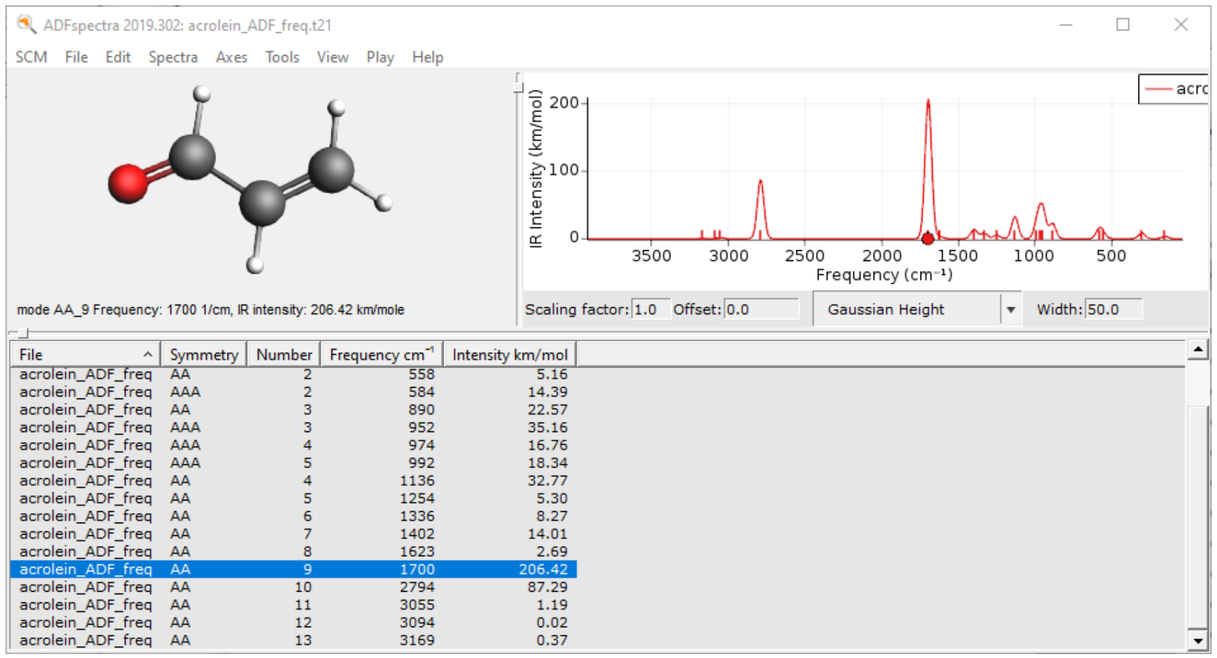
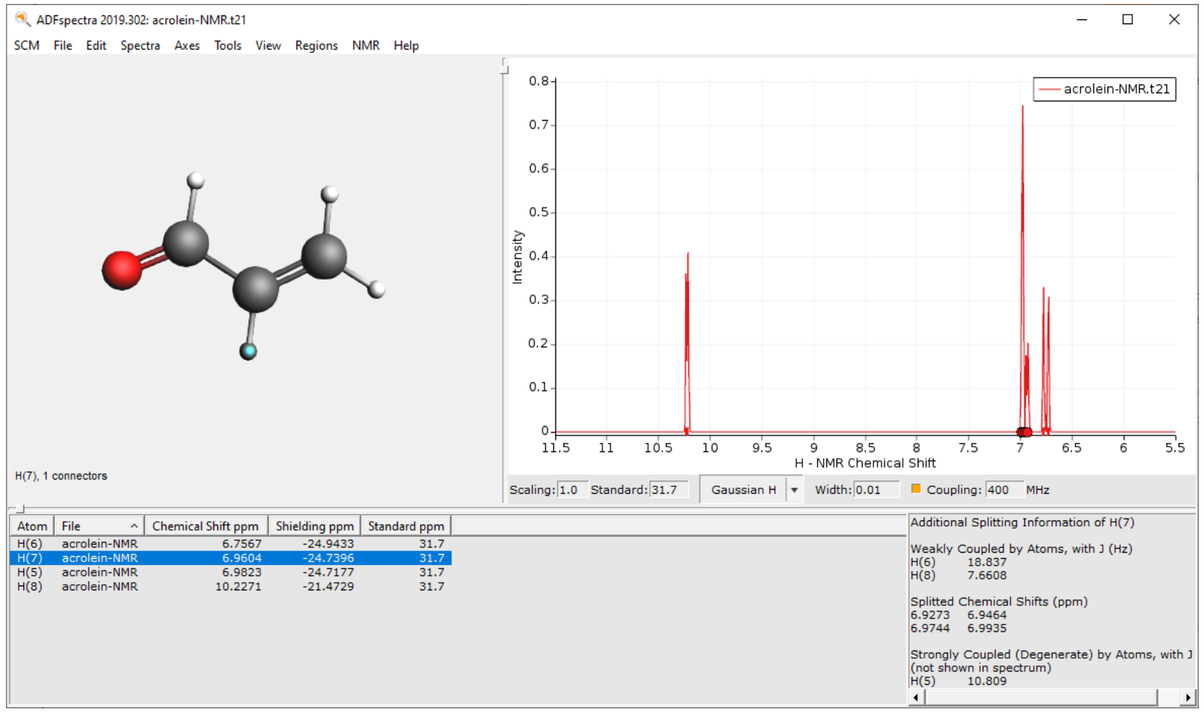
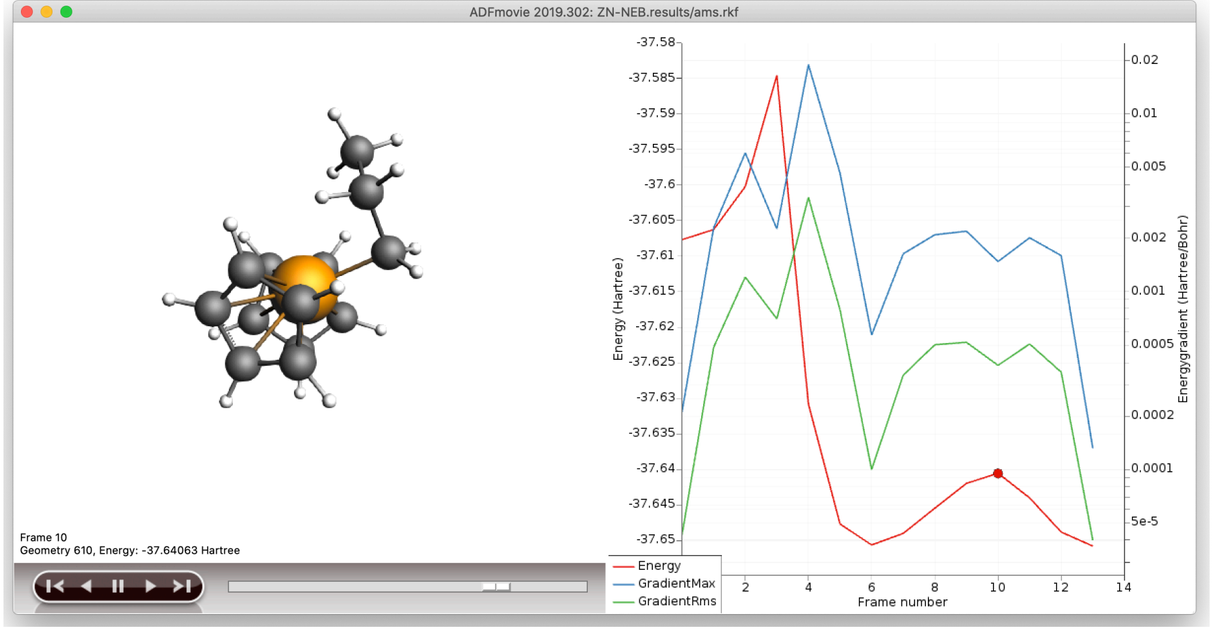
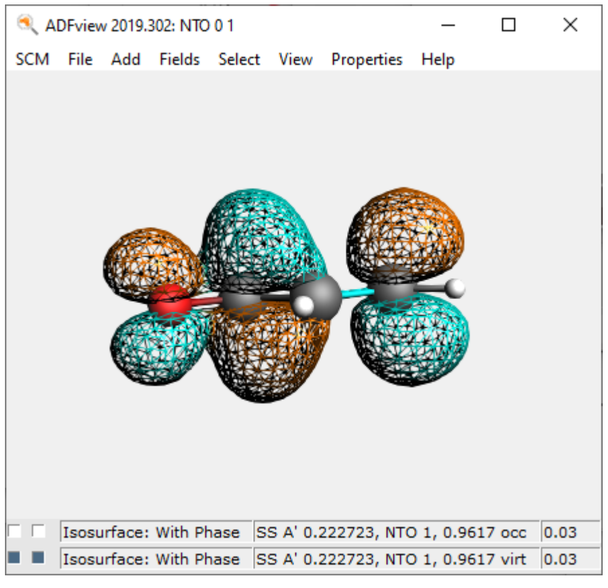
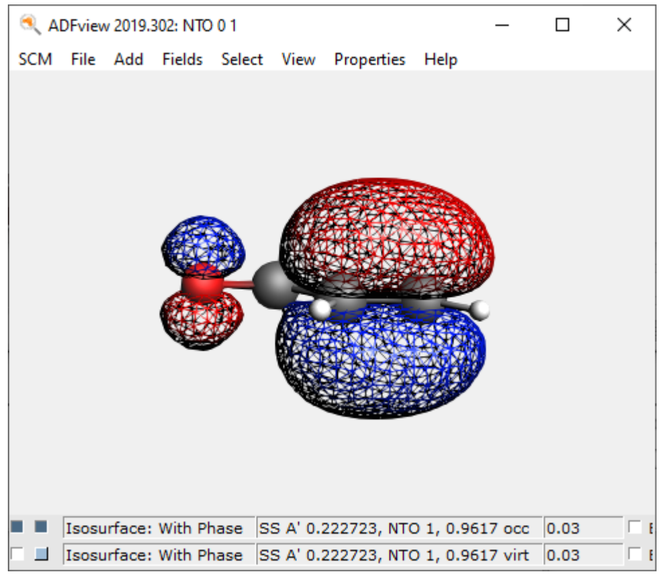
Hands-on exercise 1: molecules











SCM
Software for Chemistry & Materials

Virtual Winter School on Computational Chemistry, 20 February 2020

Fedor Goumans, goumans@scm.com

Ole Carstensen, carstensen@scm.com

Thomas Soini, soini@scm.com

SCM support: support@scm.com

Getting started with the GUI

Starting ADFjobs: job bookkeeping tool

- Win: dbl-click desktop item
- Mac: open Application
- Linux: run $ADFBIN/adfjobs

- ADF is a bit separate concerning setting up tasks
- There is ‘classic’ ReaxFF besides ReaxAMS
  - Both will move to AMS driver – engine set up in 2020

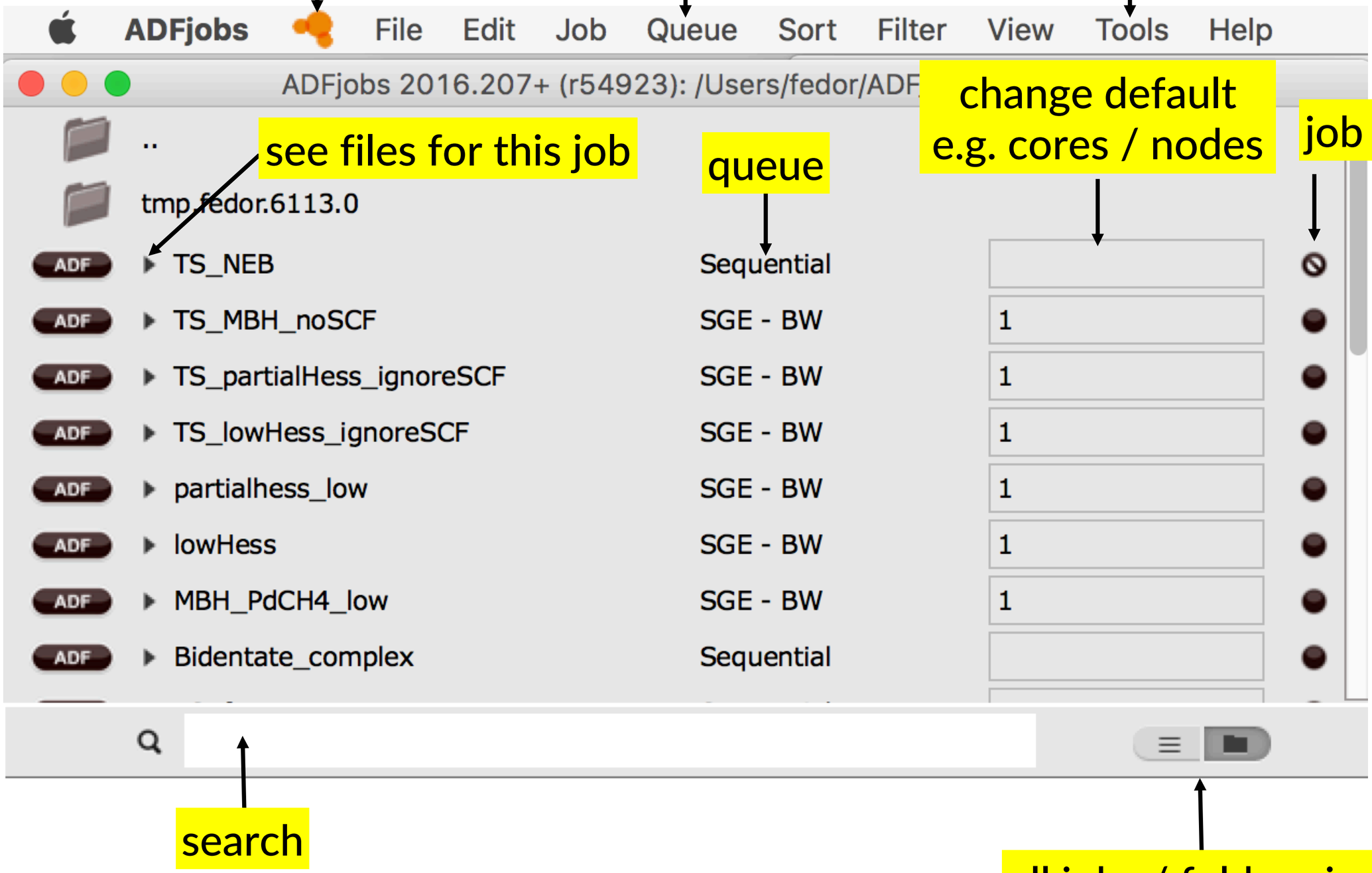
- Other GUI modules: (Input, View, Levels, Movie, Spectra, Band Structure, ADFTrain, Microkinetics, COSMO-RS, …)
  - Can be opened by dbl-clicking ‘.exe’ (Win) or opening e.g. ‘$ADFBIN/adfinput’

ADFjobs: job bookkeeping

switch GUI functionality

define & switch queues

reports & templates



see files for this job

queue

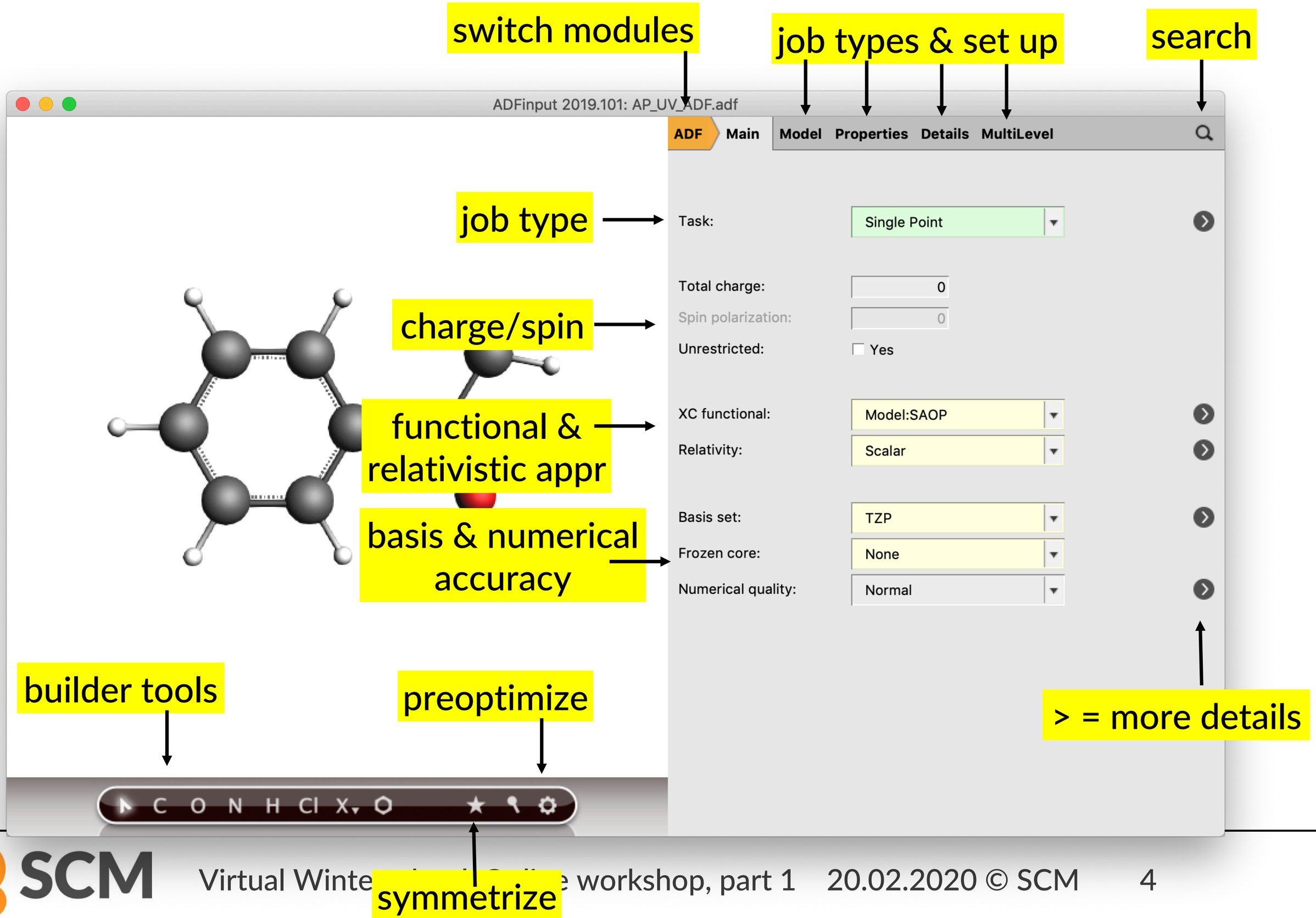
change default
e.g. cores / nodes

job status

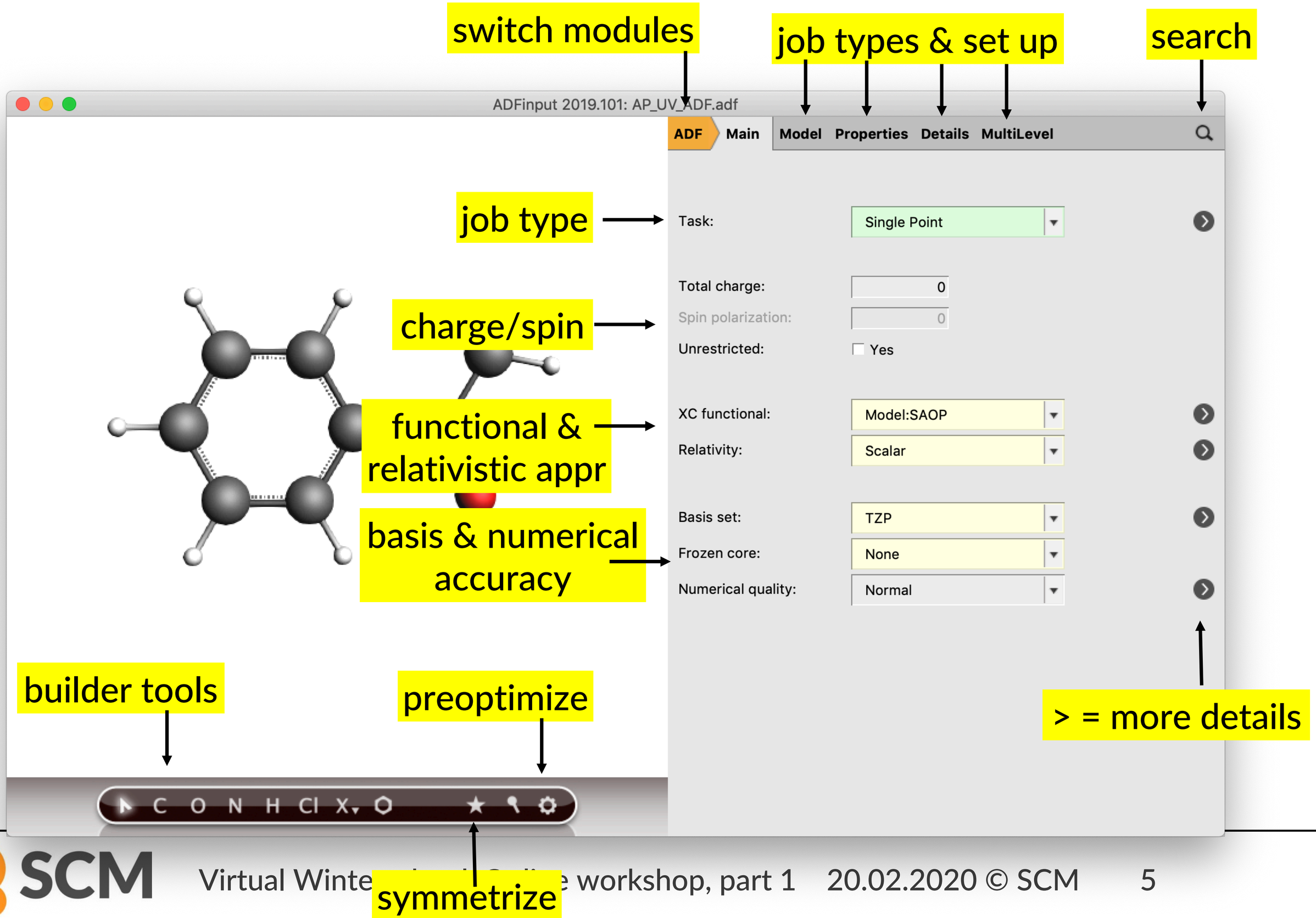
search

all jobs / folder view

Basic calculations & settings



Basic calculations & settings



GUI input editor controls

Free rotation	**left mouse button** (**LMB**) & drag
In-plane rotation	**ctrl** + **LMB** & drag
In-plane shift	**right mouse button** (**RMB**) & drag
Zoom	**mouse wheel** / **alt** & drag
Area selection	**shift** + **LMB**
Deselect	**LMB** on drawing space
Undo	**ctrl** + **Z**
Redo	**shift** + **ctrl** + **Z**
View along x- / y- / z-axis	**ctrl** + **1** / **ctrl** + **2** / **ctrl** + **3**

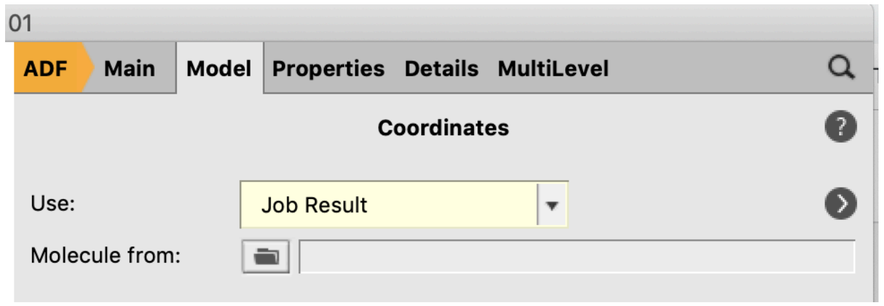
GUI input editor controls

Selection free rotation	**LMB** & drag from a selected atom
Selection in-plane rotation	**ctrl** + **LMB** & drag from atom
Selection in-plane shift	(**shift** +) **RMB** & drag from atom
Select all atoms	**ctrl** + **A**
Add hydrogen atoms	**ctrl** + **E**
Link selected atoms	**ctrl** + **L**
Delete selected atoms	**del** / **backspace**

- More shortcuts: **Help** → **Shortcuts**

Using the GUI more efficiently

1. Chained jobs
   - Model -> coordinates use Job results
   - E.g. first do pre / partial optimization
   - Can not be used to also read in Hessian
     - Python scripting could work (do check on nimag e.g.)



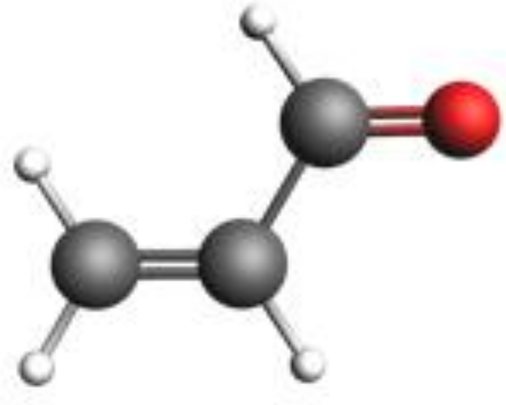
2. Preset
   - If you always use same XC, basis set, relativity & quality, etc. you can save it:
     - File -> Save as preset (all fields different from default)
     - File -> Save as full preset (all input options)
   - Load this: File -> Preset -> 'Your preset' on future jobs with the same setting

3. Adfprepare (& report)
   - In adfjobs select a job, tools -> prepare
   - Now you can run the same job but with different settings (e.g. basis set, xc, …)
   - With adfreport you can build a report to visualize results (e.g. distances)
   - (also consider Python scripting with PLAMS)

Building molecules

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

- Search molecules
- Import: InChI, SMILES, xyz, cif, pdb, …



- Included library + building

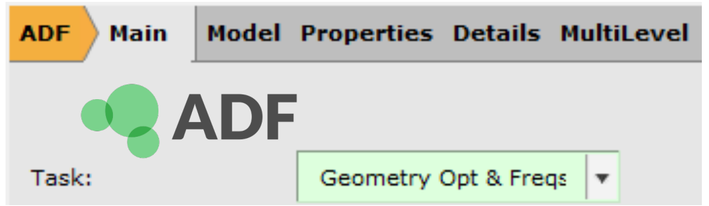
- **Excercise:** Build acrolein / propenal
  - By searching for it in the GUI
  - By starting from the builder tools
    use ‘2’ for double bonds, Ctrl+E to add H atoms
  - By importing SMILES, InChI (e.g. from Wikipedia, PubChem or Chemspider)

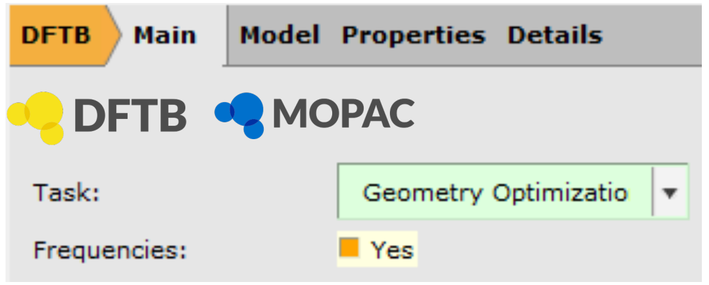
- Symmetrize (Cs), pre-optimize (UFF, MOPAC, DFTB)

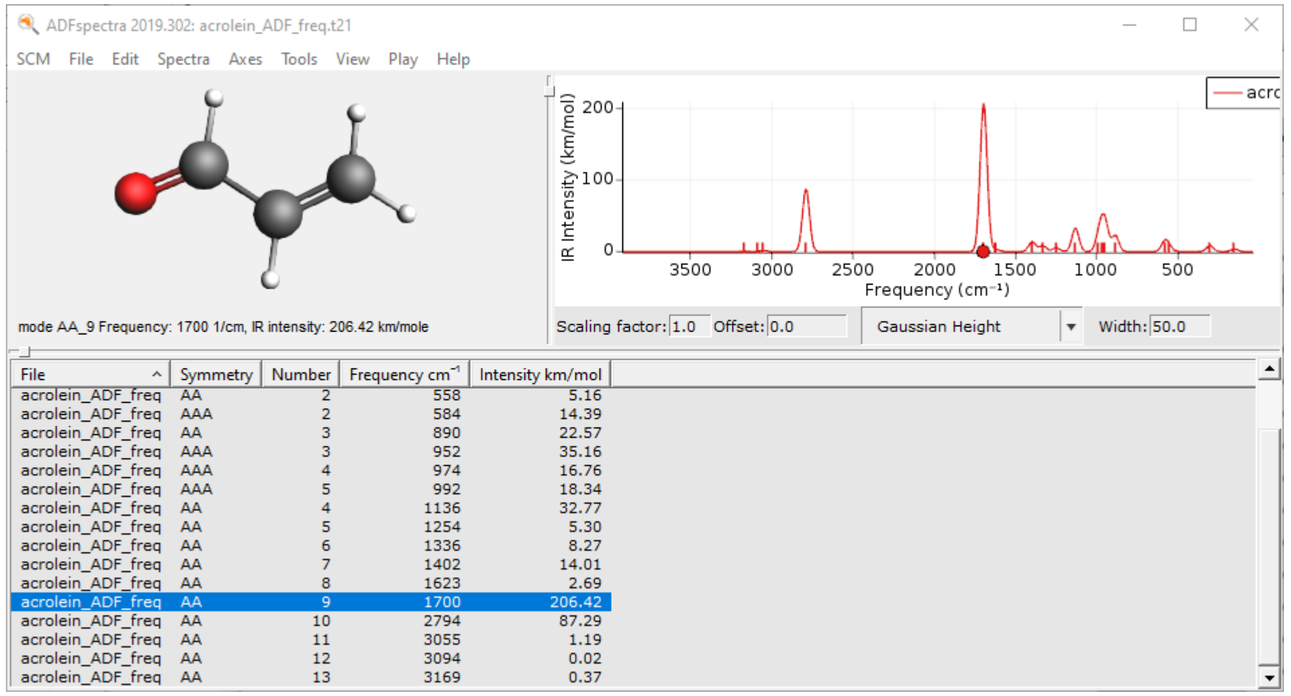
Spectra: IR

https://www.scm.com/doc/Tutorials/ADF/Vibrational_frequencies_and_IR_spectrum_of_ethane.html

- **Excercise:** Calculate & visualize frequencies
  - Geometry needs to be optimized at same level as frequency calc.
  - ADF (not yet part of AMS): Task = Geometry Opt & Freq
  - MOPAC, DFTB: Task = Geometry Opt + Frequencies = Yes
  - Try a few different methods:
    - ADF: PBE-D4/DZP + Scalar (.adf)
    - DFTB: DFTB3-D3-BJ/3ob-3-1 (.adf)
    - MOPAC
  - Visualize: ADFSpectra; tweak broadening
  - Compare to NIST

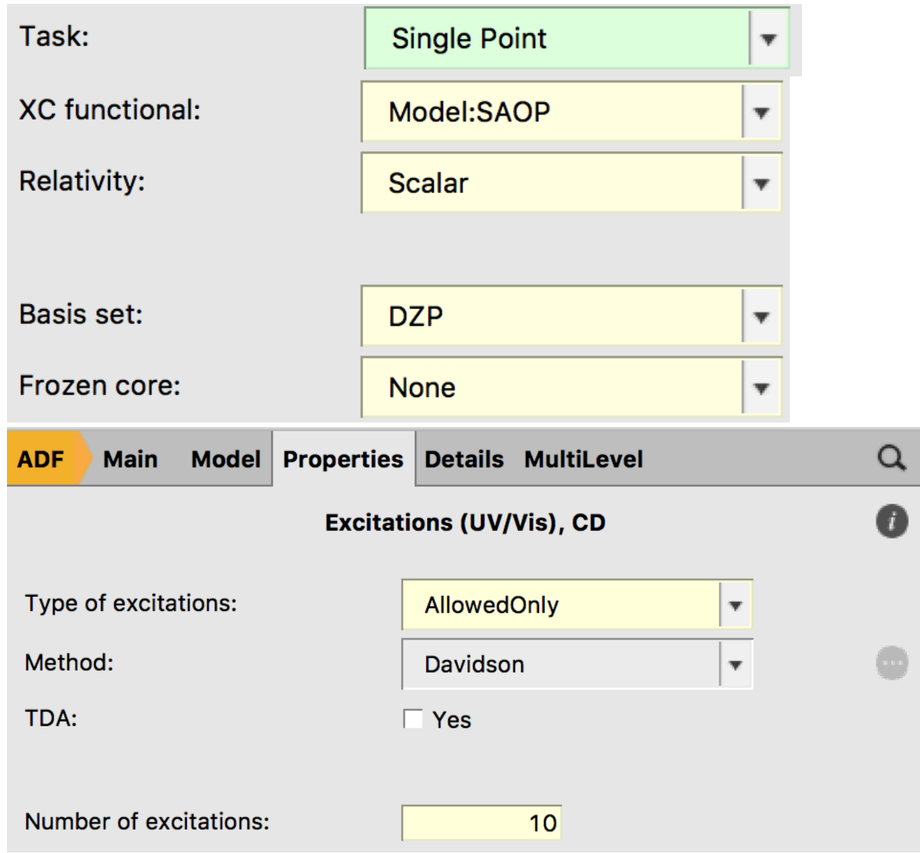


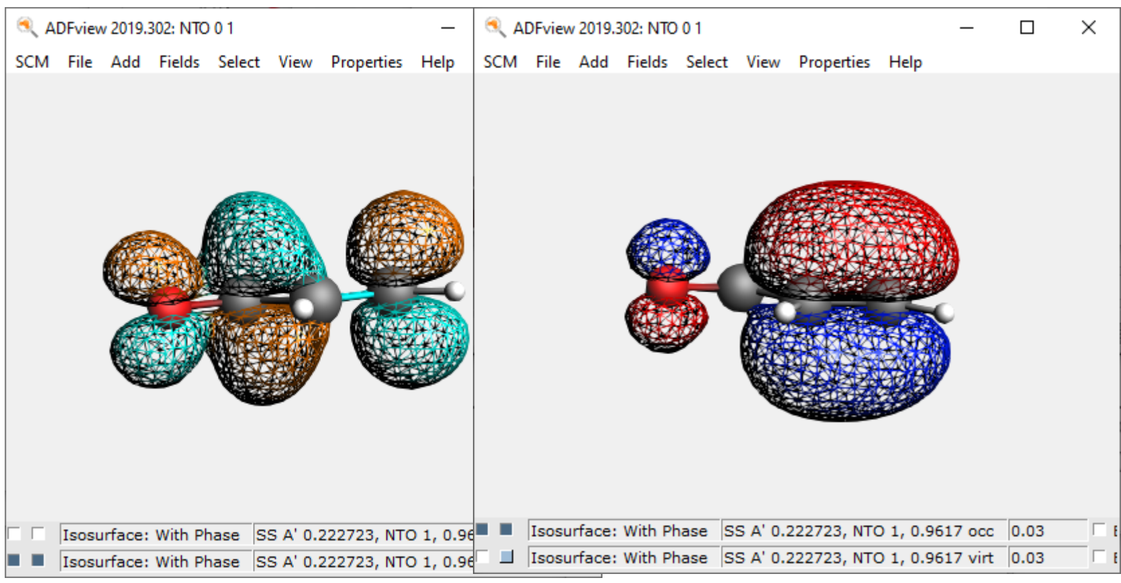




Spectra: UV/VIS

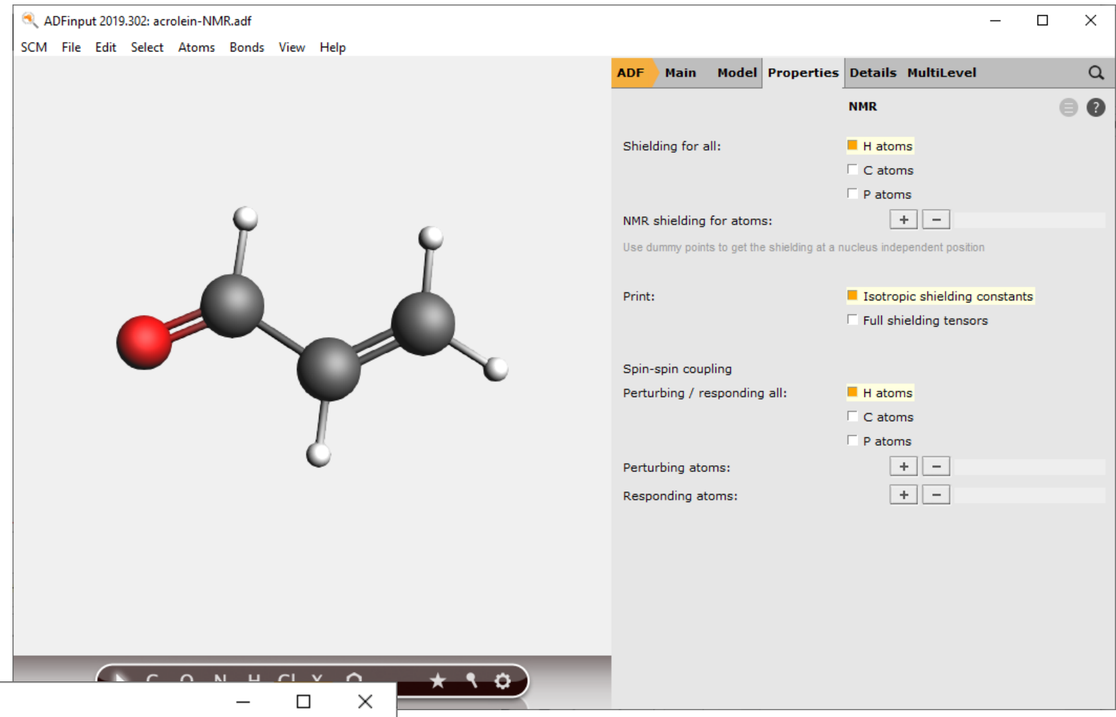
- Exercise:
  - With ADF: calculate 10 allowed excitations
    - use SAOP model potential, DZP (or TZP), no core (.adf)
  - See also UV/VIS FAQ for tips
  - Go to spectra, change x-axis to nm
  - Increase the line width to ~10
  - Visualize the pi-pi* NTOs at ~205nm (click on NTO1)
  - Visualize the MOs strongest Single Orbital Transition
  - Compare to NIST data
    - Rerun with method ‘sTDA’ and tick TDA
    - Also try TD-DFT+TB (ADF)
    - and TDDFTB (DFTB3/3ob-3-1, GFN-xTB)
    - (can use the same PBE-D4 optimized geometry)

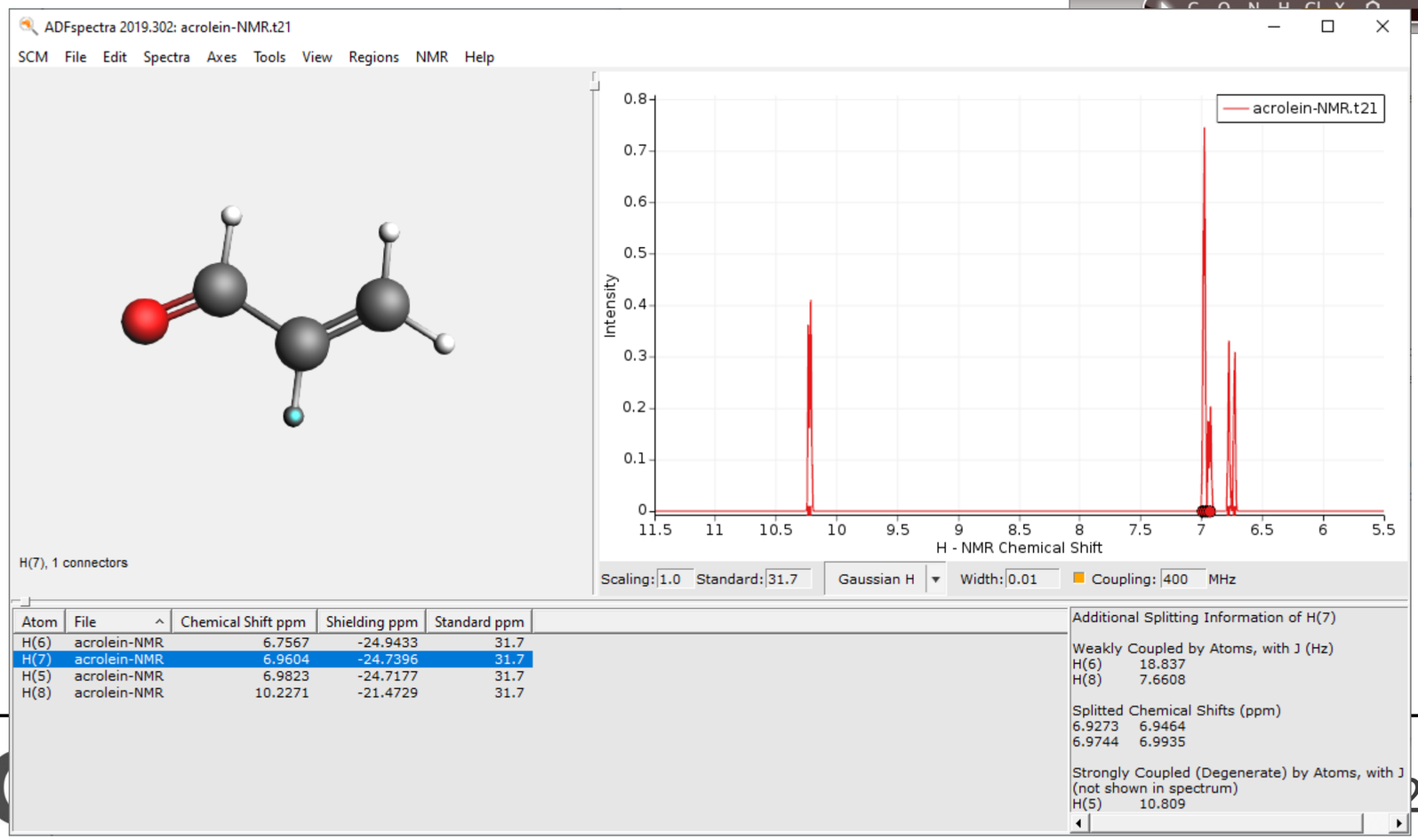




Spectra: NMR

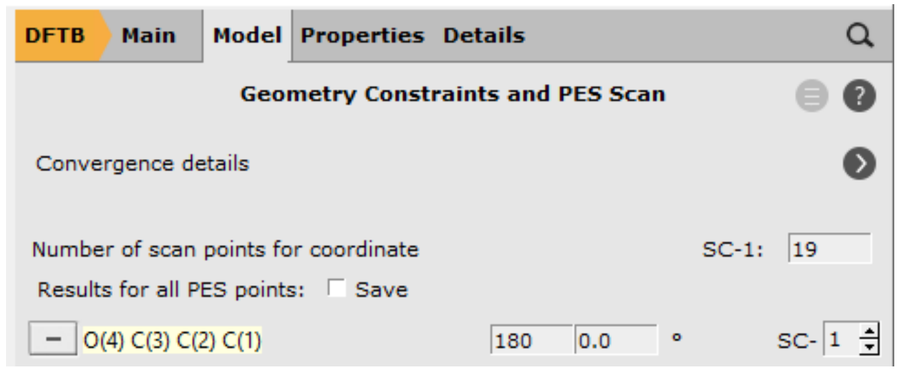
- Exercise:
  - See also NMR FAQ for tips + advanced tutorials
  - Use PBE0 + TZP, Scalar, no core (.adf)
  - Select Properties -> NMR
    - select shielding & coupling for all H
    - Set 400 MHz and tick coupling, compare
  - Note the internal ref. uses different settings!
    - Recalculate TMS with same set up

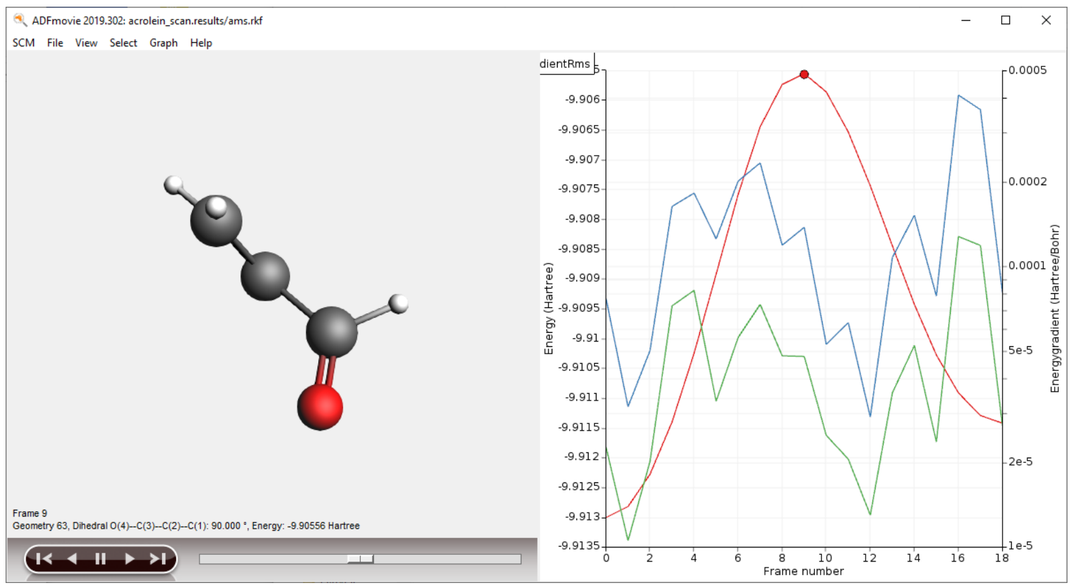




PES: conformers, scan dihedral

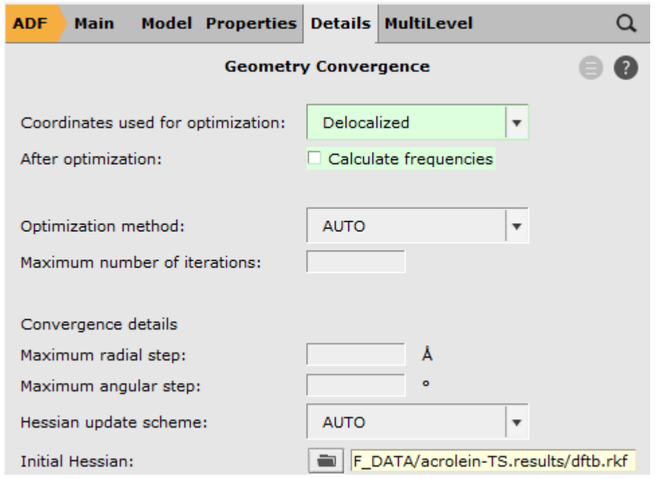
- Exercises:
  - Take any acrolein, switch the engine to Conformers, run, visualize -> ADFMovie
    - Does it find all conformers :) ? Maybe try a larger molecule?
    - Switch to, e.g. DFTB, and from Model -> Coordinates, Use: Selected File, select your.sdf
    - Do a frequency run on all geometries and visualize a Boltzmann-averaged spectrum
  - Take a DFTB input, set task to PES Scan, click >
    - Select dihedral and scan in 19 points from 180-0 (.adf)
    - Wait for calculation to finish -> ADFMovie
    - Select highest, save geometry (to import for TS search)



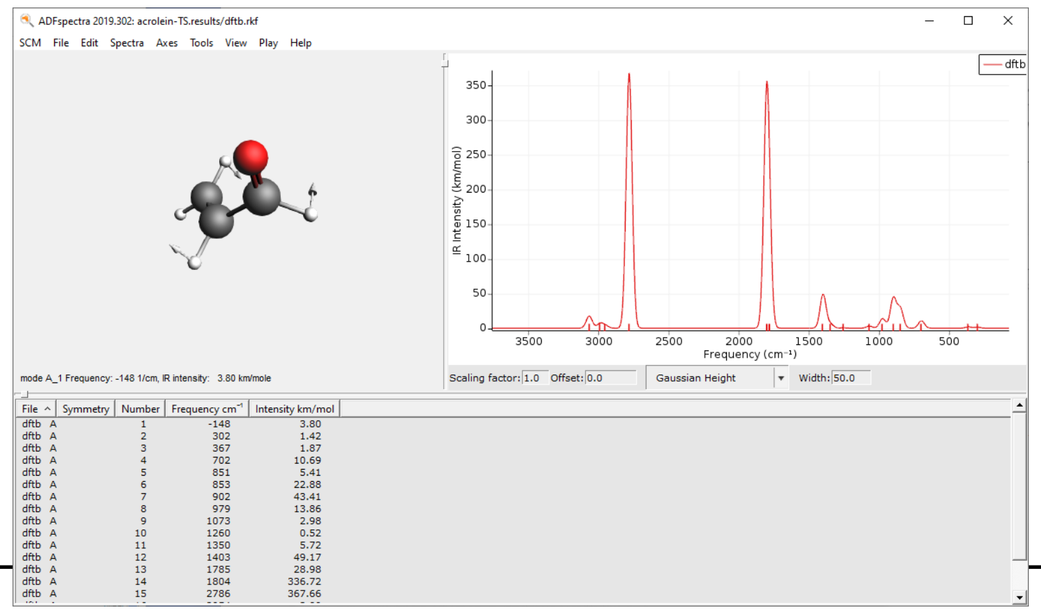


Transition State (I)

- Exercises:
  - New DFTB input, DFTB3-D3-BJ/3ob-3-1
    - Import highest point from PES scan
    - Change Task: Transition State, and calculate frequencies (.adf)
    - Leave all defaults and run, verify 1 imaginary mode



  - Update geometry and switch to ADF
    - Change Task: Transition State, click >
    - Next to initial Hessian click again >
    - Choose the dftb.rkf from the DFTB TS as initial Hessian
    - On the main tab, choose Meta -> MN15L, DZP, no core (.adf – check restart file!)
    - Verify imaginary modes?
    - Can also use 'TSRC' if no lower-level Hessian



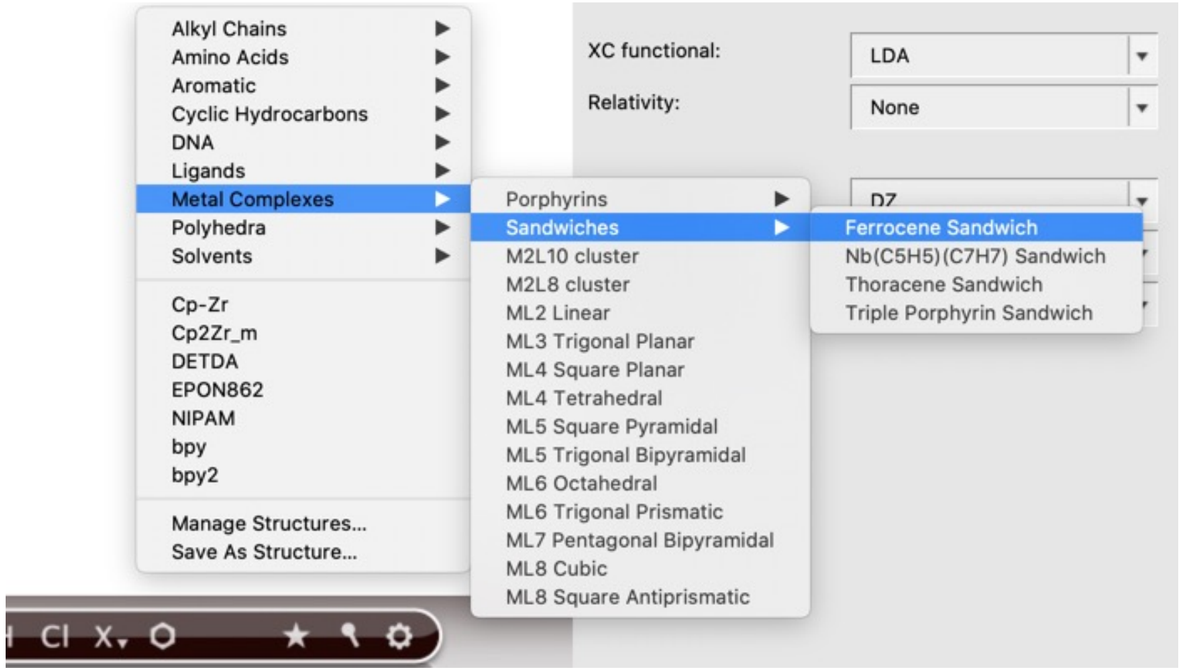
Quick thermodynamic properties

- Exercise:
  - Open SCM -> COSMO-RS (no need to install database)
  - In the SMILES input, put C=CC=O and Add
  - Properties -> Pure compound
  - Compare some properties (density, boiling point) (e.g. Wikipedia)

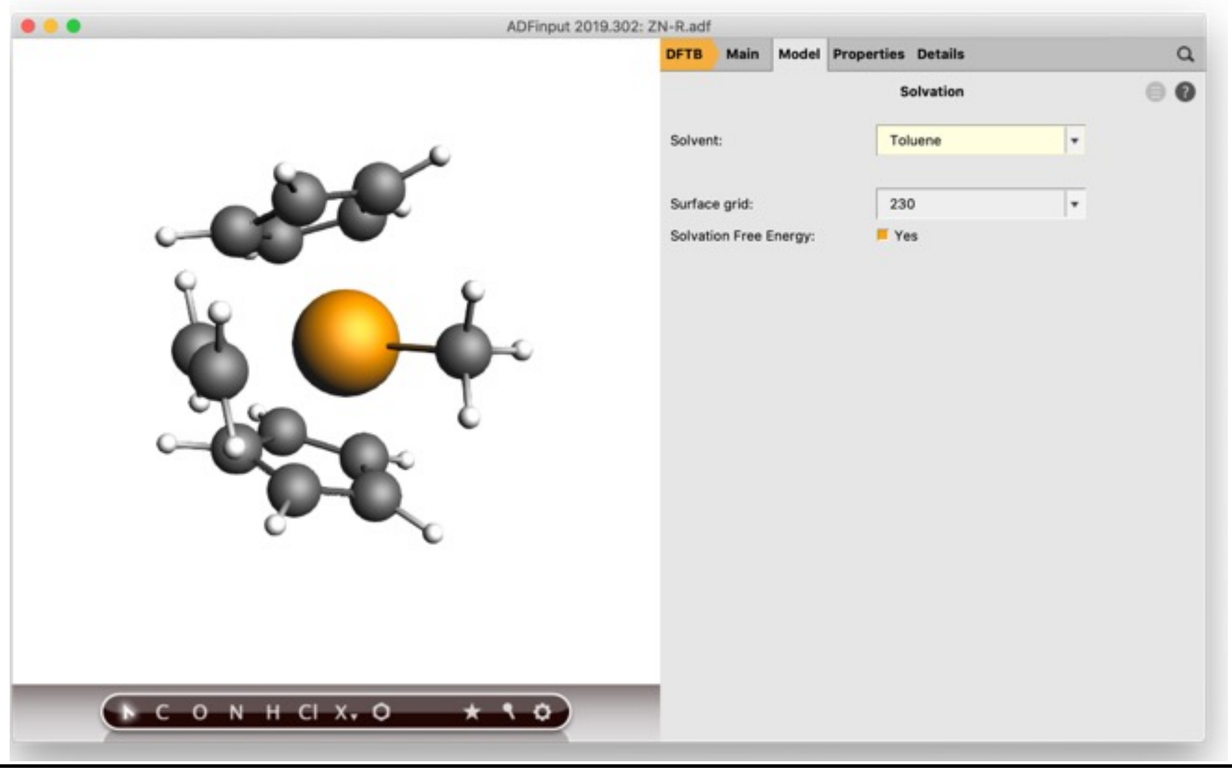
Property		Unit
Boiling point	346.746	K
Critical pressure	51.21	bar
Critical temperature	524.603	K
Critical volume	0.195	L/mol
Liquid density	0.816	kg/L
Dielectric constant	10.985	
Absolute entropy (ideal gas)	309.848	J/(mol K)
Flash point	270.523	K
Gibbs energy of formation (ideal gas)	-111.468	kJ/mol
Net enthalpy of combustion	-1652.692	kJ/mol
Std. state enthalpy of formation	-188.906	kJ/mol
Enthalpy of fusion	17.129	kJ/mol
Enthalpy of formation (ideal gas)	-157.71	kJ/mol
Enthalpy of sublimation	49.534	kJ/mol
Melting point	213.82	K
Liquid molar volume	0.069	L/mol
Parachor	161.085	
Solubility parameter	10.098	√(MPa)
Triple point temperature	213.778	K
Van der Waals area	91.576	Å^2
Van der Waals volume	63.229	Å^3

Transition State (II): Ziegler-Natta

- Exercises:
  - New DFTB input, GFN-xTB
  - 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 (.adf)

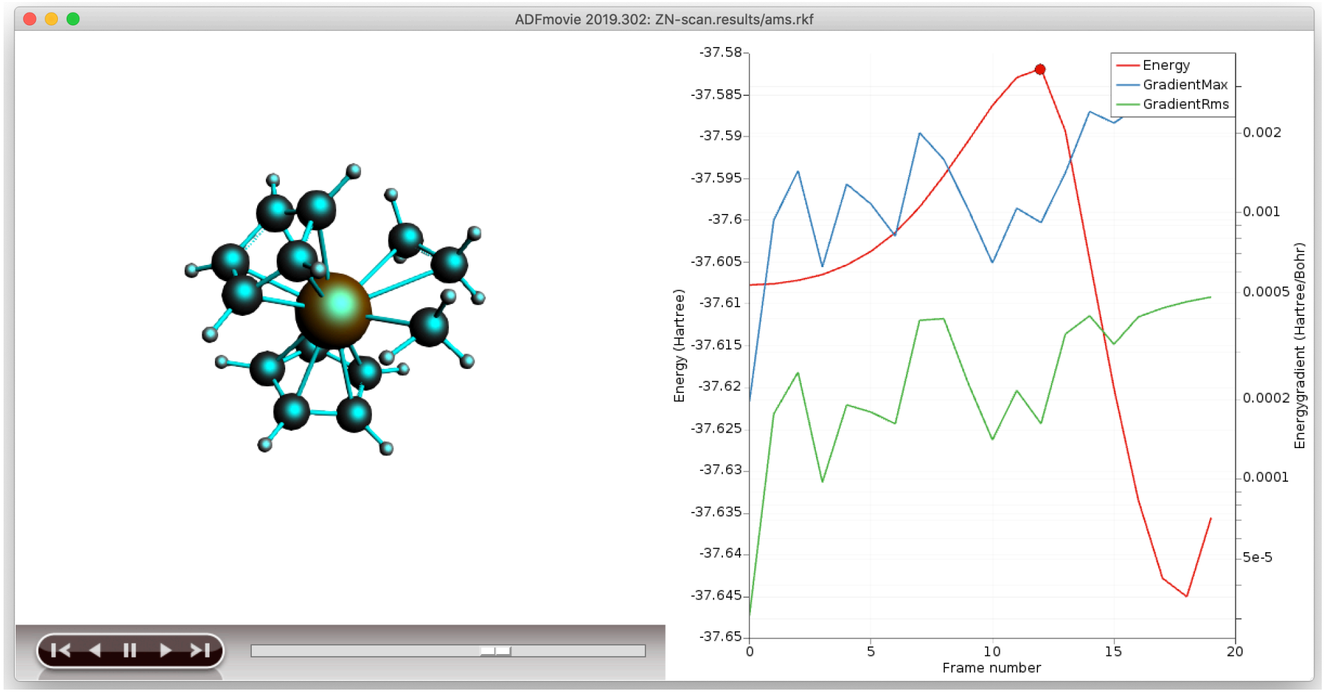


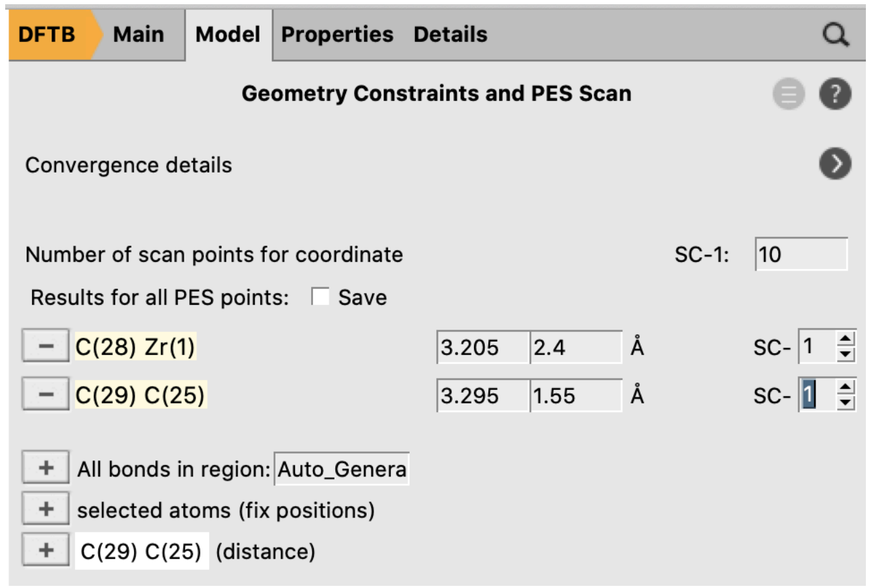
- Add ethene (use the 🔍)
  - Manipulate it in position
  - Right-click + drag = translate
  - Left-click + drag = rotate
  - Ctrl+M = select molecule
  - Remove dummies (.adf)
  - Optimize



Transition State (II): Ziegler-Natta

- Exercise:
  - Set up a PES scan, scanning 1 coordinte
    - Zr-C to 2.4 & C-C to 1.55
  - Loosen the Convergence criteria by a factor of 5 (.adf)
  - When finished, open ADFMovie



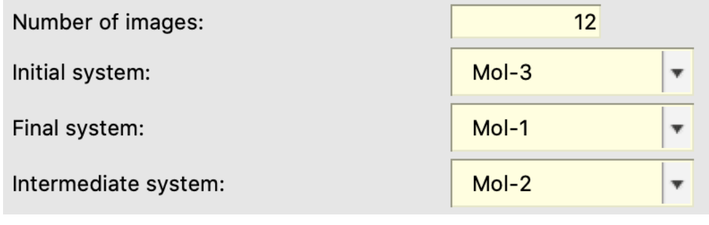


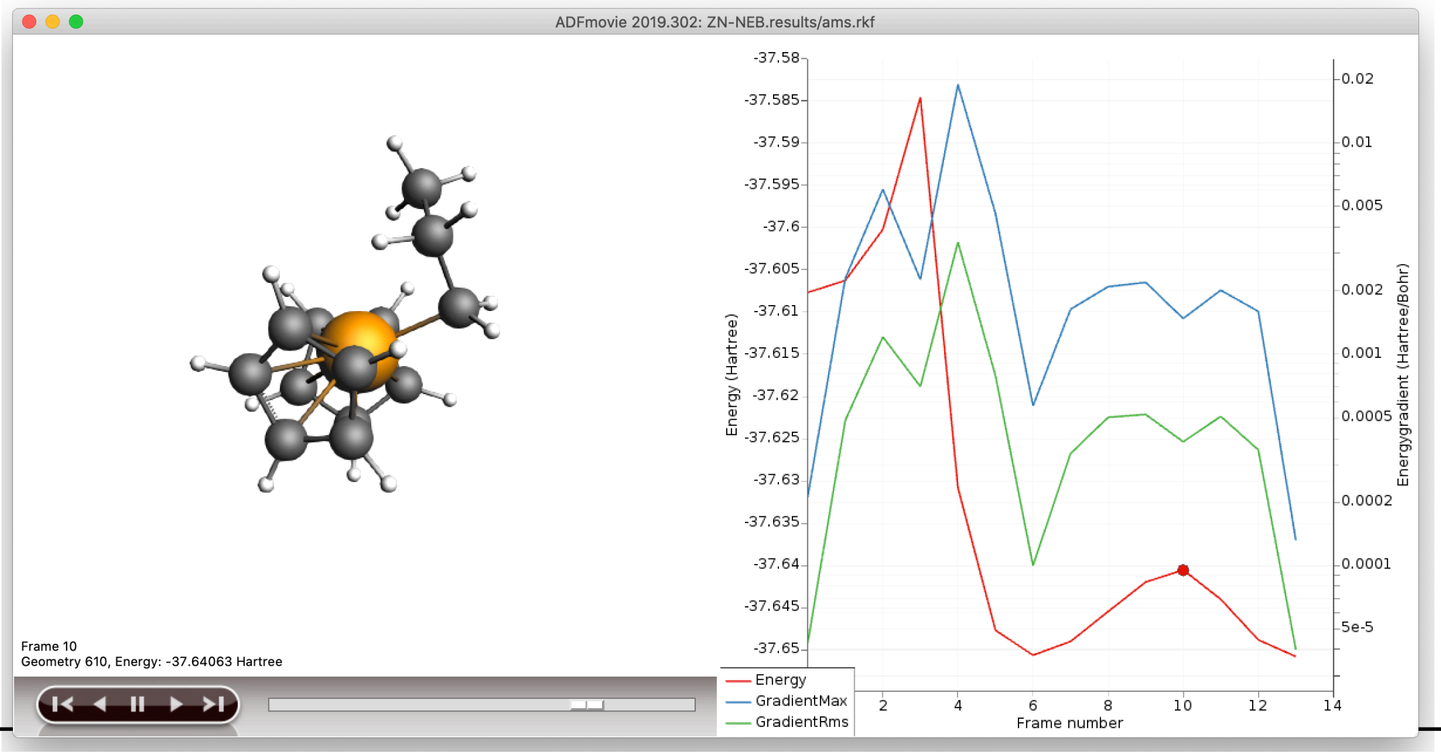
Gradient convergence:	5.0e-3	Hartree/Å
Energy convergence:	5.0e-5	Hartree
Step convergence:	5.0e-3	Å

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

Transition State (III): Ziegler-Natta

- Exercise:
  - Optimize the product from the last PES scan point (.adf)
  - Rotate the Zr-C-C-H dihedral to ~0 (metallacycle Zr-C-C-H) & optimize (.adf)
  - 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 the ams.rkf) and choose 12 points
  - Don't optimize R&P, relax convergence by factor 4* (.adf)
  - Open ADFMovie when finished
    - Which is the rate-determining step?





* Tip: use NEB to get close to TS, then use Hessian-based optimization to find it

Transition States: Further considerations

- Reaction rates:
  - Calculate $\Delta G^{\#}$: include H_{vib}, S (ADFoutput -> Other Properties -> Statistical Thermal Analsyis)

Temp		Transl	Rotat	Vibrat	Total
298.15	Entropy (cal/mole-K):	42.601	31.219	51.511	125.331
	Internal Energy (Kcal/mole):	0.889	0.889	161.150	162.927
	Constant Volume Heat Capacity (cal/mole-K):	2.981	2.981	55.756	61.718

Summary of energy terms

	hartree	eV	kcal/mol	kJ/mol
Bond Energy:	-37.588359904200161	-1022.8313	-23587.05	-98688.22
Internal Energy:	0.259640981269797	7.0652	162.93	681.69
pV/n = RT:	0.000944186013486	0.0257	0.59	2.48
Enthalpy H:	-37.327774736916879	-1015.7404	-23423.53	-98004.06
-T*S:	-0.059548659150599	-1.6204	-37.37	-156.34
Gibbs free energy:	-37.387323396067480	-1017.3608	-23460.90	-98160.40

  - Use harmonic TST as first approximation: k = exp (-$G^{\#}$/RT)
  - Could also try mircokinetics. More underway (ReaxPro)

- Suggestions / troubleshooting
  1. get close to TS: NEB, PES Scan, constrained opt, previous TS + change ligands (PLAMS script!), ….
  2. get a good curvature (Hessian): pre-calc with GFN-xTB, MOPAC; partial Hessian
  3. check final curvature / path: Frequency calculation, PES point characterization, IRC
  4. Spurious imag. Freq.: displace along that mode (ADFMovie) & retry