

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

The screenshot shows the ADFinput 2016.207+ (r54923) software interface. The main window is divided into several sections, with yellow callout boxes and arrows pointing to specific features:

- switch modules**: Points to the top navigation bar containing **ADF**, **Main**, **Model**, **Properties**, **Details**, and **MultiLevel**.
- job types & set up**: Points to the **Model** tab.
- search**: Points to a search icon in the top right corner.
- job type / template**: Points to the **Preset:** dropdown menu, which is currently set to **Single Point**.
- charge/spin**: Points to the **Task:** dropdown menu, which is currently set to **SinglePoint**.
- functional & relativistic appr**: Points to the **XC functional:** dropdown menu, which is currently set to **LDA**.
- basis & numerical accuracy**: Points to the **Basis set:** dropdown menu, which is currently set to **DZ**.
- builder tools**: Points to the bottom toolbar, which includes buttons for **C**, **O**, **N**, **H**, **Cl**, **X**, and **O**, along with a star icon, a magnifying glass, and a gear icon.
- ... = more details**: Points to the ellipsis (...) buttons next to the **Task**, **XC functional**, **Relativity (ZORA)**, **Basis set**, **Frozen core**, and **Numerical quality** settings.

The main window displays the following settings:

- 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

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?

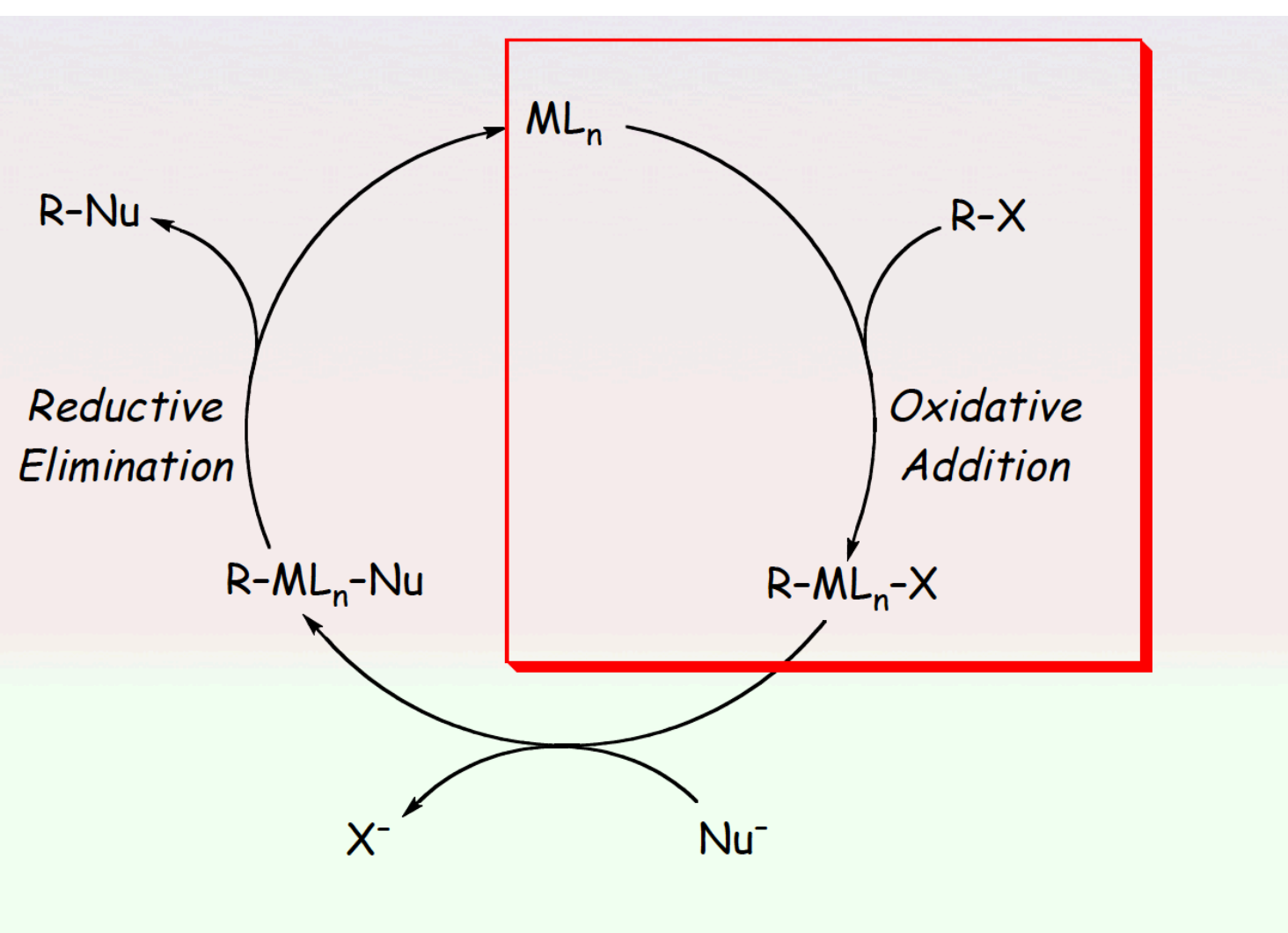
Remember: a TS has 1 and only 1 negative Hessian eigenvalue

Example: Pd-catalysed oxidative addition

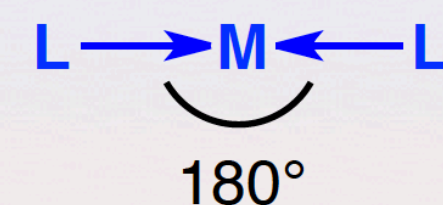
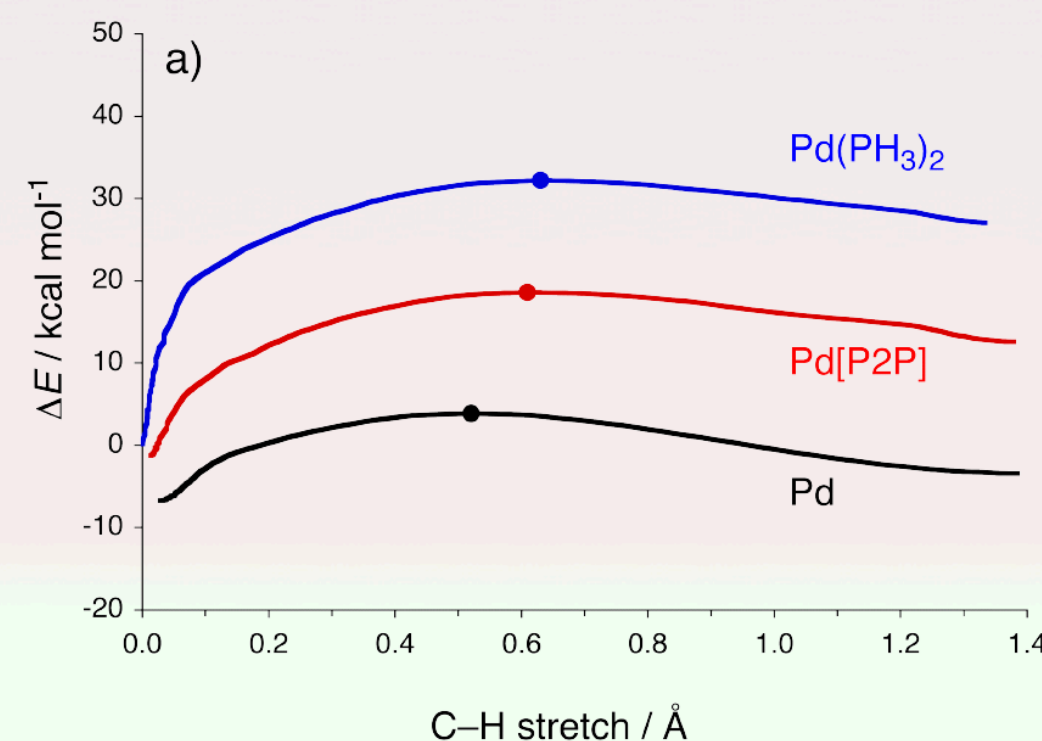
Goal: find reactant and transition states, understand

- Get a good geometry: LT, previous geometry, NEB
- Good Hessian: TSRC, partial Hessian
- Bonding analysis: Activation Strain Model (ASM)

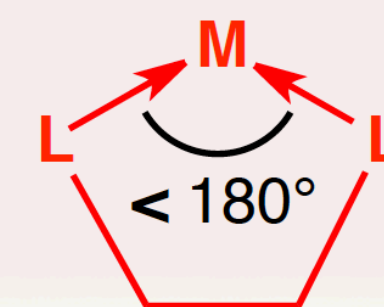
- Example: Pd catalyzed oxidative addition: Wolters & Bickelhaupt



Methane C–H activation:



- ligands raise barriers

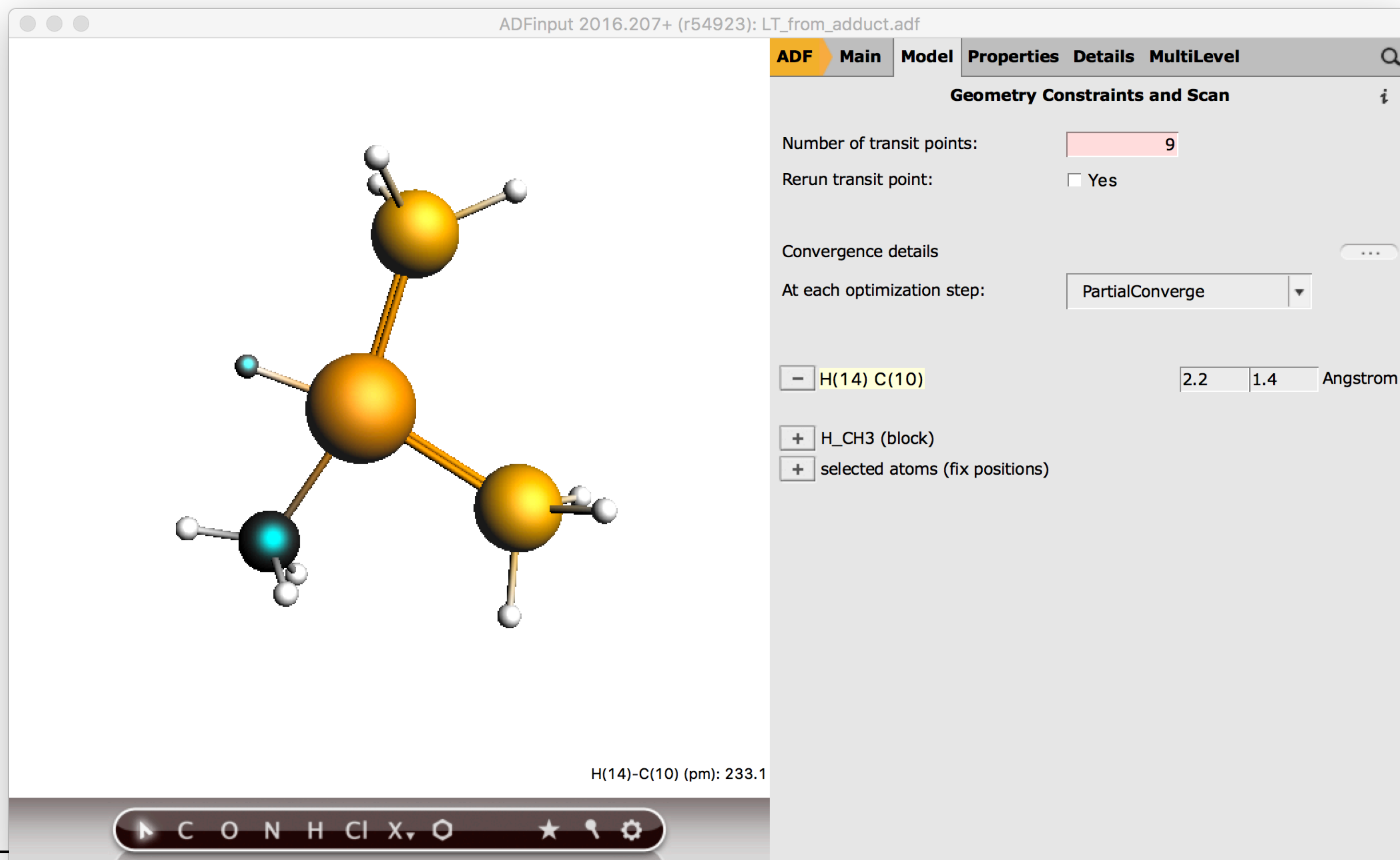


- smaller bite angle \rightarrow lower barrier

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

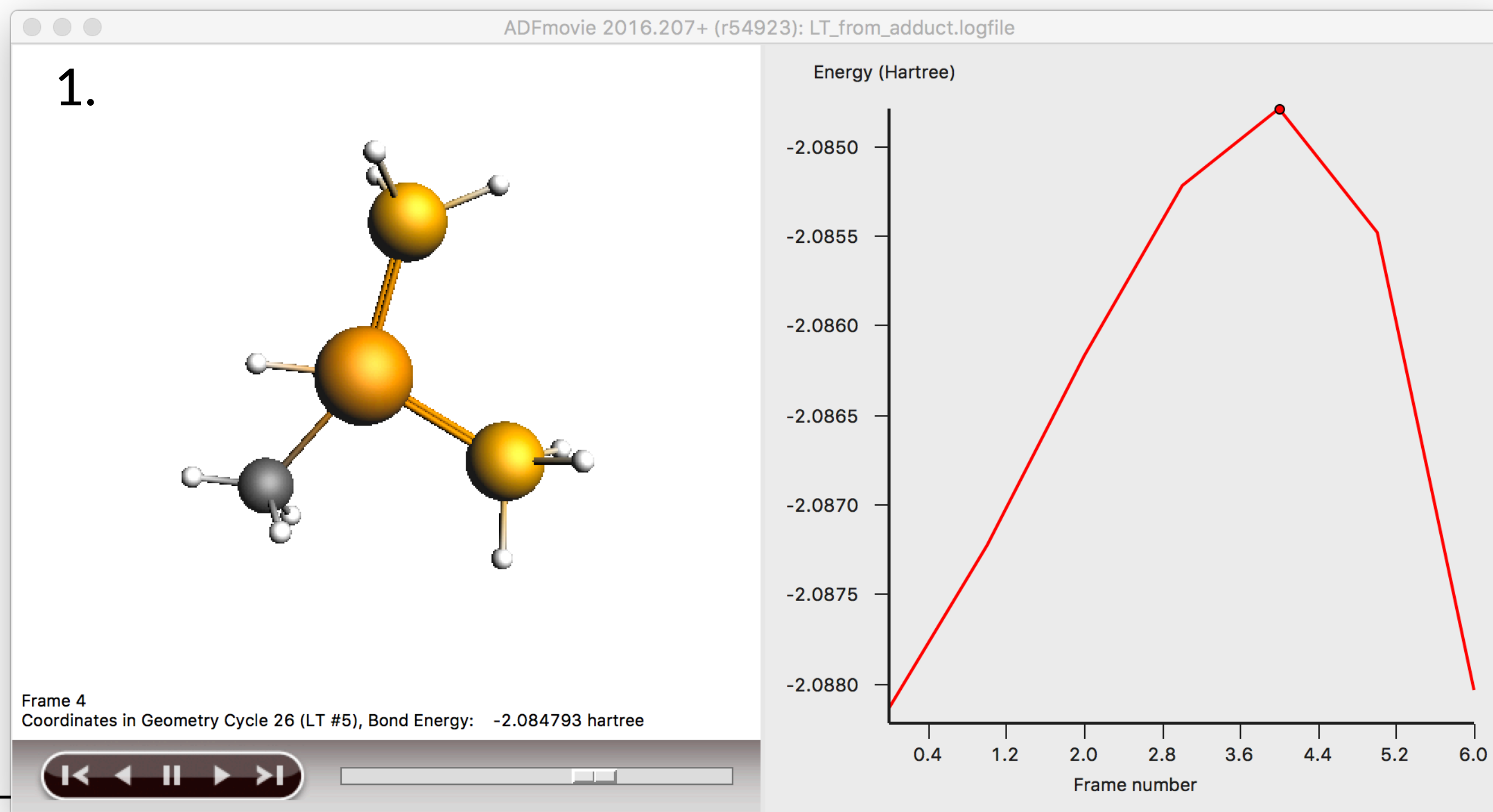
Good geometry guess: 1. LT

1. Build $(\text{CH}_3)(\text{H})\text{Pd}(\text{PH}_3)_2$ - 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)



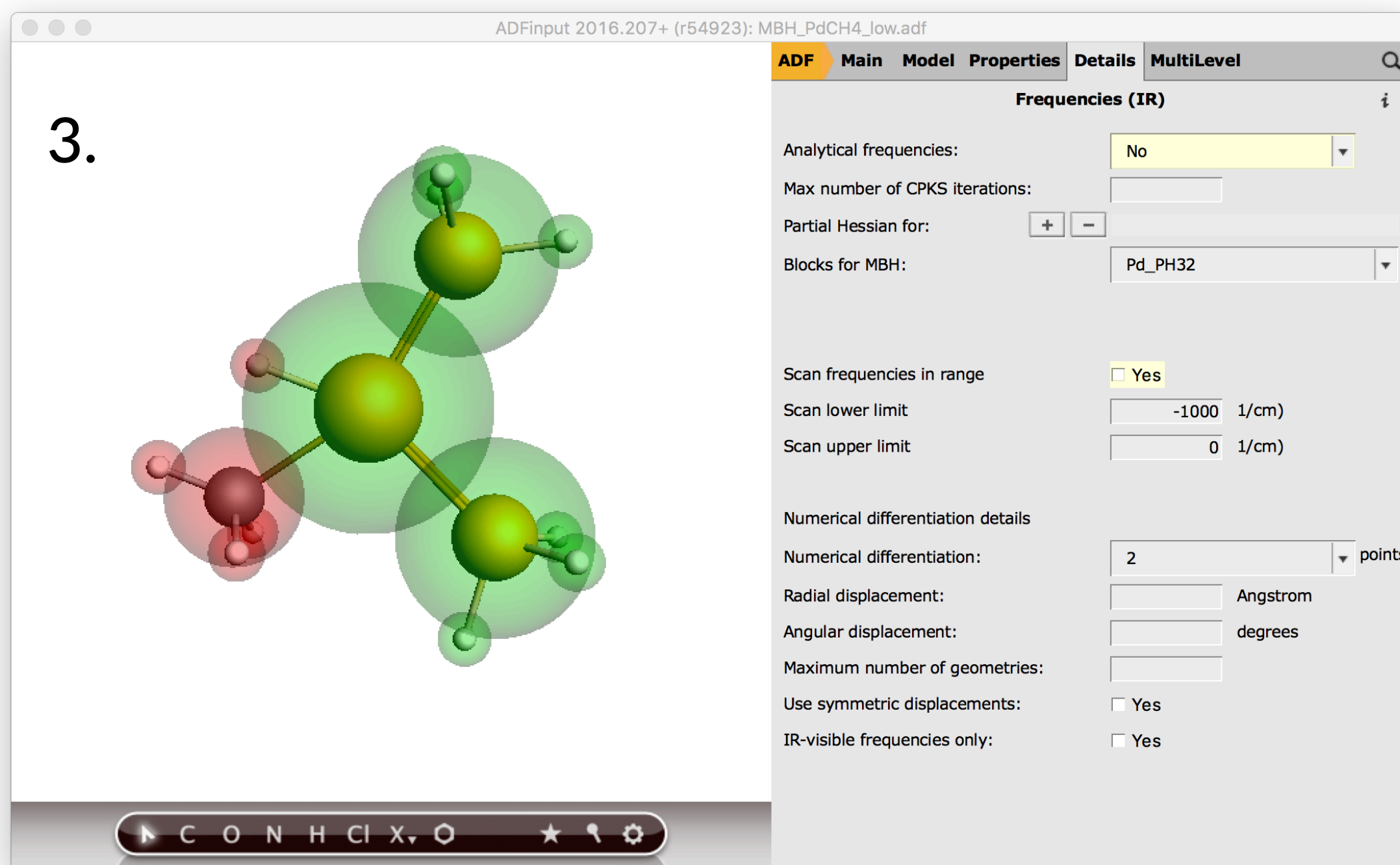
Good Hessian: 1. TSRC

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_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)
 - Can be combined with 1. & 2.
5. Restart with Hessian (TS_MBH.adf, TS_pHess.adf, TS_lowHess.adf)



3): TS_MBH.adf

ADF Main Model Properties Details MultiLevel

5.

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

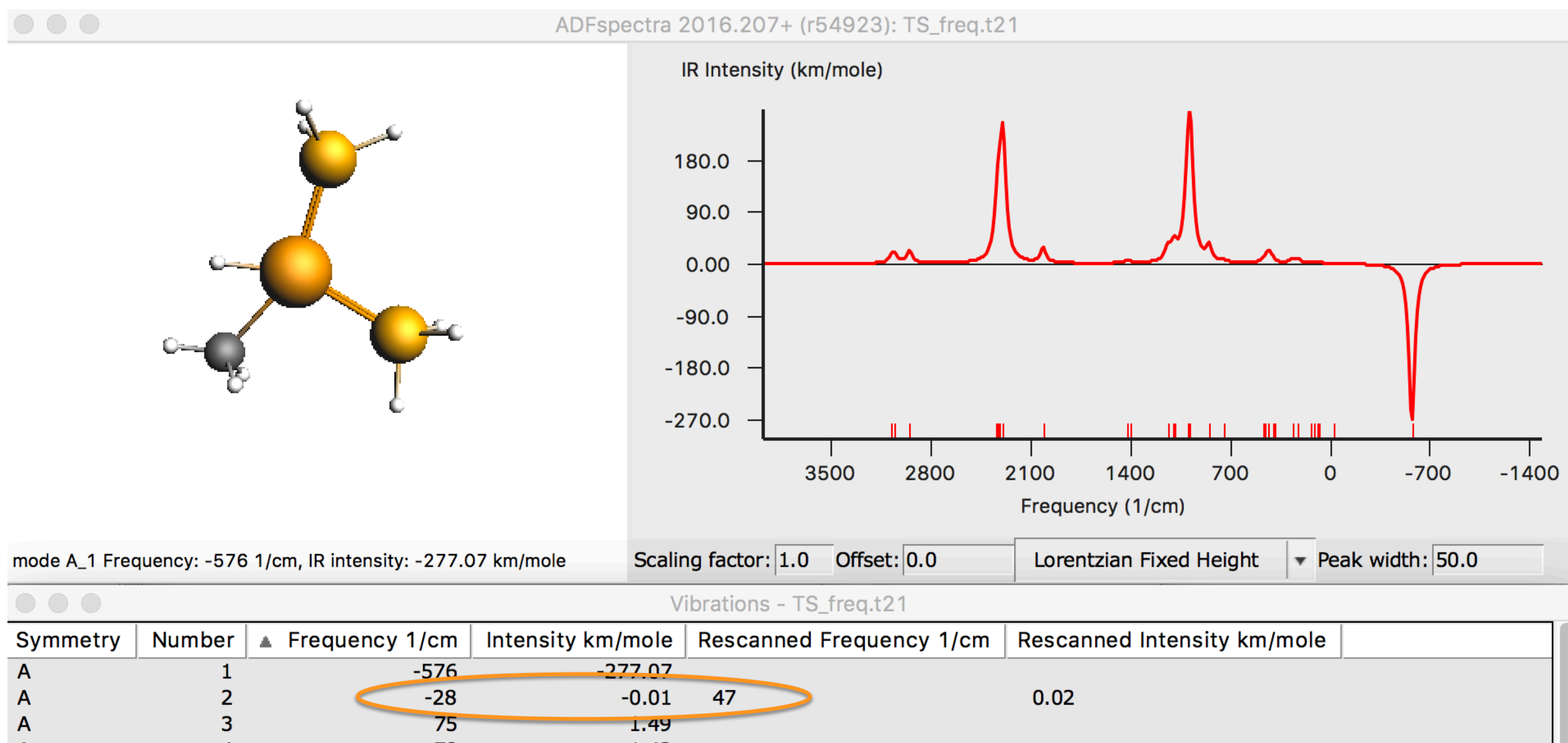
Checkpoint: ☐ TAPE13

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

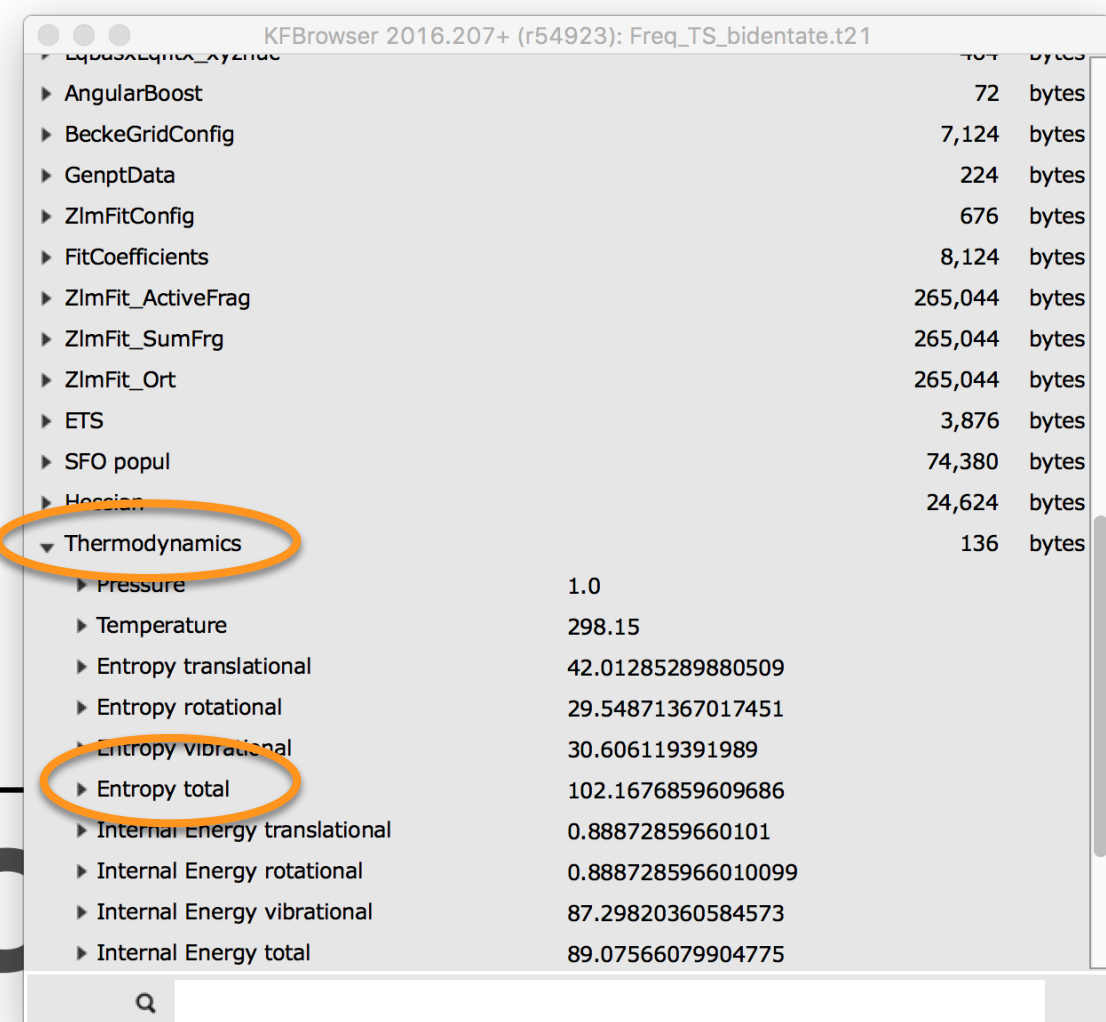


Calculate $\Delta E^\#$, $\Delta H^\#$, $\Delta G^\#$

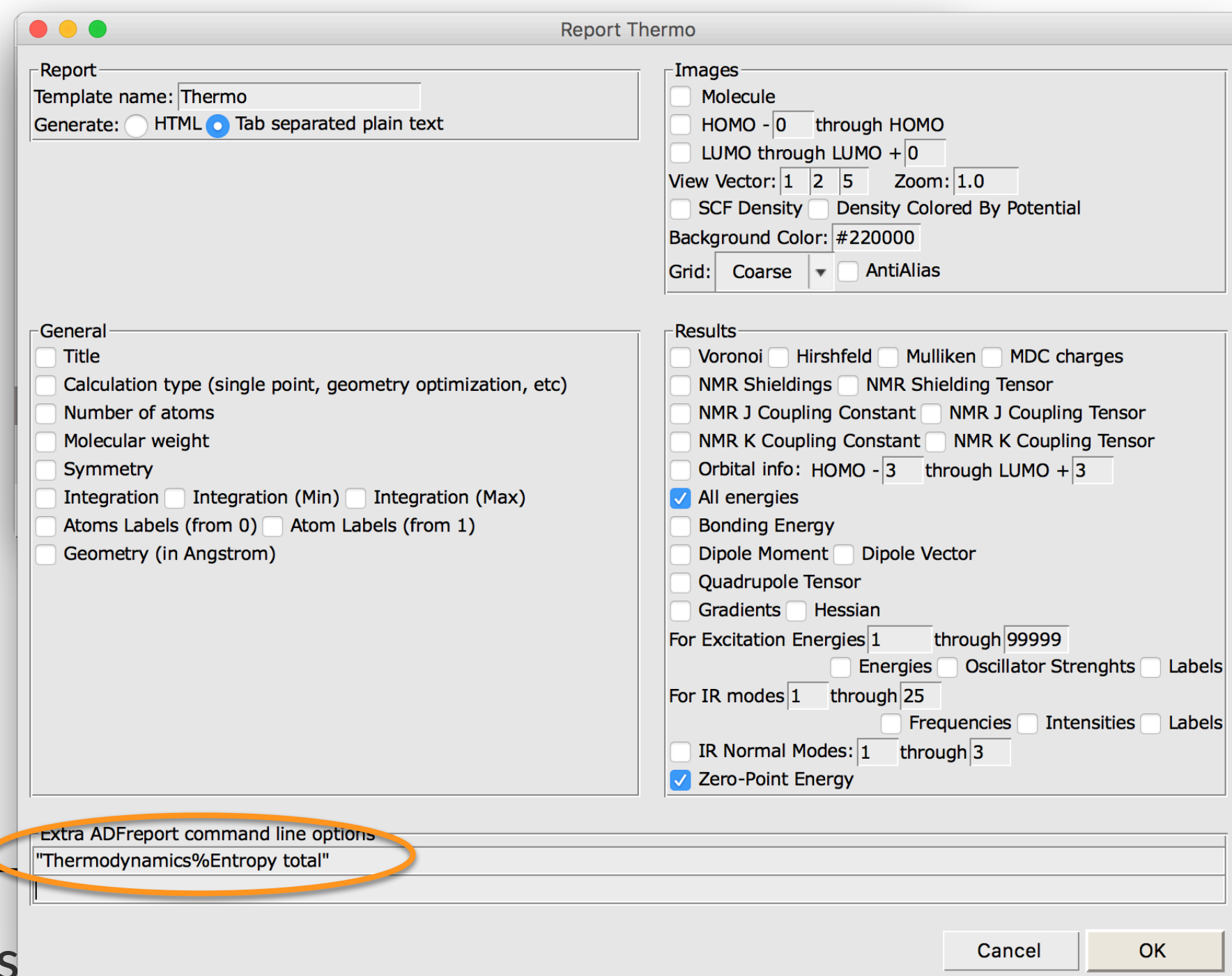
- Get the binding energy for reactants $\text{CH}_4 + \text{Pd}(\text{PH}_3)_2$
 - First optimize reactants separately, run frequencies for ZPE
 - Read from logfile, outputfile, use PLAMS / adfreport, or use report tool in GUI

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)

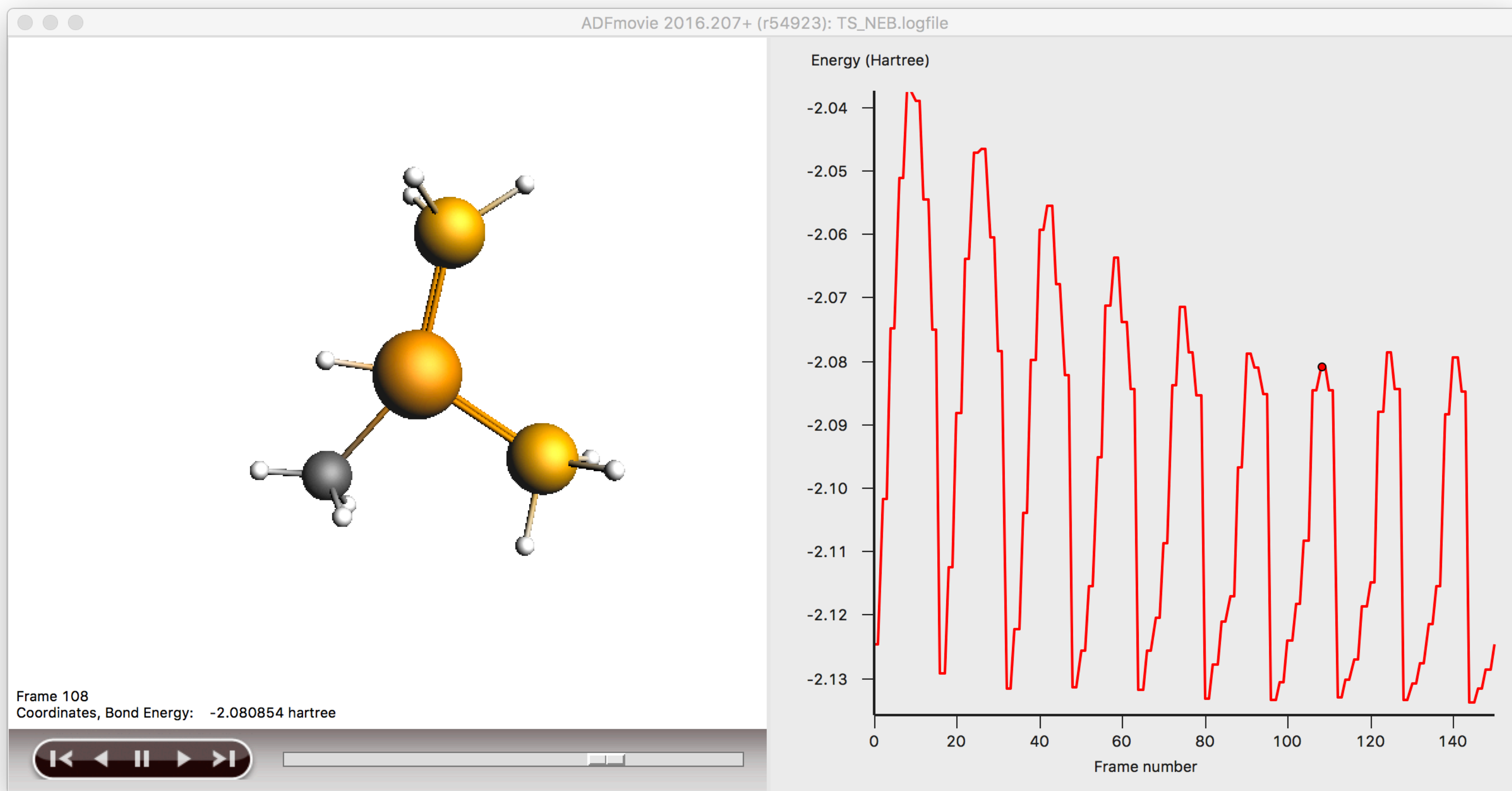


AngularBoost	72	bytes
BeckeGridConfig	7,124	bytes
GenptData	224	bytes
ZImFitConfig	676	bytes
FitCoefficients	8,124	bytes
ZImFit_ActiveFrag	265,044	bytes
ZImFit_SumFrg	265,044	bytes
ZImFit_Ort	265,044	bytes
ETS	3,876	bytes
SFO popul	74,380	bytes
Hessian	24,624	bytes
Thermodynamics	136	bytes
Pressure	1.0	
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	



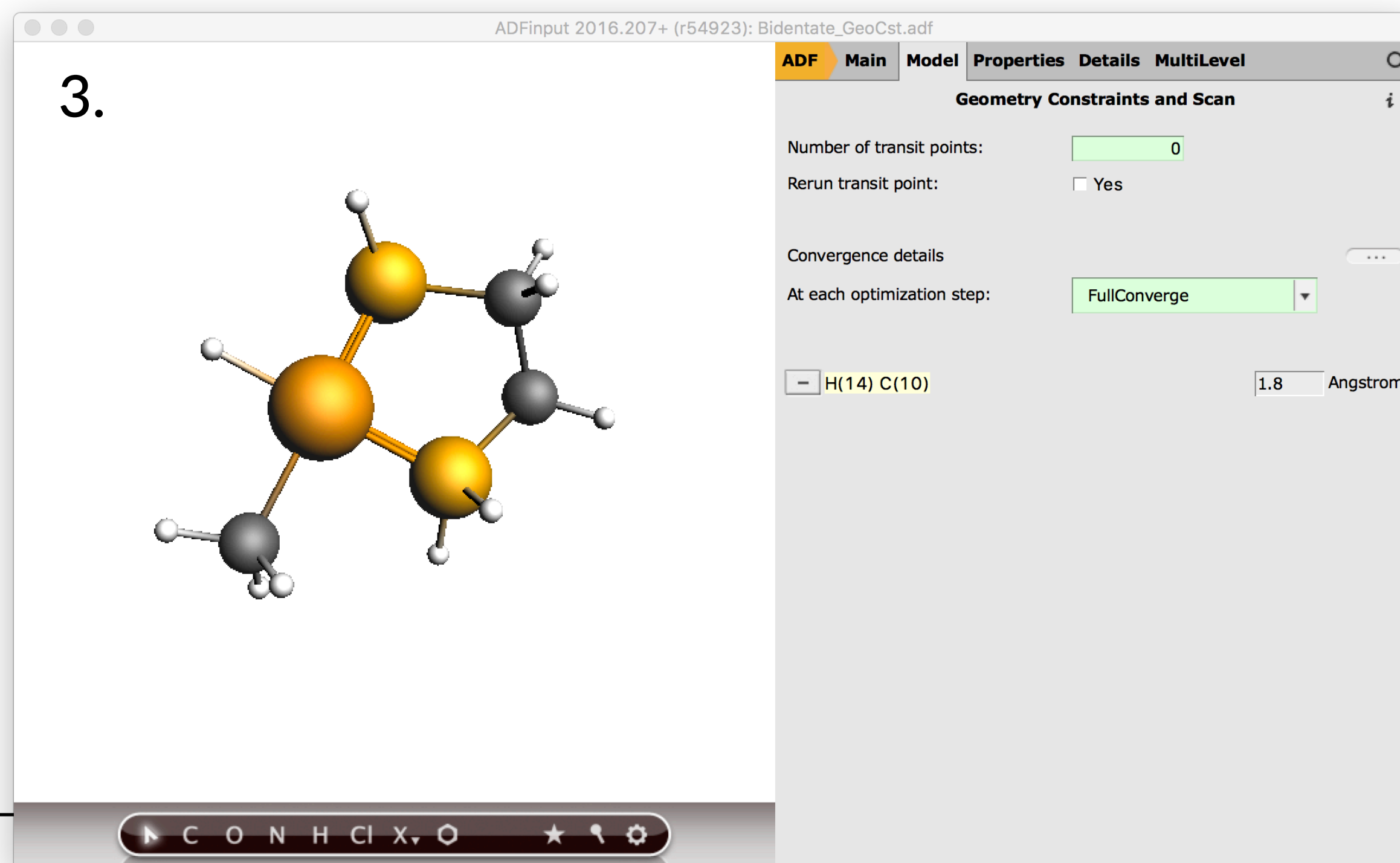
Good geometry guess: 2. NEB

1. Optimize reactant state complex $\text{CH}_4 \cdots \text{Pd}(\text{PH}_3)_2$
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

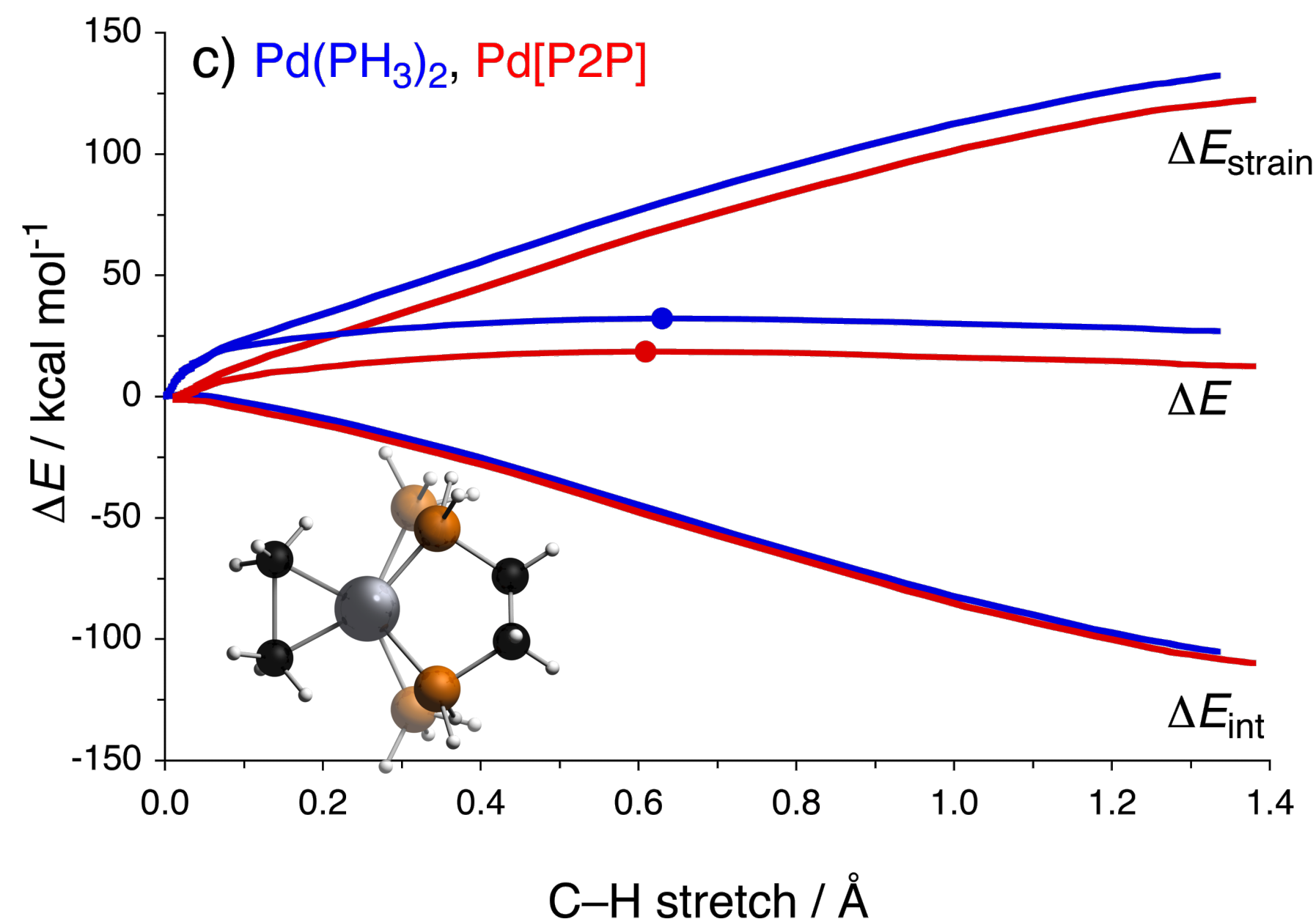
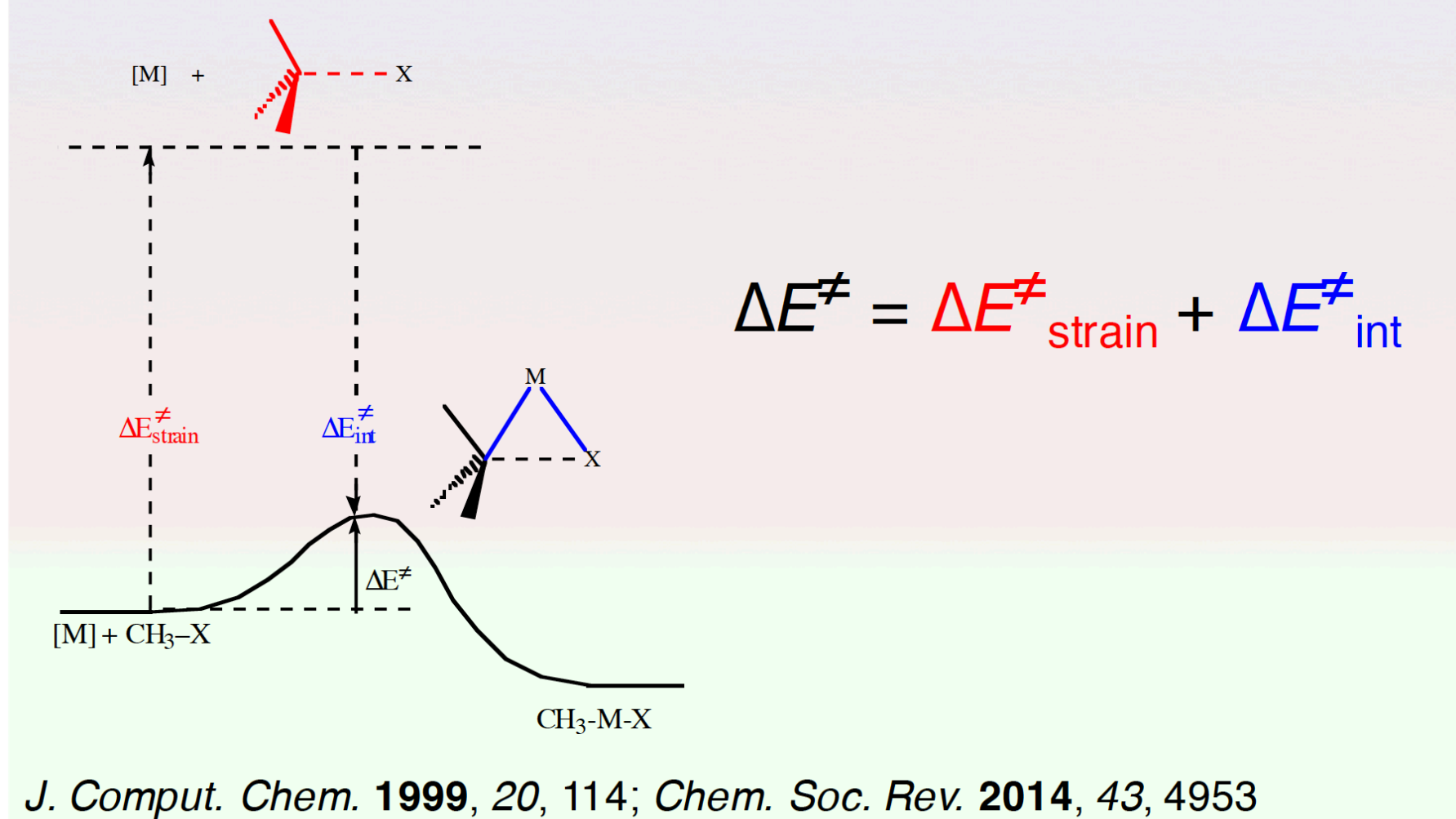
- Start from a TS from a comparable reaction (e.g. change ligands)
 1. Take TS or product from $\text{Pd}(\text{PH}_3)_2$
 2. Make a bidentate ligand (diphosphinoethane, dpe)
 3. Run with a constraint: C-H distance $\sim 1.8\text{\AA}$ (Bidentate_GeoCst.adf)
(may use sloppy accuracy as well, or get xyz 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:



EDA along the reaction path

Bite-Angle Effect: Activation Strain analyses:

- HOMO-LUMO interaction marginally improved
- But: strain reduced by building it into catalyst

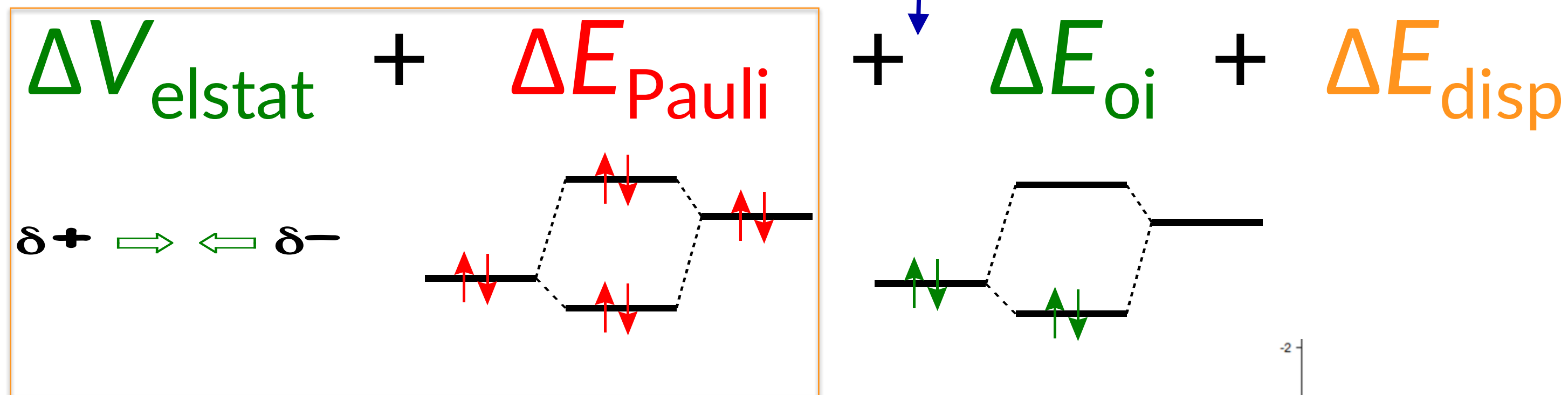
Exercise: check $\text{Pd}(\text{PH}_3)_2$ vs $\text{Pd}(\text{diphosphinoethane})$ TSs: C-H distance, EDA

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

Energy decomposition analysis

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

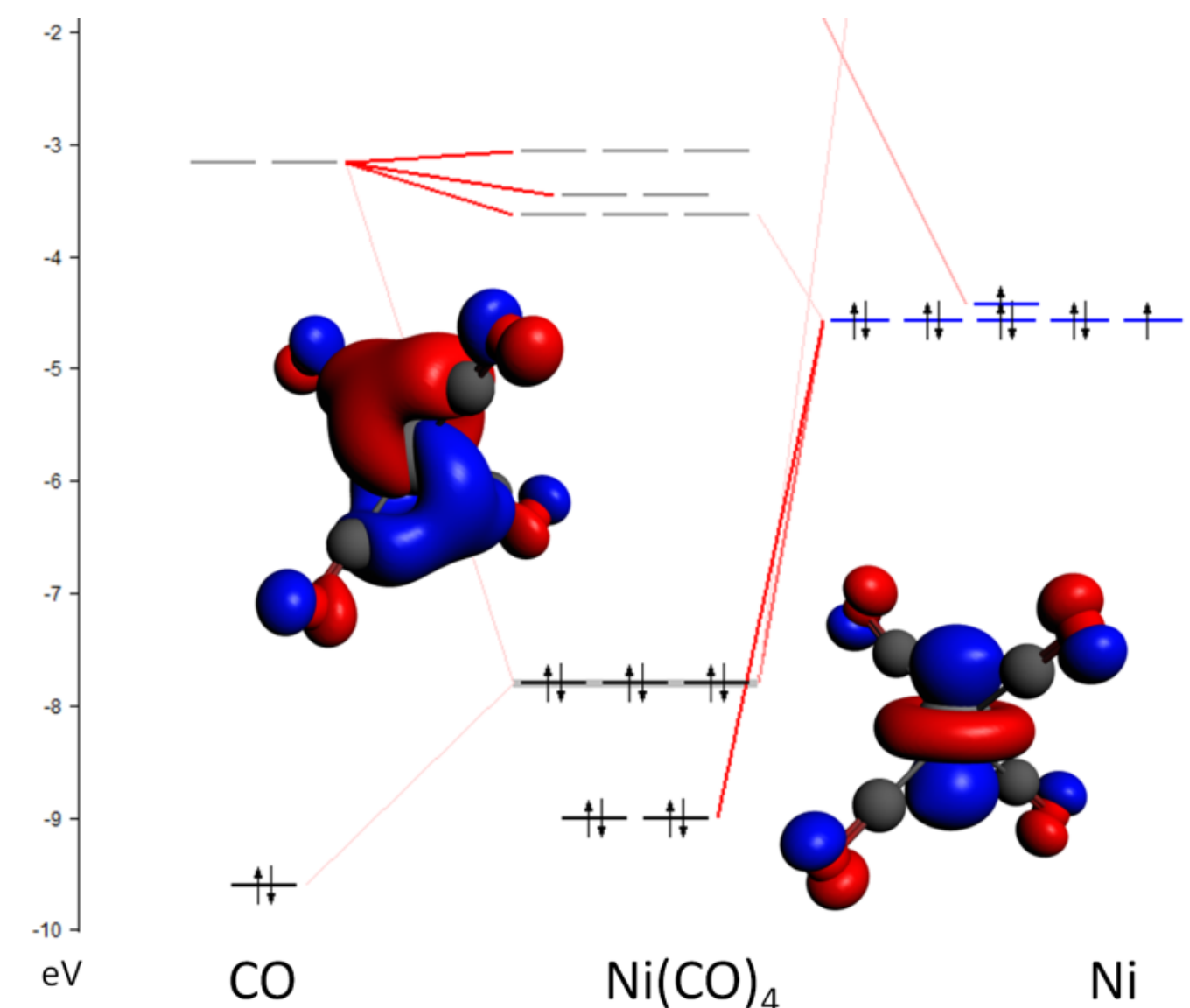
Rev. Comput. Chem. 2000, 15, 1



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

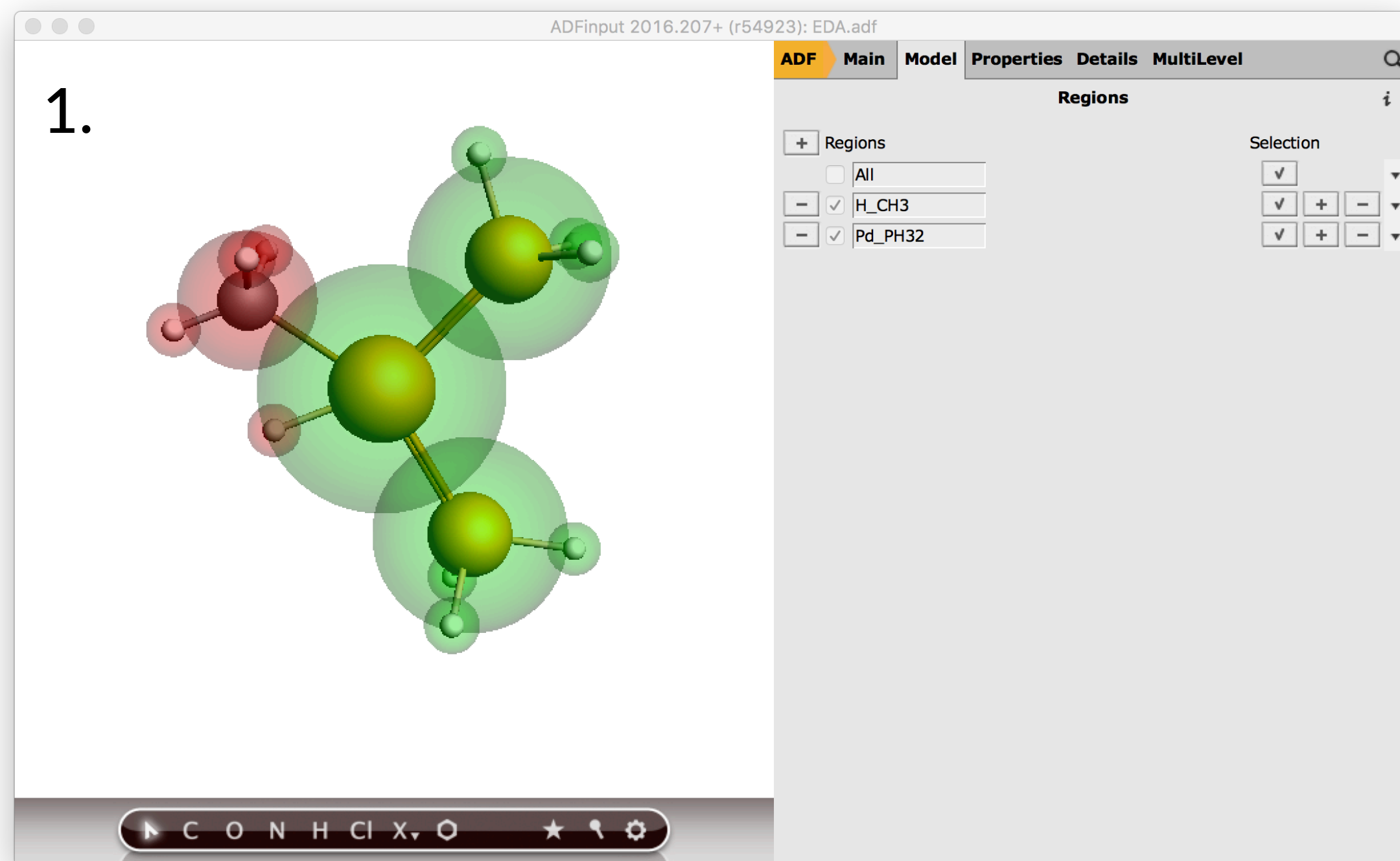
Extensions:

- 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

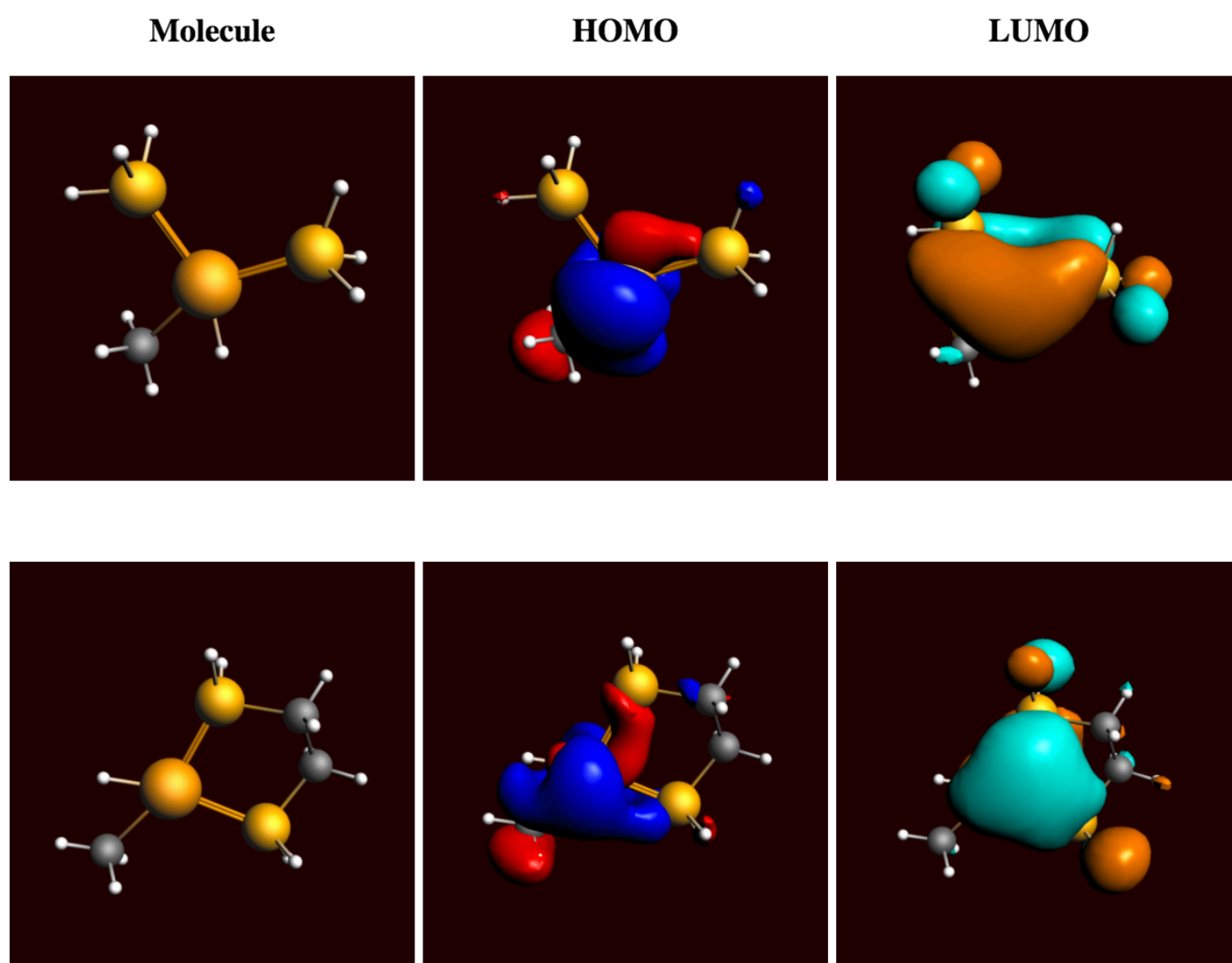
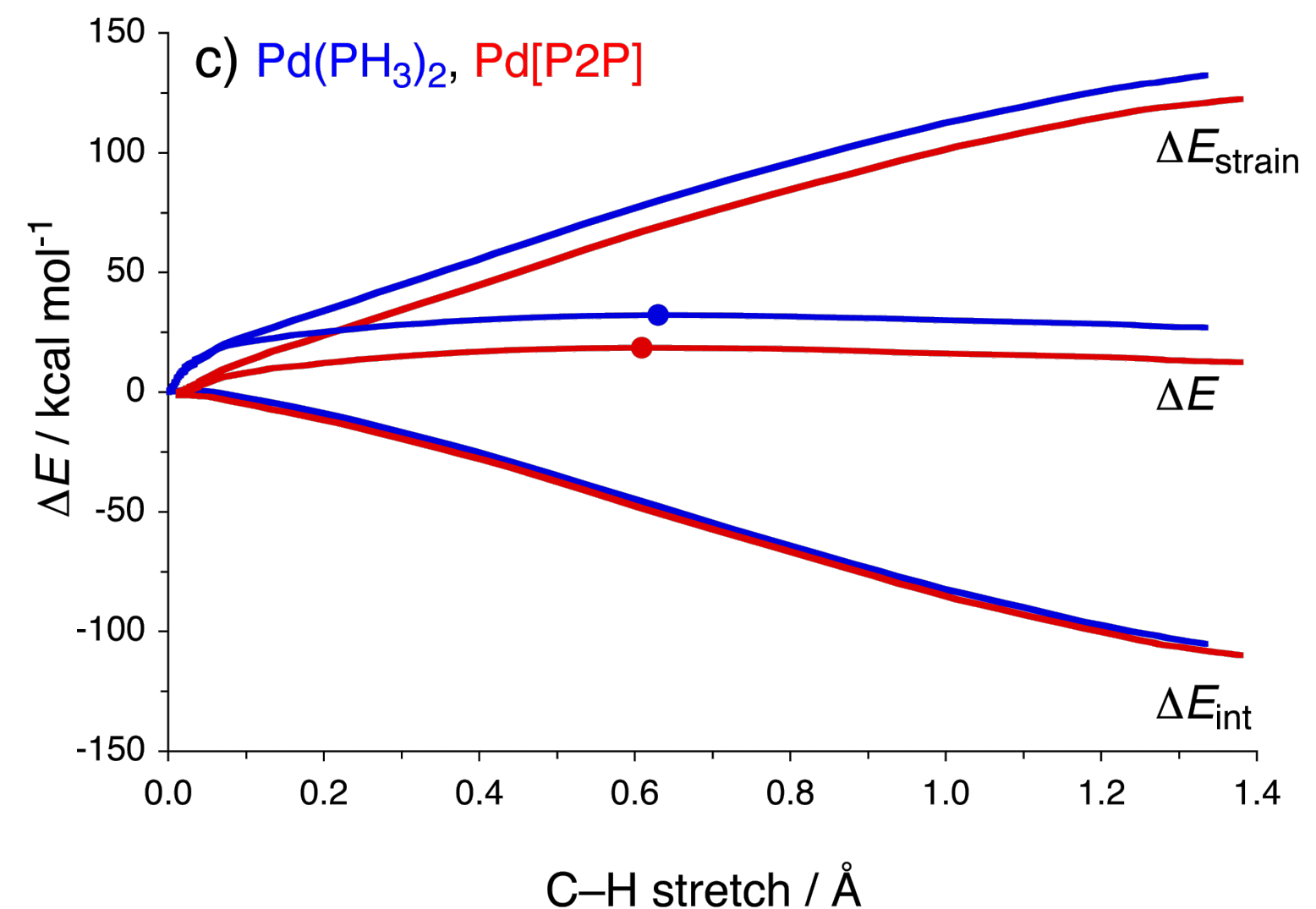
1. Define your fragments (regions)
2. Run your EDA or ETS-NOCV calculation
 - Single point calculation; check 'Use fragments' in MultiLevel tab
 - (Select ETS-NOCV type calculation in Properties => ETS-NOCV)
 - Results: ADFoutput => Properties => Bonding Energy Decomposition
3. Optimize fragments to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



Energy decomposition analysis

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

	Pd(PH ₃) 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

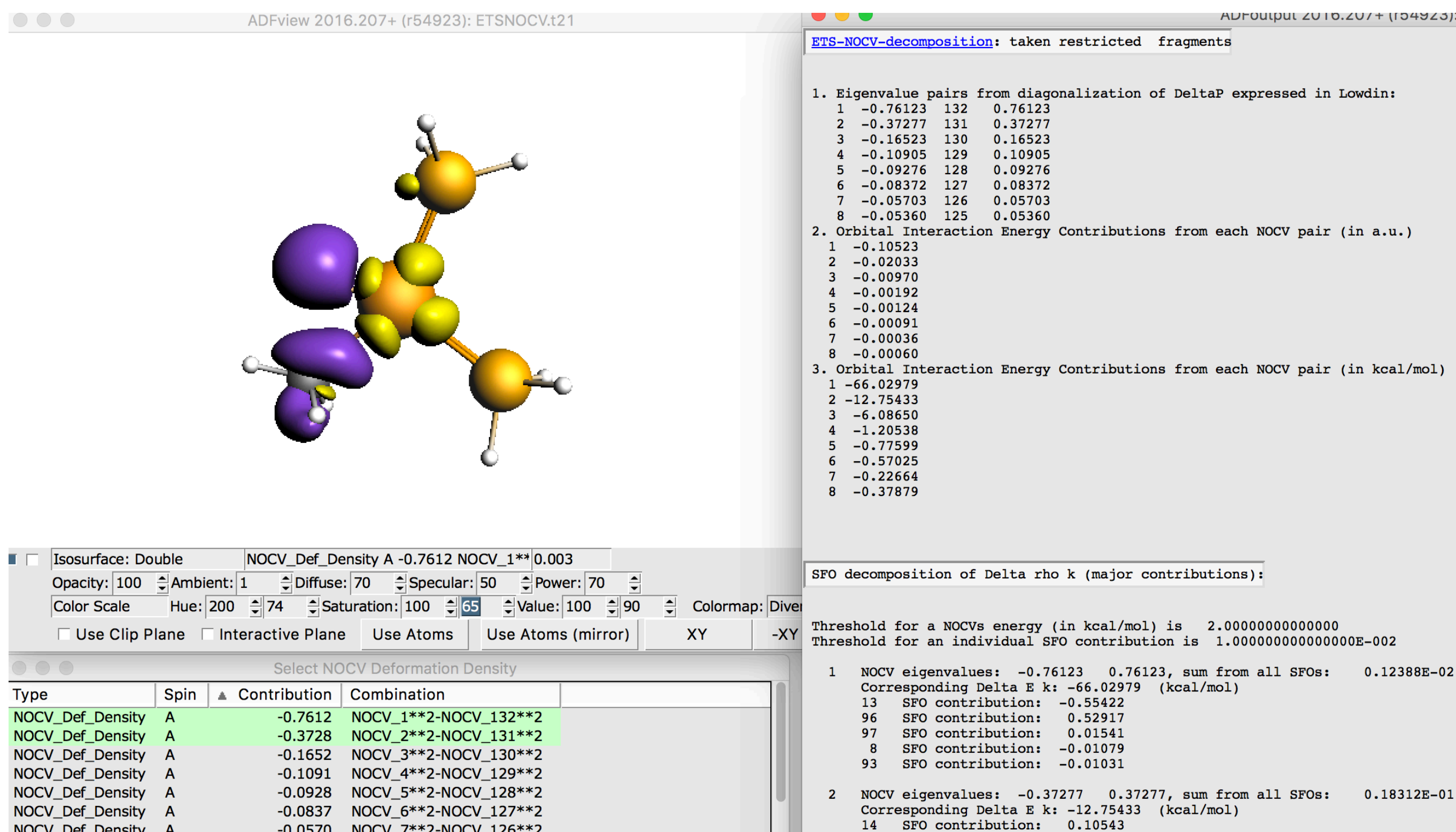


Strain built into bidentate

- Reduces *activation strain*
- Earlier TS
- Lower ΔE^\ddagger

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/>

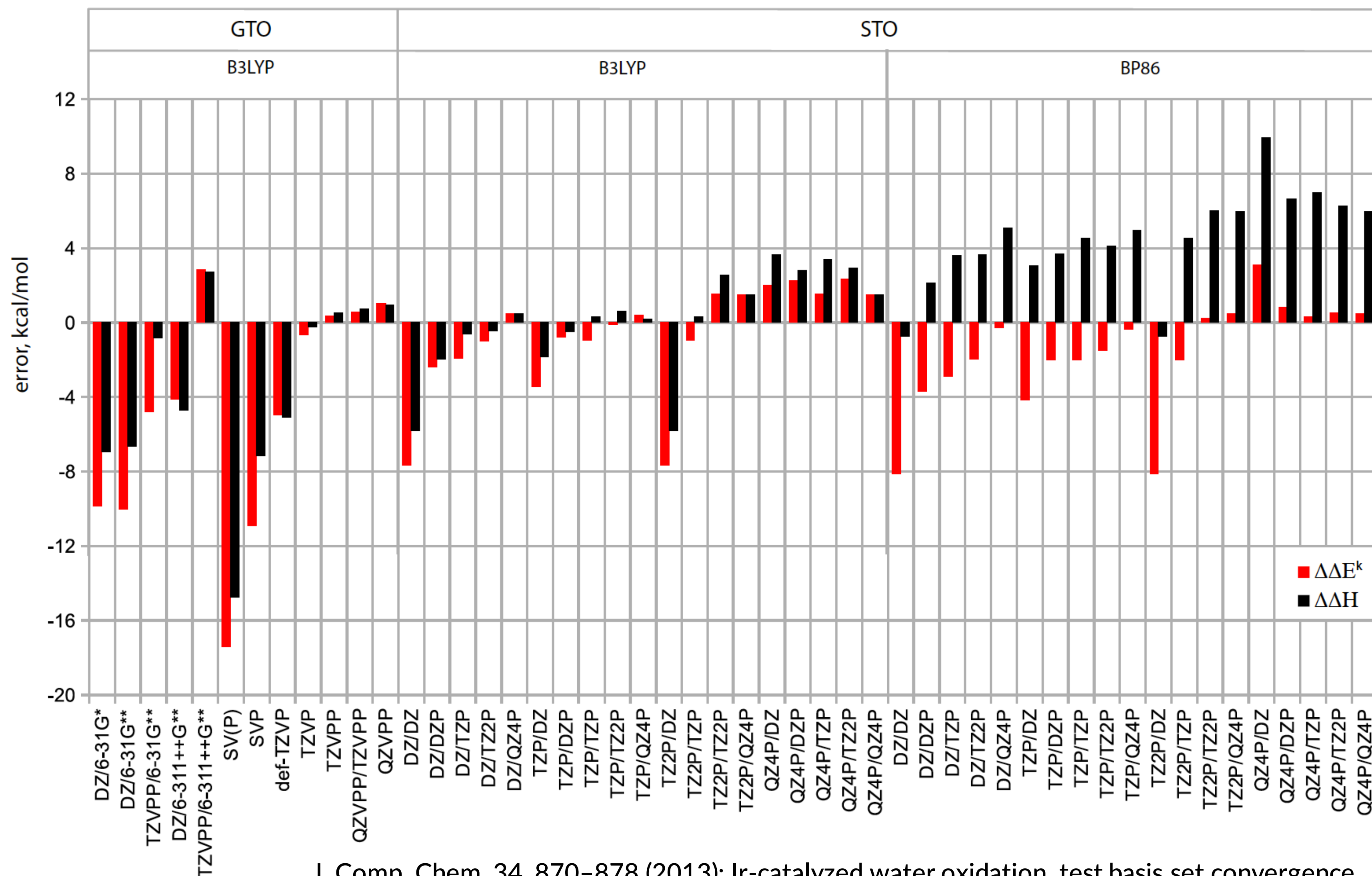
<https://www.scm.com/adf-modeling-suite/adf-hands-on-workshops/>

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 ΔE^\ddagger)
 - 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