)

Numerical differentiation details
Numerical differentiation: 2 point
Radial displacement: Angstrom
Angular displacement: degrees
Maximum number of geometries:
Use symmetric displacements: ☐ Yes
IR-visible frequencies only: ☐ Yes



3): TS_MBH.adf

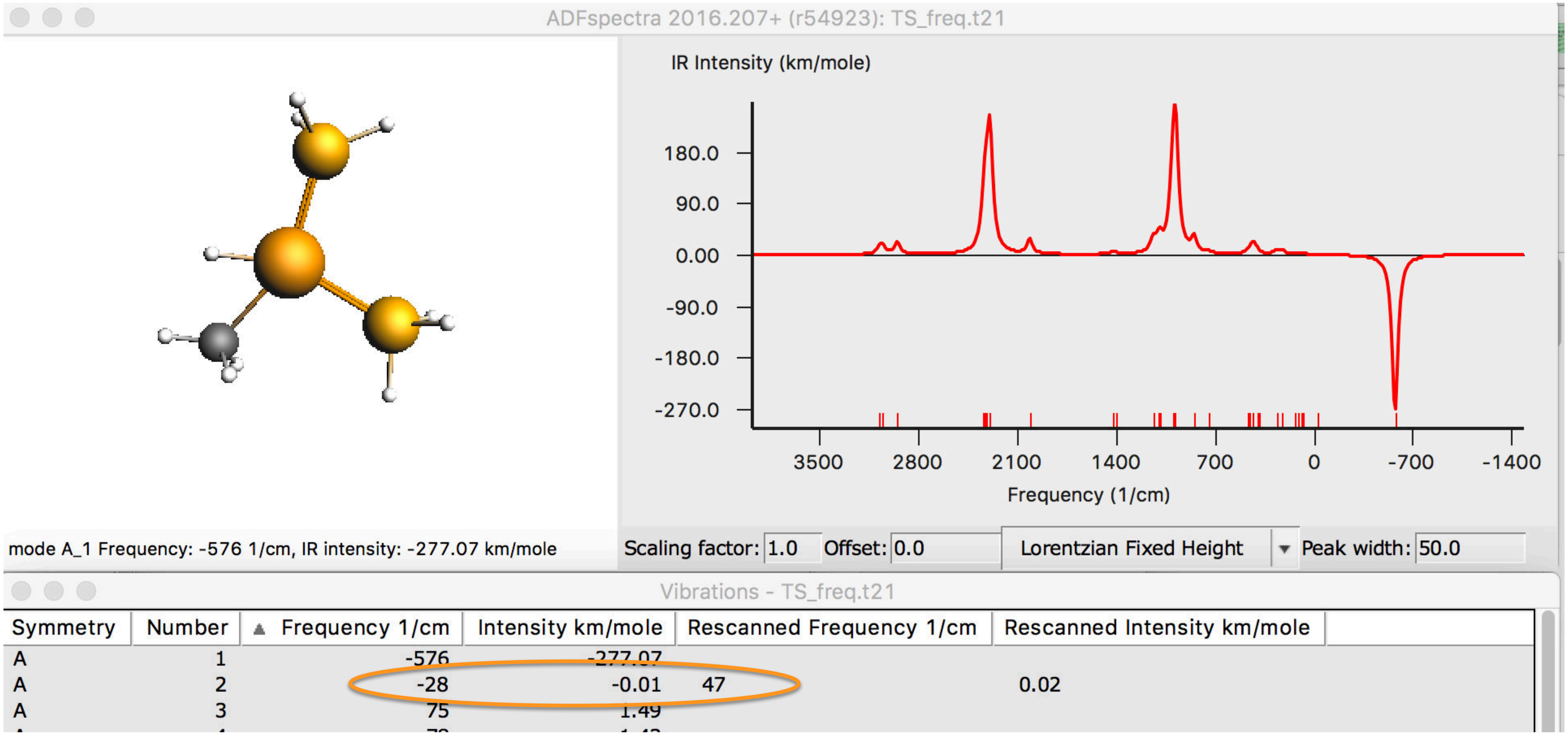
Files (Restart)

Restart options
Restart file: MBH_PdCH4_low.t21
Ignore: ☑ SCF results
Ignore: ☐ Geometry
Ignore: ☐ Hessian

Save files
☐ gzipped
Grid-based data: ☑ TAPE41
Numint data: ☐ TAPE10
Fit integrals: ☐ TAPE11
Checkpoint: ☐ TAPE13
Scratch data: ☐ TAPE15
COSMO data: ☐ COSKF

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



mode A_1 Frequency: -576 1/cm, IR intensity: -277.07 km/mole

Scaling factor: 1.0 Offset: 0.0 Peak width: 50.0

Symmetry	Number	▲ Frequency 1/cm	Intensity km/mole	Rescanned Frequency 1/cm	Rescanned Intensity km/mole
A	1	-576	-277.07		
A	2	-28	-0.01	47	0.02
A	3	75	1.49		

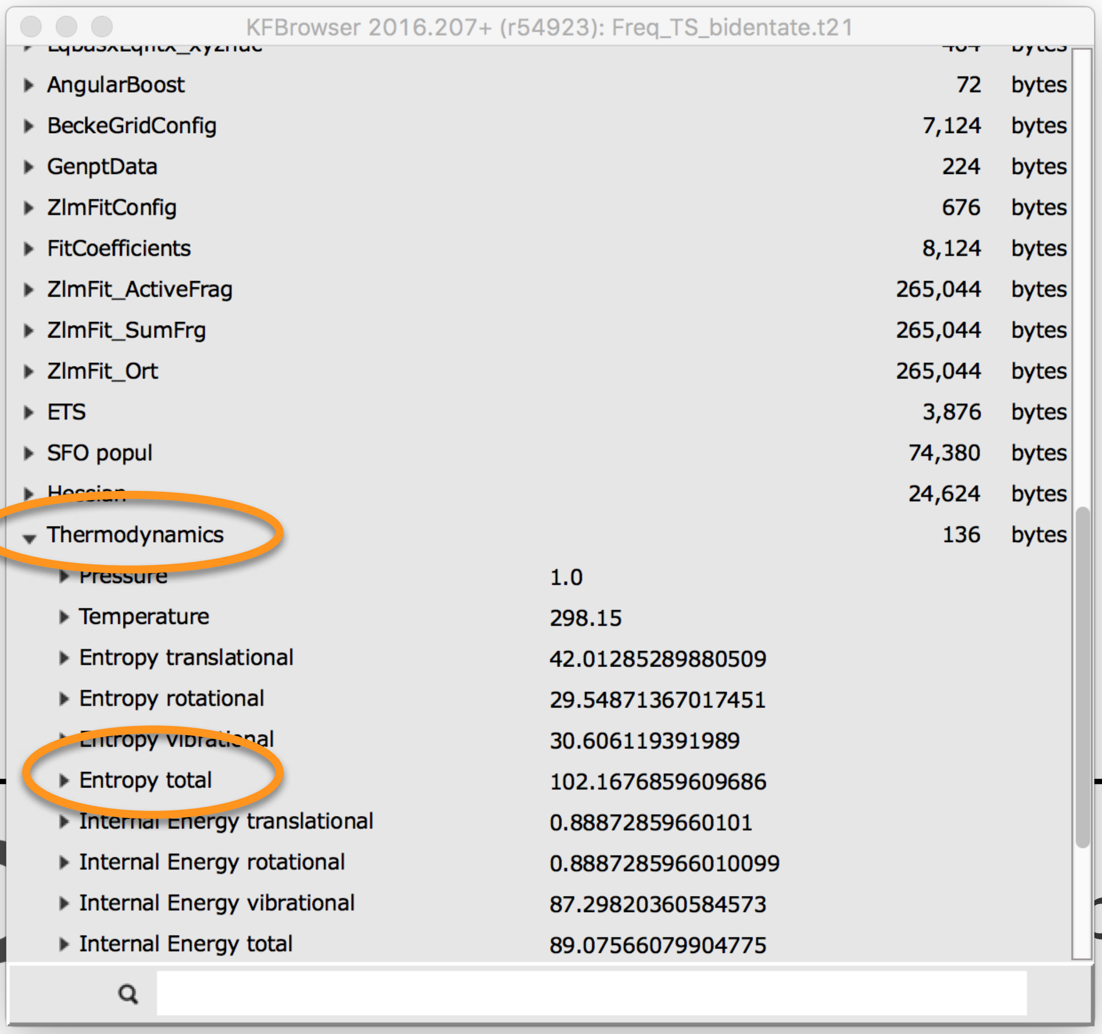
Calculate ΔE#, ΔH#, ΔG#

- 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

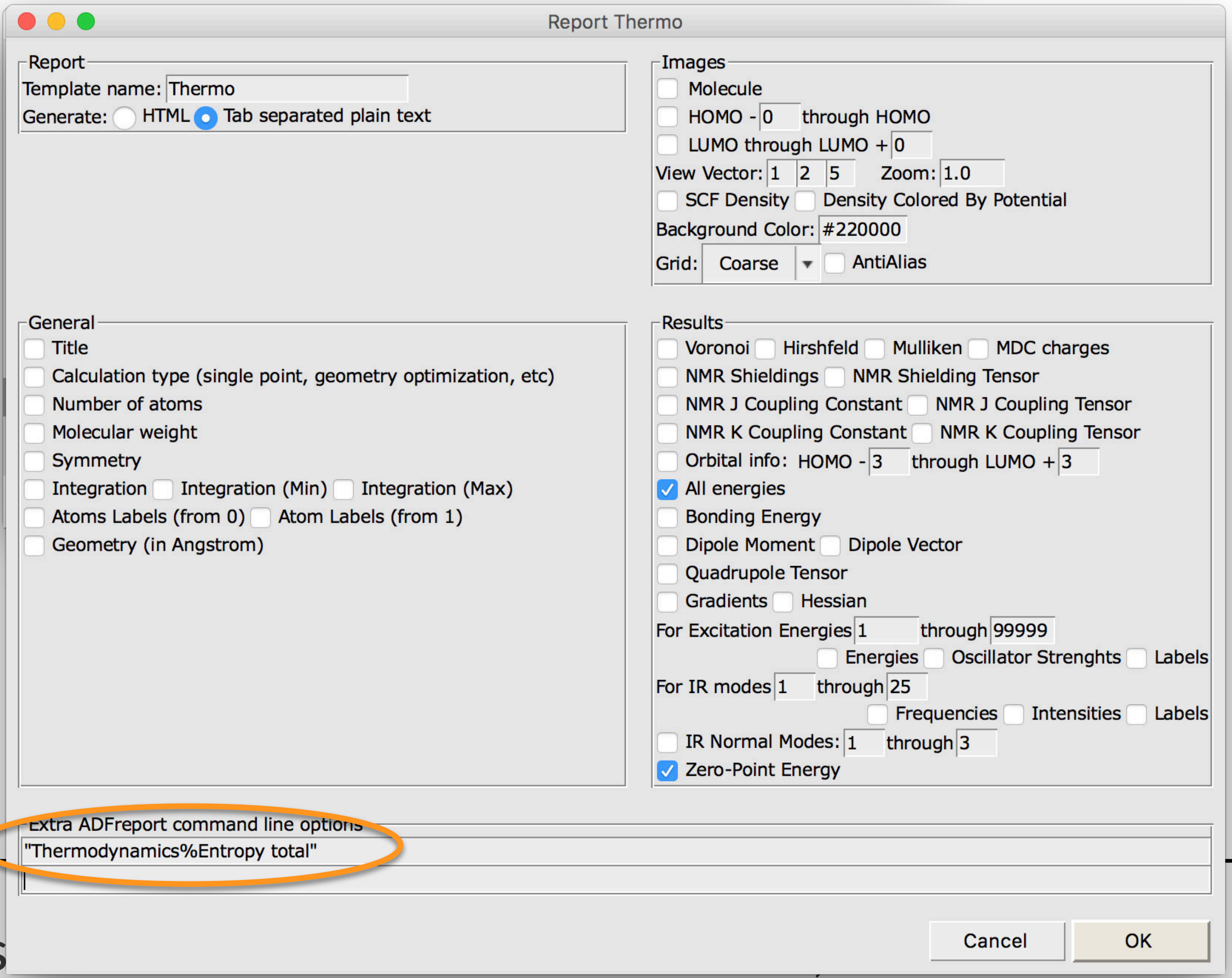
- $\Delta E^{\#}$ = E(TS) – E(reactants), same for H, G (add ZPEs, pV term, S)

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



KFBrowser 2016.207+ (r54923): Freq_TS_bidentate.t21

AngularBoost	72	bytes
BeckeGridConfig	7,124	bytes
GenptData	224	bytes
ZlmFitConfig	676	bytes
FitCoefficients	8,124	bytes
ZlmFit_ActiveFrag	265,044	bytes
ZlmFit_SumFrg	265,044	bytes
ZlmFit_Ort	265,044	bytes
ETS	3,876	bytes
SFO popul	74,380	bytes
Hessian	24,624	bytes
Thermodynamics	136	bytes
Pressure	1.0	
Temperature	298.15	
Entropy translational	42.01285289880509	
Entropy rotational	29.54871367017451	
Entropy vibrational	30.606119391989	
Entropy total	102.1676859609686	
Internal Energy translational	0.88872859660101	
Internal Energy rotational	0.8887285966010099	
Internal Energy vibrational	87.29820360584573	
Internal Energy total	89.07566079904775	



Report Thermo

Report
Template name: Thermo
Generate: ○ HTML ● Tab separated plain text

Images
☐ Molecule
☐ HOMO - 0 through HOMO
☐ LUMO through LUMO + 0
View Vector: 1 2 5 Zoom: 1.0
☐ SCF Density ☐ Density Colored By Potential
Background Color: #220000
Grid: Coarse ☐ AntiAlias

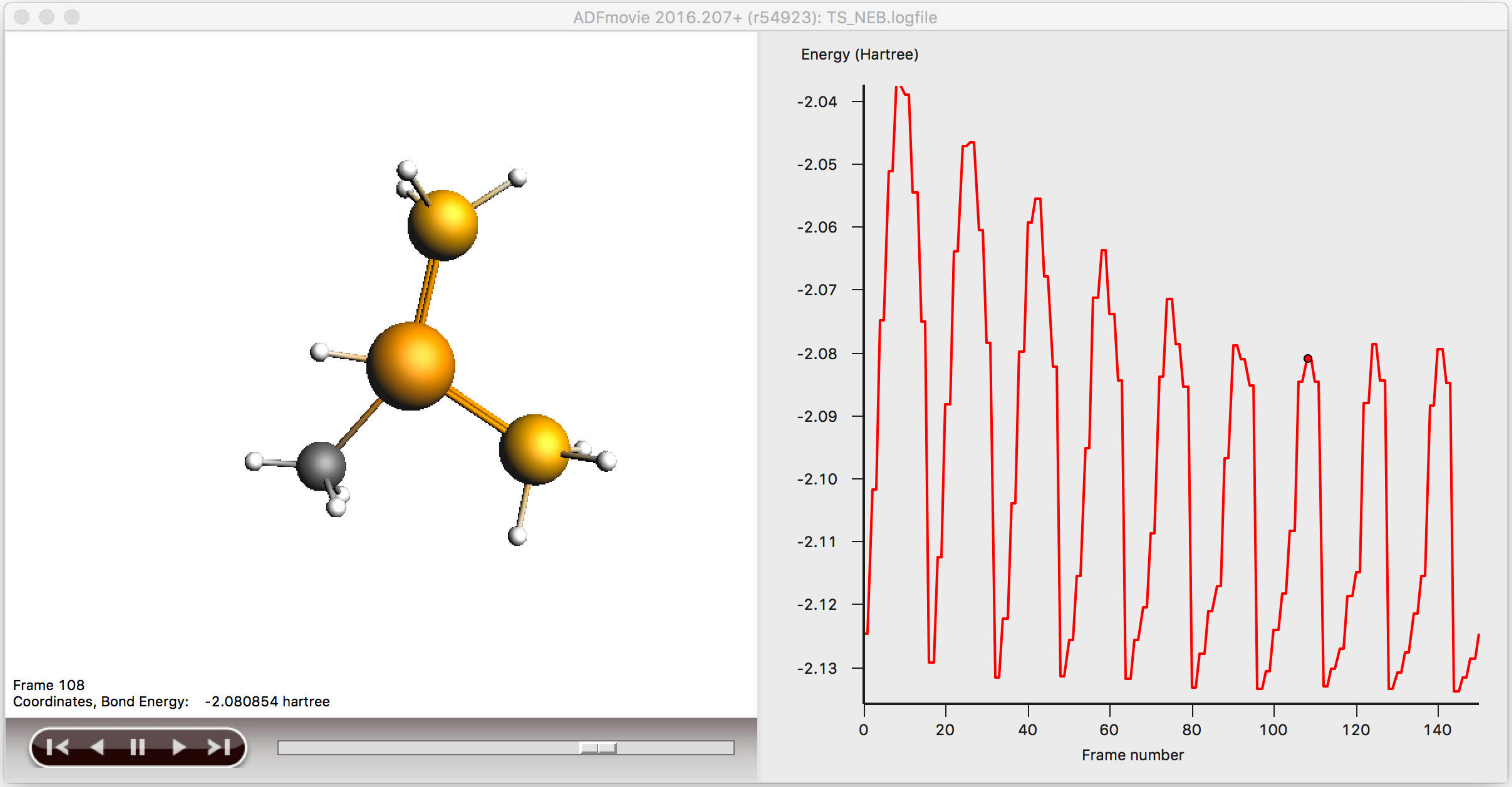
General
☐ Title
☐ Calculation type (single point, geometry optimization, etc)
☐ Number of atoms
☐ Molecular weight
☐ Symmetry
☐ Integration ☐ Integration (Min) ☐ Integration (Max)
☐ Atoms Labels (from 0) ☐ Atom Labels (from 1)
☐ Geometry (in Angstrom)

Results
☐ Voronoi ☐ Hirshfeld ☐ Mulliken ☐ MDC charges
☐ NMR Shieldings ☐ NMR Shielding Tensor
☐ NMR J Coupling Constant ☐ NMR J Coupling Tensor
☐ NMR K Coupling Constant ☐ NMR K Coupling Tensor
☐ Orbital info: HOMO - 3 through LUMO + 3
☑ All energies
☐ Bonding Energy
☐ Dipole Moment ☐ Dipole Vector
☐ Quadrupole Tensor
☐ Gradients ☐ Hessian
For Excitation Energies 1 through 99999
☐ Energies ☐ Oscillator Strenghts ☐ Labels
For IR modes 1 through 25
☐ Frequencies ☐ Intensities ☐ Labels
☐ IR Normal Modes: 1 through 3
☑ Zero-Point Energy

Extra ADFreport command line options
"Thermodynamics%Entropy total"

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)



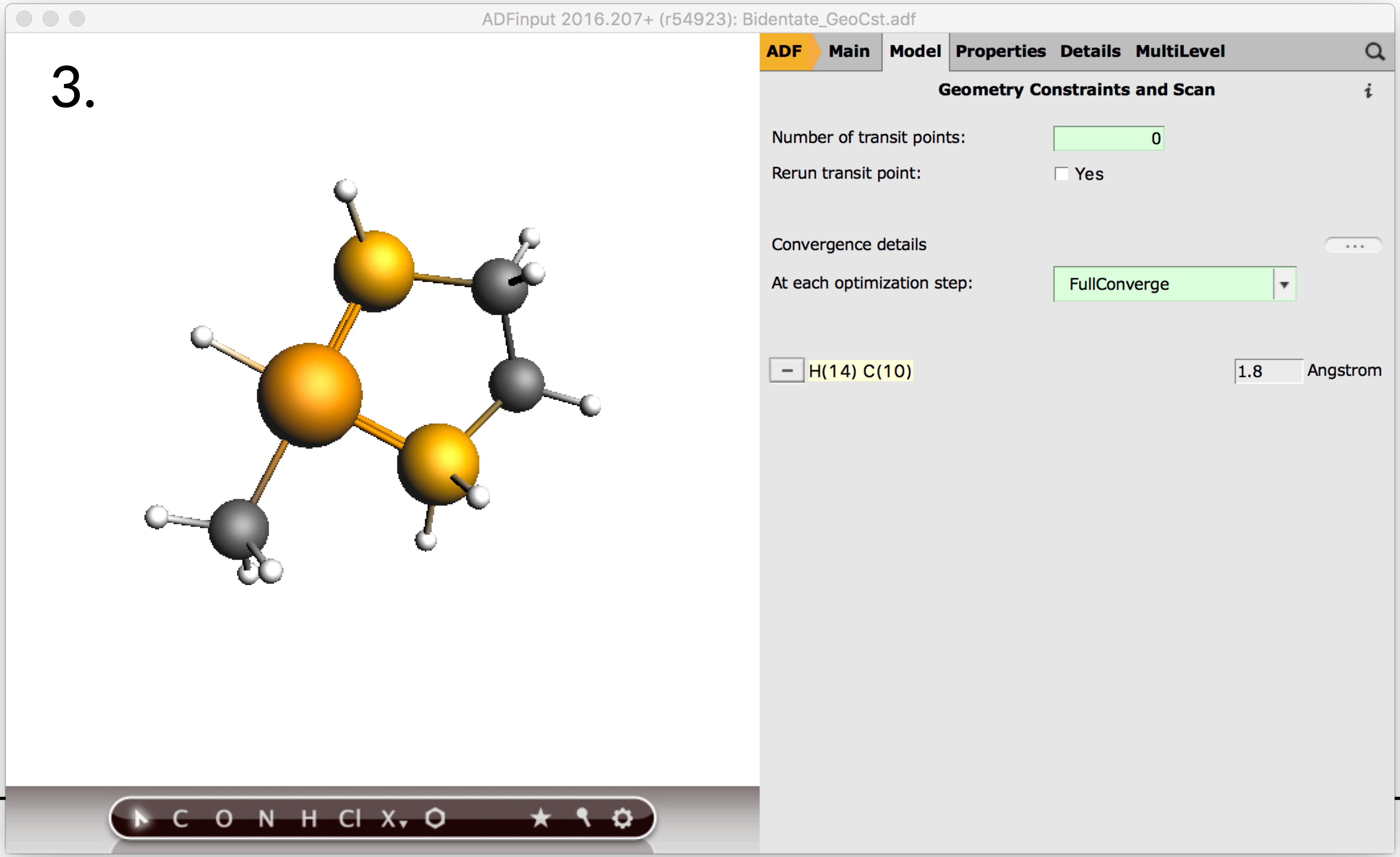
Frame 108
Coordinates, Bond Energy: -2.080854 hartree

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)



Number of transit points: 0

Rerun transit point: ☐ Yes

Convergence details

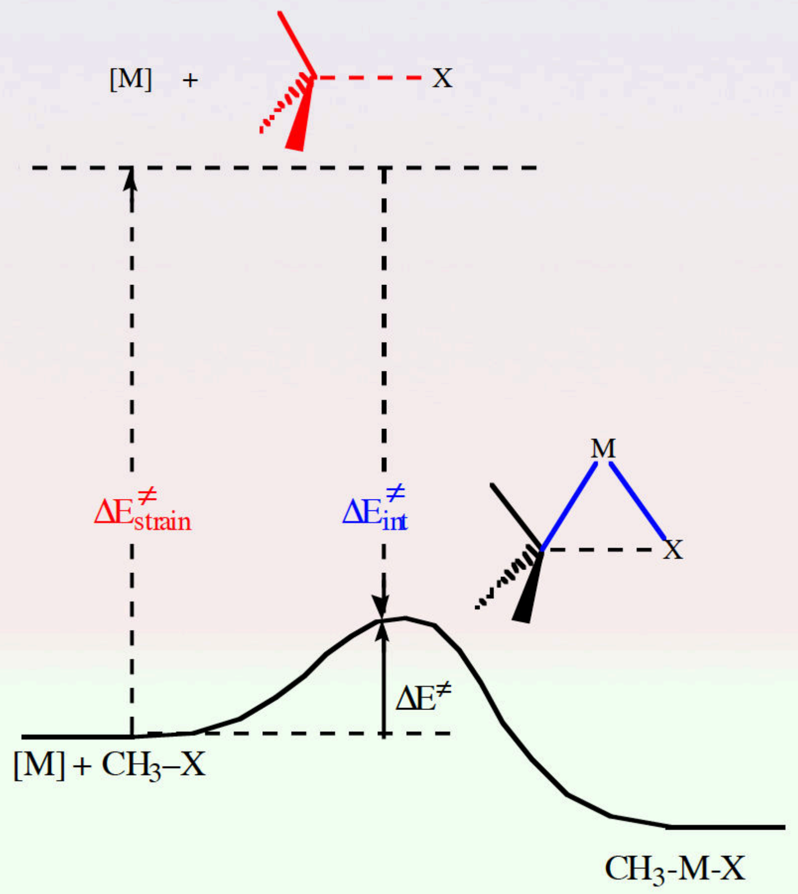
At each optimization step: FullConverge

H(14) C(10) 1.8 Angstrom

Bonding analysis: ASM, EDA, NOCV

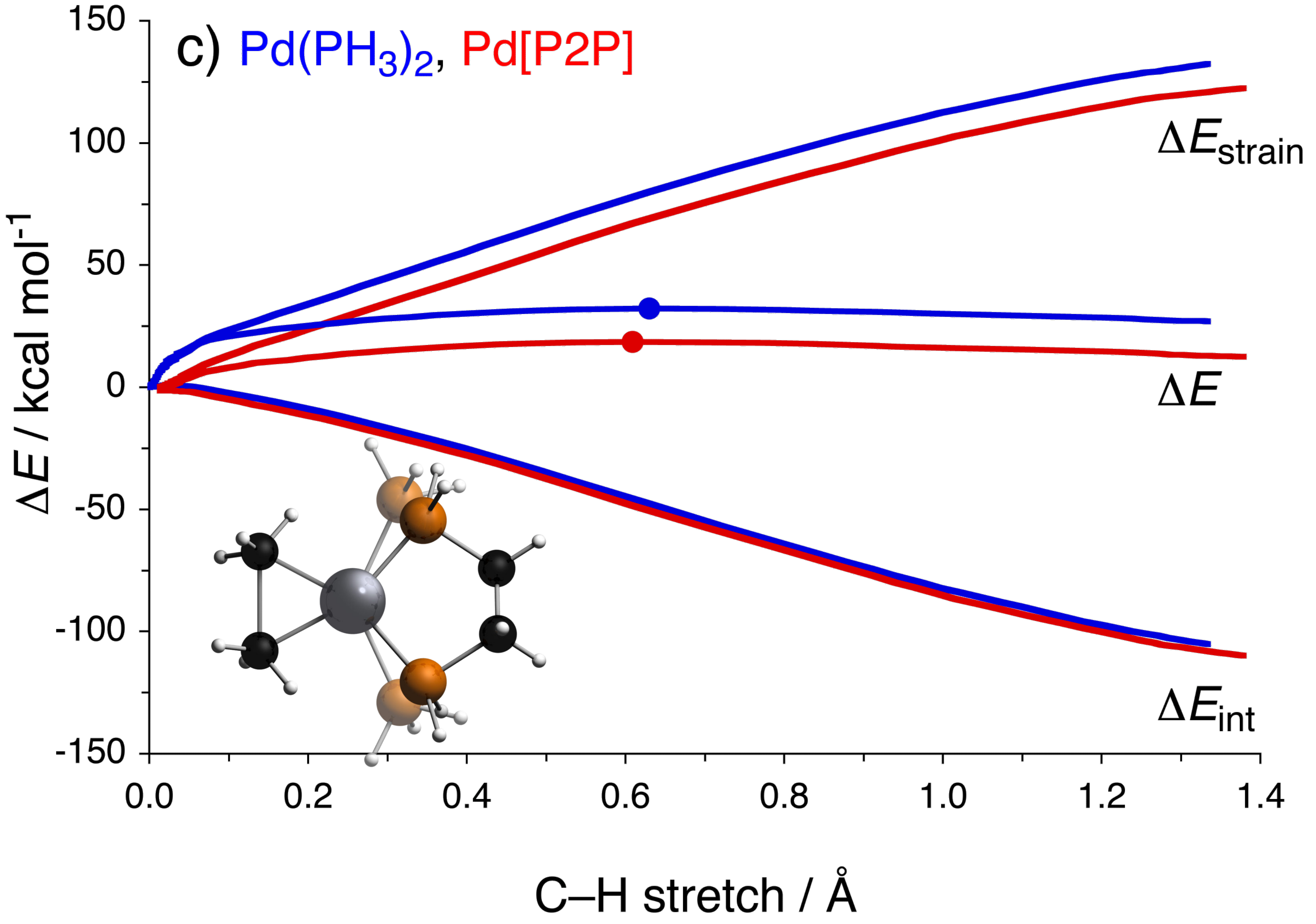
Activation Strain Model Bickelhaupt & co. based on Fragment MOs

- Decompose barrier:



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

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

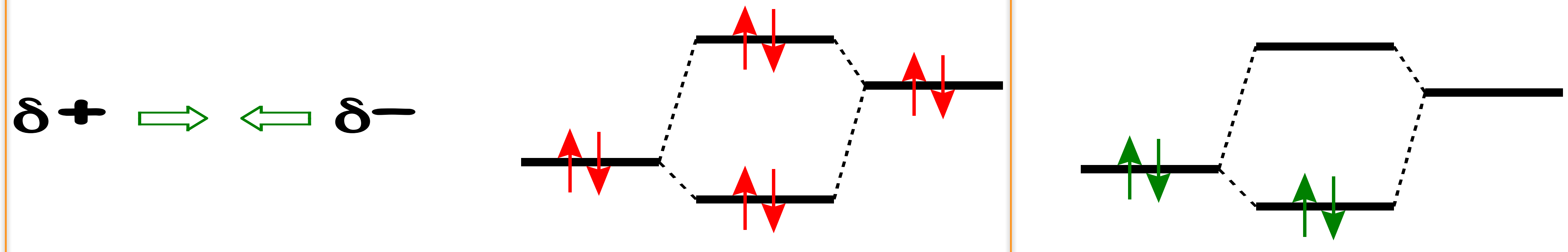
Rev. Comput. Chem. 2000, **15**, 1; Chem. Soc. Rev. 2014, **43**, 4953; WIRES Comput. Mol. Sci. 2015, **5**, 324

Energy decomposition analysis

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

Rev. Comput. Chem. 2000, 15, 1

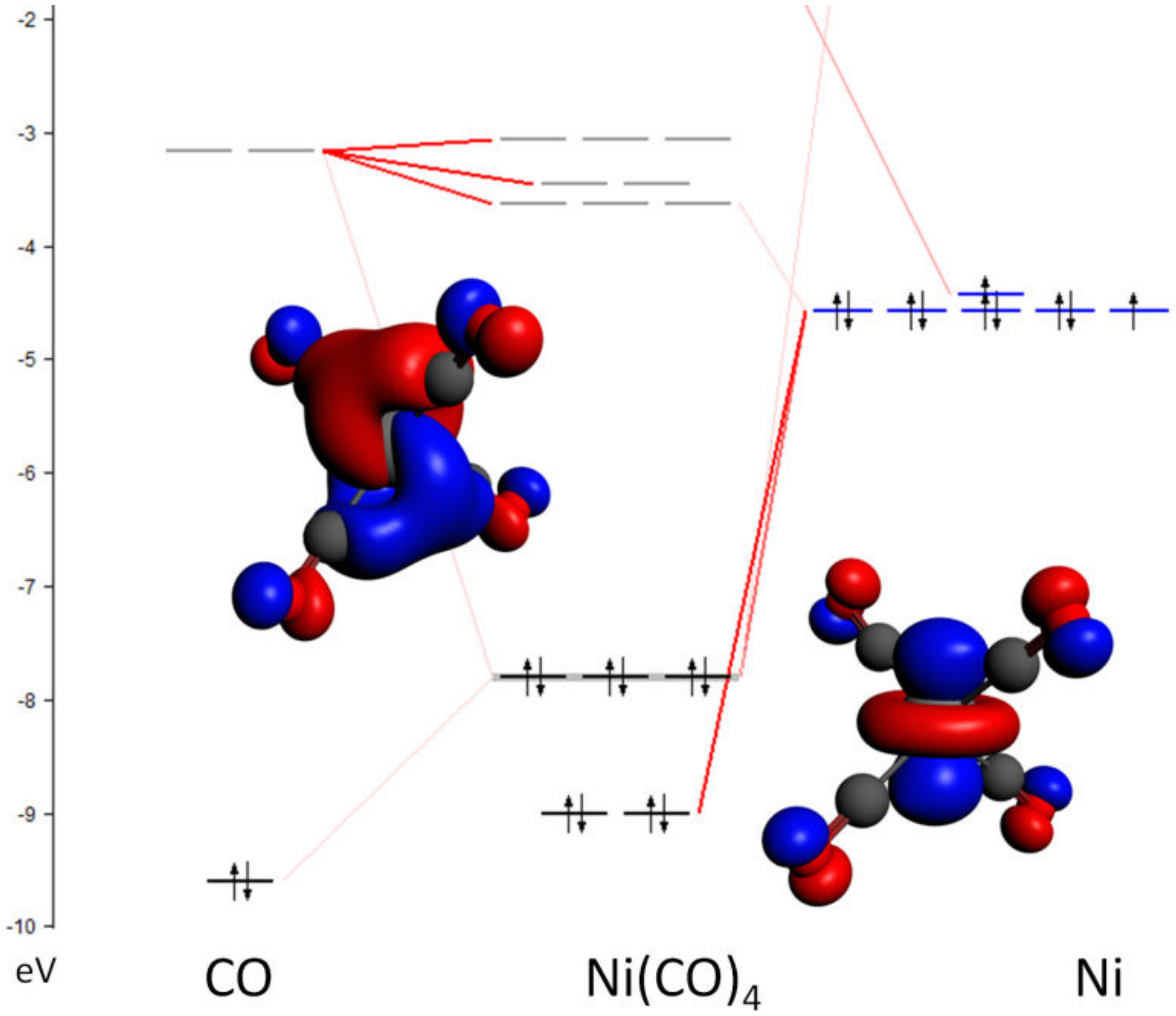
$$\boxed{\Delta V_{elstat} + \Delta E_{Pauli}} + \Delta E_{oi} + \Delta E_{disp}$$



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

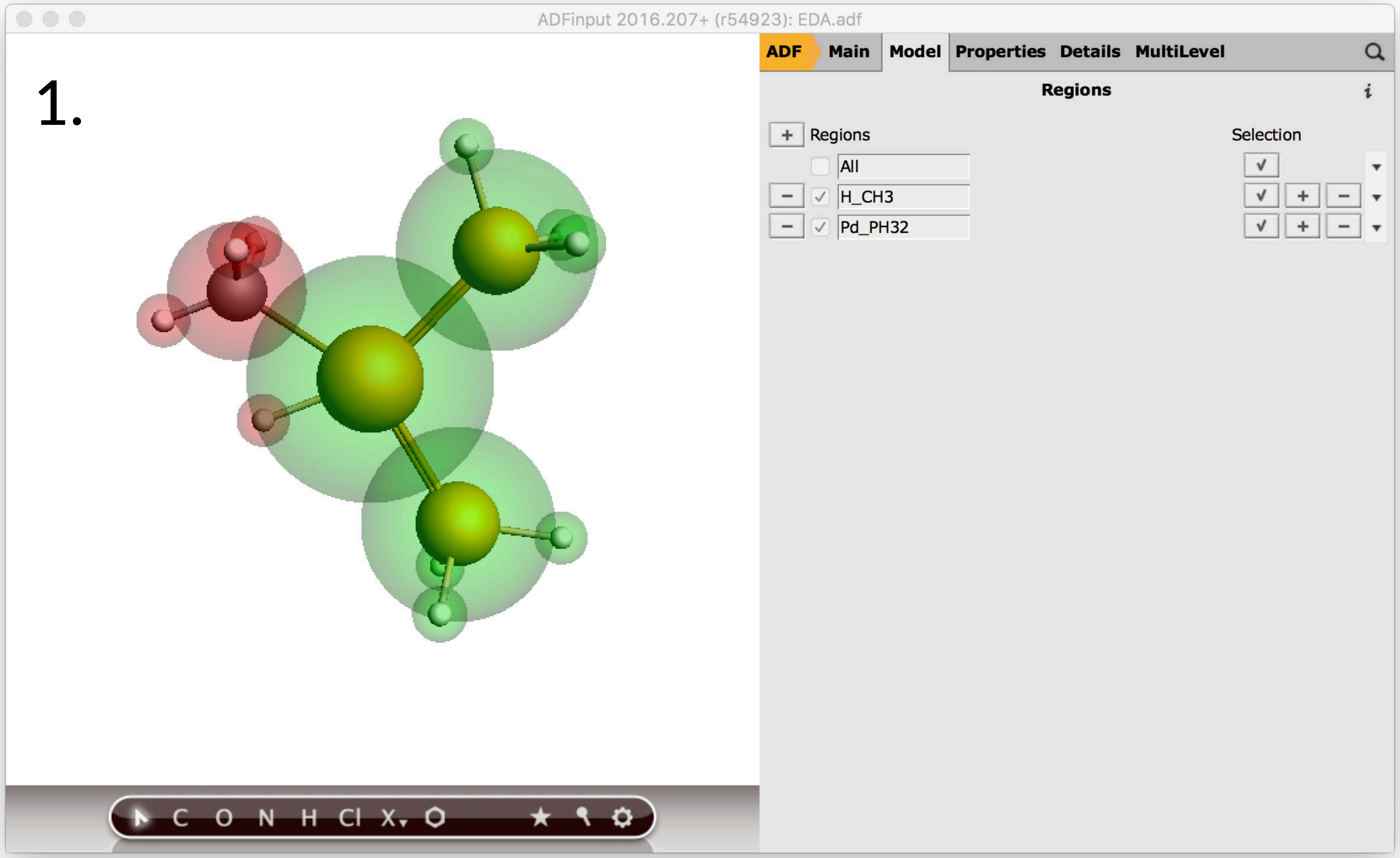
Extensions:

- 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 $\Delta E_{\text{prep}} = E_{(\text{fragments, relaxed})} - E_{(\text{fragments in complex})}$



All

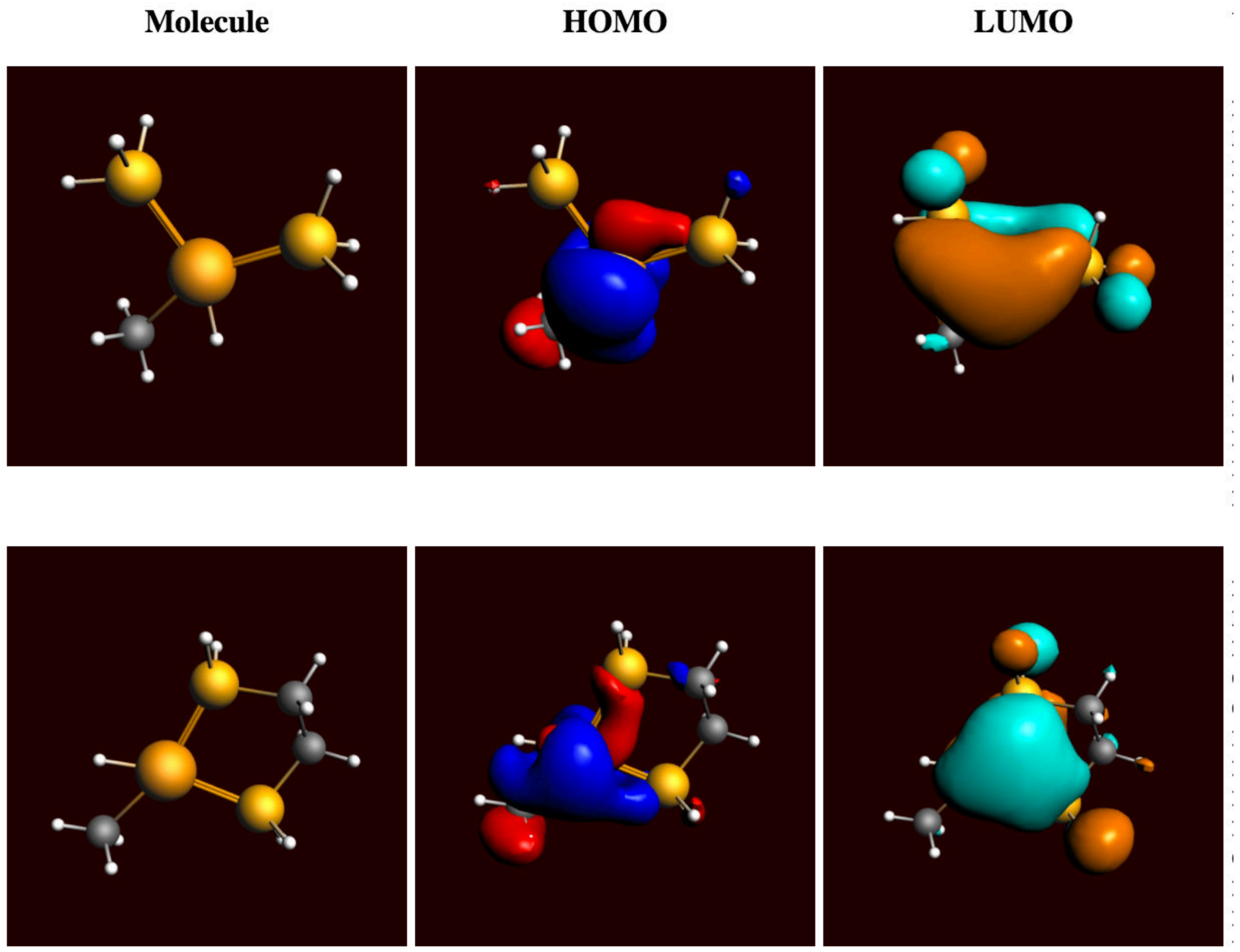
H_CH3

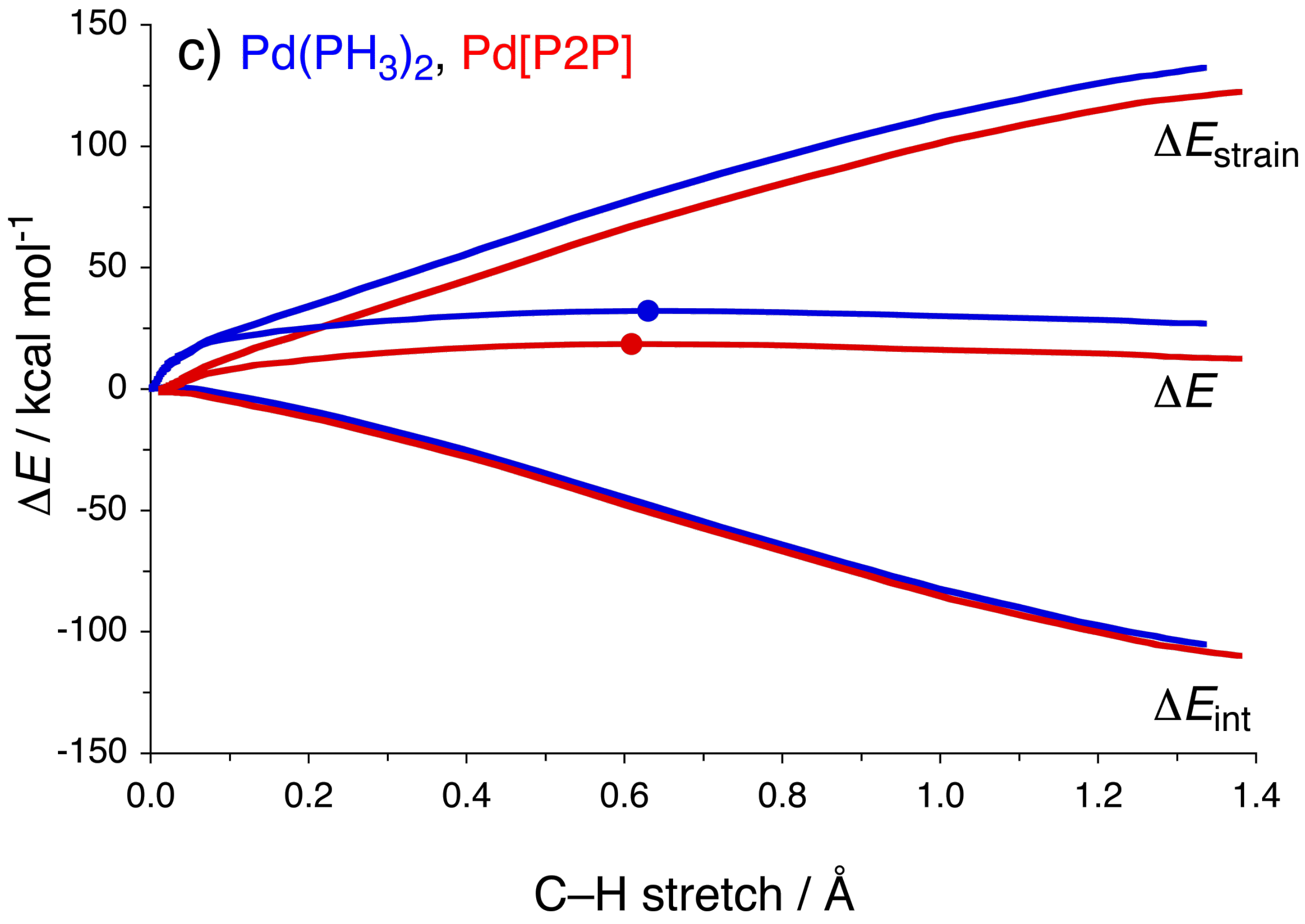
Pd_PH32

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



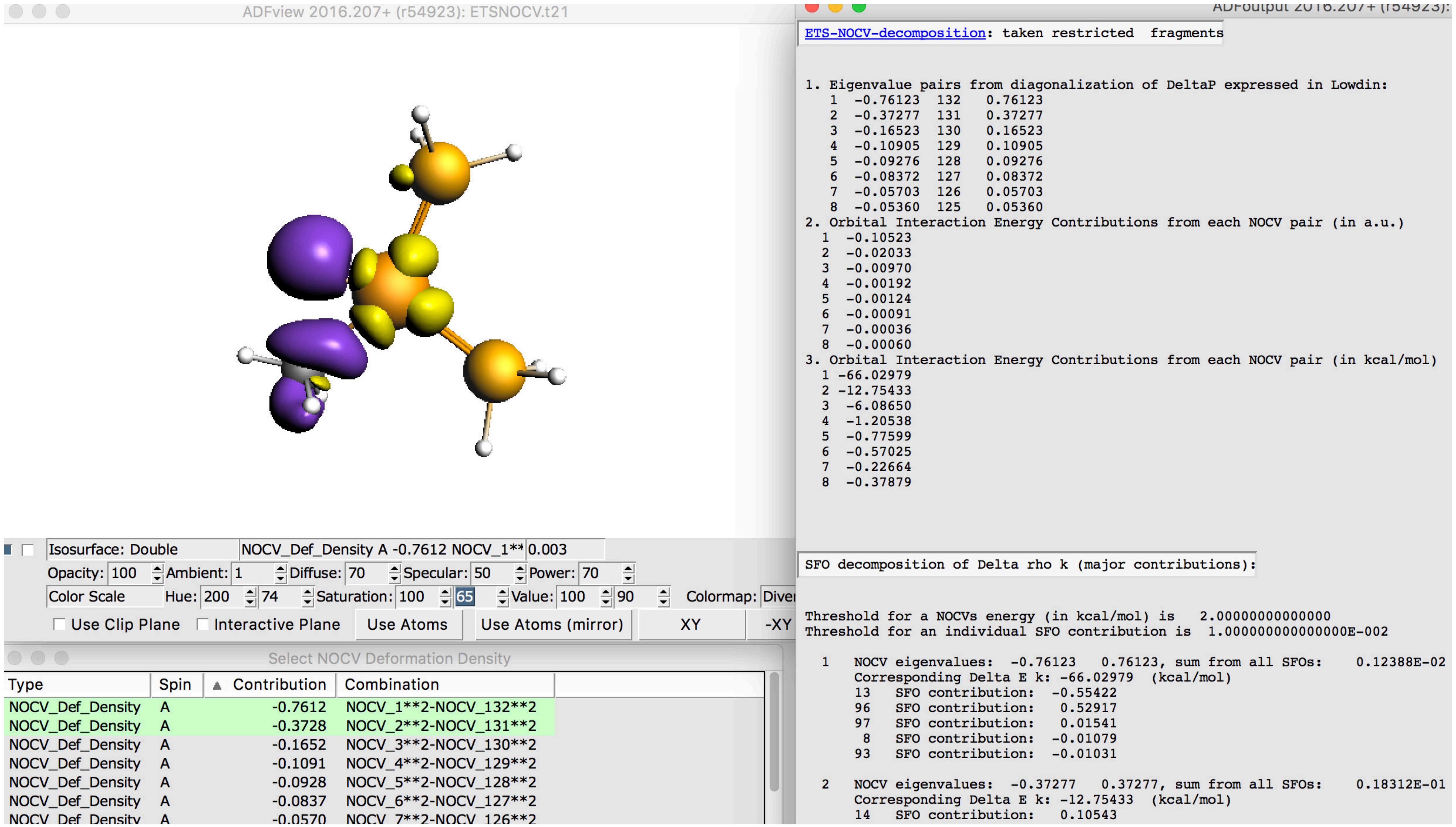


Strain built into bidentate

- 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



☐ Isosurface: Double NOCV_Def_Density A -0.7612 NOCV_1** 0.003

Opacity: 100 Ambient: 1 Diffuse: 70 Specular: 50 Power: 70

Color Scale Hue: 200 74 Saturation: 100 65 Value: 100 90 Colormap: Diver

☐ Use Clip Plane ☐ Interactive Plane

Type	Spin	▲ Contribution	Combination
NOCV_Def_Density	A	-0.7612	NOCV_1**2-NOCV_132**2
NOCV_Def_Density	A	-0.3728	NOCV_2**2-NOCV_131**2
NOCV_Def_Density	A	-0.1652	NOCV_3**2-NOCV_130**2
NOCV_Def_Density	A	-0.1091	NOCV_4**2-NOCV_129**2
NOCV_Def_Density	A	-0.0928	NOCV_5**2-NOCV_128**2
NOCV_Def_Density	A	-0.0837	NOCV_6**2-NOCV_127**2
NOCV_Def_Density	A	-0.0570	NOCV_7**2-NOCV_126**2

```
ETS-NOCV-decomposition: taken restricted  fragments


1. Eigenvalue pairs from diagonalization of DeltaP expressed in Lowdin:
   1  -0.76123  132   0.76123
   2  -0.37277  131   0.37277
   3  -0.16523  130   0.16523
   4  -0.10905  129   0.10905
   5  -0.09276  128   0.09276
   6  -0.08372  127   0.08372
   7  -0.05703  126   0.05703
   8  -0.05360  125   0.05360
2. Orbital Interaction Energy Contributions from each NOCV pair (in a.u.)
  1  -0.10523
  2  -0.02033
  3  -0.00970
  4  -0.00192
  5  -0.00124
  6  -0.00091
  7  -0.00036
  8  -0.00060
3. Orbital Interaction Energy Contributions from each NOCV pair (in kcal/mol)
  1 -66.02979
  2 -12.75433
  3  -6.08650
  4  -1.20538
  5  -0.77599
  6  -0.57025
  7  -0.22664
  8  -0.37879


SFO decomposition of Delta rho k (major contributions):


Threshold for a NOCVs energy (in kcal/mol) is   2.00000000000000
Threshold for an individual SFO contribution is  1.000000000000000E-002

  1   NOCV eigenvalues:  -0.76123   0.76123, sum from all SFOs:    0.12388E-02
      Corresponding Delta E k: -66.02979  (kcal/mol)
      13   SFO contribution:  -0.55422
      96   SFO contribution:   0.52917
      97   SFO contribution:   0.01541
       8   SFO contribution:  -0.01079
      93   SFO contribution:  -0.01031

  2   NOCV eigenvalues:  -0.37277   0.37277, sum from all SFOs:    0.18312E-01
      Corresponding Delta E k: -12.75433  (kcal/mol)
      14   SFO contribution:   0.10543
```

More (workshop) materials:

https://www.scm.com/adf-modeling-suite/wizard/teaching/adf-teaching-materials/

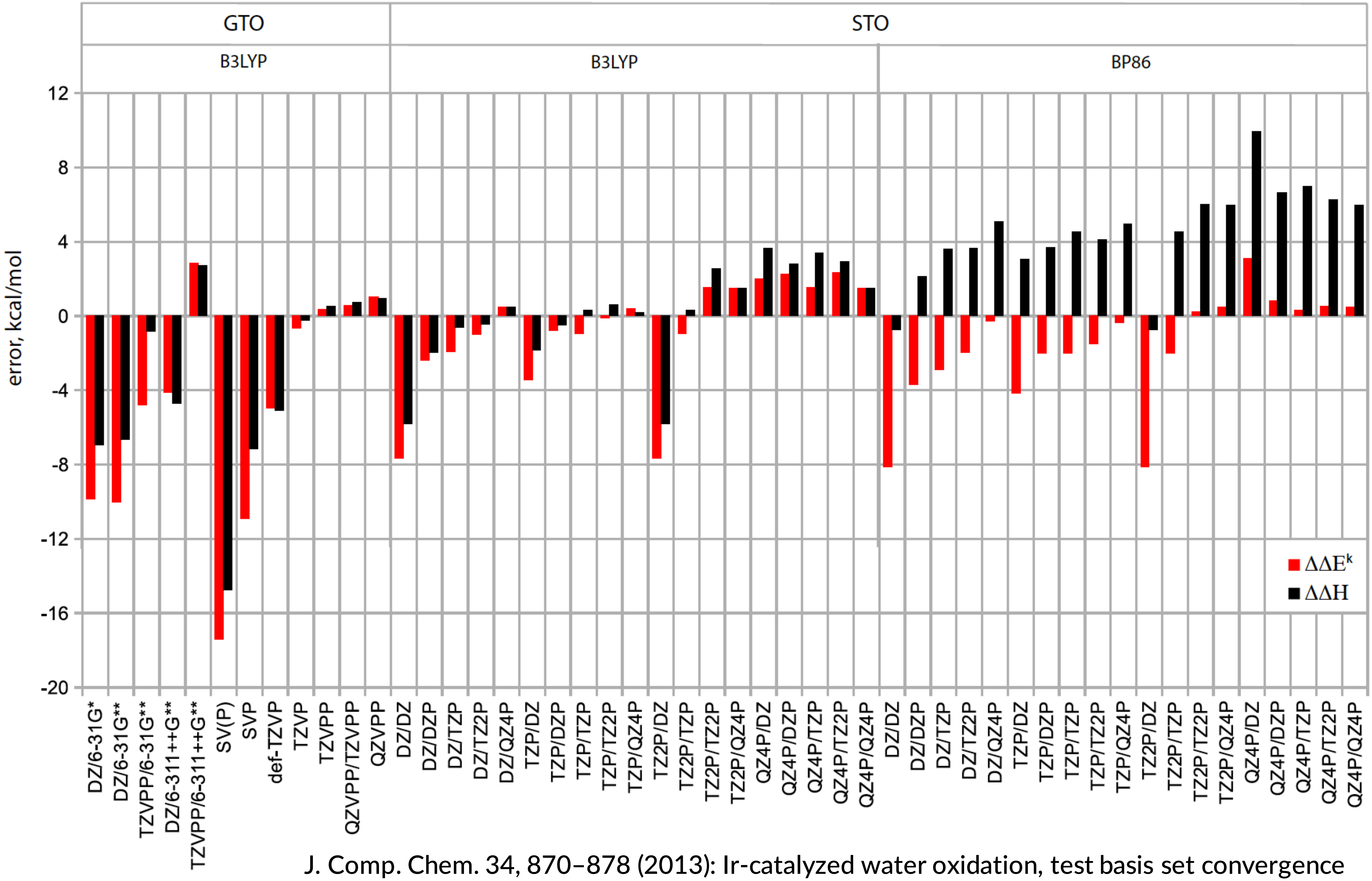
https://www.scm.com/adf-modeling-suite/adf-hands-on-workshops/

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