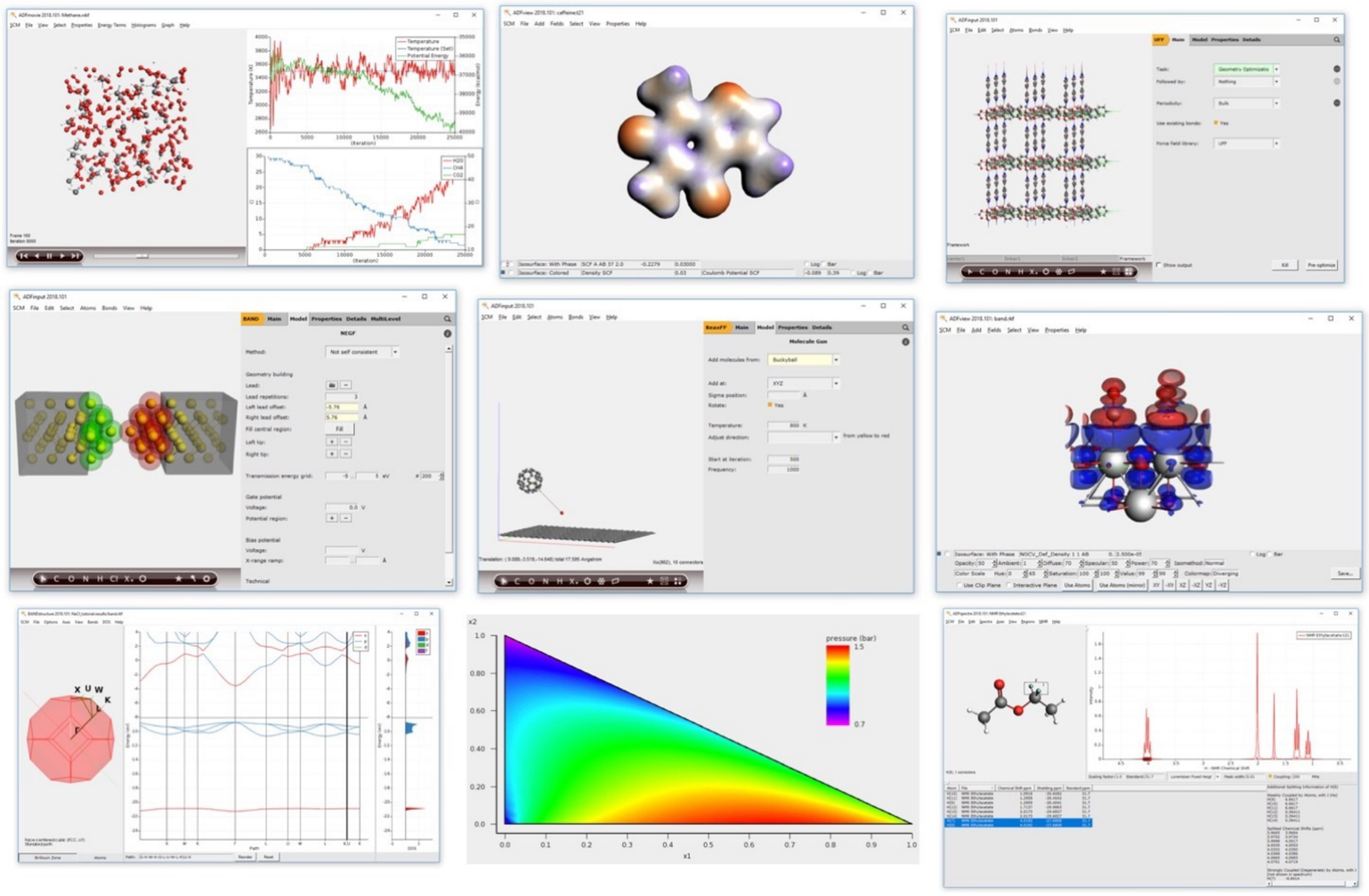
Hands-on workshop:
Chemistry & Materials
with the Amsterdam Modeling Suite



School of Chemistry, Glasgow University, hands-on workshop, 19 Jun 2023

Maria Jose Aliaga, aliaga@scm.com

SCM support: support@scm.com

SCM
Software for
Chemistry &
Materials

Program

- Brief introduction Amsterdam Modeling Suite
- Hands on:
  - https://www.scm.com/about-us/news-agenda/adf-hands-on-workshops/
- Q&A

- NOTE: we'll be using AMS2023 (released in April)
- www.scm.com/doc2023
- www.scm.com/bin2023

- Slides: www.scm.com/news/19-june-2023-1-day-ams-workshop-in-glasgow/

Background: SCM, ADF & AMS

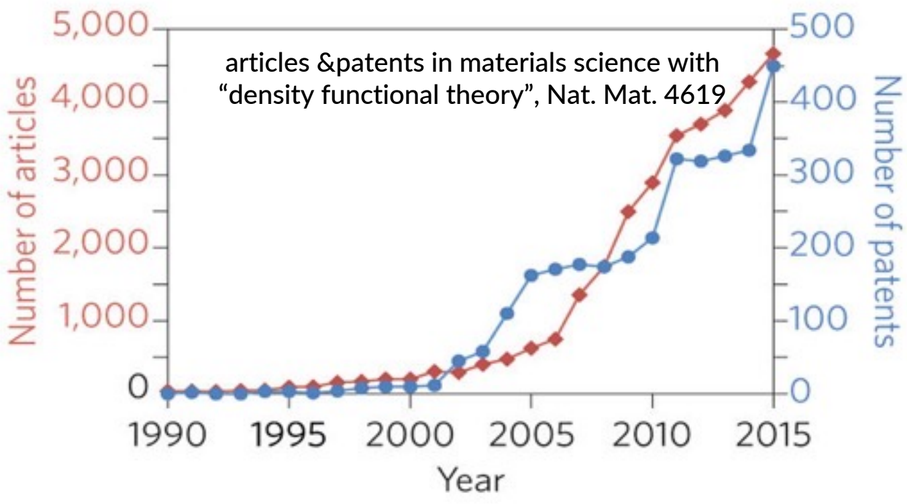
- ADF = first DFT code for chemistry (1970s)
  Baerends@VU (>'73), Ziegler@Calgary(+) (>'75)
  - 80s: support industrial users Mitsui, Shell, Akzo, Unilever

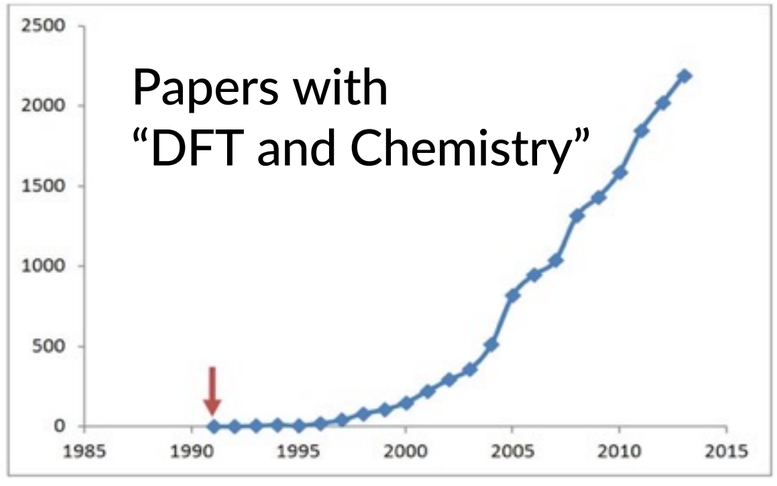
- SCM: Spin-off company 1995

- 24 people (17 senior PhD's) + 3 EU fellows

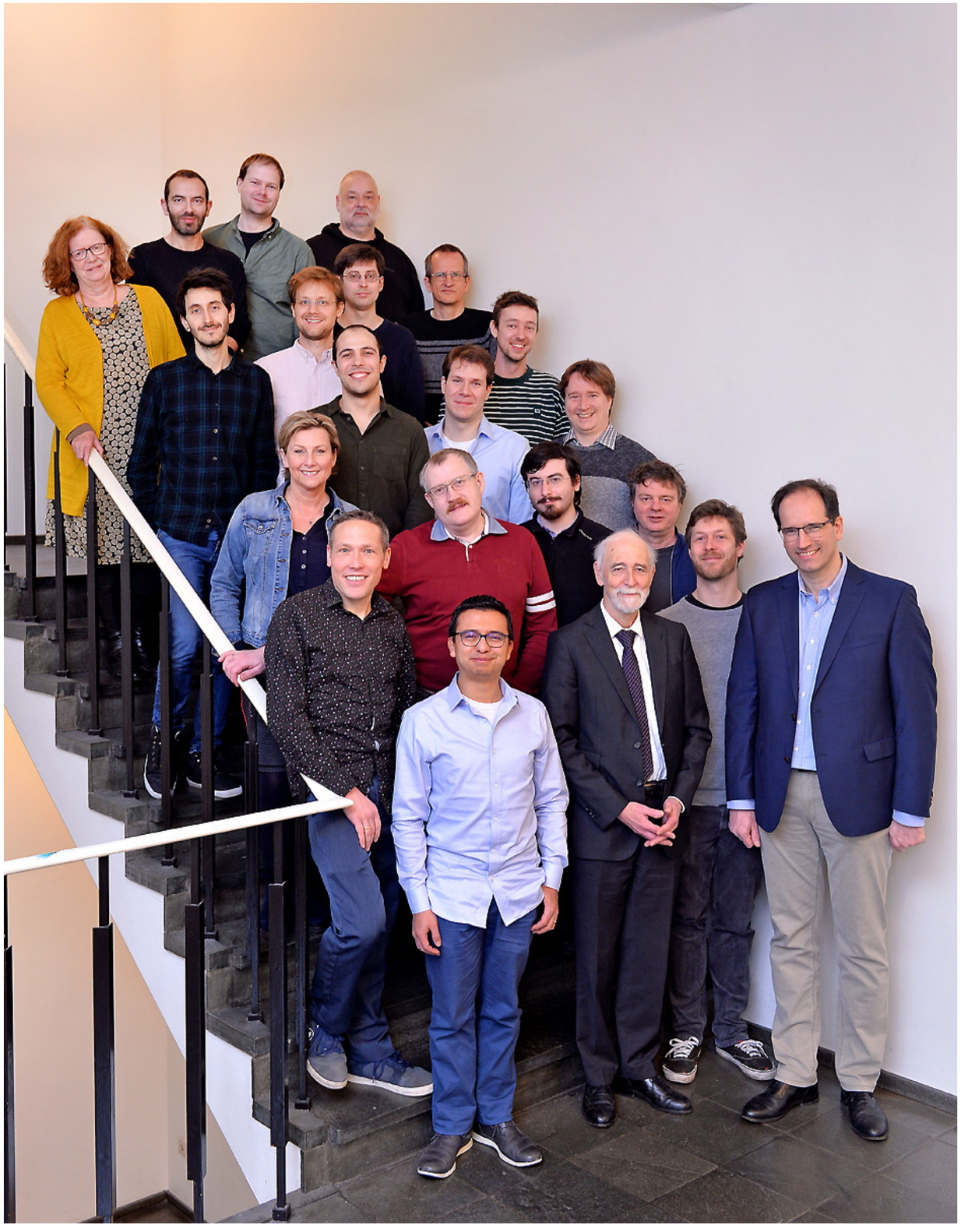
- Many academic collaborators / EU networks
  - ~160 authors
  - New functionality
  - Academia, government & industry users worldwide

- SCM: development, debug,
port, optimize, docs & <u>support</u>





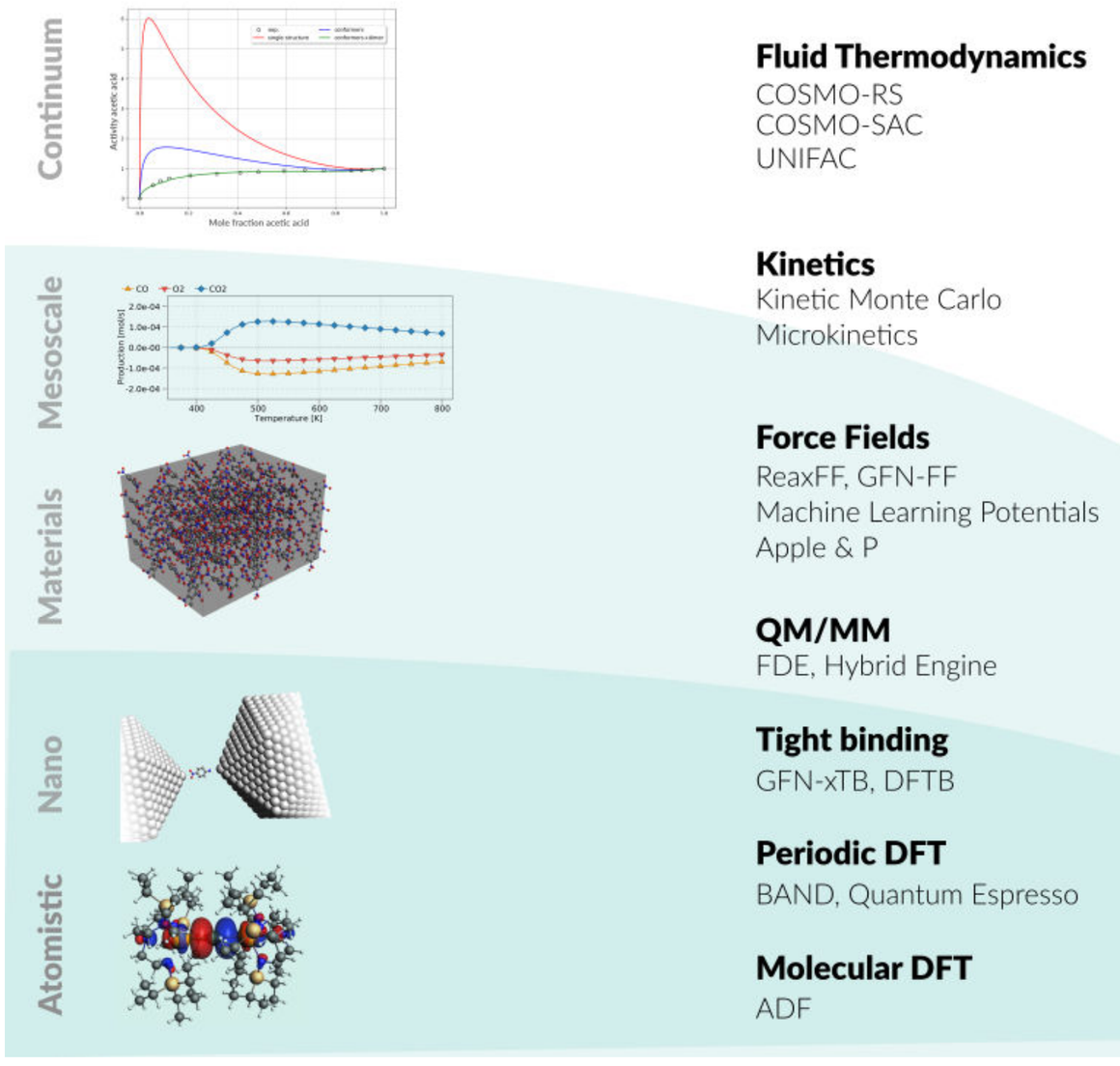
The SCM team in Amsterdam



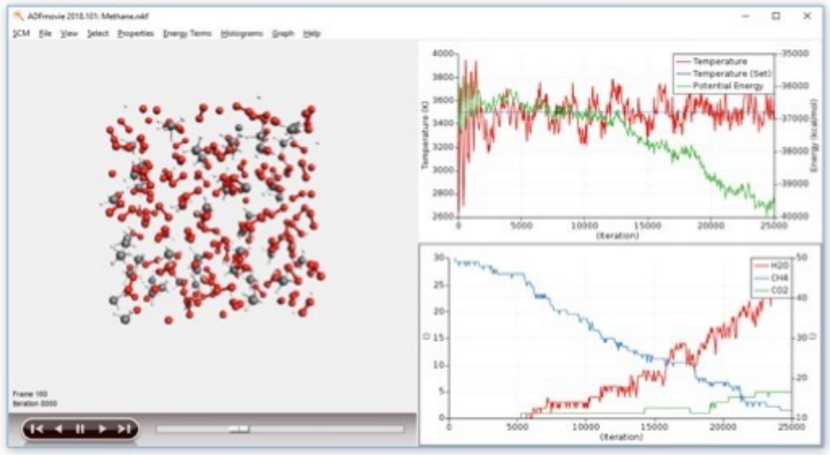
- 17 developers
- 4 support scientists
- 3 office / business
- 3 PhD students (EU)

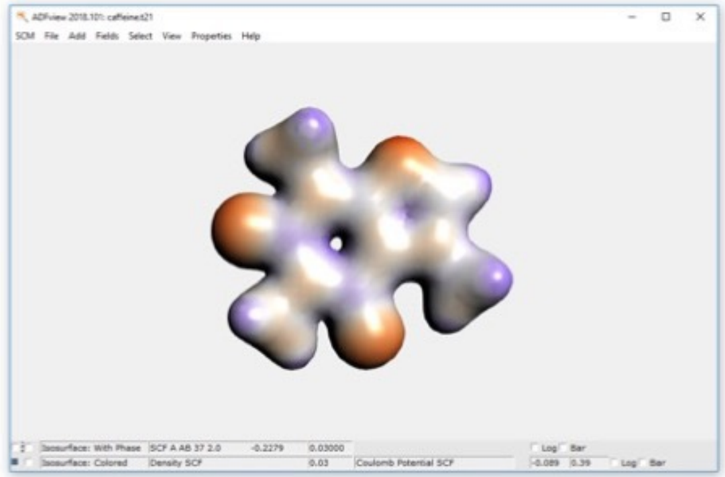
Amsterdam Modeling Suite

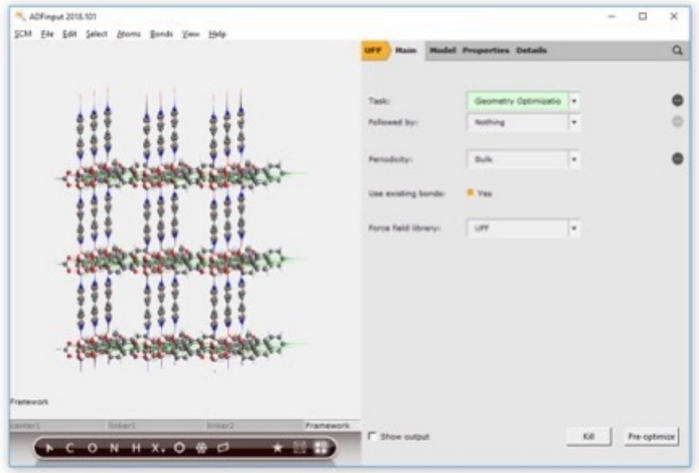
- ADF: powerful molecular DFT
  - Reactivity, spectroscopy
  - Spectroscopy: NMR, EPR, VCD, UV, XAS
- BAND: periodic DFT
  - (2D) Materials, spectroscopy, analysis
  - Interface with QE, VASP
- DFTB & MOPAC: fast electronic structure
- ReaxFF: Reactive MD
  - Dynamics of large complicated systems
- MLPotential
  - Several backends, ANI-2x, M3GNet
- COSMO-RS: fluid thermodynamics
  - VLE, LLE, logP, solubility
- AMSdriver: PES exploration, MD, MC
  - Hybrid: multi-layer, QM/MM, QM/QM'
- Integrated GUI, python scripting (workflows), ParAMS: parametrize ReaxFF & xTB

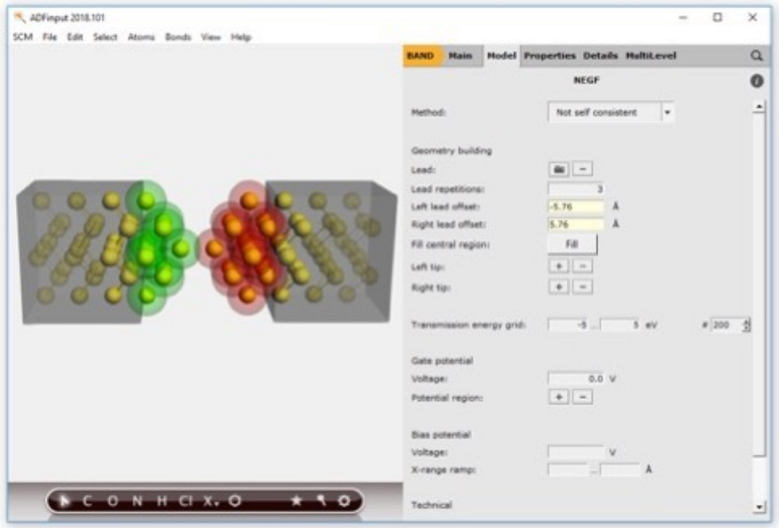


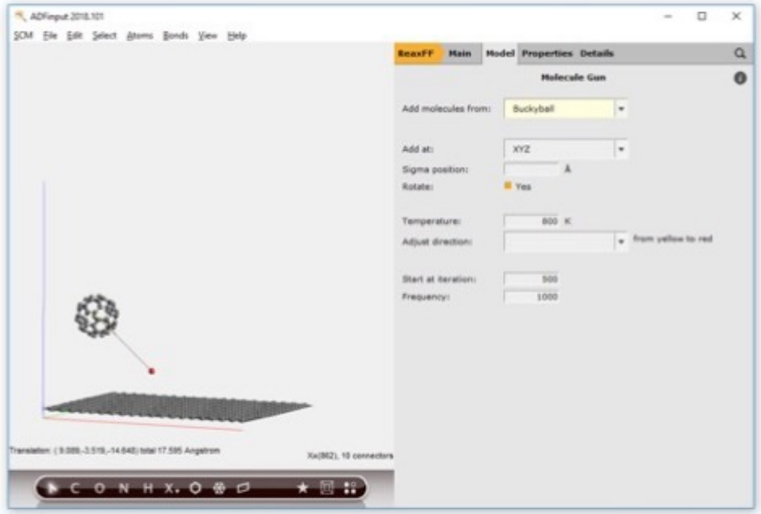
1 GUI: build, run & analyze

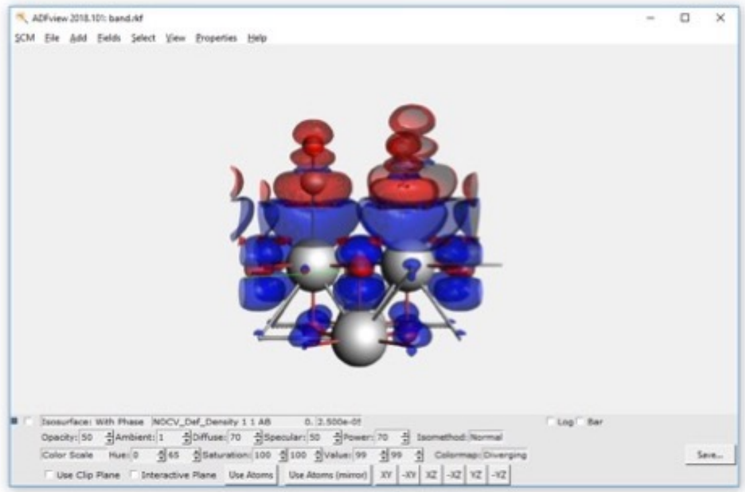


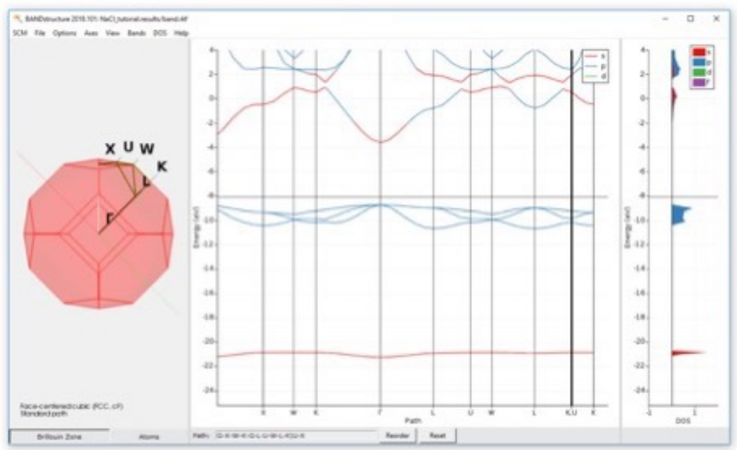


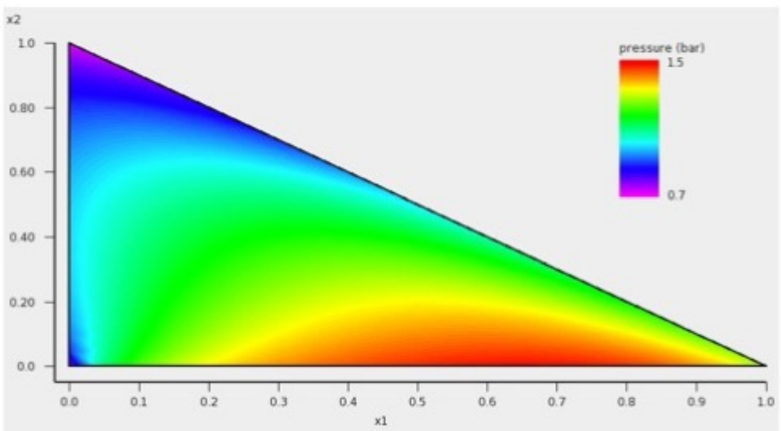


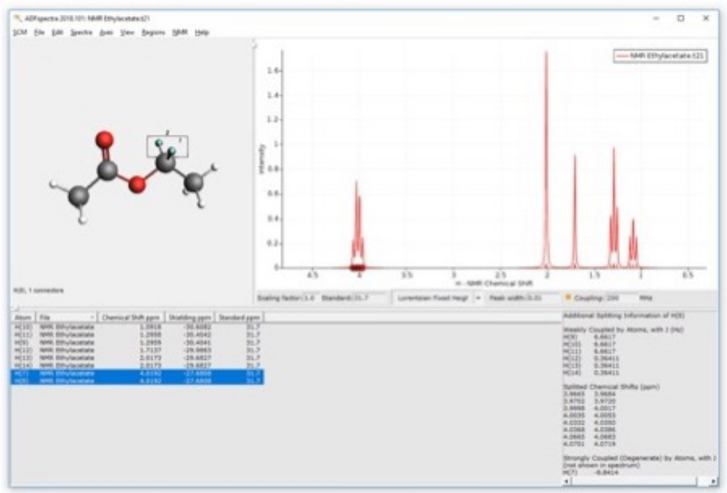






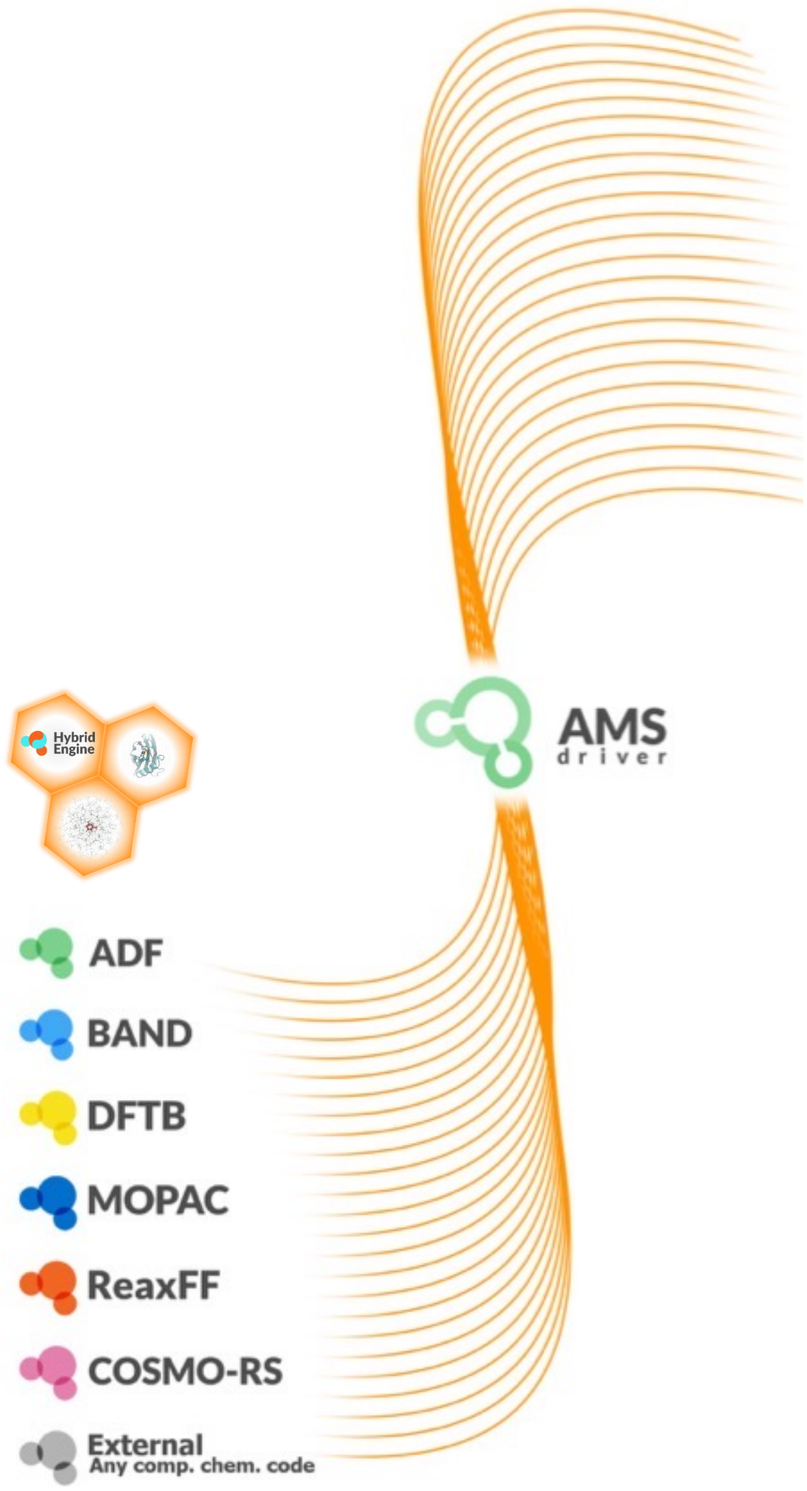


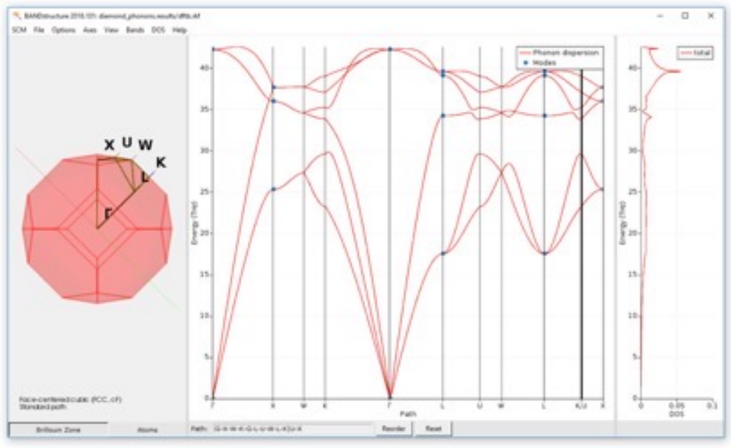


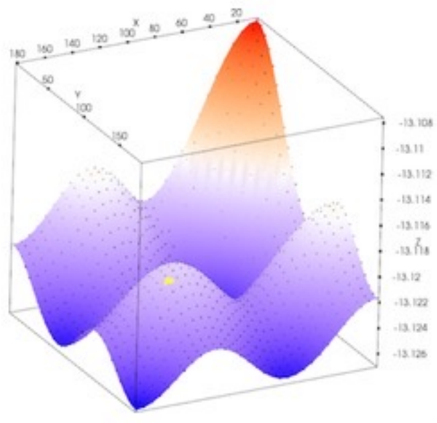


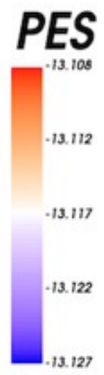
The AMS driver: decouple from Engine

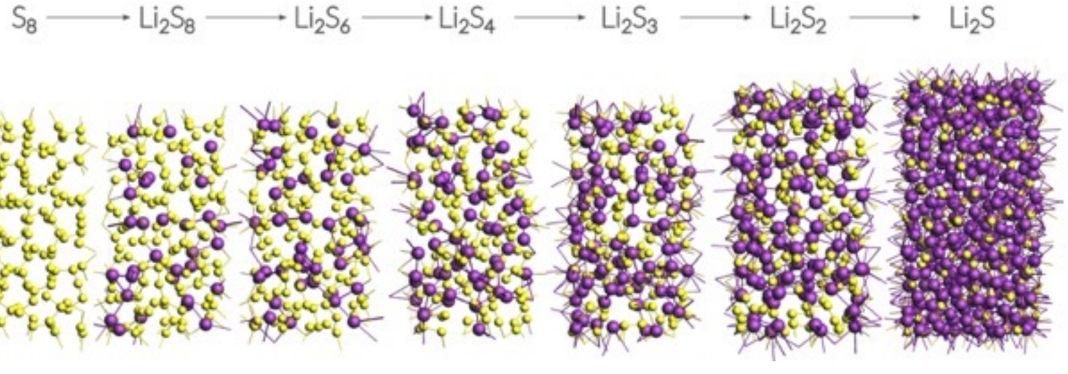
- Frequencies (+ analysis) & phonons
- Stress & elastic tensors
- Scan (multiple) coords, any periodicity
- Geometries, TS, IRC
- Advanced Molecular Dynamics
- (Grand Canonical) Monte Carlo



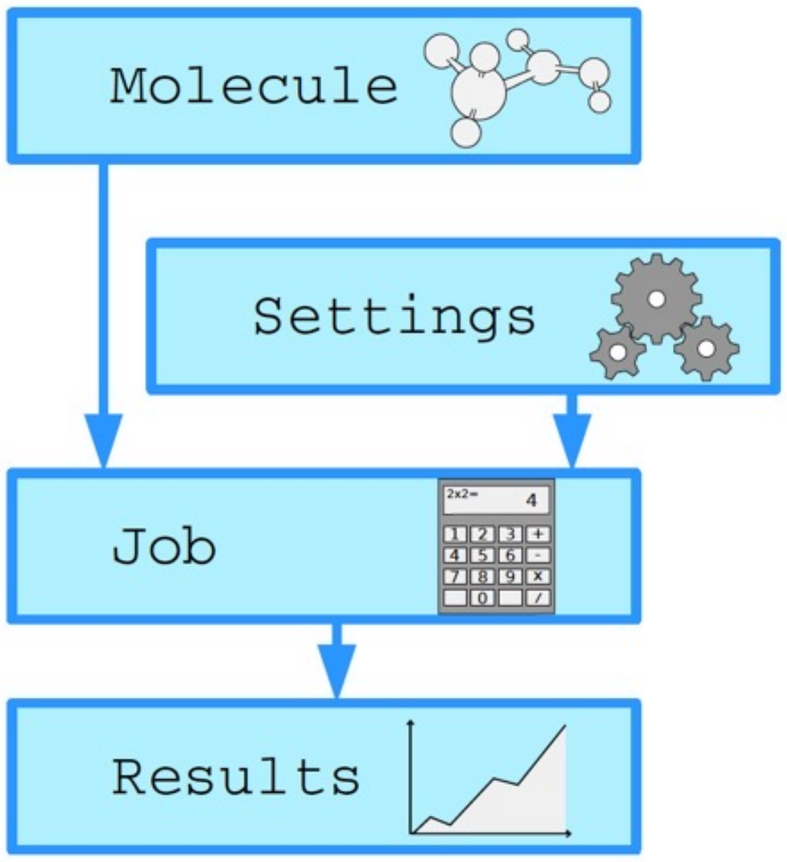


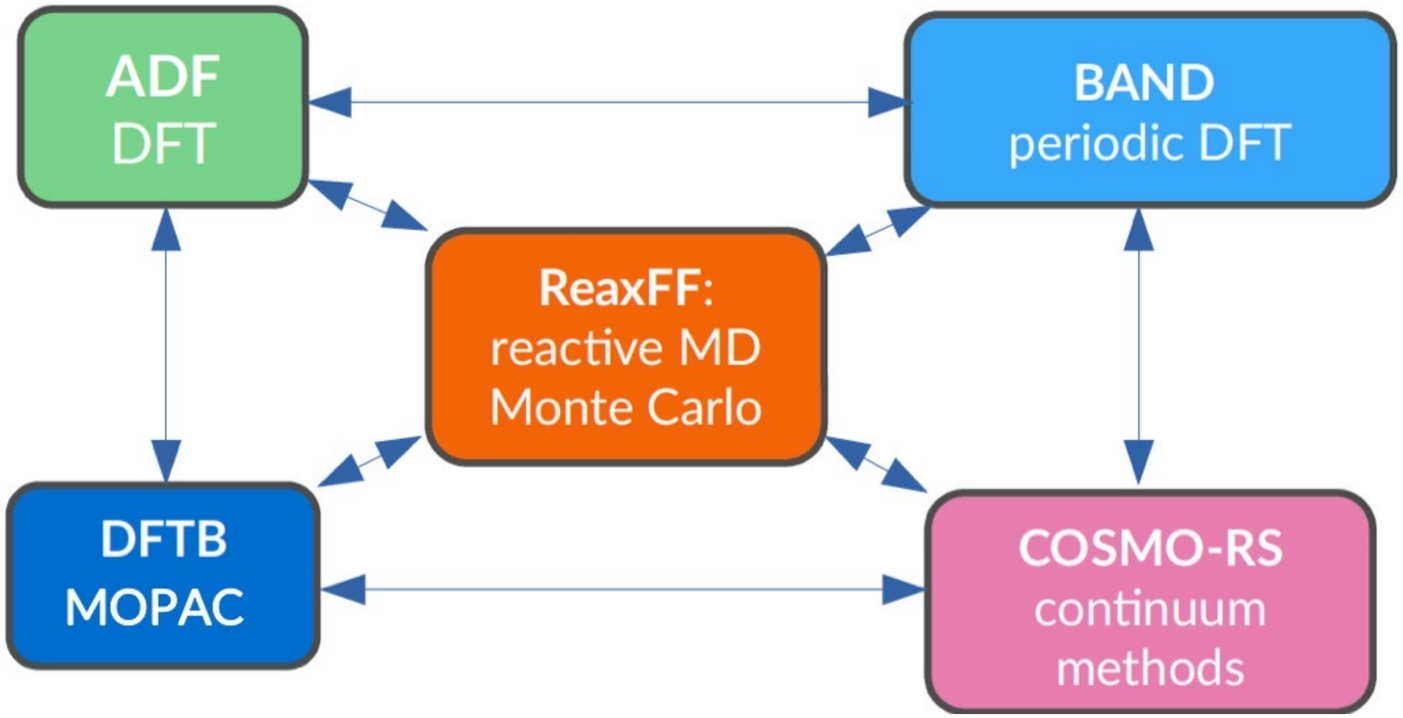






PLAMS: python scripting



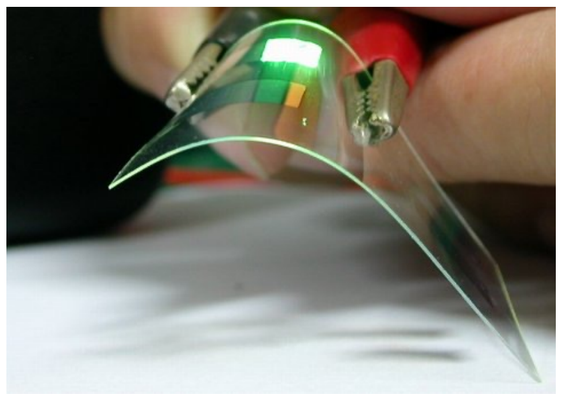


PLAMS python

Links all modules + various tools
→ workflows & screening
→ (custom) post-processing
→ rapid prototyping

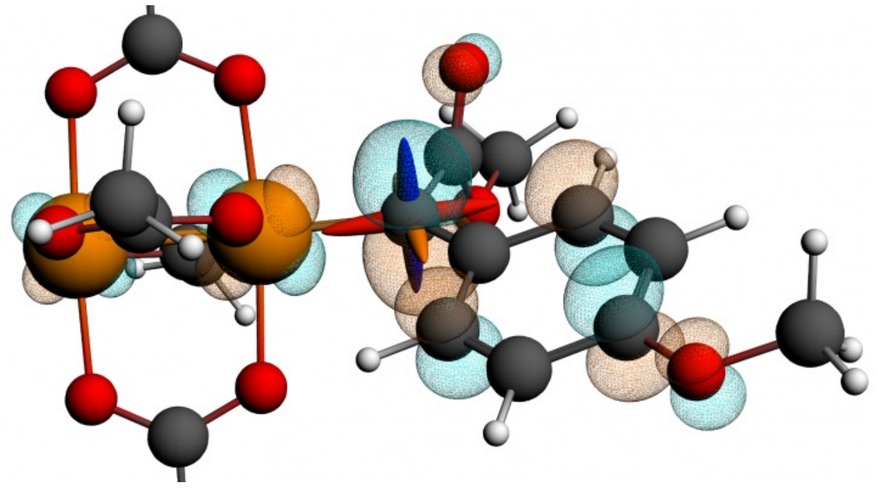
ADF: Molecular DFT

Organic electronics



Strong & unique points

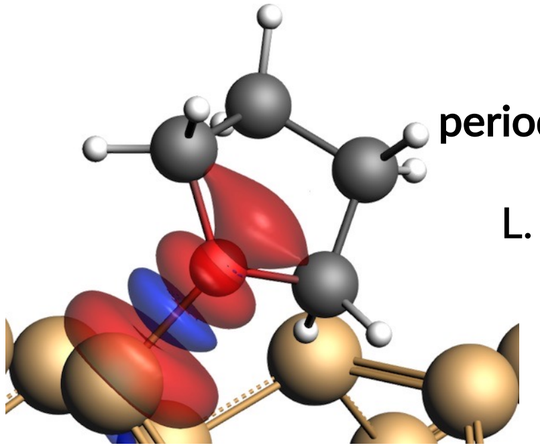
- All-electron Slaters, H-Og
- Relativity: ZORA (SR, **SOC**)
- Spectroscopy
  - EPR, NMR, IR (VCD), UVVIS, XAS
  - qsGW+BSE
  - Phosphorescence
- Bonding analysis:
  - Fragment-based approach
  - ETS-NOCV, QTAIM, MO diagrams, NCI, ...
  - Transfer integrals (charge mobility)
- Environments
  - Subsystem DFT (FDE), DIM/QM, QM/MM, QM/FQ, 3D-RISM, COSMO, SM12



NMR calculations locate ^{13}C di-Rh carbene catalyst intermediate, Science, **342**, 351 (2013)

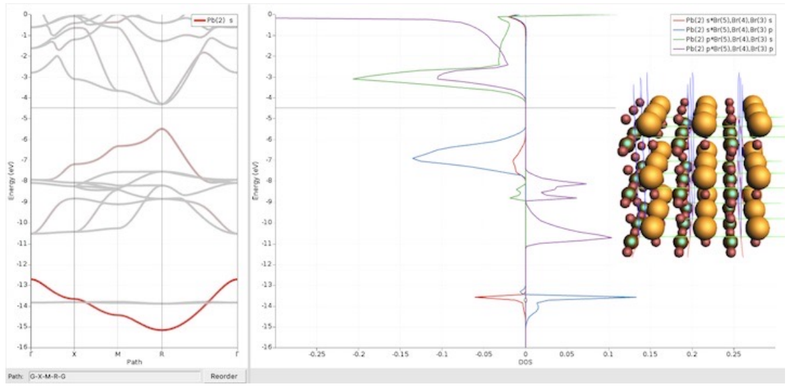
Periodic DFT: BAND vs Plane Waves

- Atom centered basis functions, STO or NAO
  - Compare cluster with periodic
  - No pseudopotentials, all elements
  - Core spectroscopy (core holes)
  - Easy orbital **analysis:** pDOS, COOP, EDA
  - Fast for empty (1D, 2D, porous)
  - xc: r2SCAN, MN15-L, HSE06, GLLB-sc, D3(BJ), D4, DFT-1/2
  - Self-consistent NEGF
    - Gate & bias potential
    - Spin transport



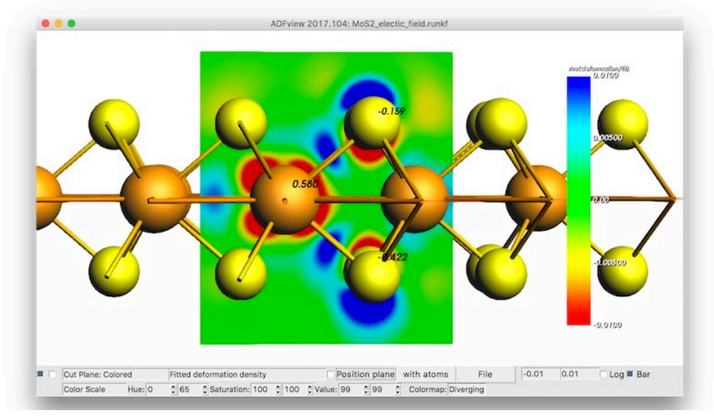
periodic energy decomposition analysis (tutorial)
L. Pecher and R. Tonner
WIREs CMS, (2018)

- True 2D surfaces, 1D polymers
  - Het. catalysis: polarization, COSMO, SM12
  - 2D electronics (homogeneous E field)
  - Nanotubes
  - QM/MM and QM/QM' for 2D



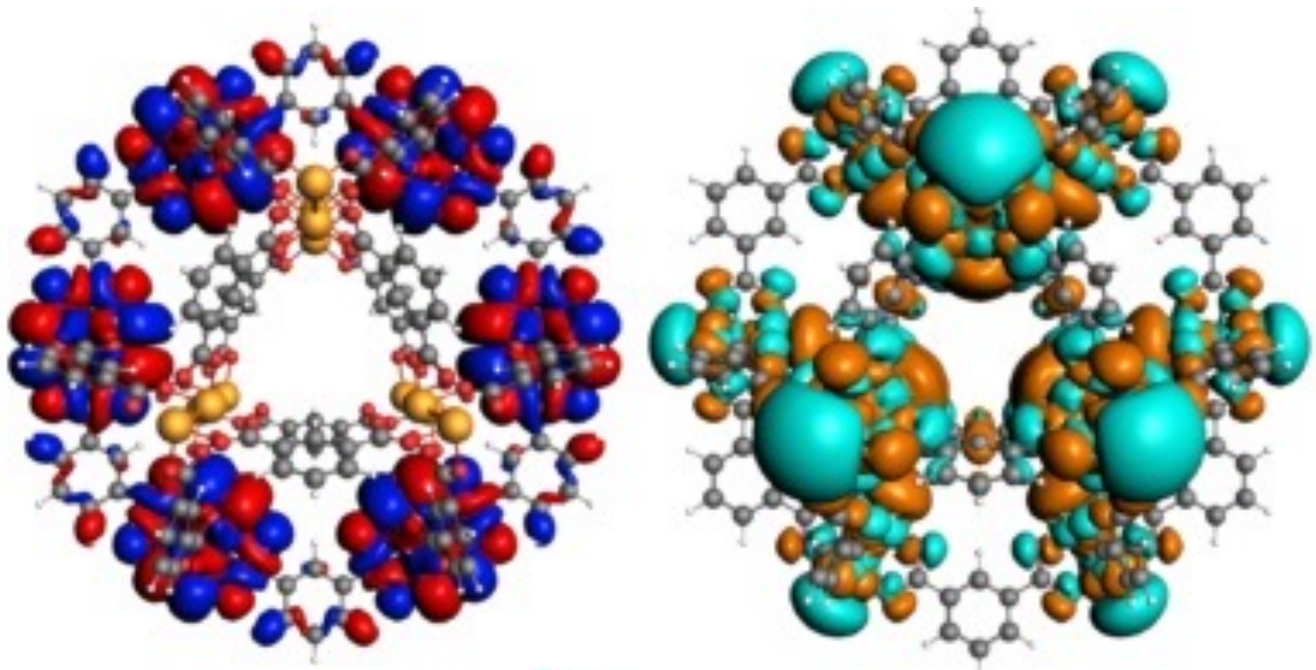
COOP in perovskites (tutorial)
Goesten & Hoffmann
JACS (2018)

- Integrated Graphical Interface:
  - Easy set up & analysis
  - Switch: ADF, BAND & Quantum Espresso, VASP



Polarizing 2D semiconductor (tutorial)
N. Zibouche et al.
PCCP (2014)

DFTB: ‘fast DFT’ for molecules & periodic



Approximated DFT

- Nearest neighbor & minimal basis
- Tabulated elec & rep. parameters:
  - Grimme GFN-xTB (Z = 1-86)
  - QuasiNaNo & DFTB.org

Capabilities & Features

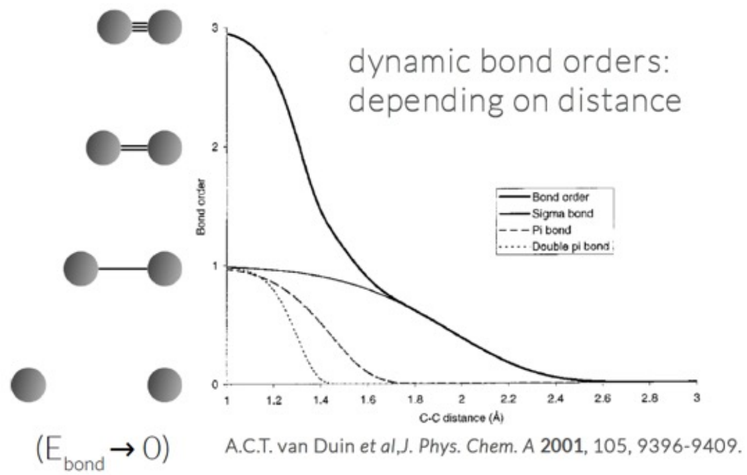
- UV/VIS (fast!)
- MOs, band structures, DOS

Through AMS

- Geometries, frequencies, phonons
- Stress tensors (optimize under p)
- Advanced MD, PES scans
- GCMC, molecule gun
- Multi-layer, QM/MM, QM/QM’
- Reparametrize xTB

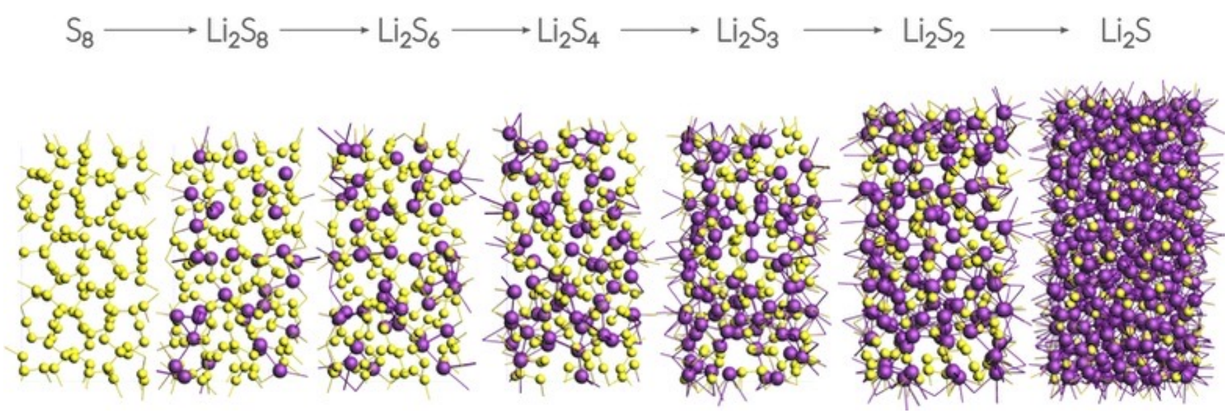
ReaxFF – reactive molecular dynamics

- No discontinuities in energy or forces
- No pre-defined reaction sites or types
  - Dynamic bond orders, charge equilibration
  - Only 1 atom type per element

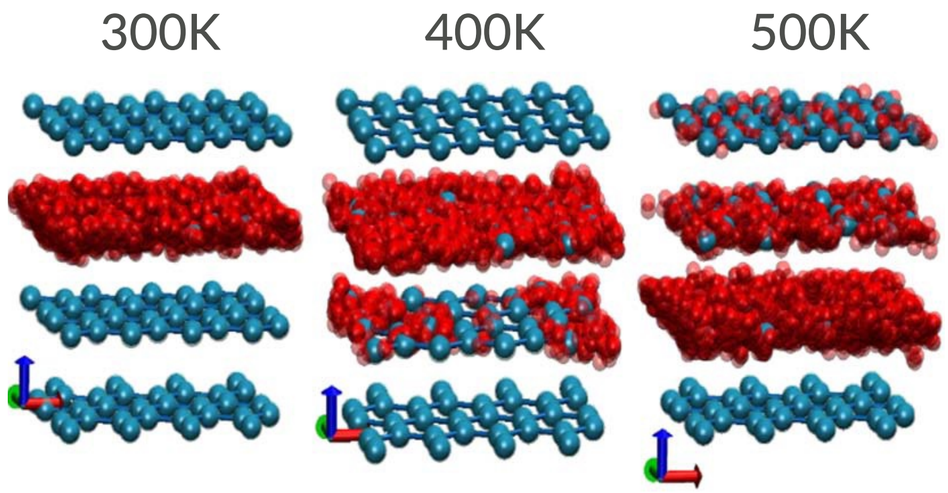


$(E_{bond} \rightarrow 0)$ A.C.T. van Duin *et al*,*J. Phys. Chem. A* **2001**, 105, 9396-9409.

$$E_{system} = E_{bond} + E_{lp} + E_{over} + E_{under} + E_{val} + E_{pen} + E_{coa} + E_{C_2} + E_{tors} + E_{conj} + E_{H-bond} + E_{vdWaals} + E_{Coulomb}$$



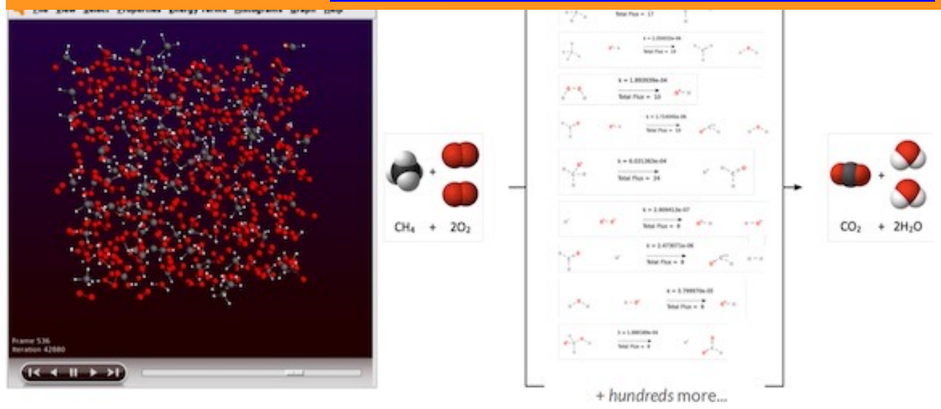
Li battery discharge: J. Electrochem. Soc. **161**, E3009 (2014); PCCP, **17**, 3383 (2015), tutorial



eReaxFF to study electron mobility & Li ion reduction, explicit electrons & electric field, *J. Electrochem. Soc.* **169** ,110540 (2022)

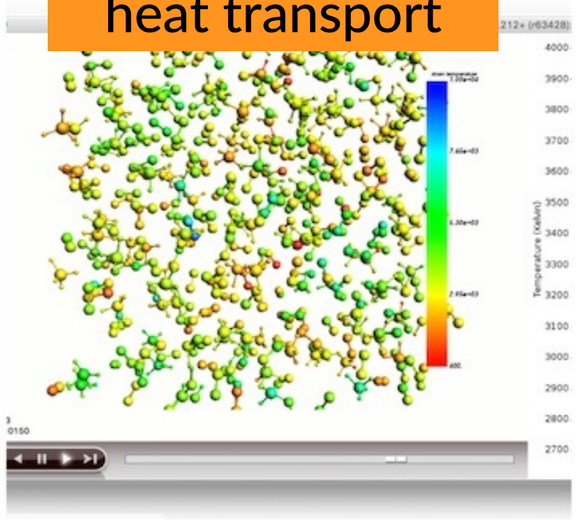
Reactive MD tools Amsterdam Modeling Suite

ChemTraYzer: Automated rates & pathways
New: Analyze surface reactions

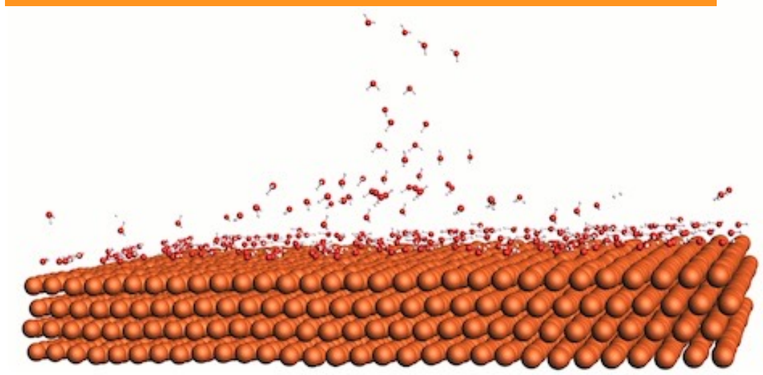


Tools += complete reaction networks
elementary reactions, rate constants, fluxes, timeline

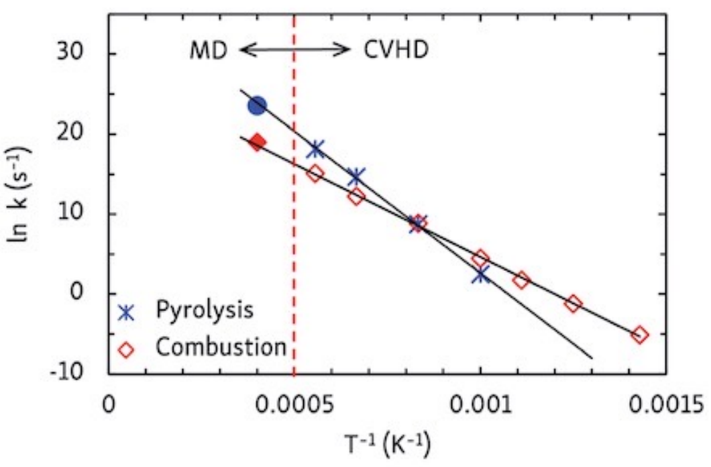
T-NEMD, local T:
heat transport

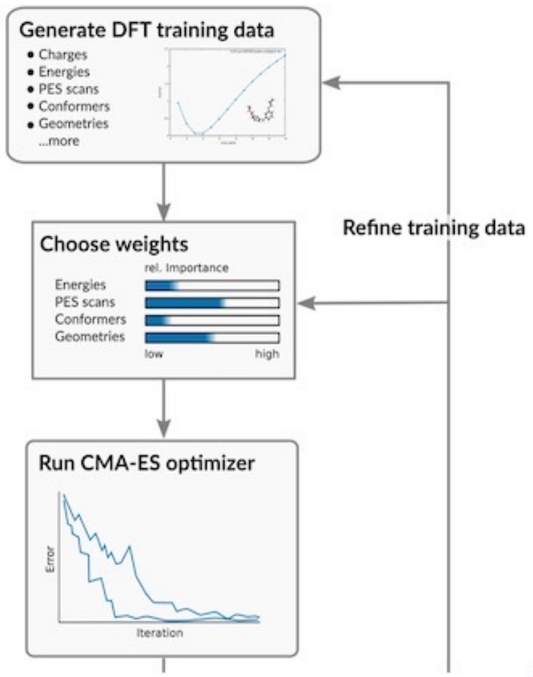


Molecule gun: depositing molecules on surfaces



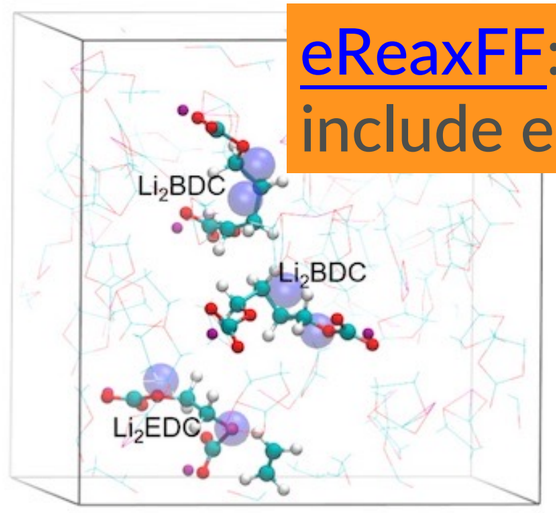
fbMC, CVHD, PRD:
speed up kinetics

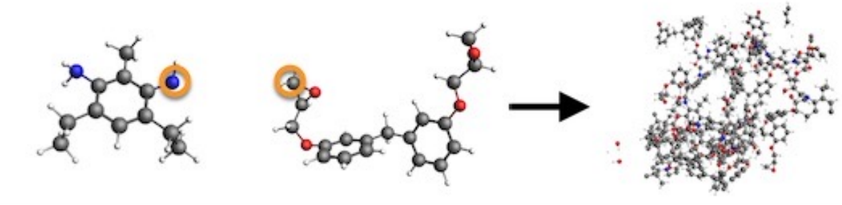




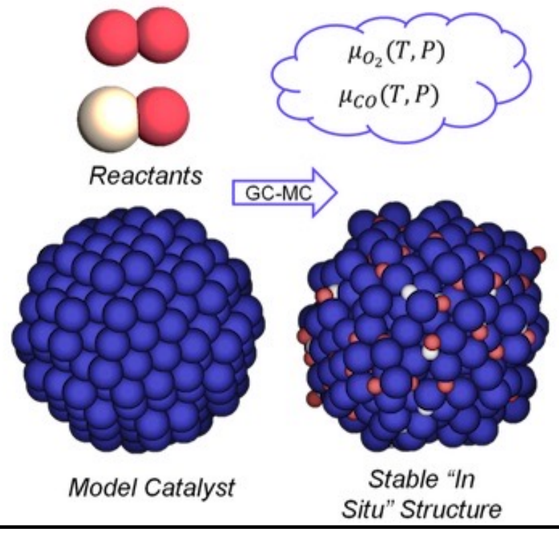
ParAMS - easy ReaxFF & DFTB (re)parameterization

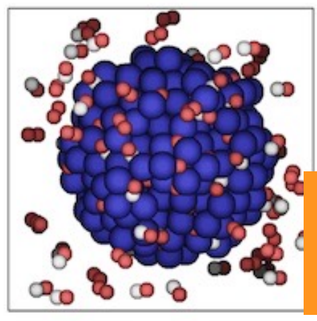
eReaxFF: include e-





bond boost
build polymers

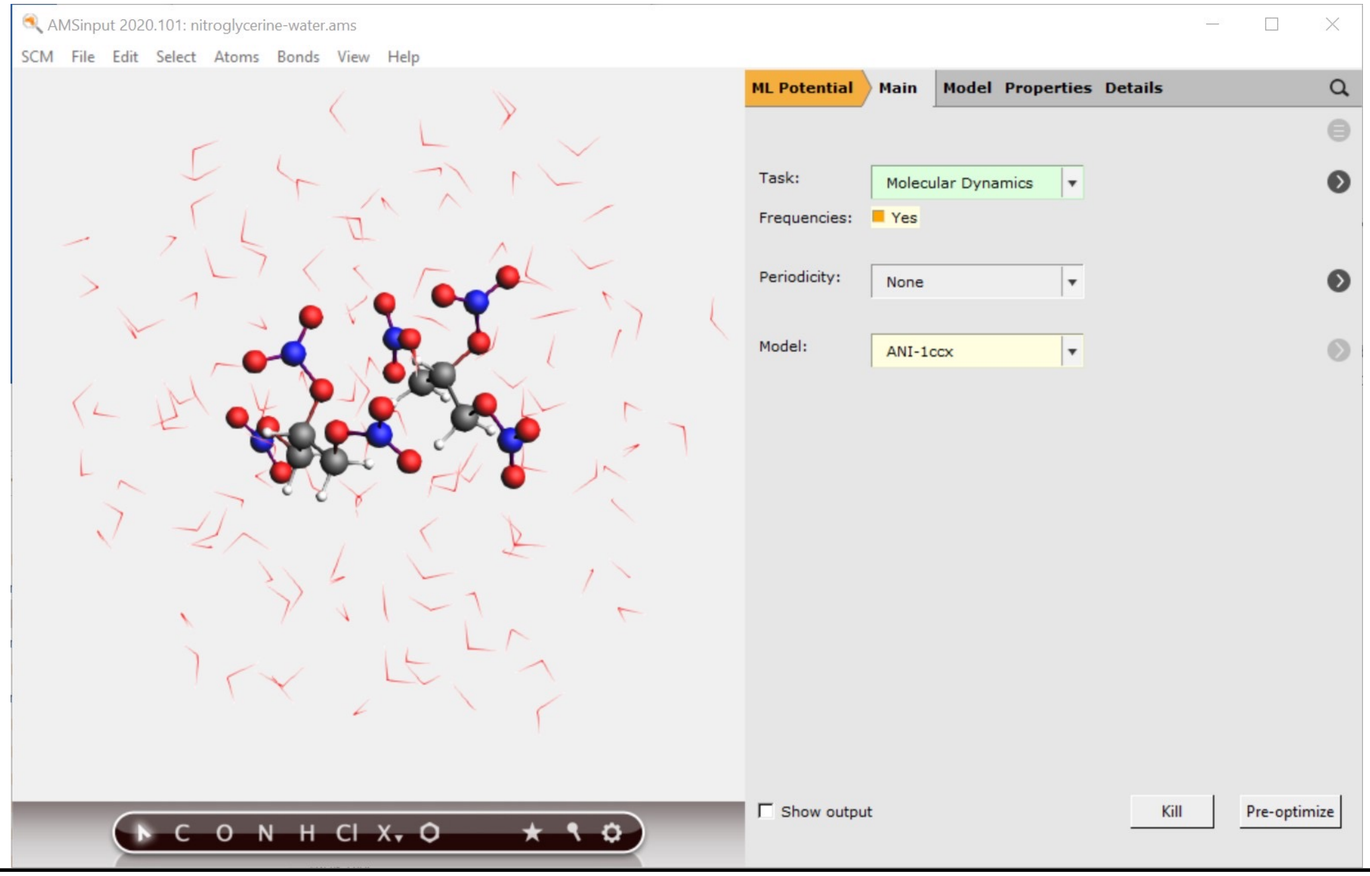




GCMC: speed up thermo

Machine Learned Potentials

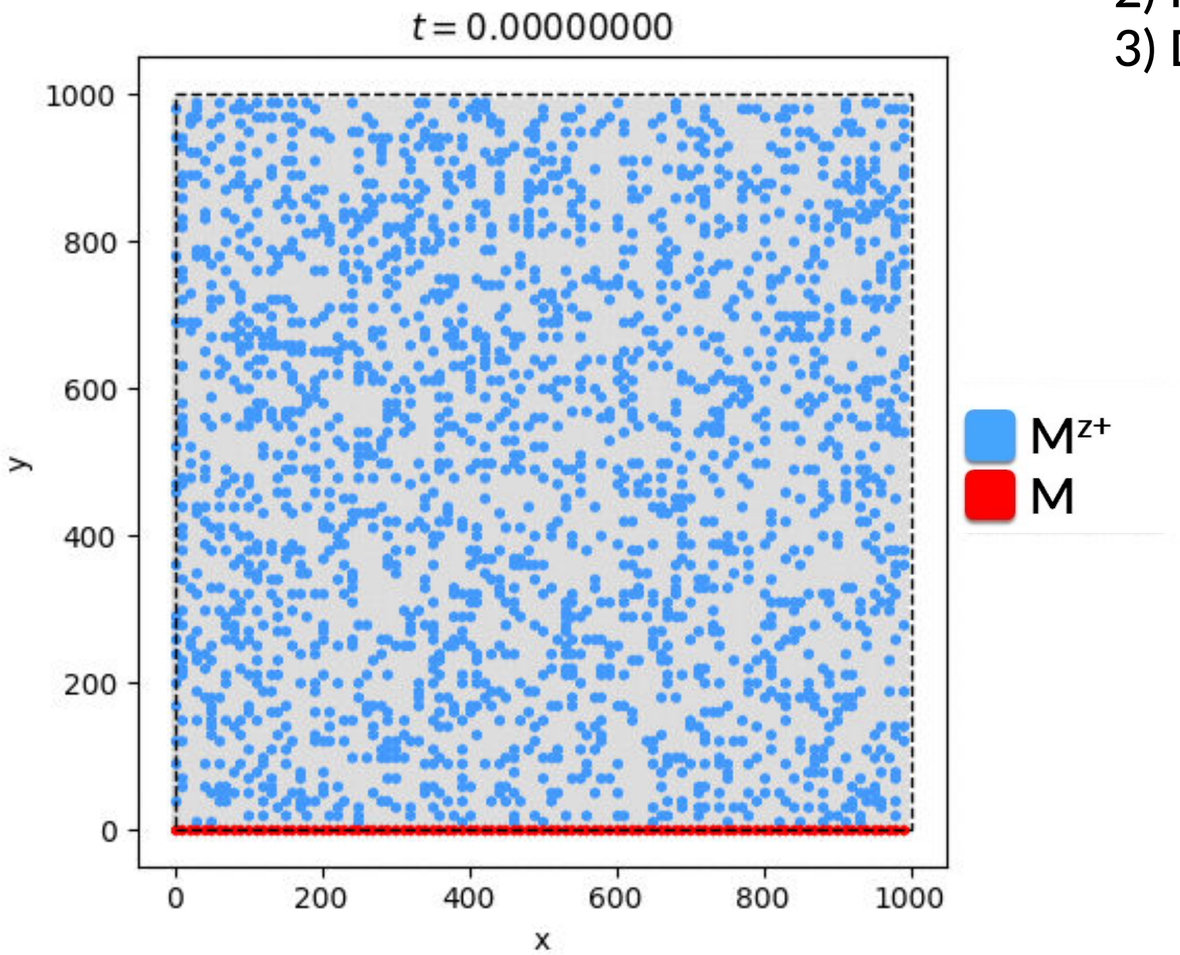
- Use machine learning potentials with AMS driver
  - PES scans, conformers, MD, reaction energies, …
  - Also with Hybrid engine (multi-layer)
- Automatically install popular ML Backends
  - SchNetPack, sGDML, PiNN, TorchANI
  - Pre-parametrized neural network potentials ANI-1ccx, ANI-2x, M3GNet-UP(2022)
  - CUDA-enabled PyTorch and Tensorflow can be used



Demo video

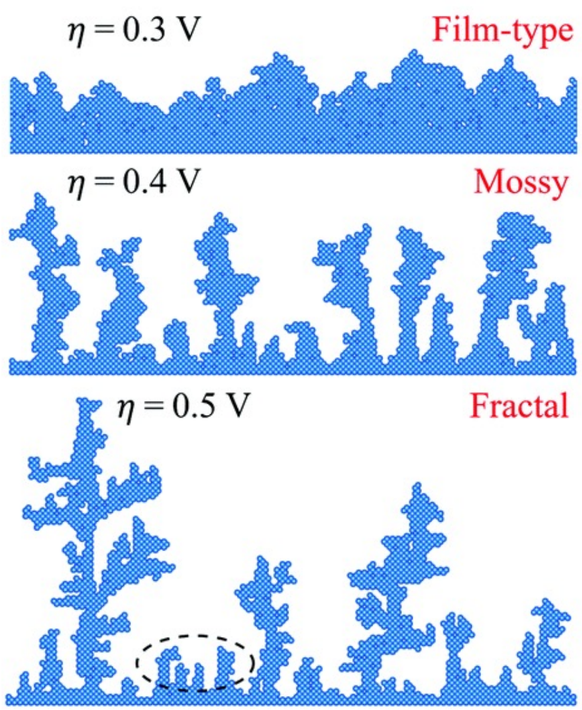
Kinetic Monte Carlo: SEI dendrite formation

Modified (py)Zacros kMC to study dendrite formation

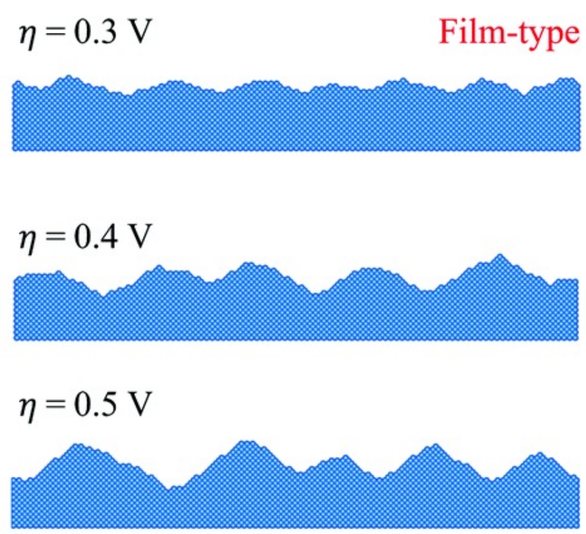


3 Processes (rates can be computed with AMS):
1) Metal ion (M^{z+}) transport across electrolyte
2) Reduction at the solid-electrolyte interface (M^{z+}->M)
3) Diffusion of the metal (M) over the electrode surface

no step diffusion



no terrace diffusion



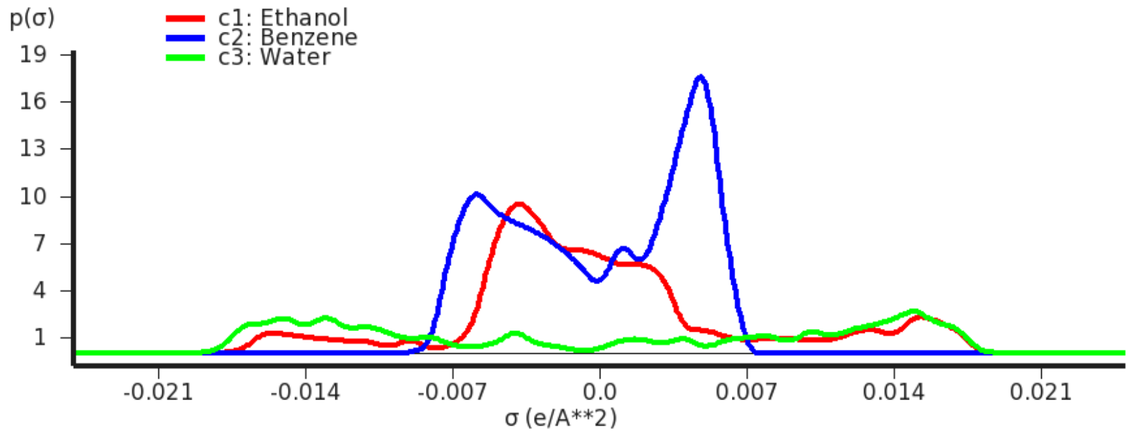
Inspired by **Surface diffusion manifestation in electrodeposition of metal anodes,** PCCP 2020 (22), 11286

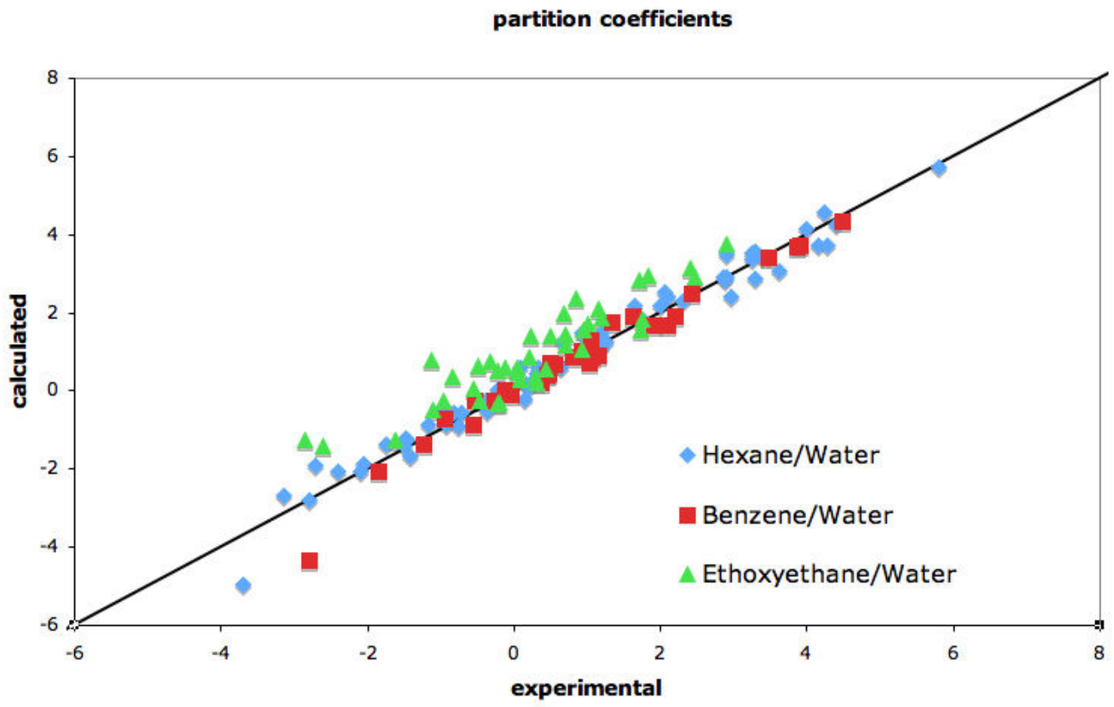
COSMO-RS/SAC: thermodynamic properties of fluids

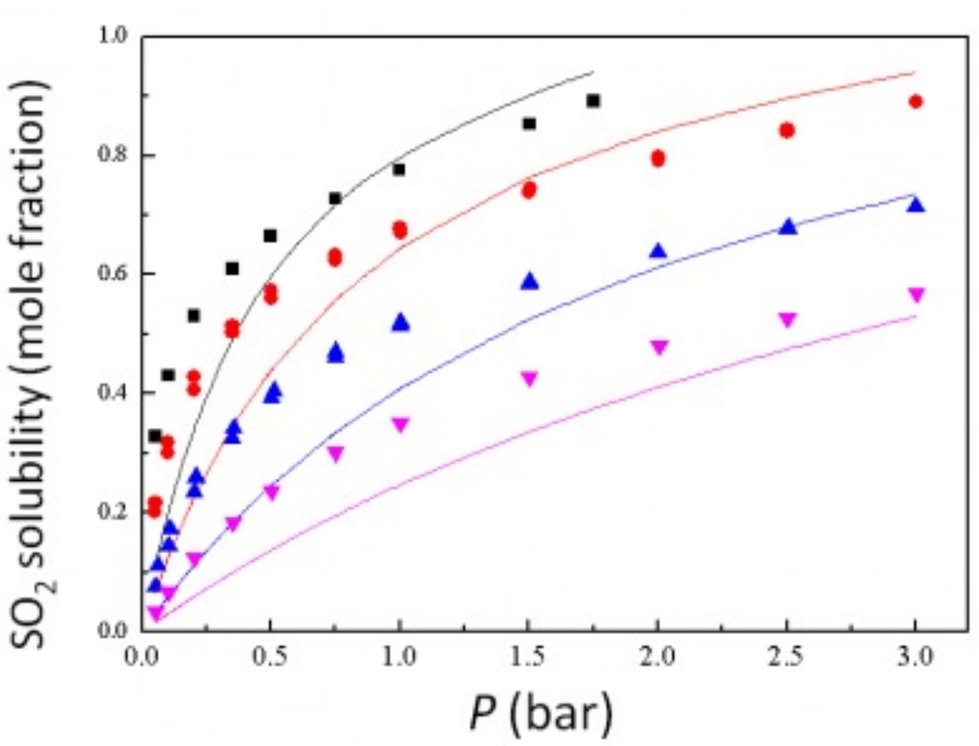
Quantum Chemistry & QSPR for quick property predictions

COntinuum Solvation MOdel + RS (Klamt), SAC (Sandler)
chemical potential => activity coefficients => instantaneous properties

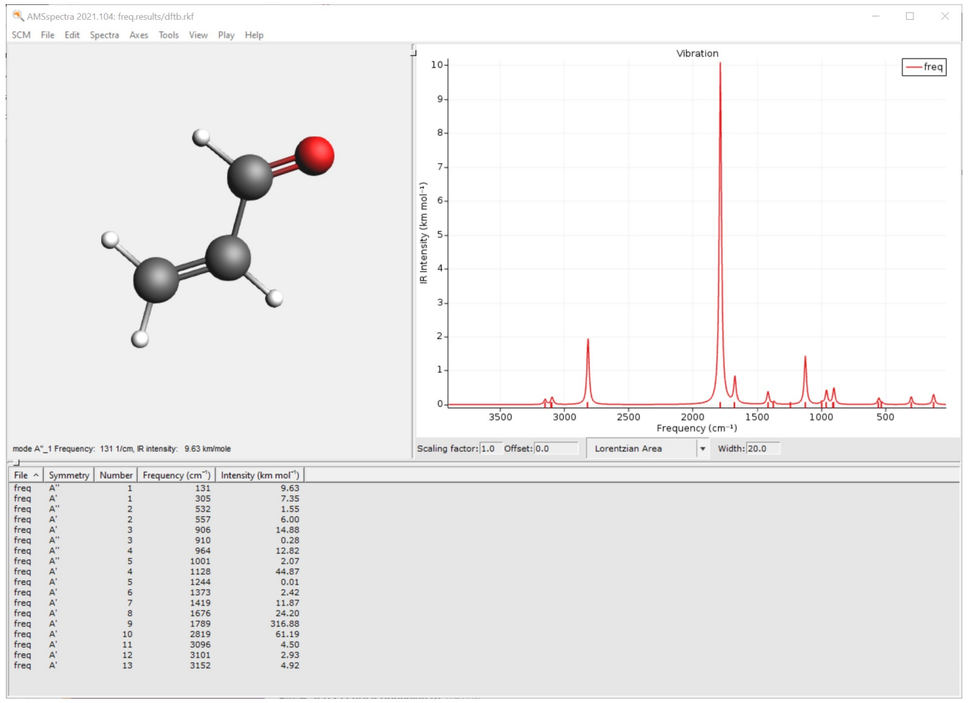
- Solvation & excess energies, pKa
- Solubilities, LLE, VLE, boiling points
- Optimize mixtures: solubility, LLE
- Polymers: Flory-Huggins X

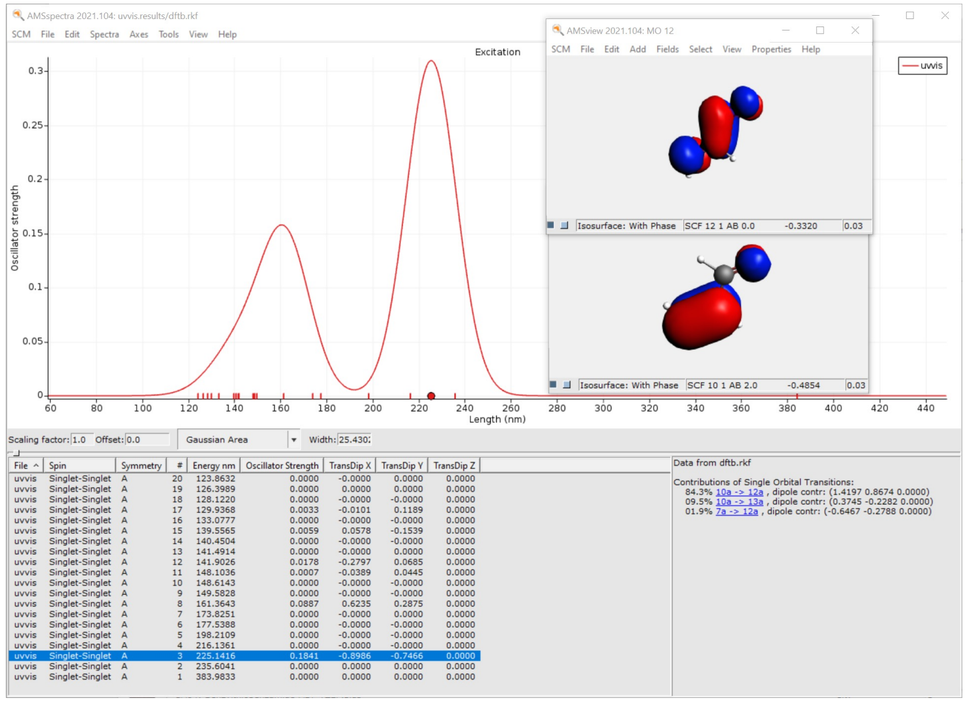


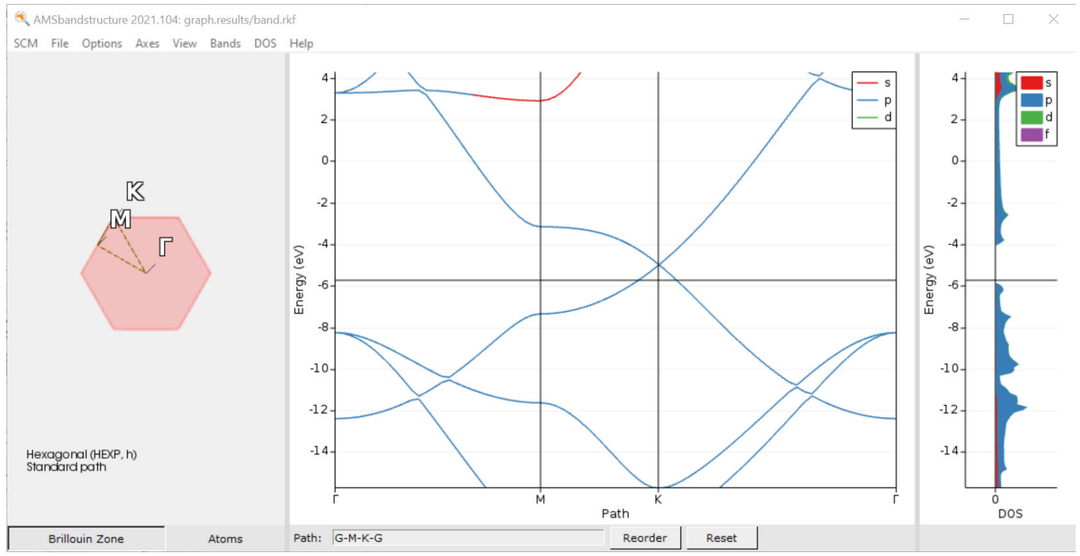


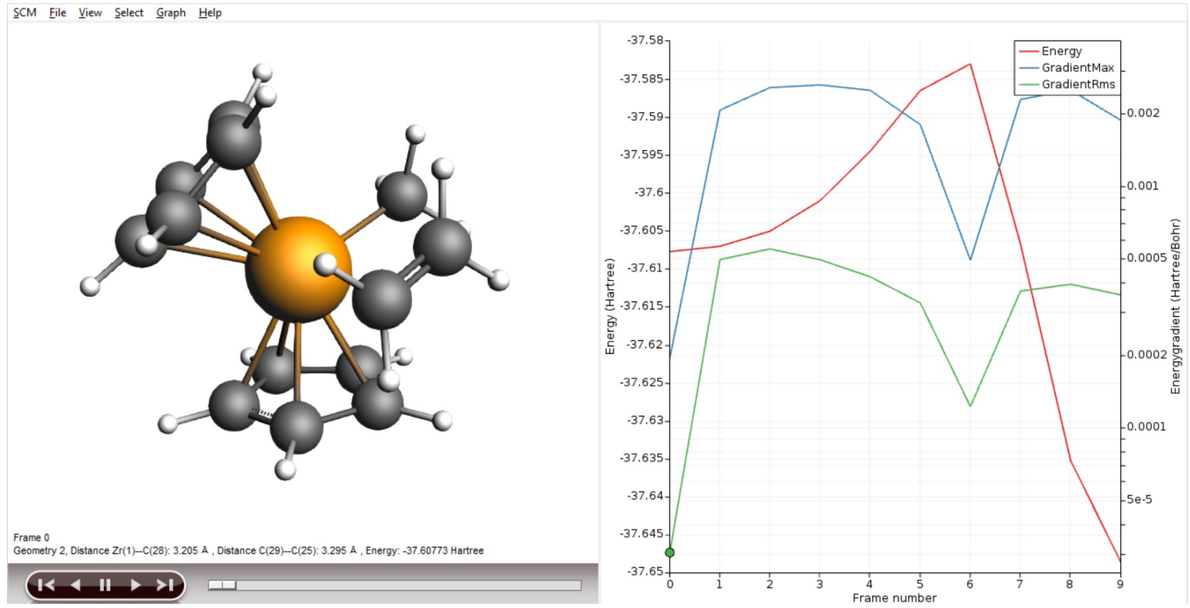


Hands on + self-learning





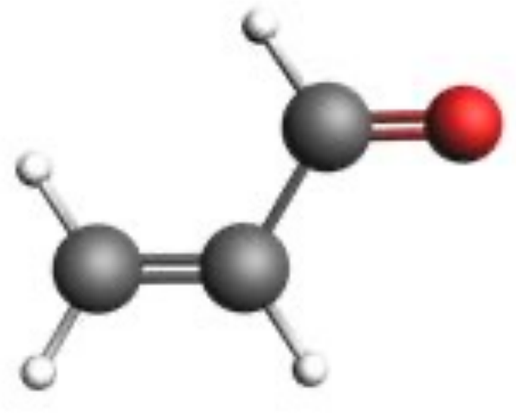




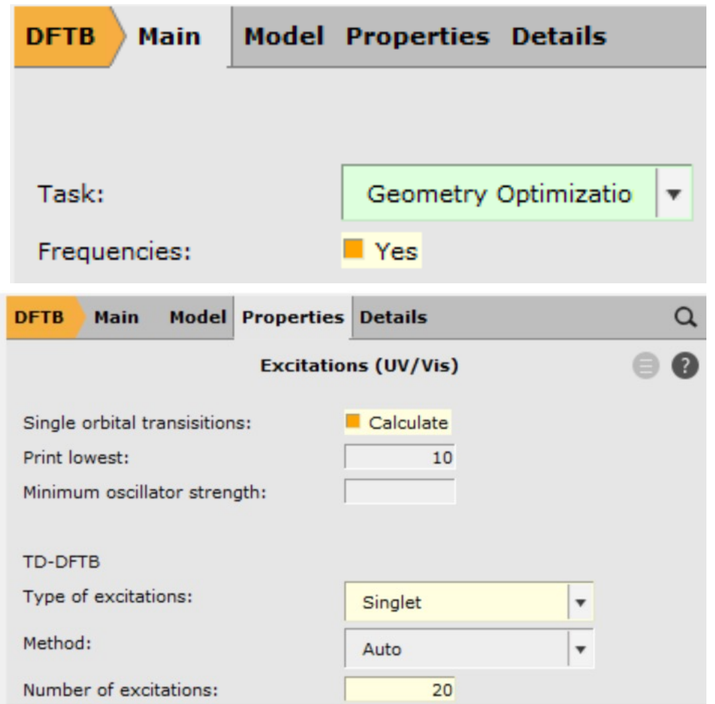
Building molecules, spectra

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

- Search molecules
- Import: InChI, SMILES, xyz, cif, pdb, …
- Included library + building



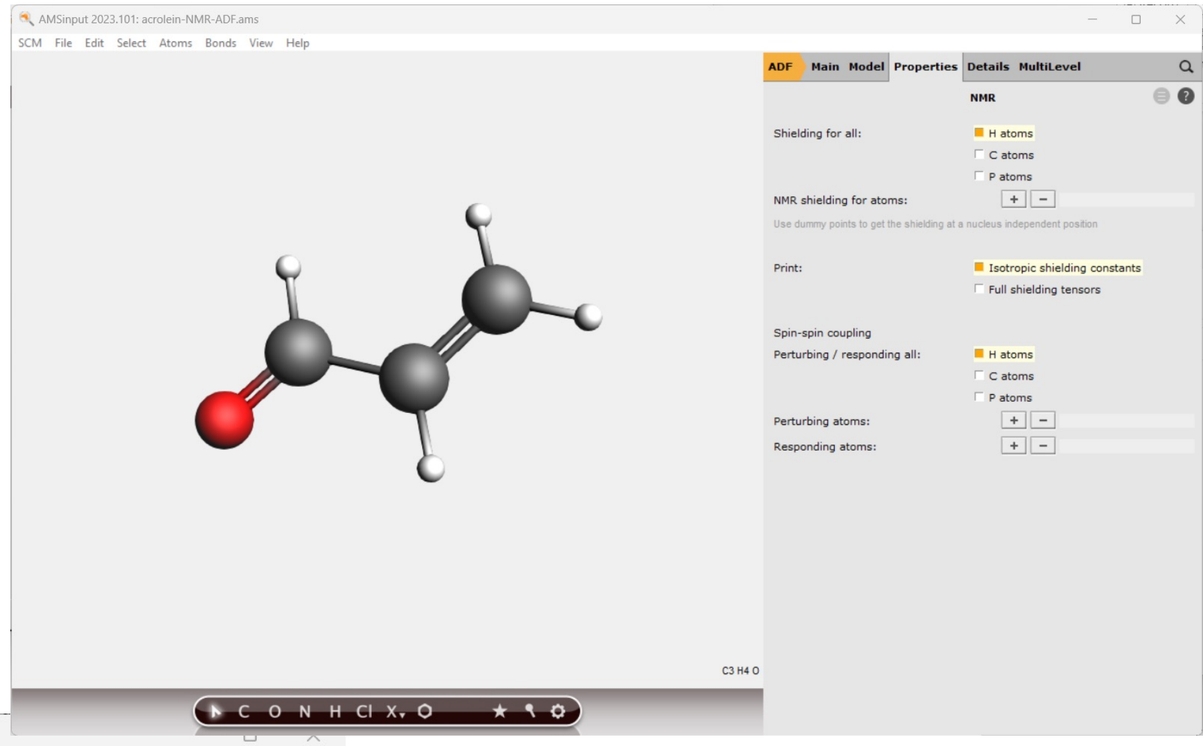
- IR frequencies (tutorial)
  - Geometry needs to be optimized at same level as frequency calc.
  - Try ADF, DFTB, MOPAC, MLPot, …
  - SCM -> Spectra
- UV/VIS FAQ for tips + links to tutorials
  - ADF: (s)TDDFT, (s)TDA, TD-DFT+TB
  - Visualize MOs Single Orbital Transition (ADF: also NTOs)
  - Compare to NIST (IR), NIST (UV/VIS)

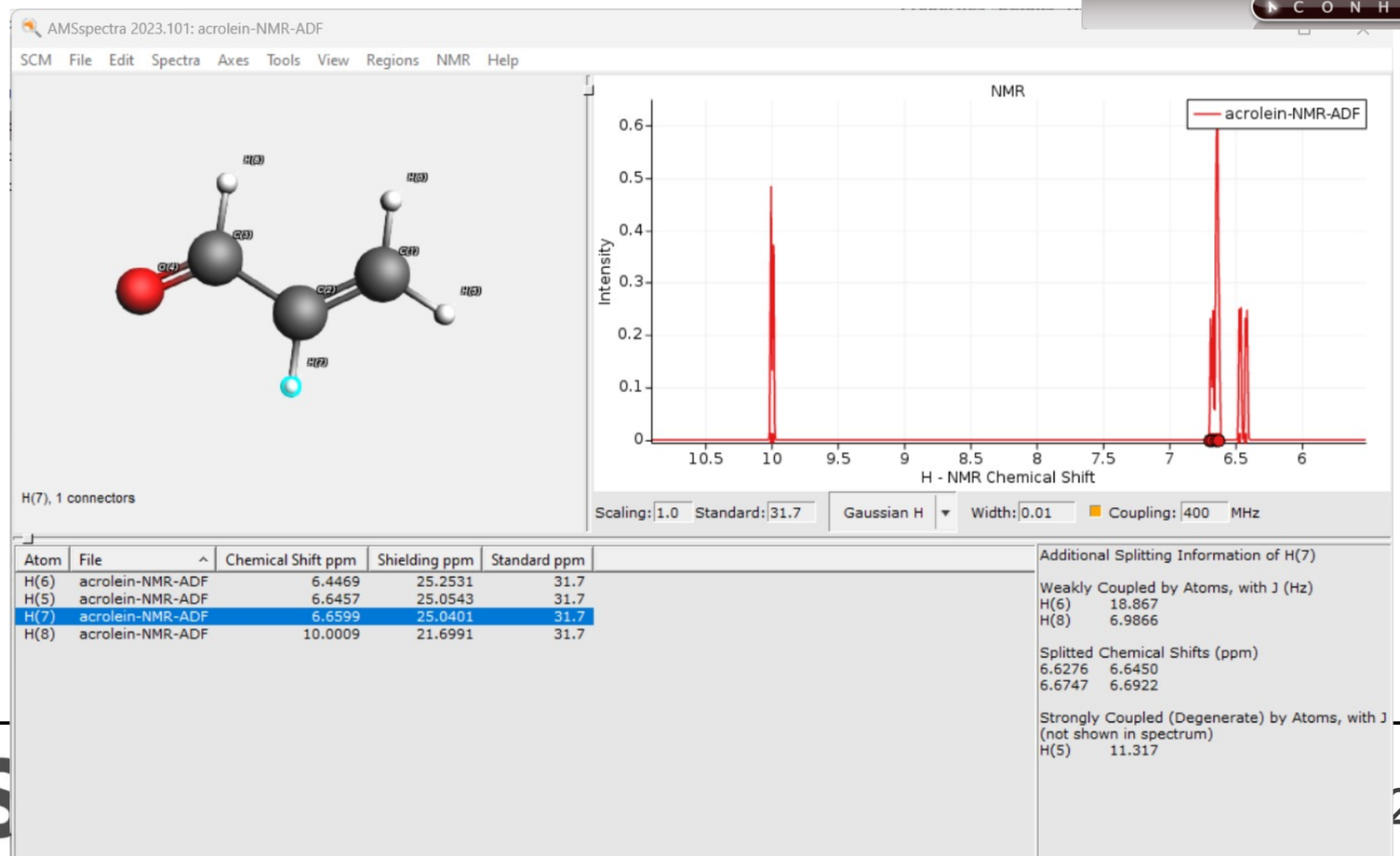


Spectra: NMR

- Exercise:
  - See also NMR FAQ for tips + advanced tutorials
  - Use PBE0 + TZP, Scalar, no core
  - 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





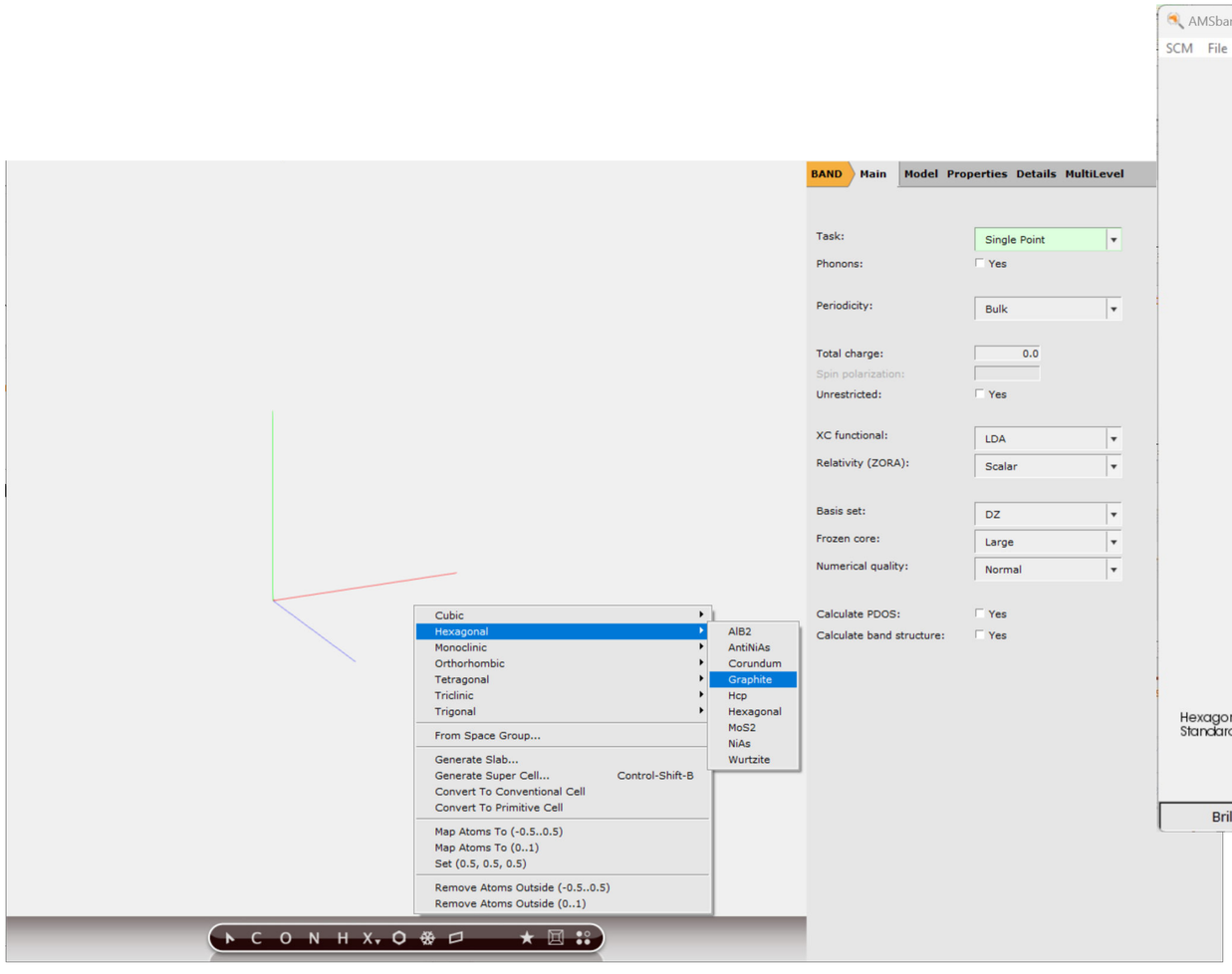
Quick thermodynamic properties

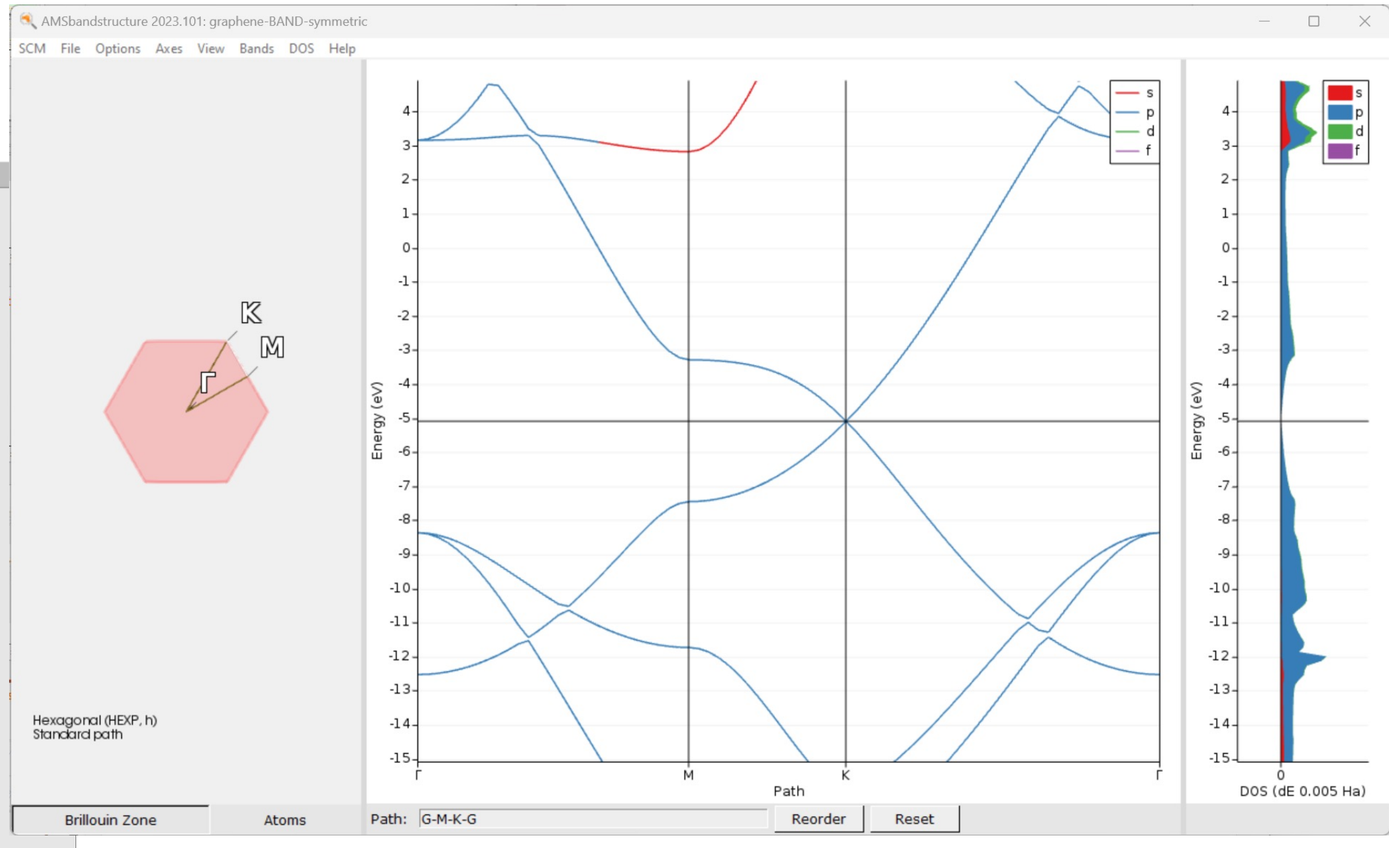
- Open SCM -> COSMO-RS (no need to install database)
- In the SMILES input, put C=CC=O and Add
- Properties -> Pure compound
- Compare some properties (density, boiling point, flash point) (e.g. Wikipedia)
- Try COSMO-RS Properties -> Boiling point pure compound

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	$Å^3$

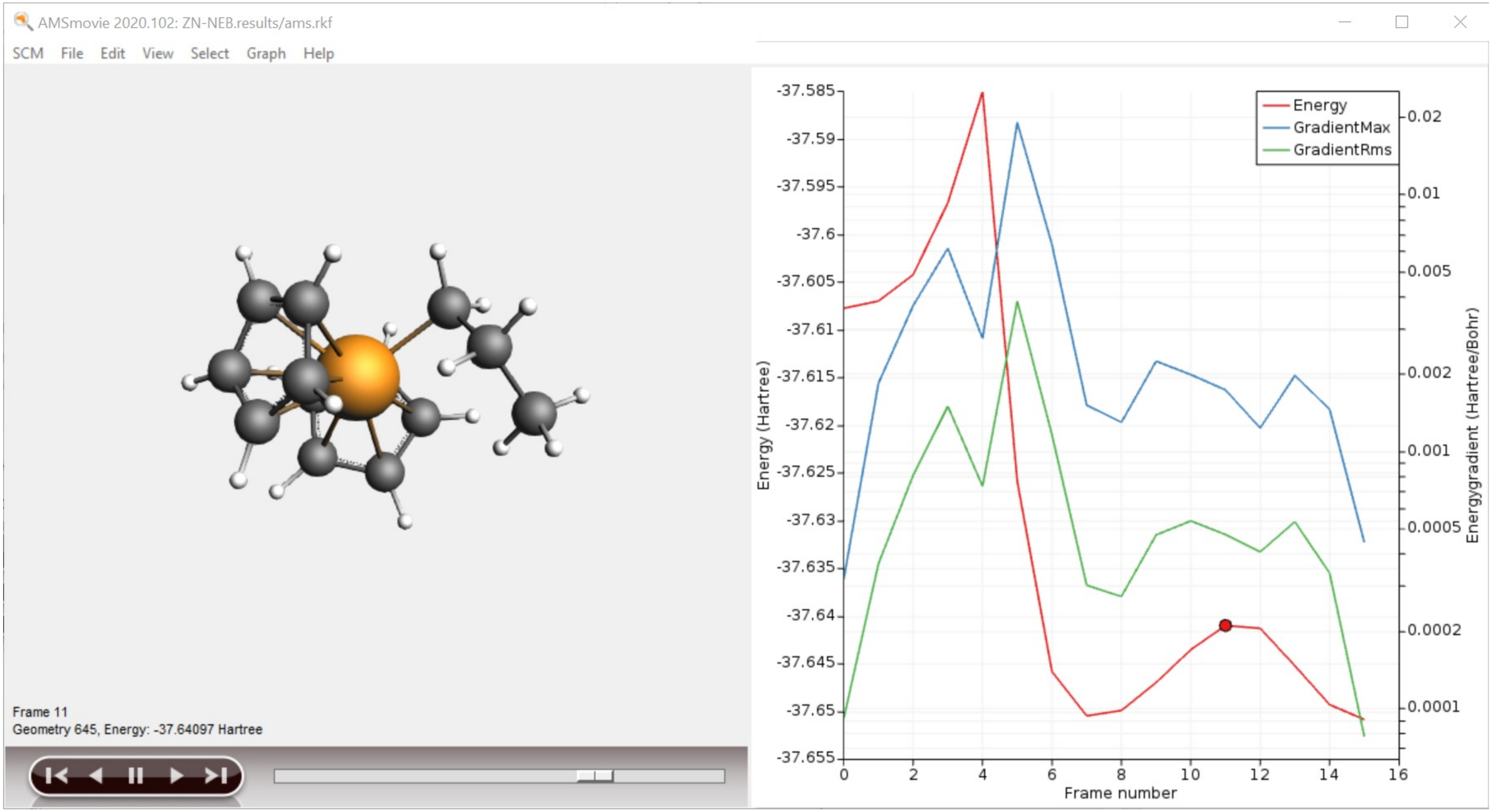
Periodic DFT(B) calculations

- Import cif, periodic pdb/xyz, use structure builder
- Run graphene 2D with BAND and DFTB
  - To get the Dirac point, right use a symmetric k-grid in BAND
  - 3D with QE (think about z lattice vector, and reorder the visualization path!)





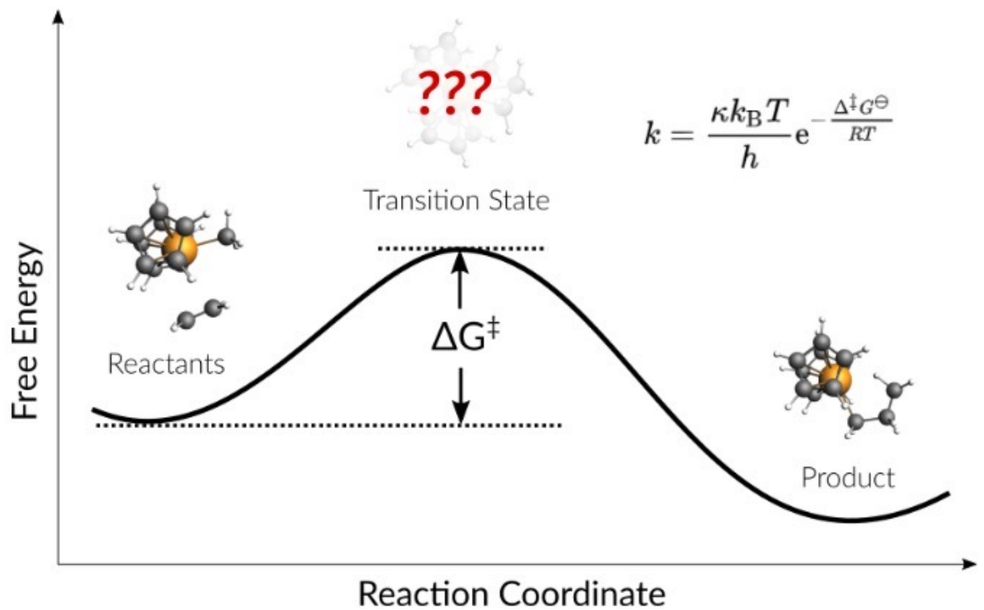
Transition States: Tips & Tricks



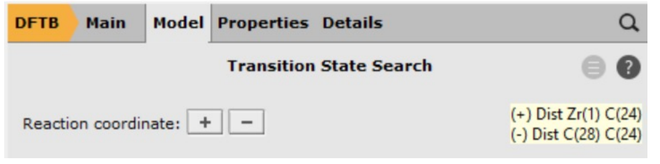
SCM
Software for Chemistry & Materials

Pointers & ideas for TS search

1. Good starting point (**geometry** close to TS)
   - First explore reactant and product
   - (Initially) use low convergence criteria
   - Scan the PES with MOPAC or GFNx-TB
     - Sometimes scanning from product side is easier
     - Can use complex composite scan coordinates
   - Use CI-NEB (tutorial)
     - Always a good idea to explore Reactants
   - Pass on coordinates (+Hessian) to ADF
   - Previous TS 'similar' system
   - Consider first doing constrained/partial optimization



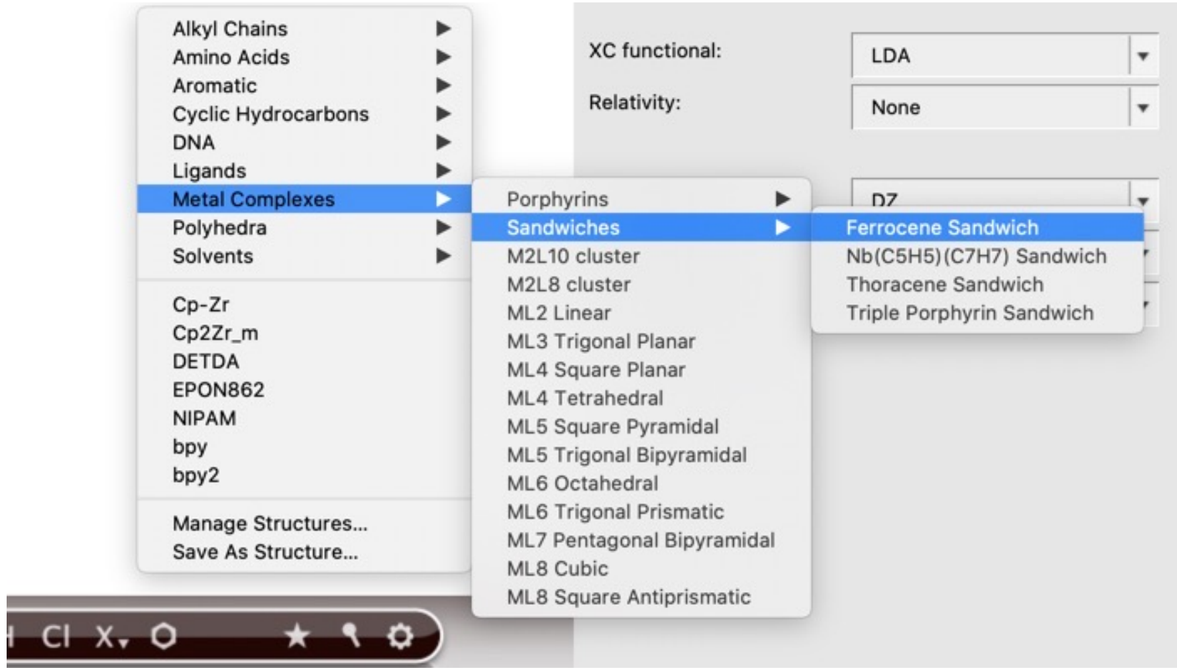
2. Good description of the **curvature**: lowest Hessian eigenmode(s)
   - Partial Hessian
   - Low-level Hessian from previous, ADF choose 'Calculate With Fast Engine'
   - TSRC: define (complex) reaction coordinate
   - Consider 'TS point characterization' to check only 1 negative eigenmode
3. Automated reaction path search (tutorial)
4. Accuracy?
   - Solvent effects: COSMO and/or SM12 (single point only), COSMO-RS
   - metaGGA? TZP/DZP? Good numerical quality?
   - Double hybrids (single point)
   - Low-eigenmode corrections to frequencies
   - Sometime spurious 2nd imaginary modes are hard to get rid of -> ScanFreq

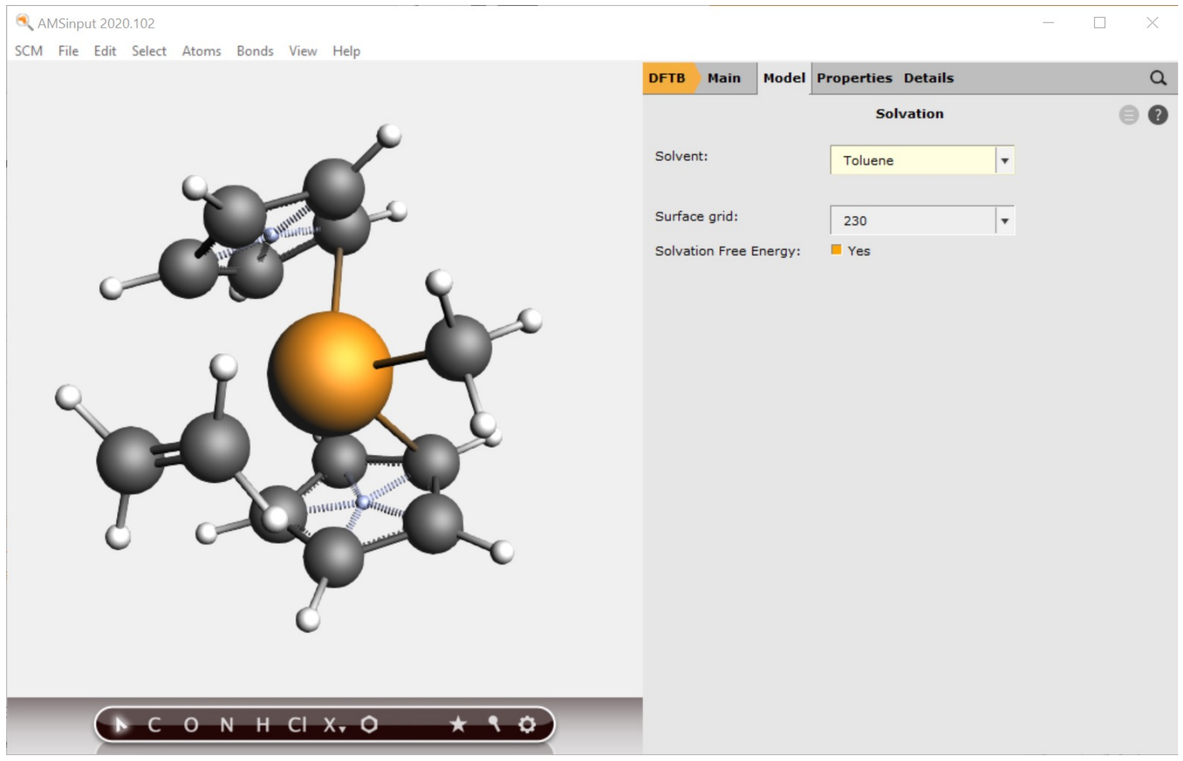


Video

Transition State through PES scan

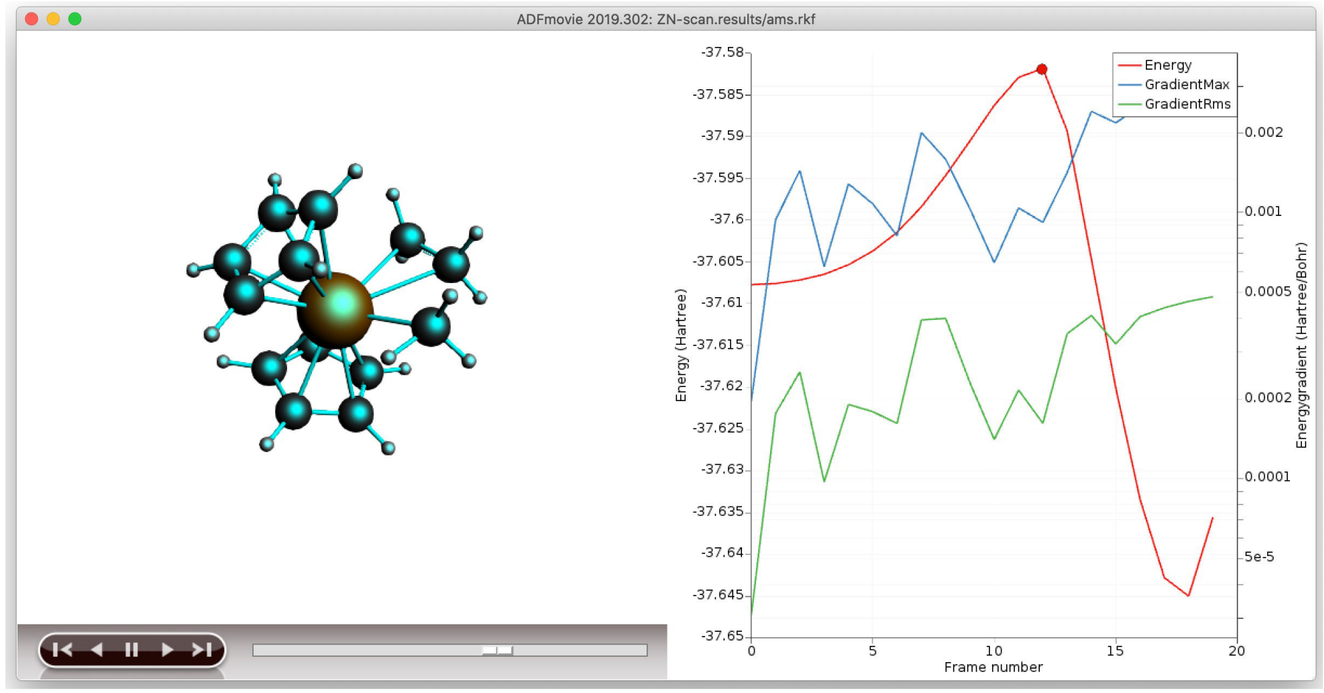
- Exercise (Ziegler-Natta tutorial):
  - New DFTB input
  - Build Cp_2ZrMe^+
    - structure tool ⬡ => ferrocene
    - Right-click Fe -> Element -> Zr
    - Add C and replace by methyl
    - (Use dummies to change CpMCp angle)
    - Model -> Solvent -> Toluene
    - Add charge and optimize
  - Add ethene (use the 🔍)
    - Manipulate it in position
    - Right-click + drag = translate
    - Left-click + drag = rotate
    - Ctrl+M = select molecule
    - Remove dummies
    - Optimize

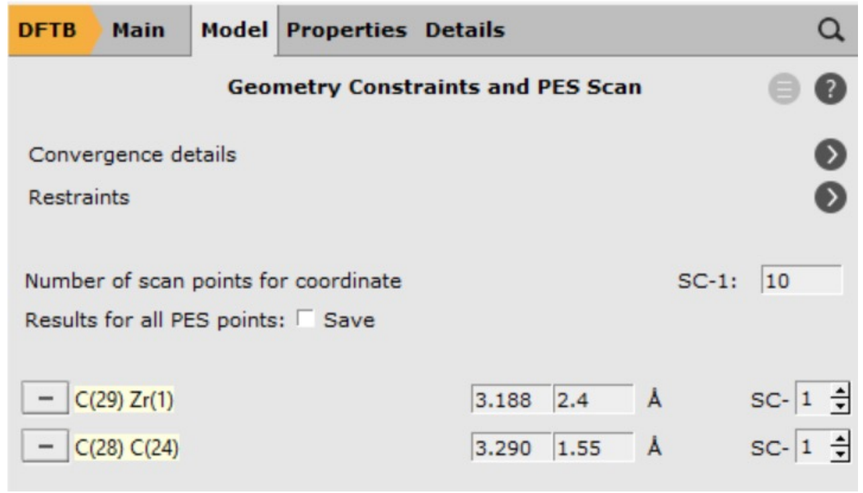




Transition State through PES scan

- Set up a PES scan, using **1 combined scan coordinate**
  - Zr-C to 2.4 & C-C to 1.55
- Details -> Geometry Optimization:
  - Loosen the Convergence criteria by a factor of 5
- Run, and when finished, open AMSMovie



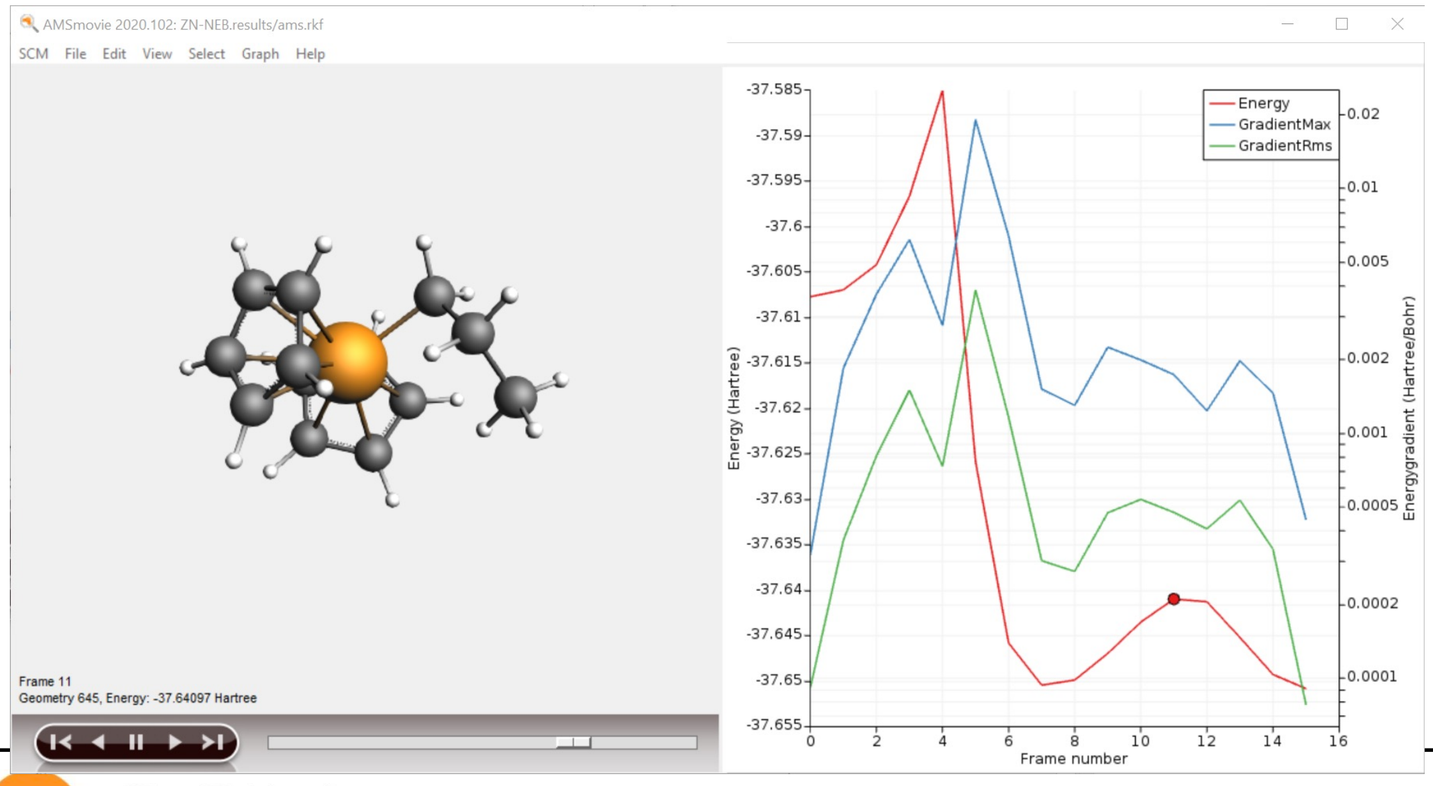


- Copy the highest energy structure (e.g. Ctrl+U), or save as structure
- Set up a TS run (ideally make a new input)
  - make sure there are no constraints, and regular convergence
  - use a calculate Hessian as initial guess and calculate frequencies

Transition State, start with NEB (Ziegler-Natta)

- Exercise:
  - Optimize reactant & product from the last PES scan points
  - Rotate the Zr-C-C-H dihedral to ~0 (metallacycle Zr-C-C-H) & optimize => alpha-agostic
  - 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 results/ams.rkf) and choose 14 points
  - Don't optimize R&P, relax convergence by factor 5
  - Open AMSMovie when finished
    - Which is the rate-determining step?

Tip: use CI-NEB to get close enough to TS, use Hessian-based optimization to find it




```
<Jan20-2021> <13:58:17>  Numerical nuclear derivatives calculation complete.
<Jan20-2021> <13:58:17>  Scanning mode: 7
<Jan20-2021> <13:58:18>  PES point character: Geometry corresponds to a transition state.
<Jan20-2021> <13:58:18>  TS barrier height from the left           0.02270445 Hartree
<Jan20-2021> <13:58:18>                                           14.247 kcal/mol
<Jan20-2021> <13:58:18>                                           59.611 kJ/mol
<Jan20-2021> <13:58:18>  TS barrier height from the right          0.06580135 Hartree
<Jan20-2021> <13:58:18>                                           41.291 kcal/mol
<Jan20-2021> <13:58:18>                                           172.761 kJ/mol
<Jan20-2021> <13:58:18>  NORMAL TERMINATION
Job ZN-NEB has finished
```

Transition States: Further considerations

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

```
   Temp                                                  Transl      Rotat     Vibrat     Total
   ----                                                  ------      -----     ------     -----

   298.15   Entropy (cal/mol-K):                         42.601     31.288     52.371    126.261
            Nuclear Internal Energy (kcal/mol):           0.889      0.889    160.907    162.684
            Constant Volume Heat Capacity (cal/mol-K):    2.981      2.981     56.260     62.222
        (c) Constant Volume Heat Capacity (cal/mol-K):    2.981      2.981     52.800     58.761

     Summary of energy terms
                                          hartree            eV         kcal/mol          kJ/mol
                                    --------------------  ----------  ----------  ----------
    Energy from Engine:             -37.585024915182686  -1022.7406   -23584.96   -98679.47
    Nuclear Internal Energy:          0.259253970109237      7.0547      162.68      680.67
(c) Nuclear Internal Energy:          0.257445594179003      7.0055      161.55      675.92
    Internal Energy U:              -37.325770945073451  -1015.6859   -23422.28   -97998.80
    pV/n = RT:                        0.000944186013486      0.0257        0.59        2.48
    Enthalpy H:                     -37.324826759059967  -1015.6602   -23421.68   -97996.32
    -T*S:                            -0.059990510871653     -1.6324      -37.64      -157.51
(c) -T*S:                            -0.058176671371776     -1.5831      -36.51      -152.74
    Gibbs free energy:              -37.384817269931617  -1017.2926   -23459.33   -98153.82


(c) The properties marked with this symbol have been corrected using 'low vibrational frequency free rotor
    interpolation corrections'. For those terms all positive frequencies are used (also ones below 20 1/cm),
    but the contribution to the partition function of small vibrational frequencies is modified as described
    in the following paper:
    S. Grimme, 'Supramolecular Binding Thermodynamics by Dispersion-Corrected Density Functional Theory'
    (Chem. Eur. J. 2012, 18, 9955-9964)
    Configuration: Dampener Frequency          :   100.000 1/cm
                   Dampener Alpha              :     4.000
                   Averaging Moment of Inertia : 1.000E-44 kg m2
```

  - hTST as first approximation: k ~ exp (-$G^{\#}$/RT), Low-level frequencies: Grimme corrections
  - 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 (AMSSpectra, Ctrl+8 *5) & retry

TS for periodic systems

- How to get good TS geometry guess?
  - Literature or previous results:
    - similar TS + constrained optimization
  - Quick (?) NEB (you want to find R & P anyway)
  - PES scan (can you use ReaxFF, MOPAC, GFN-xTB? Otherwise: cheaper DFT?) (video)
  - Maybe you can get away with periodic DFT/DFTB (video) or DFT/MM ?

- How to get good guess for lowest few Hessian eigenmodes?
  - Could try MOPAC or DFTB Hessian
    - Inspect modes first?
  - Define reaction coordinate (TSRC)
  - Use a partial Hessian ('active' region)

Video