

Day 1: Introduction to AMS2018

Getting started

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

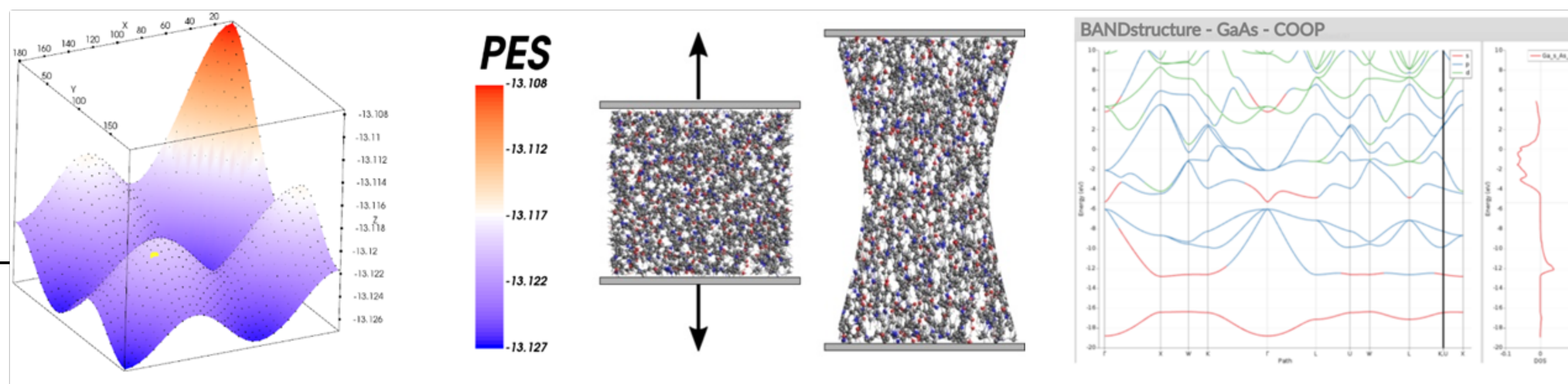
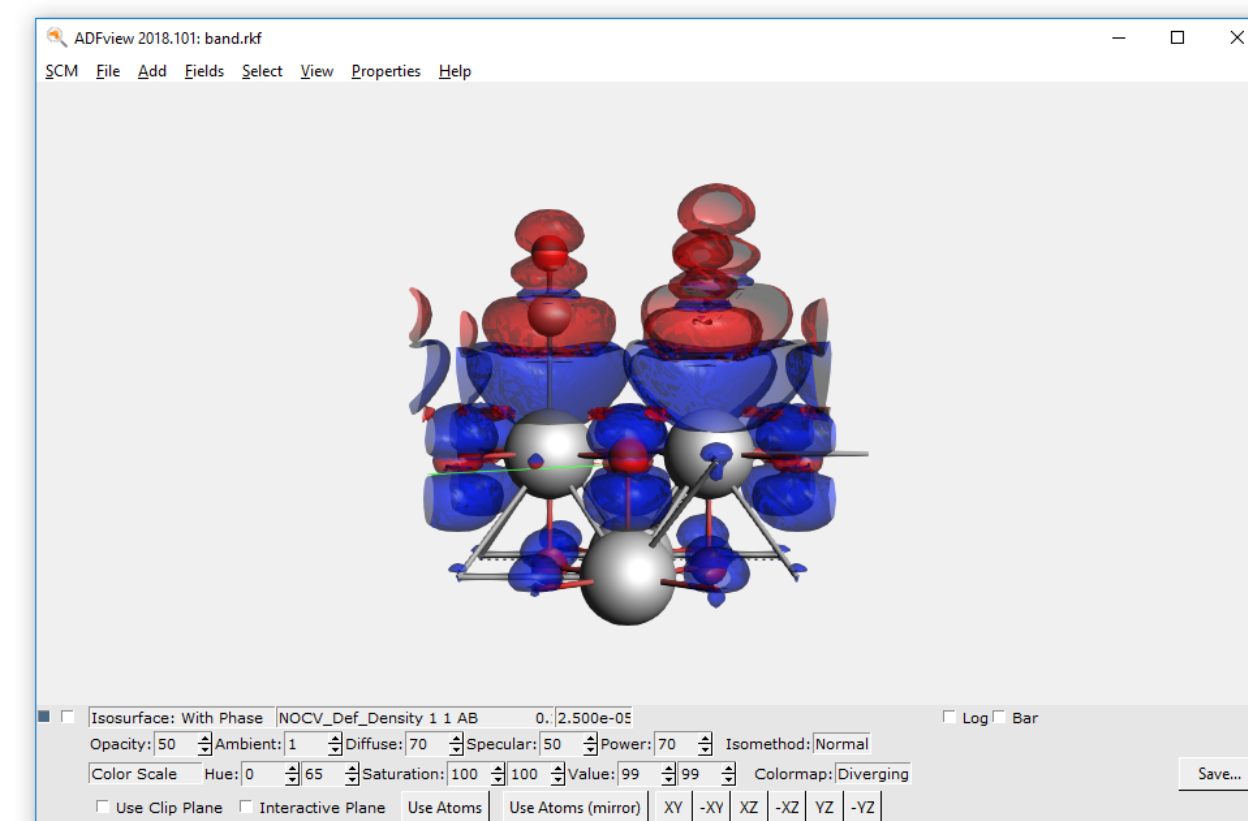
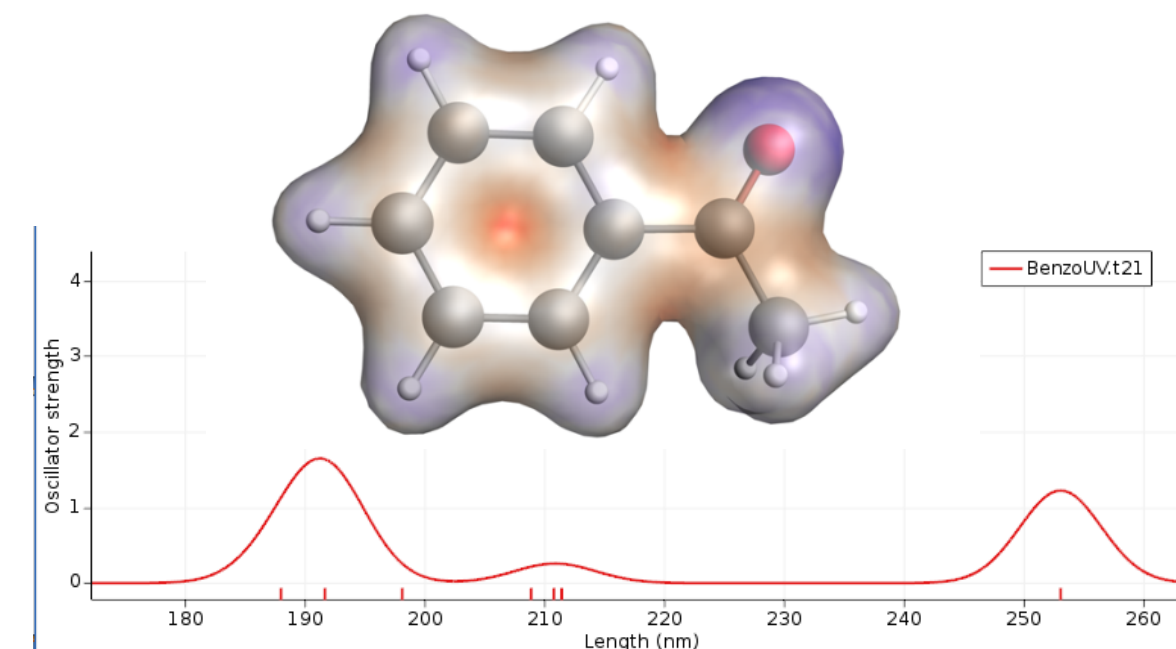


2-day workshops, October 2018, China
Fedor Goumans, goumans@scm.com SCM support: support@scm.com
FermiTech support: [wiki](#), support@fermitech.com.cn

Making Computational Chemistry Work for You

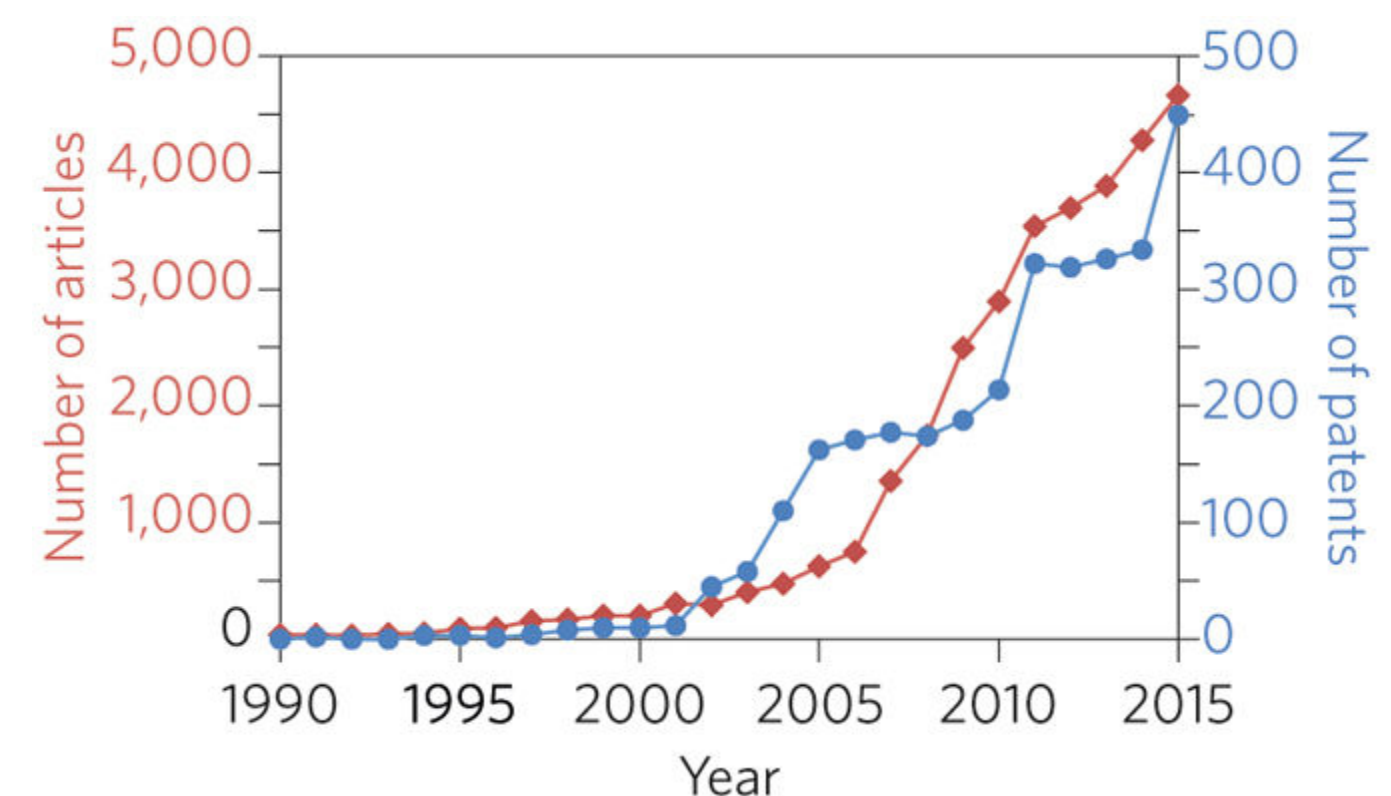
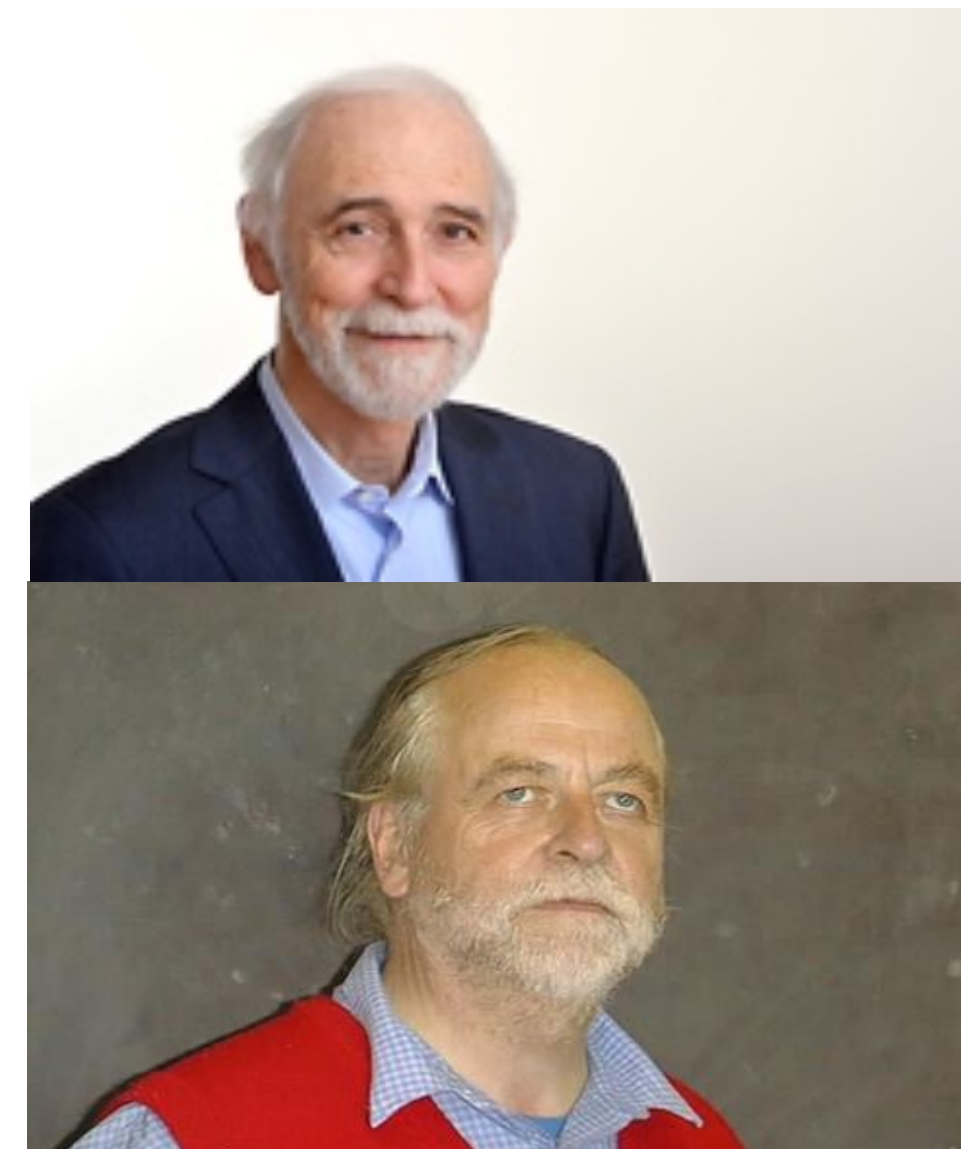
Program

- Introduction
 - SCM & AMS
 - Computational chemistry & materials science
- Molecules: builder, database, import SMILES, xyz
 - Spectroscopy
 - Advanced: bonding analysis, charge transfer, SOCME
- Periodic structures: database, cif, surfaces
 - Advanced: bonding analyses (PEDA-NOCV, COOP)
- COSMO-RS: properties, optimizing mixtures
- ReaxFF: acceleration, fitting parameters (tomorrow)



Background: SCM & ADF

- ADF = first DFT code for chemistry (1970s)
Baerends@VU (>'73), Ziegler@Calgary[†] (>'75)
- SCM: Spin-off company 1995
- 15 people (10 senior PhD's) + 5 EU fellows
- Many academic collaborators / EU networks
 - ~120 authors
 - New functionality
- SCM: development, debug, port, optimize, docs & support



articles & patents in materials science with
“density functional theory”, Nat. Mat. 4619

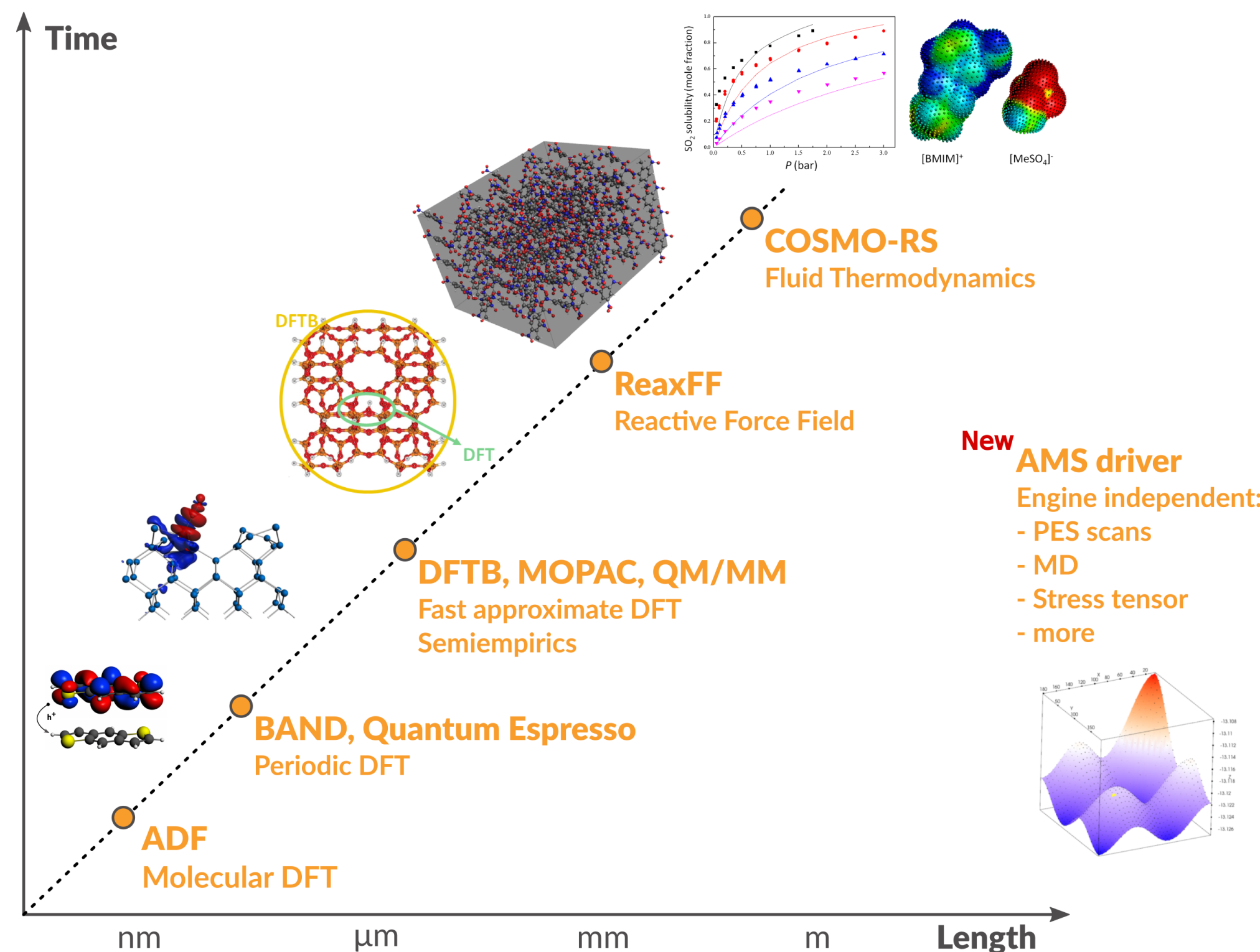
The SCM team



 <p>Olivier: GUI</p>	 <p>Alexei: ADF ReaxFF</p>	 <p>Erik: ADF COSMO-RS</p>	 <p>Pier: BAND</p>	 <p>Mirko: ADF BAND</p>
 <p>Hans: Linux GPU Python</p>	 <p>Thomas: DFTB Scripting</p>	 <p>Laurens: GUI</p>	 <p>Ole: Support Scientist</p>	 <p>Evert Jan: Adviser</p>
 <p>Michal: python scripting</p>	 <p>Robert: DFTB</p>	 <p>Anna: ReaxFF</p>	 <p>Nick: COSMO-RS</p>	 <p>Tomas: ReaxFF</p>
 <p>Stan: CEO</p>	 <p>Fedor: Marketing</p>	 <p>Sergio: Collaborations</p>	 <p>Frieda: Invoices Licenses</p>	 <p>Kitty: Finance</p>

Amsterdam Modeling Suite

- **ADF:** powerful molecular DFT
 - Spectroscopy: NMR, EPR, VCD, UV, XAS
 - Advanced solvation / environments
 - Bonding & density analysis
- **BAND:** periodic DFT
 - (2D) Materials
- **DFTB:** fast approximate DFT
- **ReaxFF:** Reactive MD
 - Dynamics of large complicated systems
- **COSMO-RS:** fluid thermodynamics
 - VLE, LLE, logP, solubility
- Integrated GUI – use out of the box
- Scripting: workflows & automation

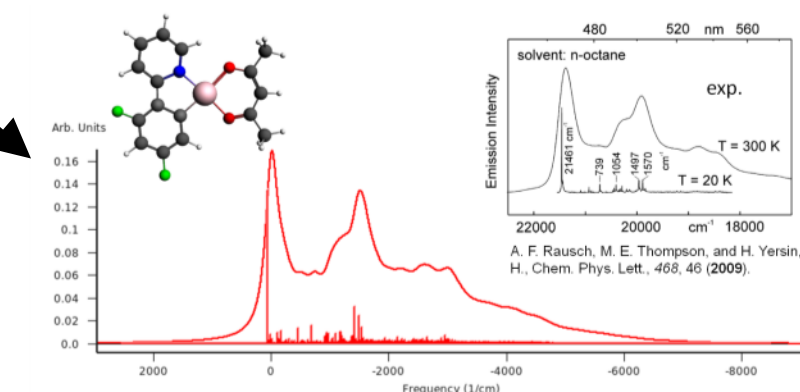
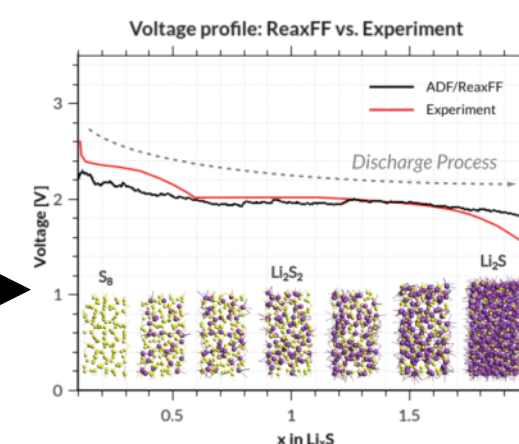
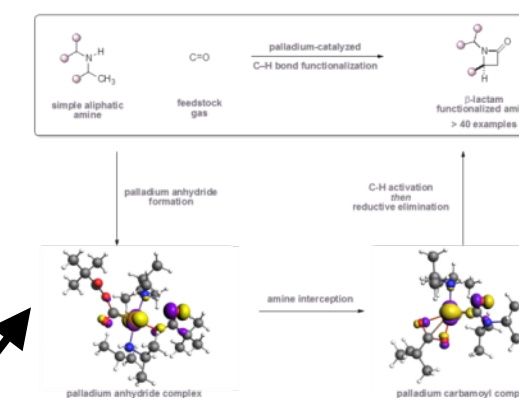
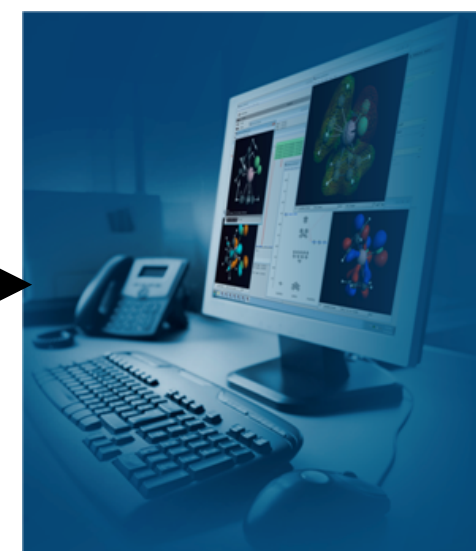


Why bother with calculations?

Computational chemistry & materials modeling

- Accelerate research, reduce costs & environmental impact
 - Reduce experimental search space
 - Analyze structure-property-reactivity
- Models: physics & empiricism
 - Accuracy?
- Synergy experiment-calculations
 - Ask relevant questions
 - Limitations model
 - Constraints experiments

???

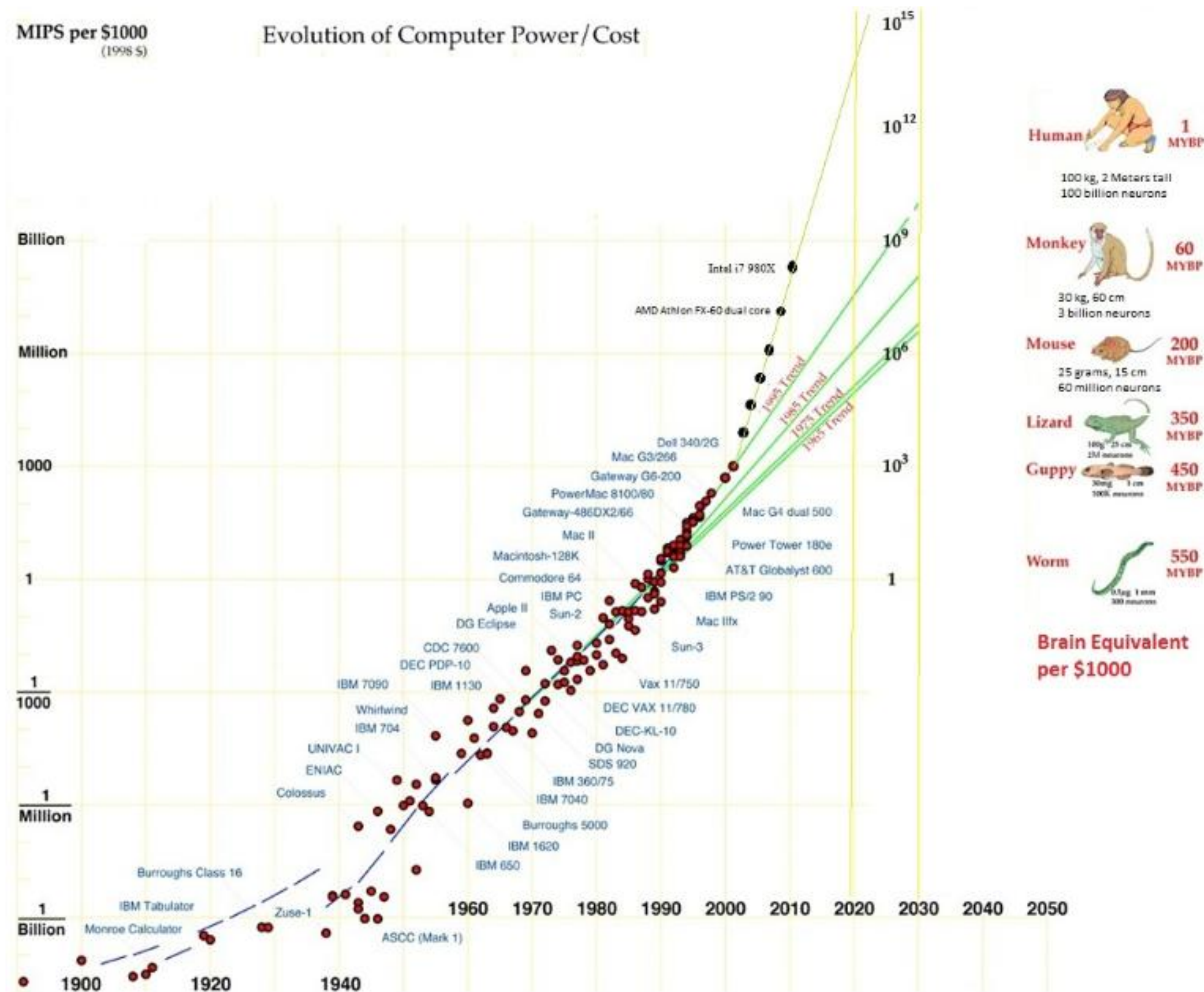


Best catalyst? => mechanism? lowest E_a ? best ligand? side reactions?

Best battery? => discharge? voltage? interaction with electrolyte?

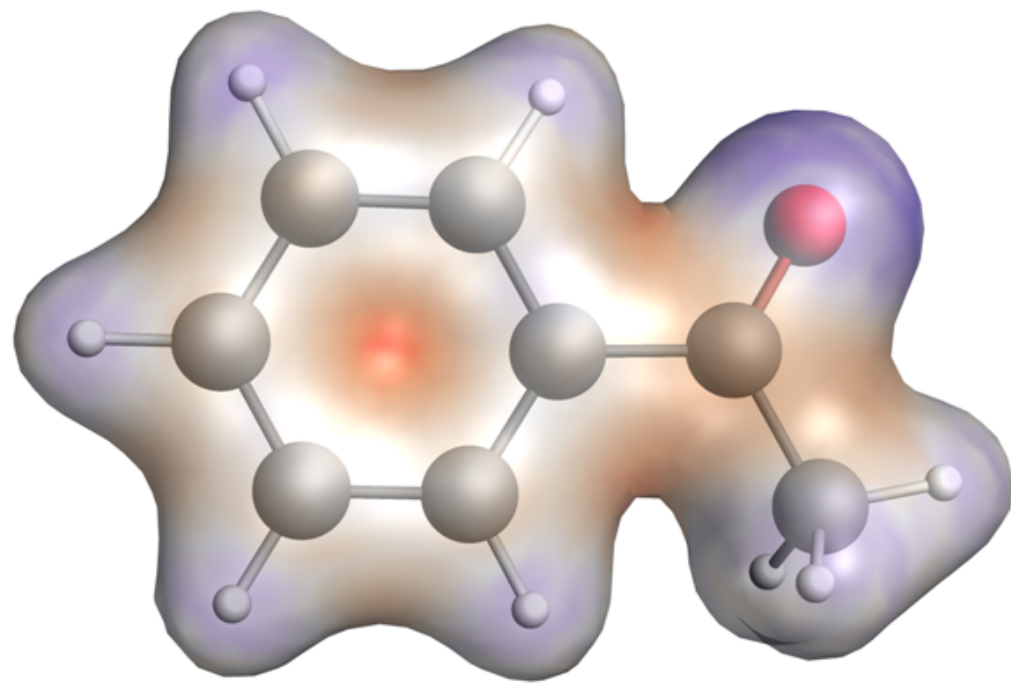
Best OLED? => charge & exciton mobility? emission speed & color?

Compute power (r)evolution

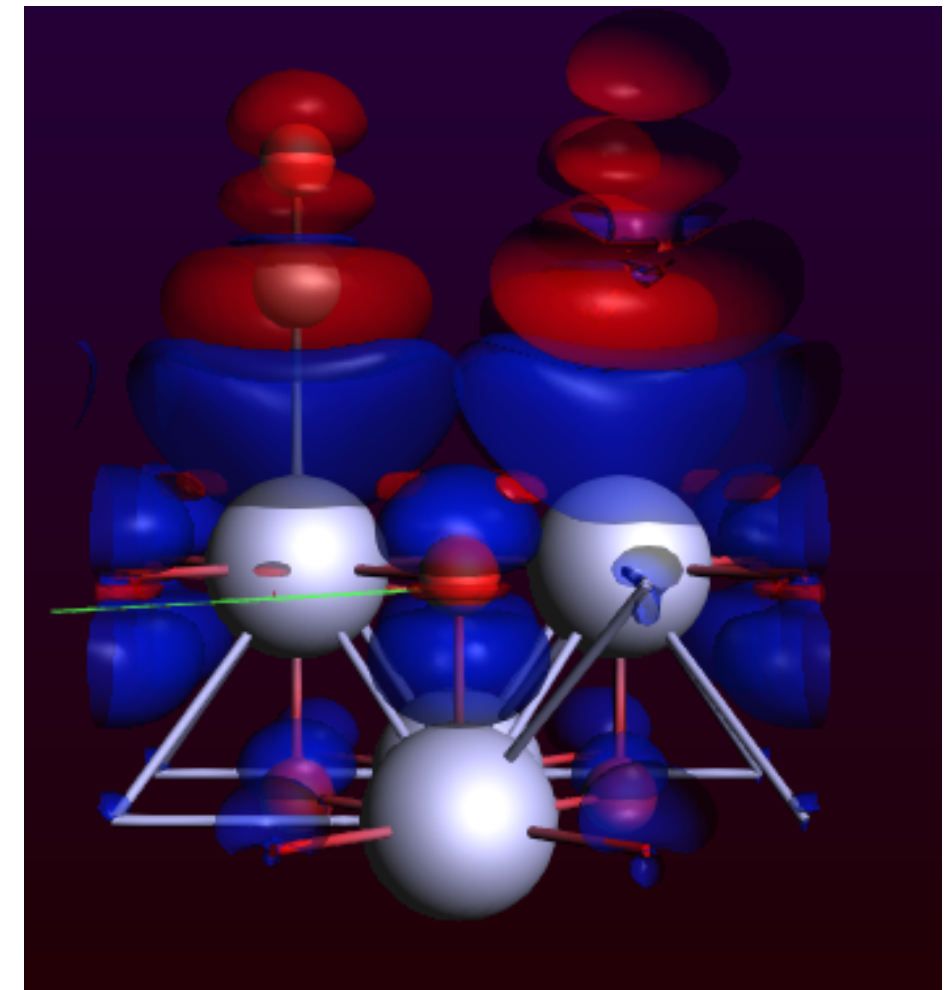


<http://www.donbot.com/Futurebot/NewTech/NT01370MoravecsGraphUpdated2020.html>

Computational Chemistry & Materials



$$H\psi = E\psi$$



Electronic structure methods: Schrödinger equation

Electrons in molecules & materials

Expand ψ : atomic orbitals / plane waves

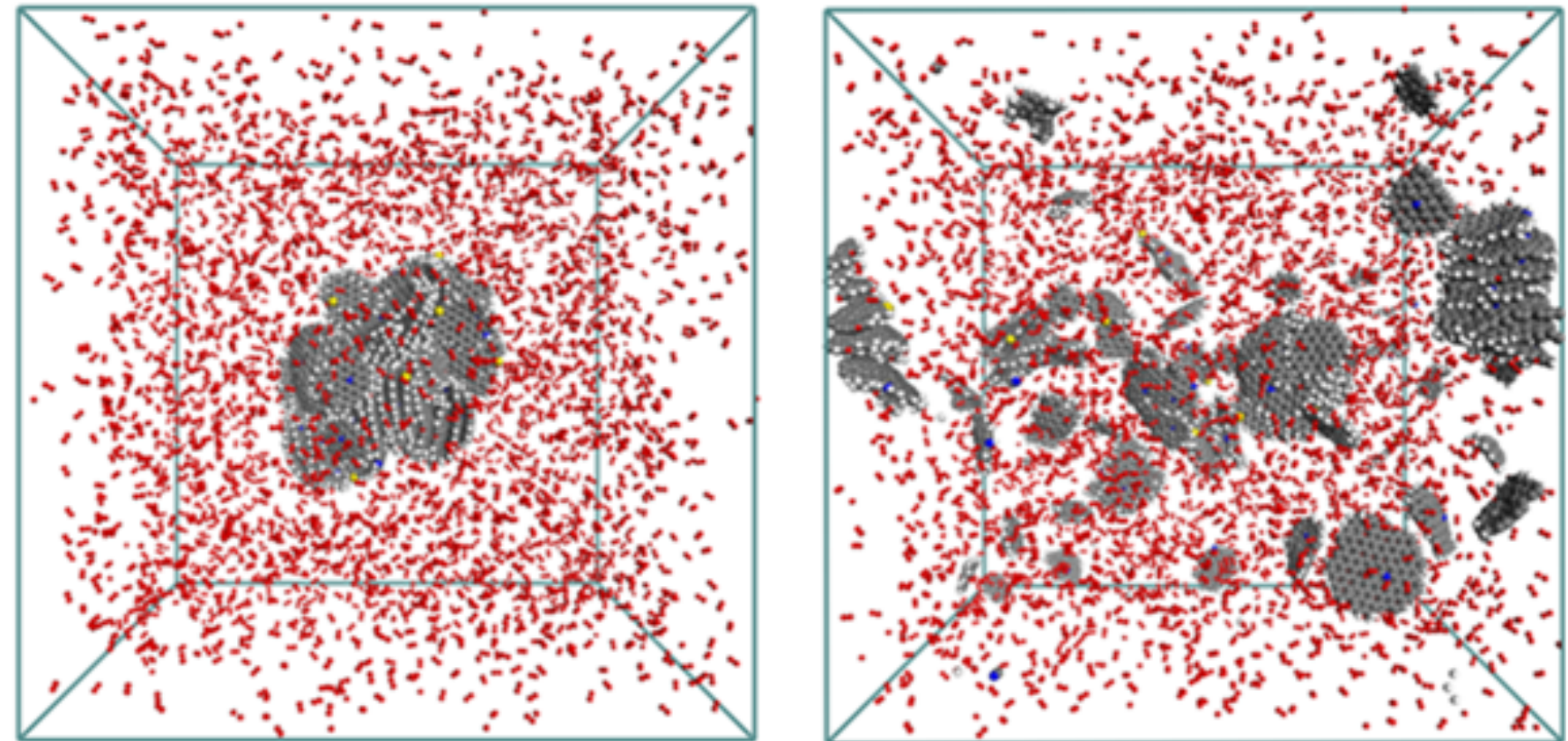
Solve self-consistently

Pragmatic: DFT

Properties: energies (gradients), MOs, densities & related, spectroscopy (EPR, NMR, IR, UV/VIS,)

Computational Chemistry & Materials

$$d^2x/dt^2 = F(x)$$
$$F(x) = - dV(x)/dx$$



Molecular dynamics: Newton's equations of motion

Movement of atoms: solve numerically + propagate,

Properties: reaction rates, diffusion coefficients, stress-strain,

Electronic Structure methods

$$H\psi = E\psi$$

- *ab initio* (basis set dependencies!)
 - Hartree-Fock (HF): mean field (no explicit e-e interaction)
 - MP2: perturbation theory (if HF = good guess)
 - CC: coupled cluster
 - CI: configuration interaction (full CI = max. Accuracy)
 - Multi-reference / active space

- Density Functional Theory (DFT)

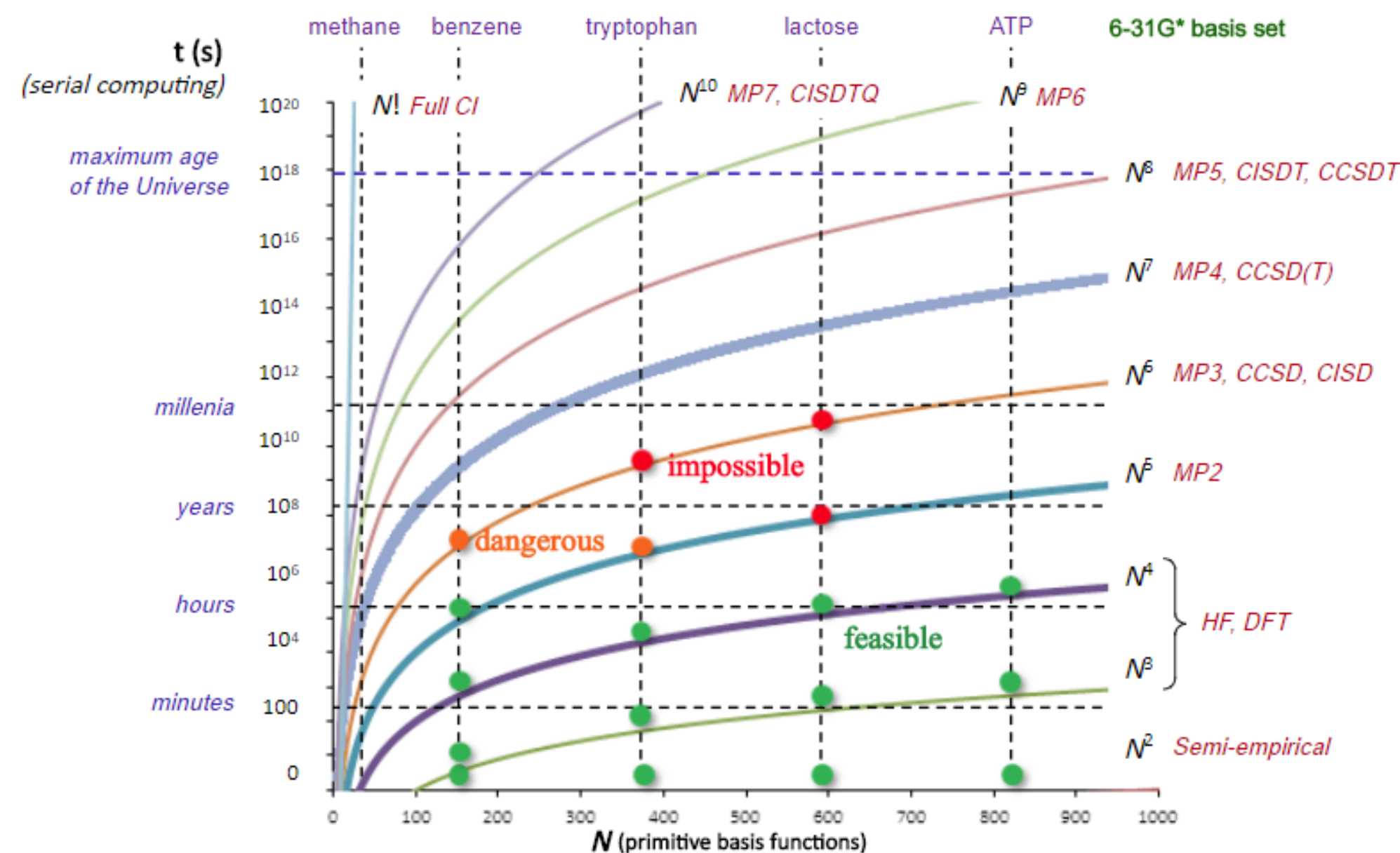
- 'first principle' functionals (physics)
- empirical functionals (fit to data)

- DFT-based tight binding (DFTB)

- Fit to DFT data
- Nearest neighbor, minimal basis

- Semi-empirical (MOPAC: PM7)

- Fit to exp. Data
- Nearest neighbor, minimal basis



(Houk, 2011)

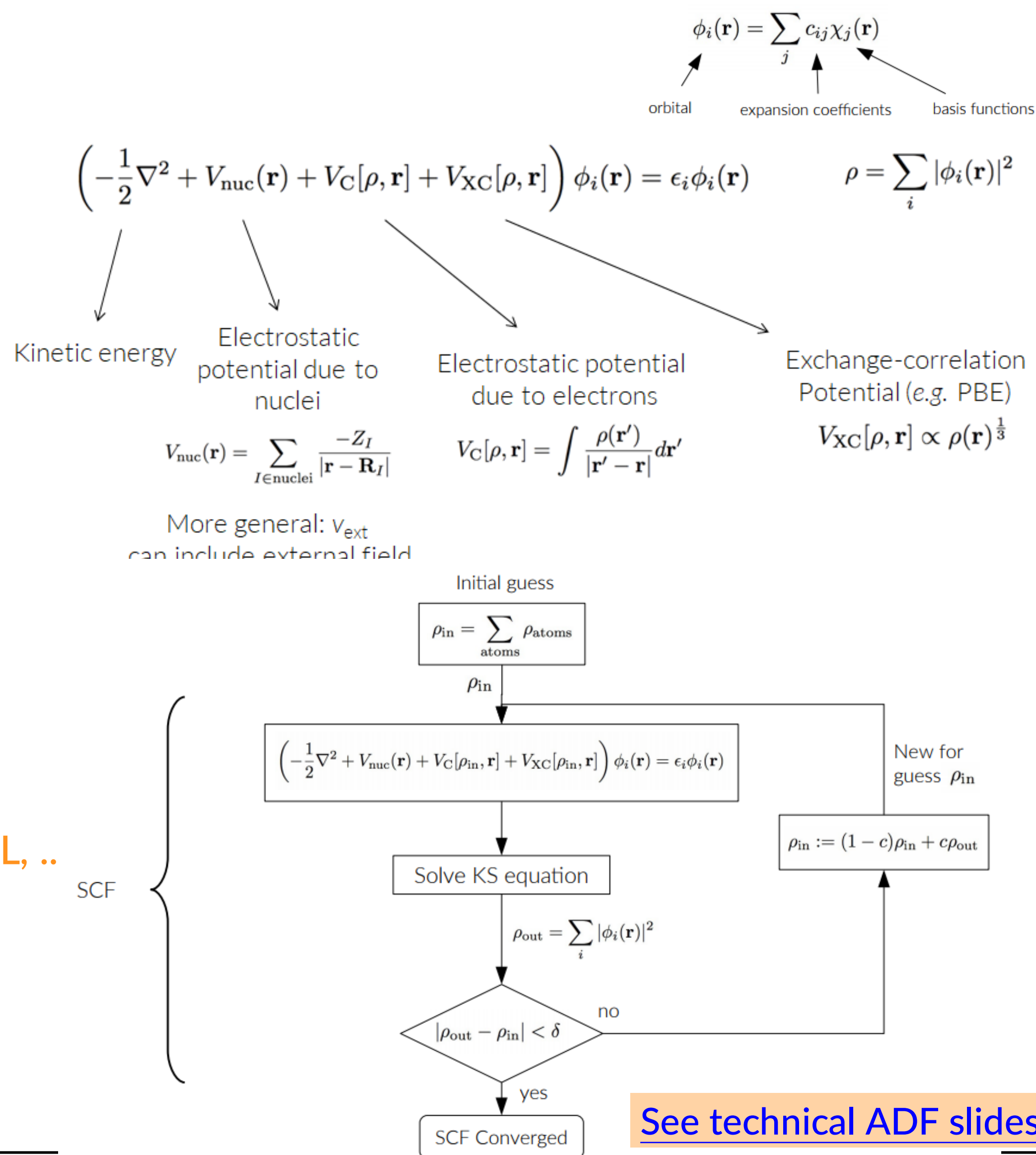
Computational Methods

Relative costs, scaling & accuracy for computational methods
(* depending also strongly on the system & property!)

Method	~ max atoms	~ relative cost	scaling	Typical Accuracy*
Classical force field (UFF, Amber, ...)	1,000,000	0.0005	N^1	<20 kcal/mol
Reactive force field (ReaxFF)	500,000	0.001	N^1	<15 kcal/mol
Semi-empirical methods (e.g. AM1, PM7)	5,000	1	$N^{1\sim2}$	<10 kcal/mol
DFTB	5,000	1	$N^{1\sim2}$	<10 kcal/mol
DFT	500	500	$N^{3\sim4}$	<5 kcal/mol
MP2	100	2000	N^5	<5 kcal/mol
CCSD(T)/cc-pVTZ	30	100000	N^7	~1 kcal/mol

Density Functional Theory

- Density ρ = central quantity
- Density functional ρ gives E
 $E[\rho] = T[\rho] + E_{ee}[\rho] + E_{ne}[\rho]$
- Usually expanded in orbitals
 - Linear combination of atomic orbitals
 - Basis set
 - Kohn-Sham DFT
 - 'Non-interacting' reference T_s
 $E[\rho] = T_s[\rho] + E_{ee}[\rho] + J[\rho] + E_{xc}[\rho]$
 - Solve self-consistently
 - $v_{xc}[\rho] = E_{xc}[\rho]/d\rho$ = 'functional'
 - approximate: LDA, BP86, PBE, M15L, ..
- Which basis & functional?
 Check literature or benchmark!

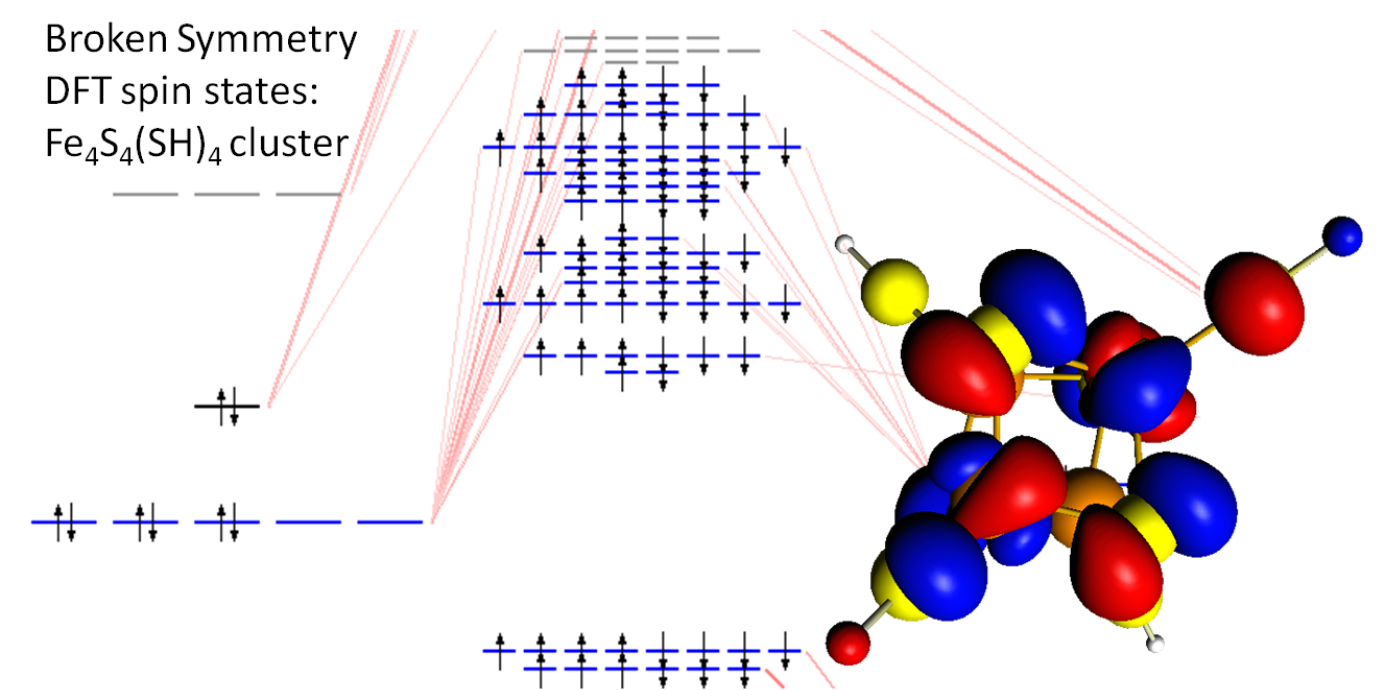
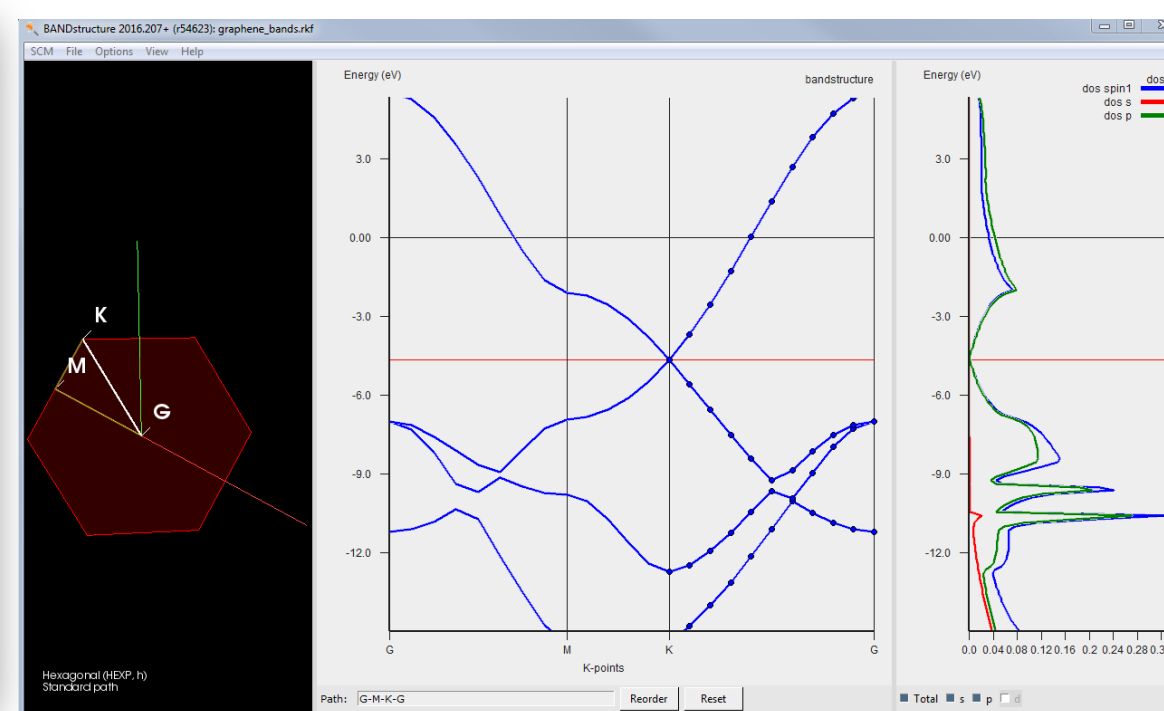
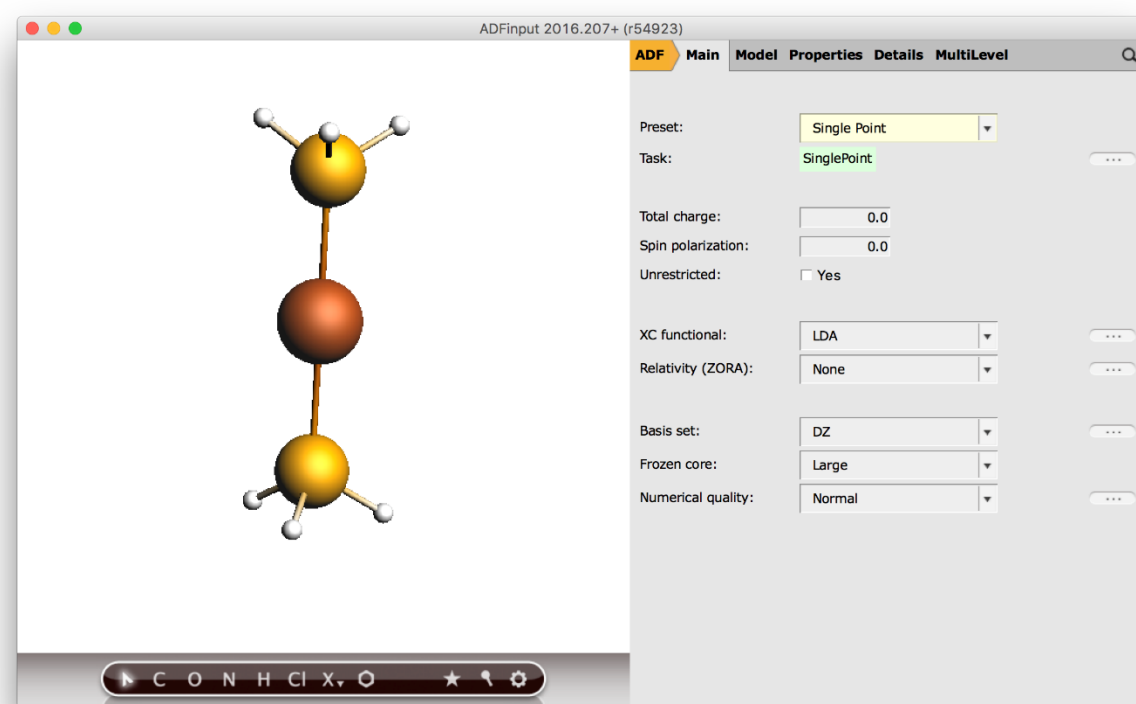
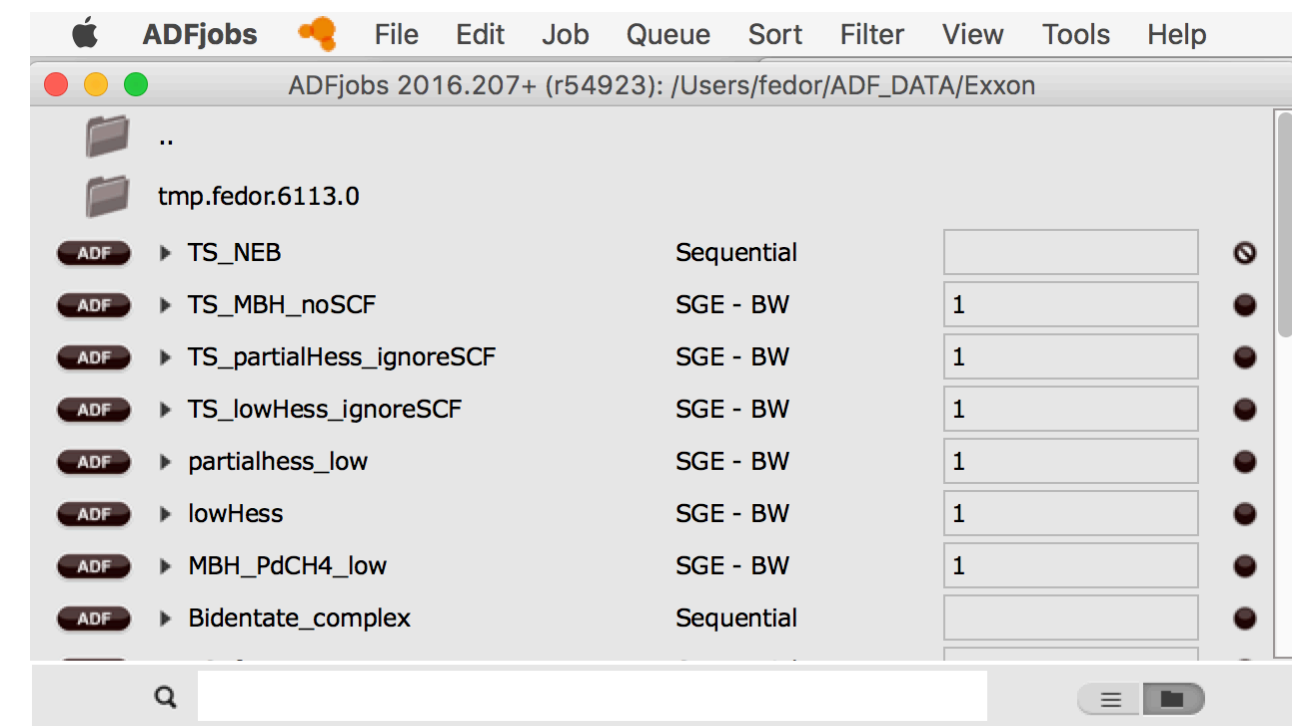


[See technical ADF slides](#)

Getting started with the GUI

Starting ADFjobs: job bookkeeping tool

- Win: dbl-click desktop item
- Mac: open Application
- Linux: run `$ADFBIN/adfjobs`
- Other GUI modules: (Input, View, Levels, Movie, Spectra, Band Structure, COSMO-RS, ...)
 - Can be opened by dbl-clicking '.exe' (Win) or opening e.g. '`$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

The screenshot shows the ADF software interface with the following components and annotations:

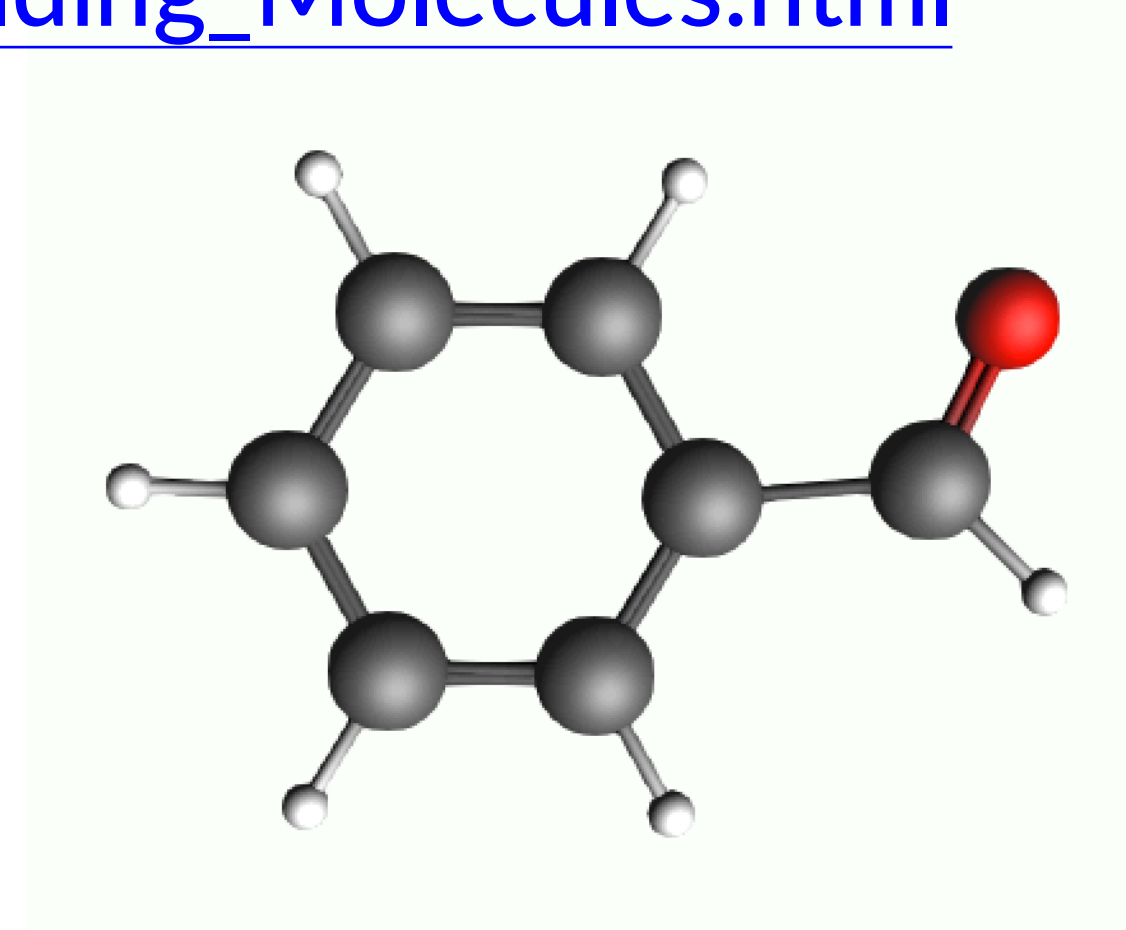
- ADFFinput 2017.212+ (r63428): acetophenone2.adf** - Title bar text.
- ADF Main Model Properties Details MultiLevel** - Tabbed menu bar.
- Task: Geometry Optimization** - Dropdown menu for job type.
- Total charge: 0** - Input field for total charge.
- Spin polarization: 0** - Input field for spin polarization.
- Unrestricted: ☐ Yes** - Checkbox for unrestricted calculation.
- XC functional: GGA:revPBE-D3(BJ)** - Dropdown menu for exchange-correlation functional.
- Relativity: Scalar** - Dropdown menu for relativistic approximation.
- Basis set: DZP** - Dropdown menu for basis set.
- Frozen core: Large** - Dropdown menu for frozen core.
- Numerical quality: Normal** - Dropdown menu for numerical quality.
- ... = more details** - Annotation pointing to the ellipsis button next to the numerical quality dropdown.
- builder tools** - Annotation pointing to the bottom toolbar.
- preoptimize** - Annotation pointing to the star icon in the bottom toolbar.
- symmetrize** - Annotation pointing to the magnifying glass icon in the bottom toolbar.
- switch modules** - Annotation pointing to the ADF tab.
- job types & set up** - Annotation pointing to the Task dropdown.
- search** - Annotation pointing to the search icon in the top right.
- charge/spin** - Annotation pointing to the Total charge and Spin polarization input fields.
- functional & relativistic appr** - Annotation pointing to the XC functional and Relativity dropdowns.
- basis & numerical accuracy** - Annotation pointing to the Basis set, Frozen core, and Numerical quality dropdowns.

SCM logo is visible in the bottom left corner.

Building molecules

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

- NB: tutorials also offline with your ADF!
- Import: SMILES, xyz, cif, pdb, ...
- Included library + building
- **Exercise 1: Build acetophenone**
 - By searching for it in the GUI
 - By starting from the benzene template (press 2 for double bond, Ctrl+E to add Hs)
 - By importing smiles CC(=O)c1ccccc1 (e.g. from Wikipedia or Chemspider)
- **Exercise 2: Symmetrize, pre-opt & optimize: SR-ZORA-PBE-D3(BJ)/DZP**



Task:	Geometry Optimization ▼	XC functional:	GGA:PBE-D3(BJ) ▼
		Relativity:	Scalar ▼

Spectra: IR

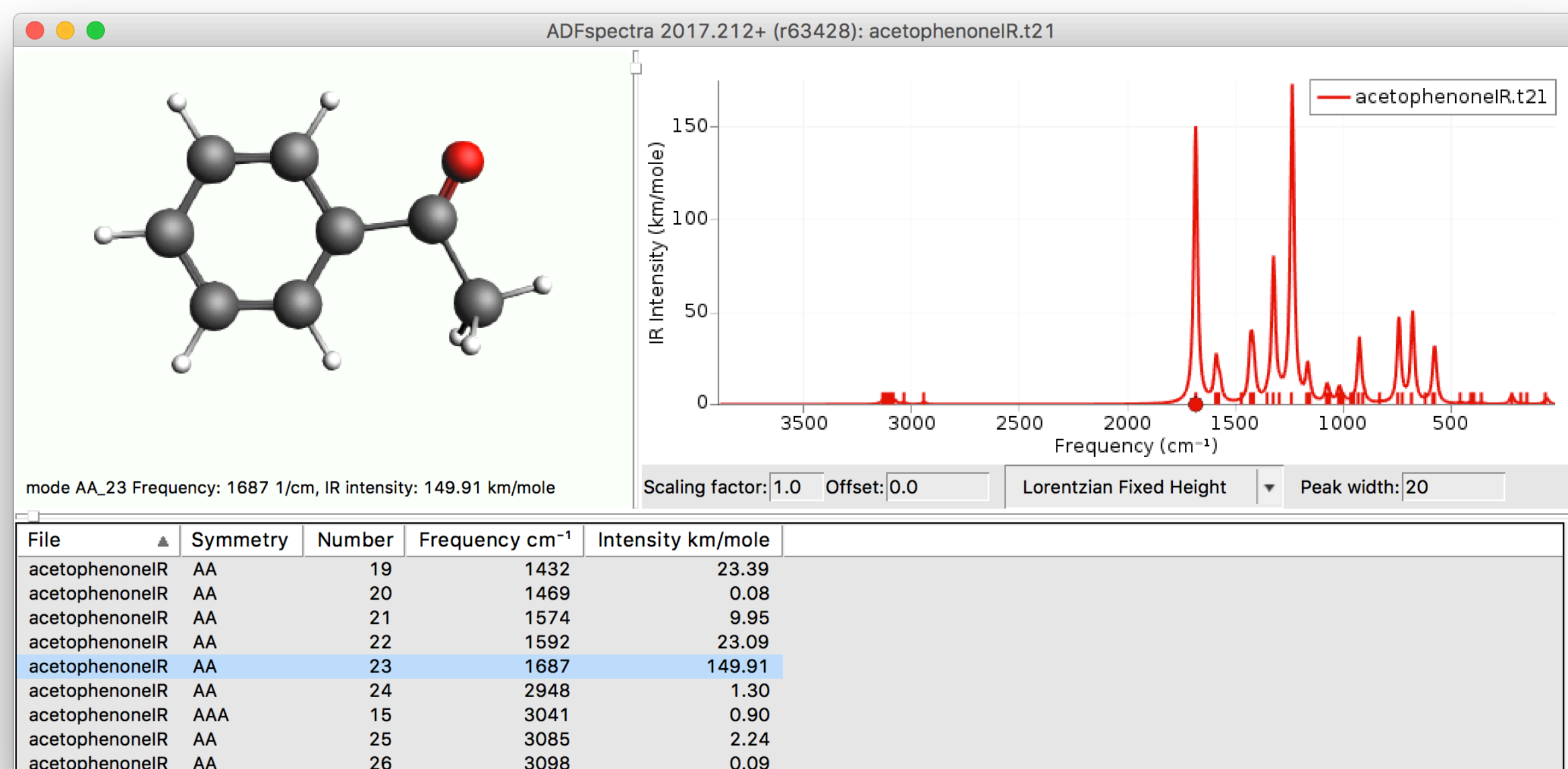
www.scm.com/doc/Tutorials/ADF/ADF-GUI_tutorials.html#spectroscopy

- **Exercise 3: Calculate & visualize frequencies**

Task:

Frequencies

- NB analytical frequencies available for most GGAs, not for hybrids
- Go to spectra, visualize the CO stretch at $\sim 1690\text{cm}^{-1}$
- Increase the line width to ~ 20
- Compare to [NIST data](#)



Spectra: UV/VIS

- Exercise 4: Calculate 10 allowed excitations with the SAOP model potential
 - See also [UV/VIS FAQ for more tips](#)
 - Go to spectra, change x-axis to nm
 - Increase the line width to ~10
 - Visualize the pi-pi* NTOs at ~250 & 285nm
 - Compare to [NIST data](#)
 - Now rerun with method 'sTDA' and tick TDA
 - Compare timings & spectra (File -> add spectra)
- AMS2018: optimize excited states also with
 - Range-separated hybrids
 - COSMO solvation

Task: Single Point

XC functional: Model:SAOP

Relativity: Scalar

Basis set: DZP

Frozen core: None

ADF Main Model Properties Details MultiLevel

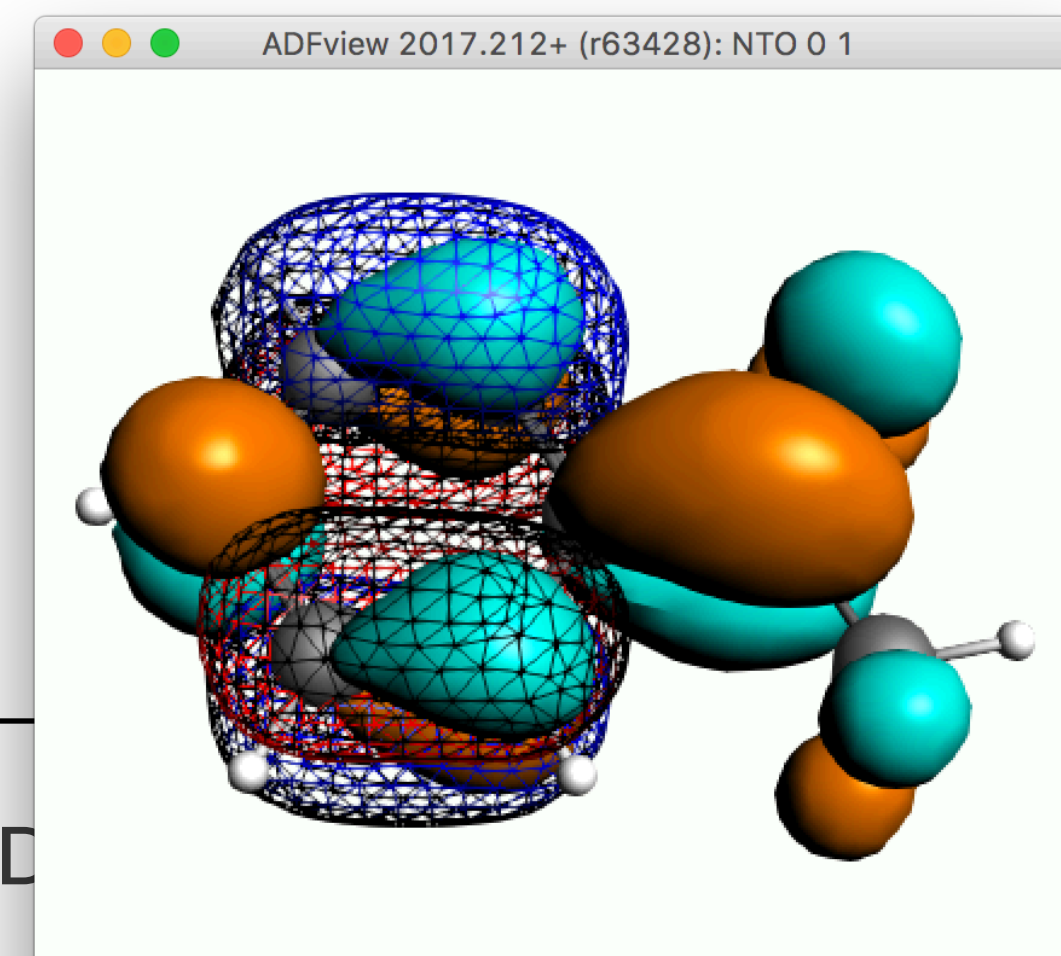
Excitations (UV/Vis), CD

Type of excitations: AllowedOnly

Method: Davidson

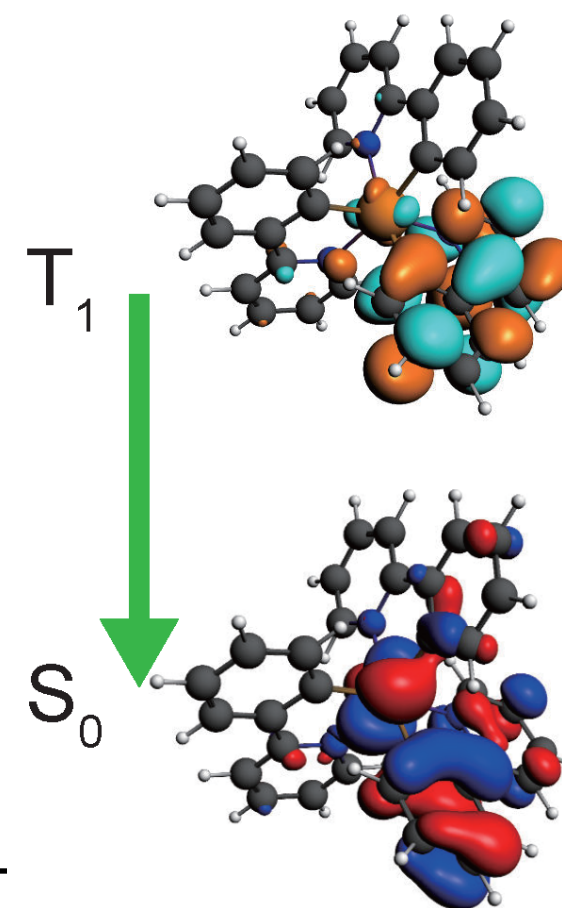
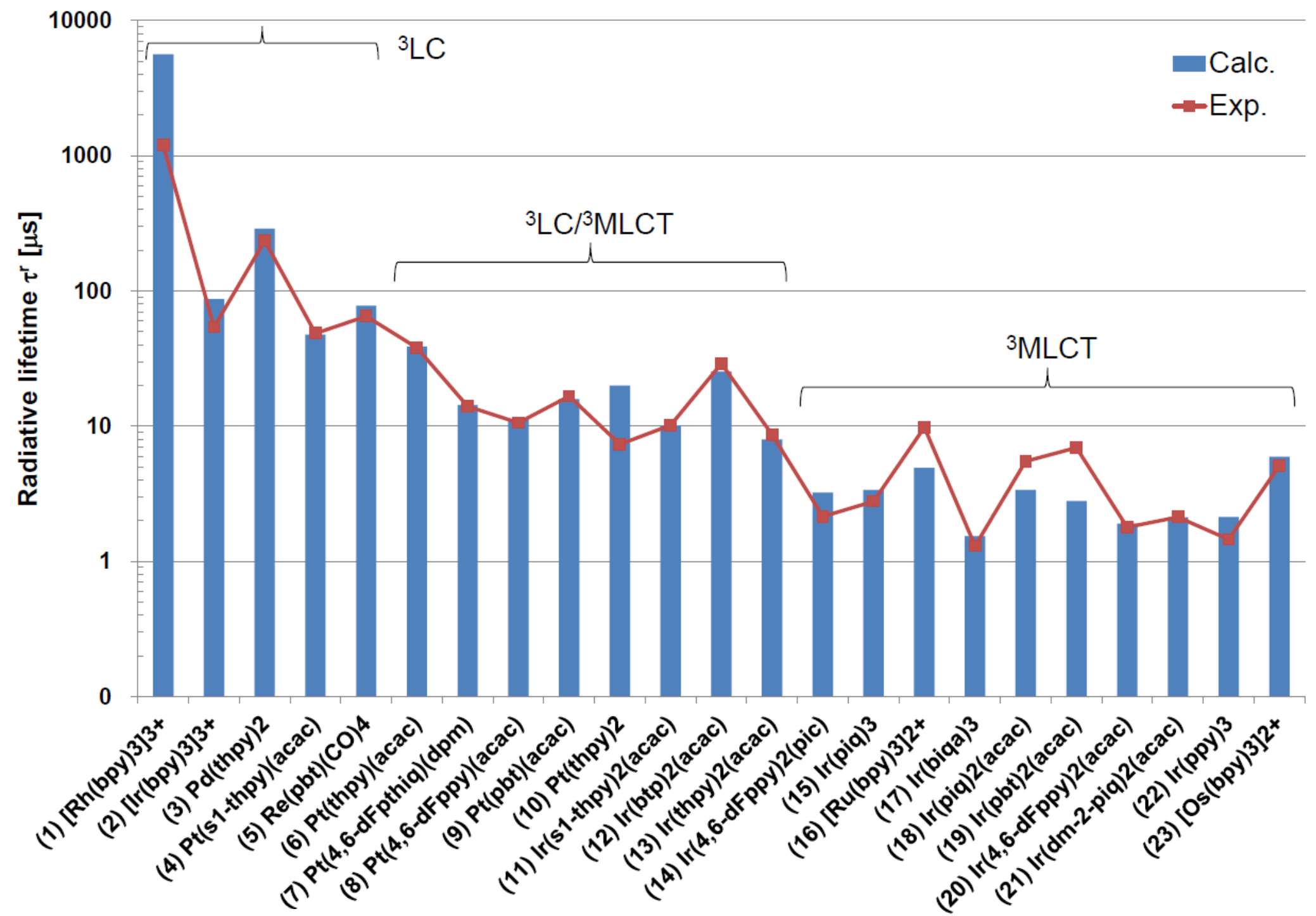
TDA: ☐ Yes

Number of excitations: 10



Phosphorescent OLED emitters

- Optimize OLED performance
 - Phosphorescence $T_1 \rightarrow S_0$
 - TADF: min. S-T, max. SOCME
 - Fast ISC: $S_n \rightarrow T_1$
 - High charge mobility
- ADF features
 - SOC-TDDFT: k_{phos}
 - SOCME: k_{ISC}
 - Transfer integrals (mobilities)
 - Other couplings (FDE)
 - Vibrationally resolved abs/em

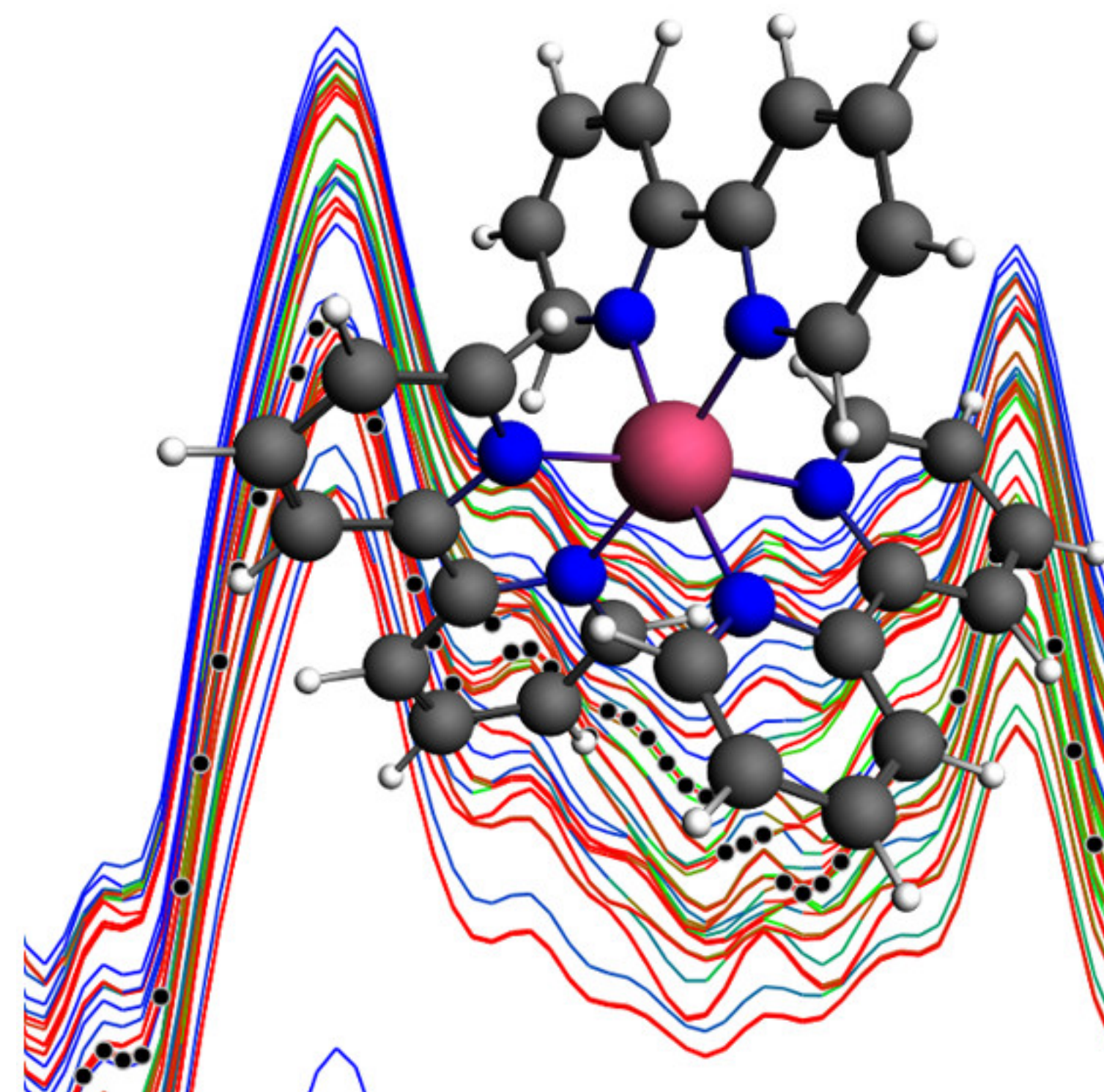
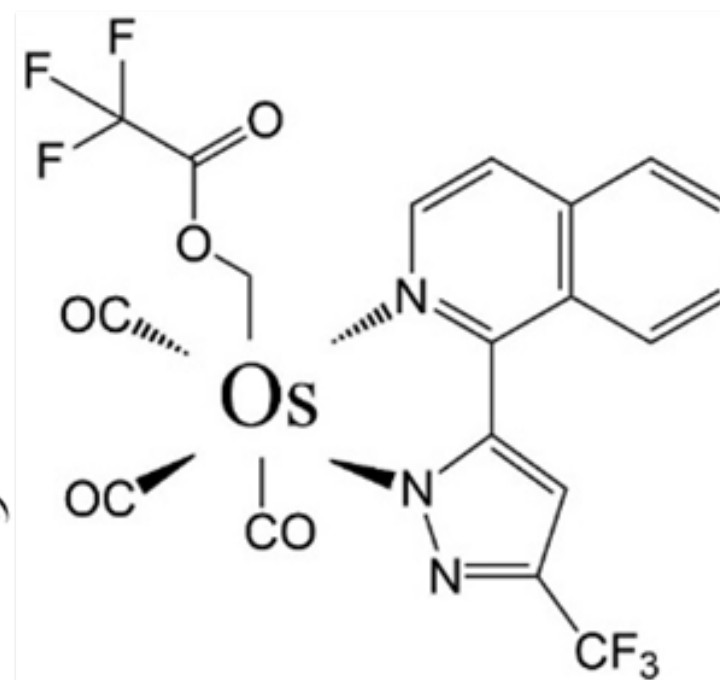
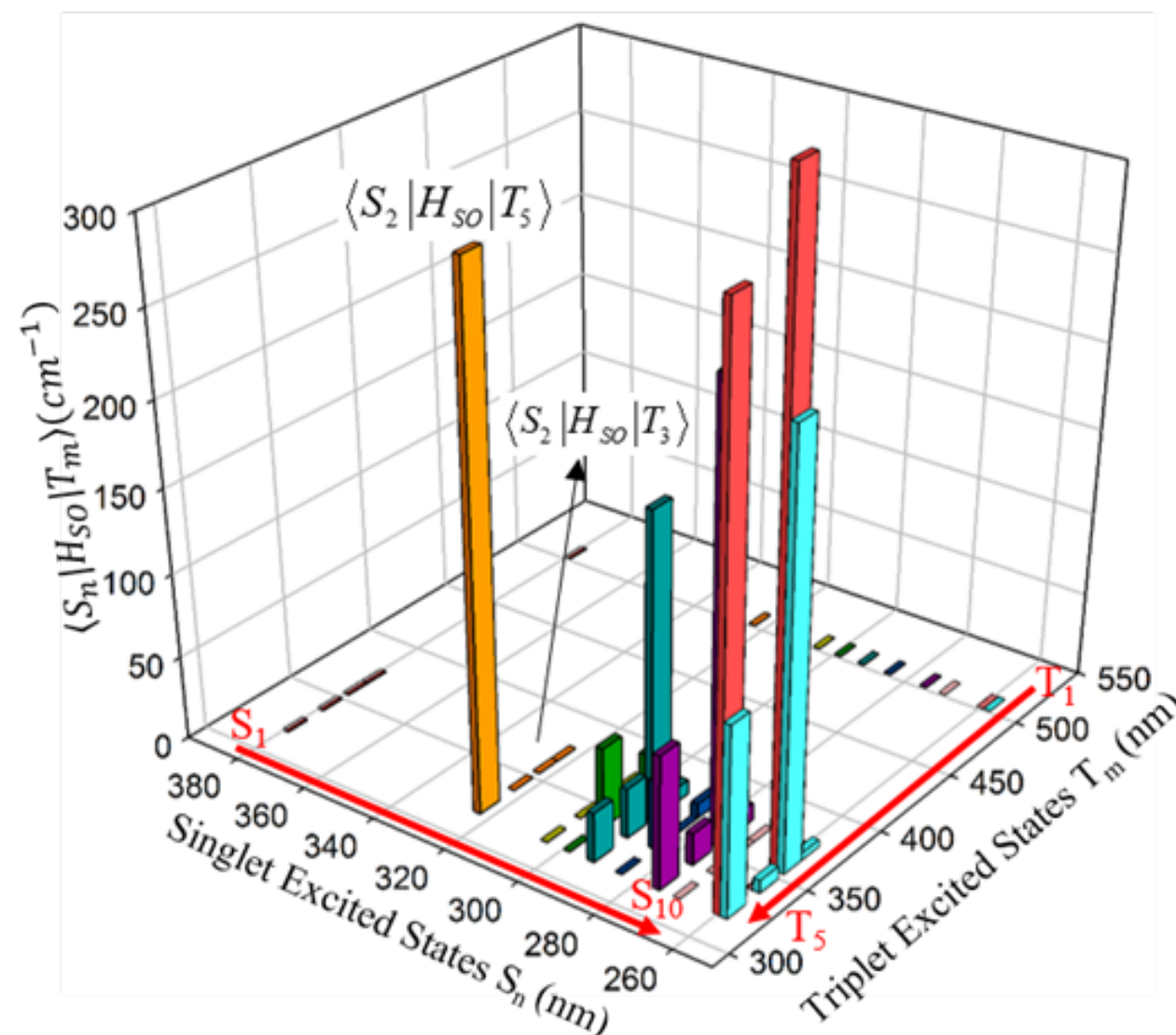


23 Ir, Rh, Ru, Os,
Pt, Re complexes

K. Mori, T. P. M. Goumans, E. van Lenthe,
F. Wang, [PCCP 16, 14523 \(2014\)](#)

[ADF tutorial](#) online

Intersystem crossing: spin-orbit coupling



El-Sayed for organometallics:

SOC is largest when:

- both S ($^1d\pi^*$) and T ($^3d'\pi^*$) are MLCT
- different d-orbitals are involved ($d \neq d'$).

λ_{exc} -dependent quantum yield

SOCME negligible for S_1 - T_n

ISC from higher S_n states

[Phys. Chem. Chem. Phys. 16, 26184-26192 \(2014\)](#)

NB: See also full k_{ISC} Paul et al. [JPCL, 2017, 8, 4893](#)

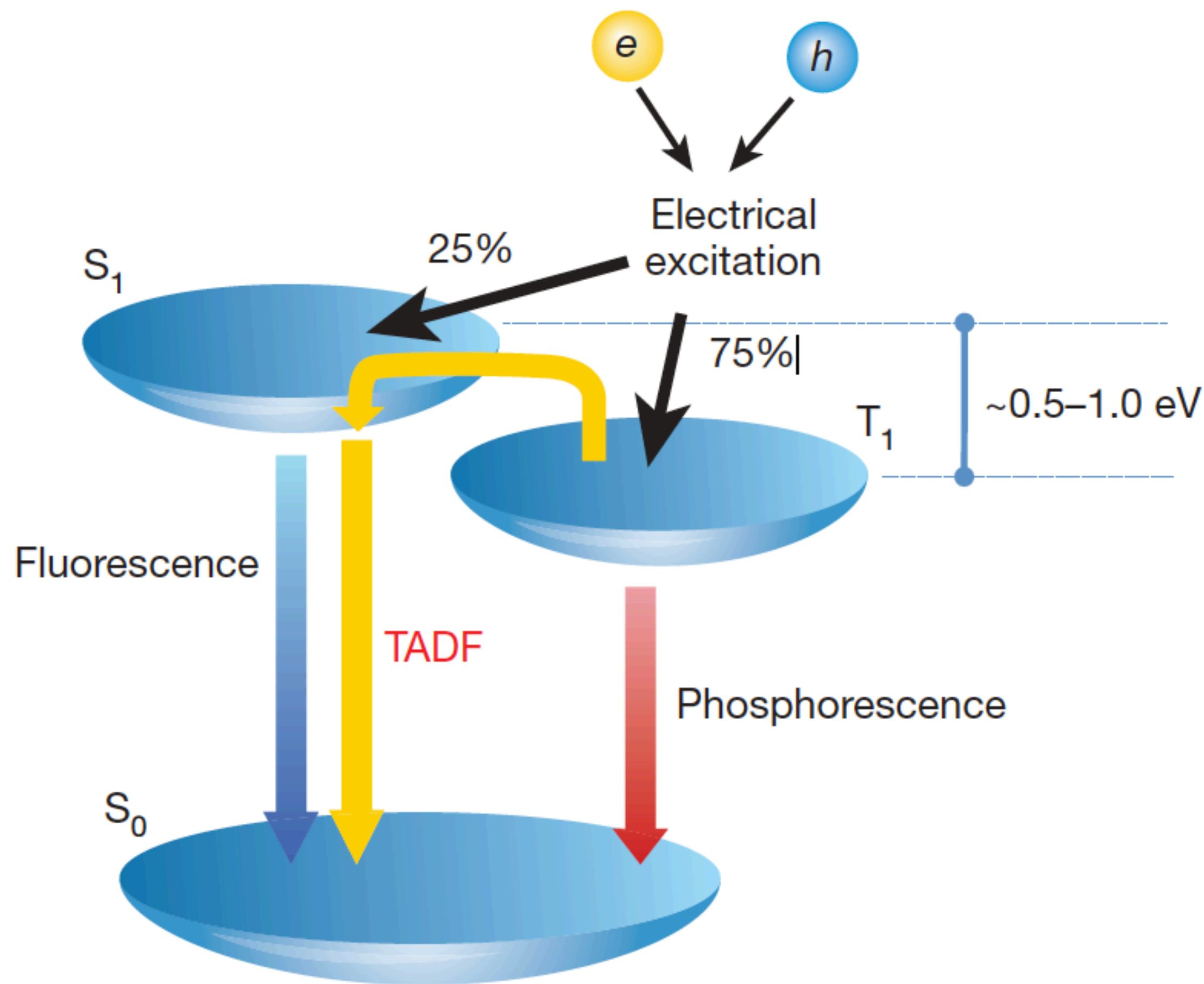
Surface-Hopping Dynamics $\text{Ru}(\text{bpy})_3^{2+}$

- Interface SHARC-ADF with ISC (SOC)
- ISC from higher S_n states within 26 ± 3 fs

Atkins & Gonzalez

[J. Phys. Chem. Lett., 8, 3840-3845 \(2017\)](#)

Thermally Activated Delayed Fluorescence



Optimize radiative rate

- Minimize S_1 - T_1 gap
- Maximize SOC
- Maximize k_{phos} & k_{TADF}

$$k_{\text{UIISC}} = \frac{2\pi}{\hbar} \rho_{\text{FC}} |\langle S_1 | \hat{H}_{\text{SO}} | T_1 \rangle|^2$$

$$\rho_{\text{FC}} = \frac{1}{\sqrt{4\pi\lambda_{\text{M}}k_{\text{B}}T}} \sum_{n=0}^{\infty} \exp(-S) \frac{S^n}{n!} \exp\left[-\frac{(\Delta E_{\text{ST}} + n\hbar\omega_{\text{eff}} + \lambda_{\text{M}})^2}{4\lambda_{\text{M}}k_{\text{B}}T}\right]$$

Z.-M. su et al. [Dyes & Pigments 145, 277-2847 \(2017\)](#)
 Bredas et al. [J. Am. Chem. Soc. 139, 4042-4051 \(2017\)](#)

ADF tutorial in progress

Spin-orbit coupling TDDFT

- Exercise 5: Calculate the SOC spectrum and the SOCME
 - Switch to perturbative Spin-Orbit and tick SOCM
 - ADF can do full and perturbative SOC
 - SOCME useful for (R)ISC, e.g. TADF/OLEDs
 - Visualize the spectrum: any effect?
 - SOC small for purely organic
 - Check SCM -> Output
 - Go to Response Properties -> All Singlet-Singlet Excitations. Compare with All Spin-Orbital Coupling Excitation Energies. Go to -> SO Matrix. This is the full matrix. Further down you will find the averaged spin-orbit coupling matrix elements (SOCMEs)

Excitations (UV/Vis), CD

Type of excitations: Spin-Orbit (Perturbative)

Show: Spin-Orbit coupling matrix

All Spin-Orbital Coupling Excitation Energies

no.	E/a.u.	E/eV	f	tau/s	Symmetry
1:	0.12004	3.26655	0.1880E-08	1.149	A'
2:	0.12004	3.26657	0.4159E-06	0.5193E-02	A'
3:	0.12004	3.26655	0.2580E-09	8.371	A''
4:	0.13339	3.62962	0.2890E-04	0.6054E-04	A''
5:	0.13363	3.63626	0.1693E-11		A'
6:	0.13363	3.63626	0.4123E-10		A''
7:	0.13367	3.63732	0.4724E-05	0.3687E-03	A''
8:	0.14001	3.80992	0.7306E-11		A'

Spin-orbit couplings calculated as root mean squares: square root of (the sum of squares of spin-orbit coupling matrix elements of all sublevels of the uncoupled states) in cm⁻¹

	T1	T2	T3	T4	T5	T6
<S Hso T>	-----	-----	-----	-----	-----	-----
S1:	0.38	21.60	3.45	3.87	0.33	0.72
S2:	3.41	0.01	0.00	0.08	5.84	0.00
S3:	0.06	0.60	1.61	5.22	0.09	19.20
S4:	16.09	0.00	0.02	0.01	2.28	0.08
S5:	14.92	3.35	1.66	0.72	0.00	0.19
S6:	1.83	0.09	0.04	0.01	19.21	0.00
S7:	3.03	0.96	0.38	1.07	0.04	0.50
S8:	12.59	6.59	1.87	1.36	0.08	0.41
S9:	0.92	0.04	0.10	0.01	4.91	0.01
S10:	31.04	0.00	0.02	0.03	3.07	0.07
<T Hso T>	-----	-----	-----	-----	-----	-----

Speeding it up: DFTB

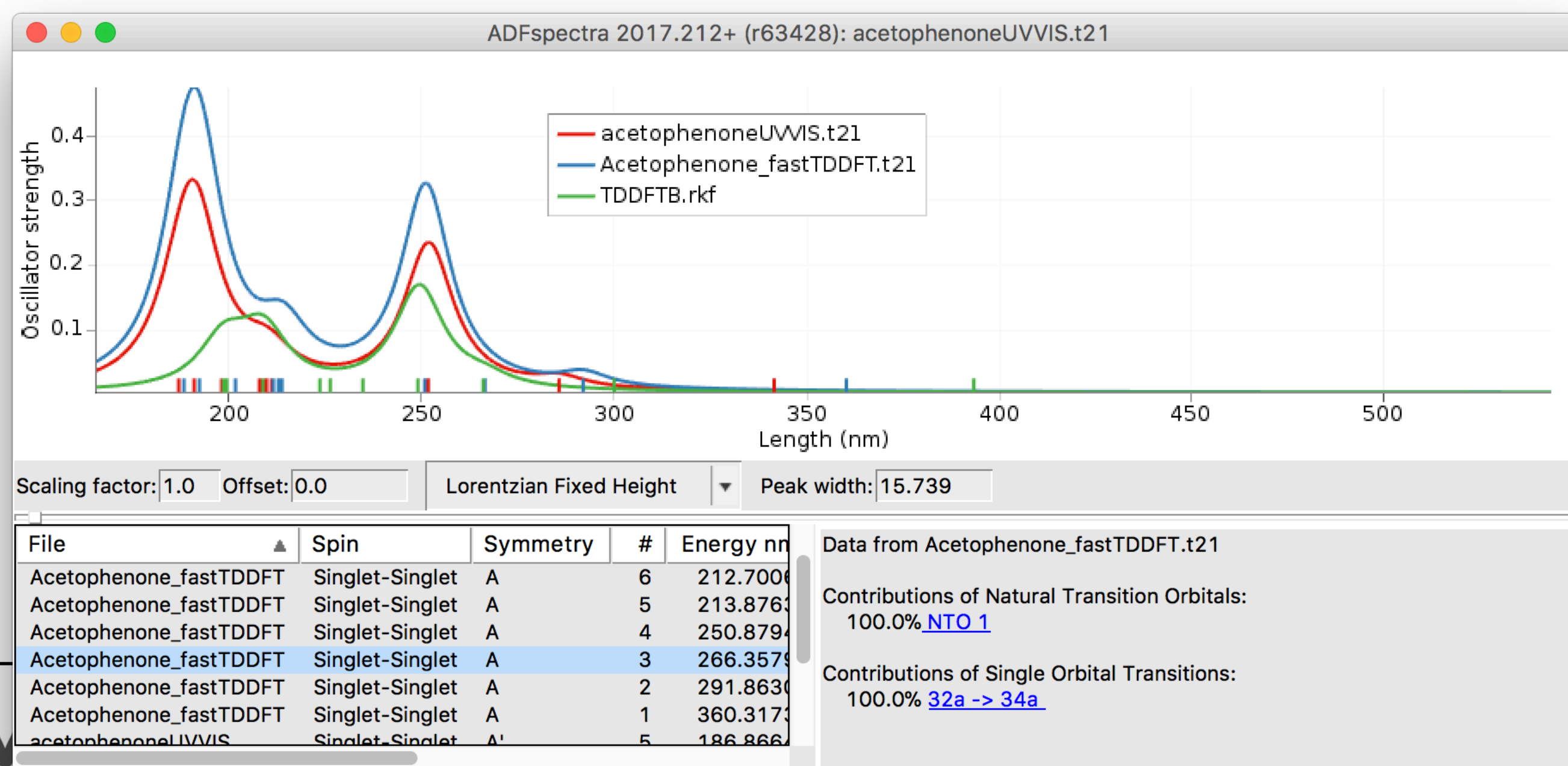
www.scm.com/doc/Tutorials/DFTB/DFTB-GUI_tutorials.html

- Exercise 6: Switch to DFTB and re-run the spectra
 - The default SCC-DFTB method is fine
 - Chose the 3ob-3-1 parameter set
 - Re-optimize, recalculate frequencies, recalculate UV/VIS spectrum
 - How do the spectra compare: TDDFT, sTDA, TDDFTB? Timings?
 - Also try the IR spectrum with DFTB & MOPAC
- To visualize DFTB MOs: single point SCC-DFTB/QuasiNano15 !

Parameter directory:



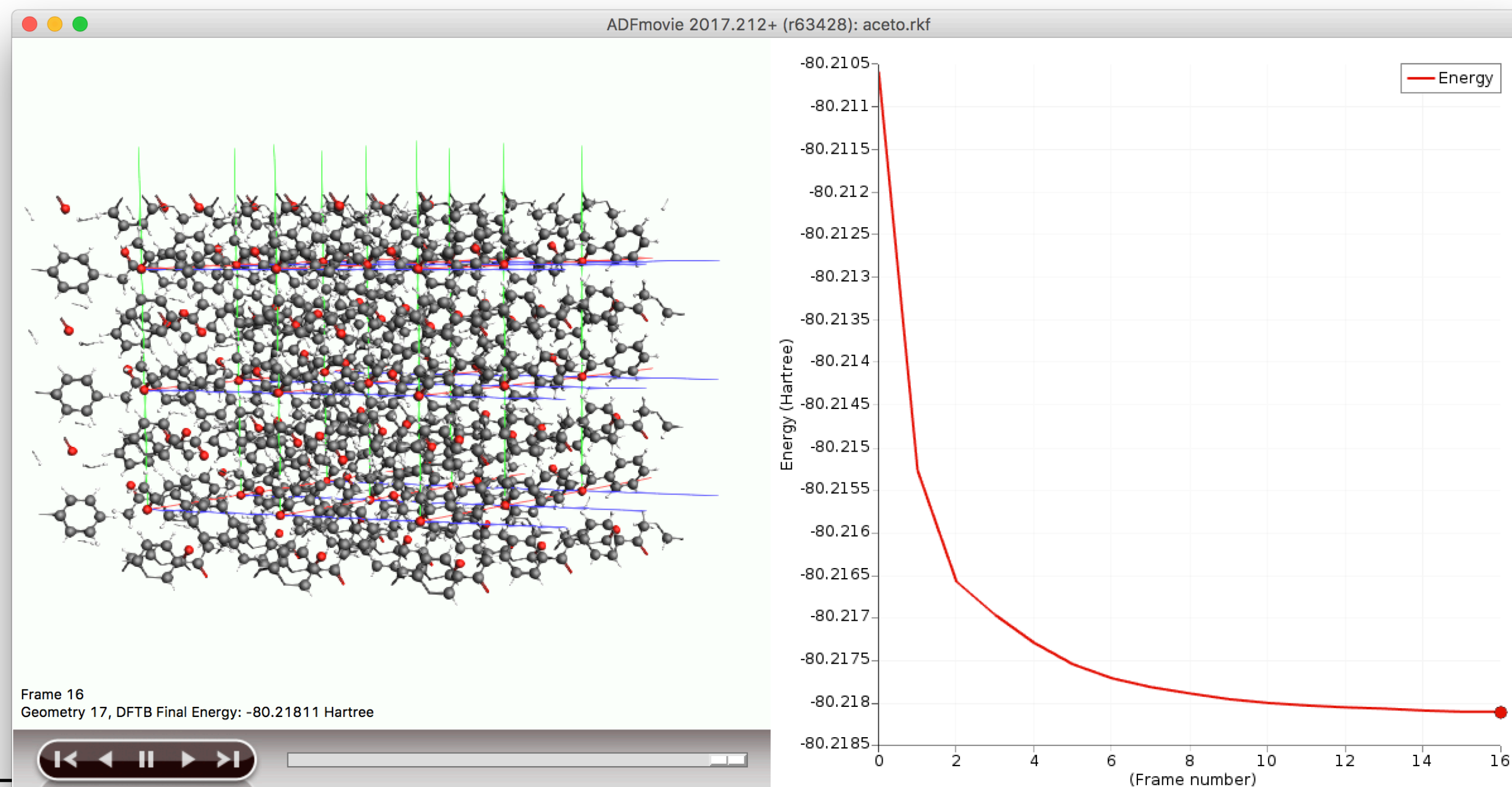
DFTB.org/3ob-3-1



Going periodic with DFTB

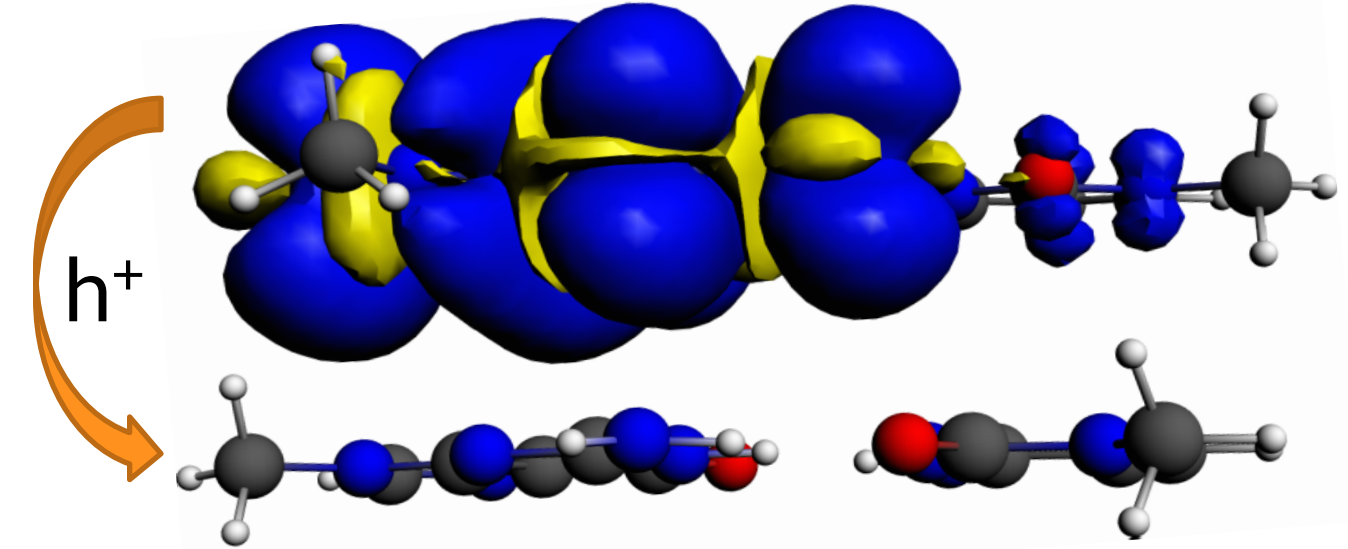
- Exercise 7: Acetophenone crystal

- Make a new input, search for acetophenone, select the crystal (optimized with MOPAC)
- Switch from BAND to DFTB and choose D3-BJ dispersion and the 3-ob-3-1 parameter set
- Ignore the small unit cell warning
 - NB: consider to go to a larger supercell instead of k-point sampling (will use FIRE)
 - You may also consider optimizing the lattice (slow)
- Check progress with SCM -> Movie

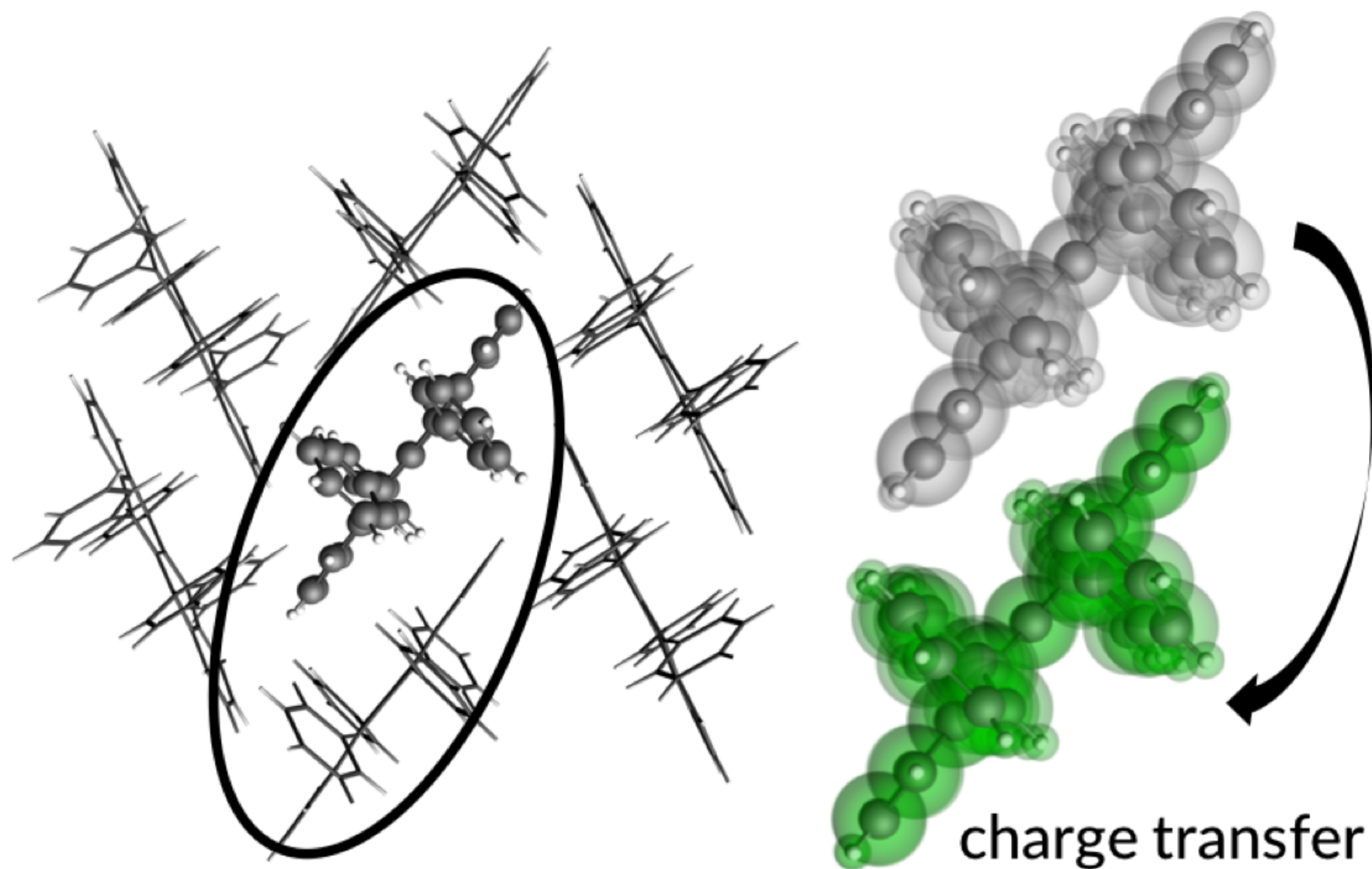


Methods to calculate charge mobilities

- Hopping transport:
 - Charge transfer integrals (FO) - easy
 - Electronic couplings from FDE
- Band transport: effective mass tensors in BAND
 - AMS2018: for any k-point & also for DFTB
 - Simulating excited state: [create a core hole](#)
- Non-equilibrium Green's Function (NEGF)
 - transmission probabilities for single-molecule junctions
 - quick calculation: wide-band limit
 - also in BAND (periodic structures, fully self-consistent, bias) and in DFTB
 - See online tutorials



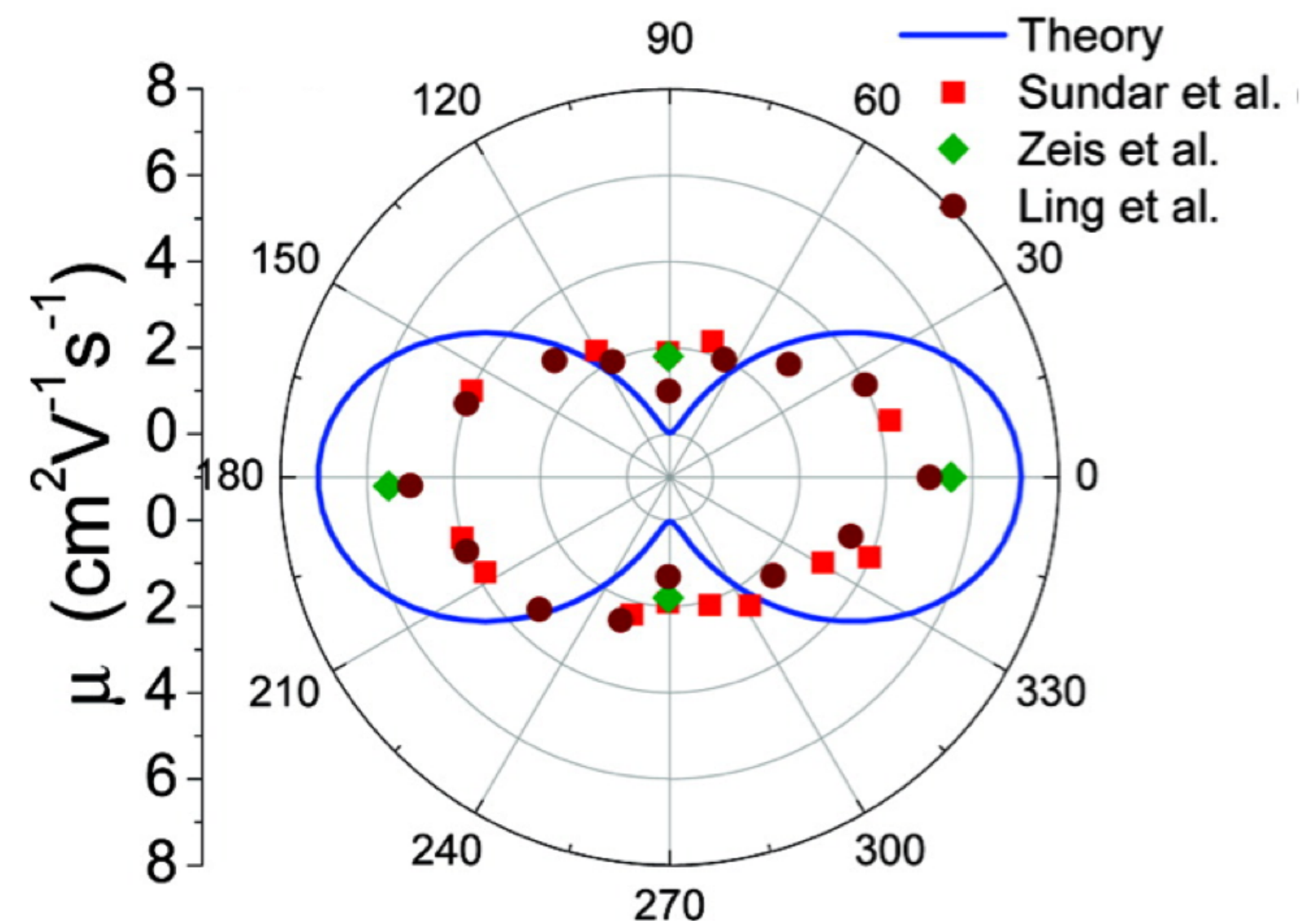
Effective transfer integral J_{eff} = electronic coupling V



extract
dimers

$$V = \frac{J_{\text{RP}} - S_{\text{RP}}(H_{\text{RR}} + H_{\text{PP}})/2}{1 - S_{\text{RP}}^2}$$

$$k = \frac{4\pi^2}{h} \frac{V^2}{\sqrt{4\pi\lambda k_B T}} \exp\left\{-\frac{\lambda}{4k_B T}\right\}$$



Anisotropic mobility:

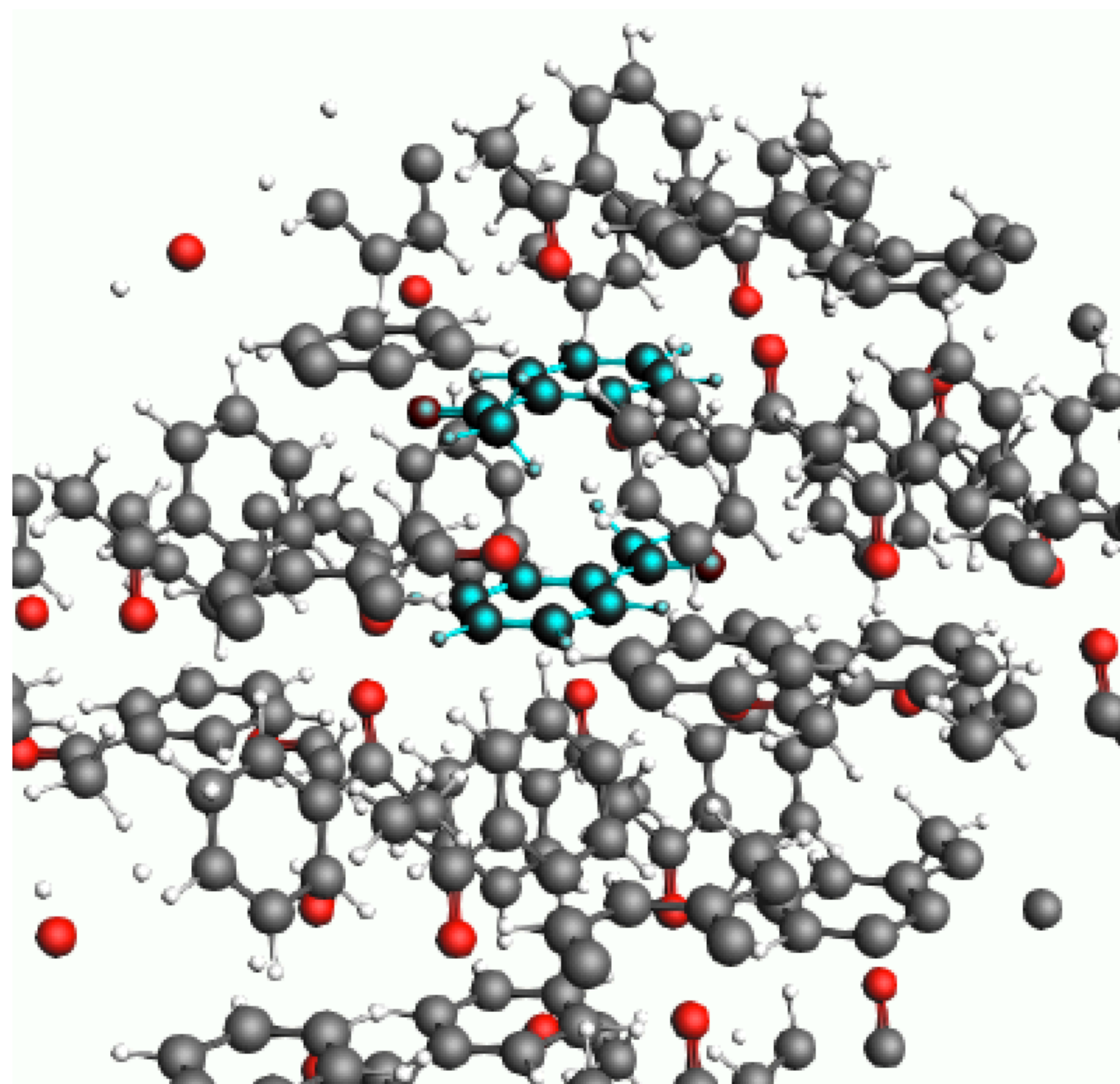
$$\mu_{\Phi} = \frac{e}{2k_B T} \sum_i W_i^2 P_i \cos^2 \gamma_i \cos^2(\theta_i - \Phi)$$

S.-H. Wen et al., J. Phys. Chem. B 113, 8813 (2009)

[ADF tutorial](#) online, ADF prints V / J_{eff} => use with Marcus theory for hopping rates

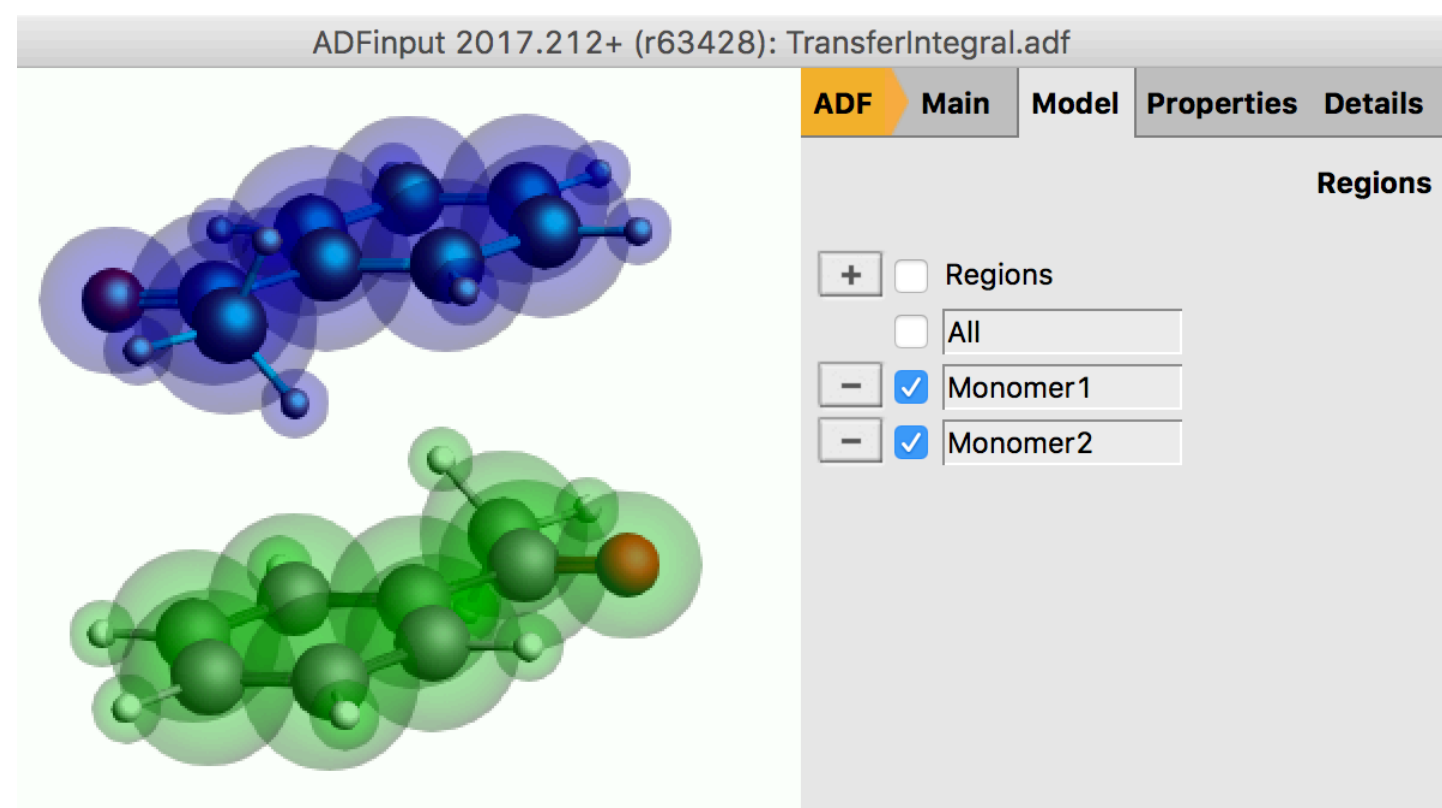
Charge transfer integrals & recombination

- Exercise 8: 1st Select the dimer for the charge transfer event
 - Update the geometry from your DFTB run
 - Make a 2x2x2 supercell (Edit-> Crystal -> Generate Supercell)
 - Switch from DFTB to ADF
 - Select 1 atom from the middle 'flat' acetophenone and one from the molecule above
 - Press Ctrl+M to select both molecules



Charge transfer integrals & recombination

- Exercise 8: Calculate the charge transfer integral
 - Select -> Invert selection. Delete all other atoms
 - In the Model Region Panel select each molecule as a new region (delete the crystal region):



- Select PW91 functional (often used) with a DZP basis
 - Frozen cores are incorrect in principle; in practice usually fine
- Find 'transfer integral' in the GUI search, and tick it.
- In Multilevel -> Fragments pane, tick 'Use fragments'
- SCM-> Output; Properties -> Charge transfer integrals
- [ADF tutorial](#): how to get mobilities
- AMS2018: [charge recombination](#)

ADFOutput 2018.105: CT_aceto.out

Charge transfer integrals relevant for hole or electron mobility calculations

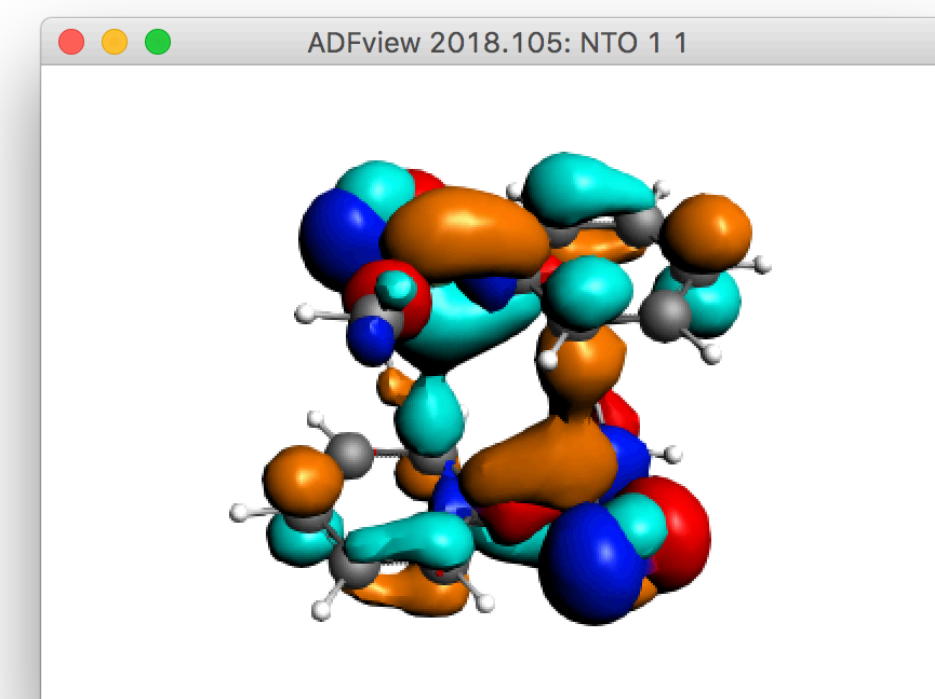
Electronic coupling V (also known as effective (generalized) transfer integrals J_{eff})
 $V = (J - S(e_1 + e_2)/2) / (1 - S^2)$

V for hole transfer:	0.00181 eV
V for electron transfer:	-0.09641 eV
V for charge_recombination 1-2:	0.00433 eV
V for charge_recombination 2-1:	-0.00434 eV

(Charge transfer) analysis excited state

- Exercise 9: Calculate the excitations with [SFO analysis](#) + [CT descriptors](#)
 - Untick charge transfer integrals
 - Properties -> Excitations: select Allowed only
 - Tick SFO Analysis + CT descriptors
 - Save as a different file & run
 - Visualize the spectrum and NTOs of two lowest states (CT)
 - In output search for Plasser (see [paper with Lischka](#))
 - CT = 1 & POS = 1.5 and CTNET = 0 => Charge resonance
 - Very small exciton splitting
 - LAMBDA = 0.4655 => perhaps use hybrid or RSH ([Tozer](#))

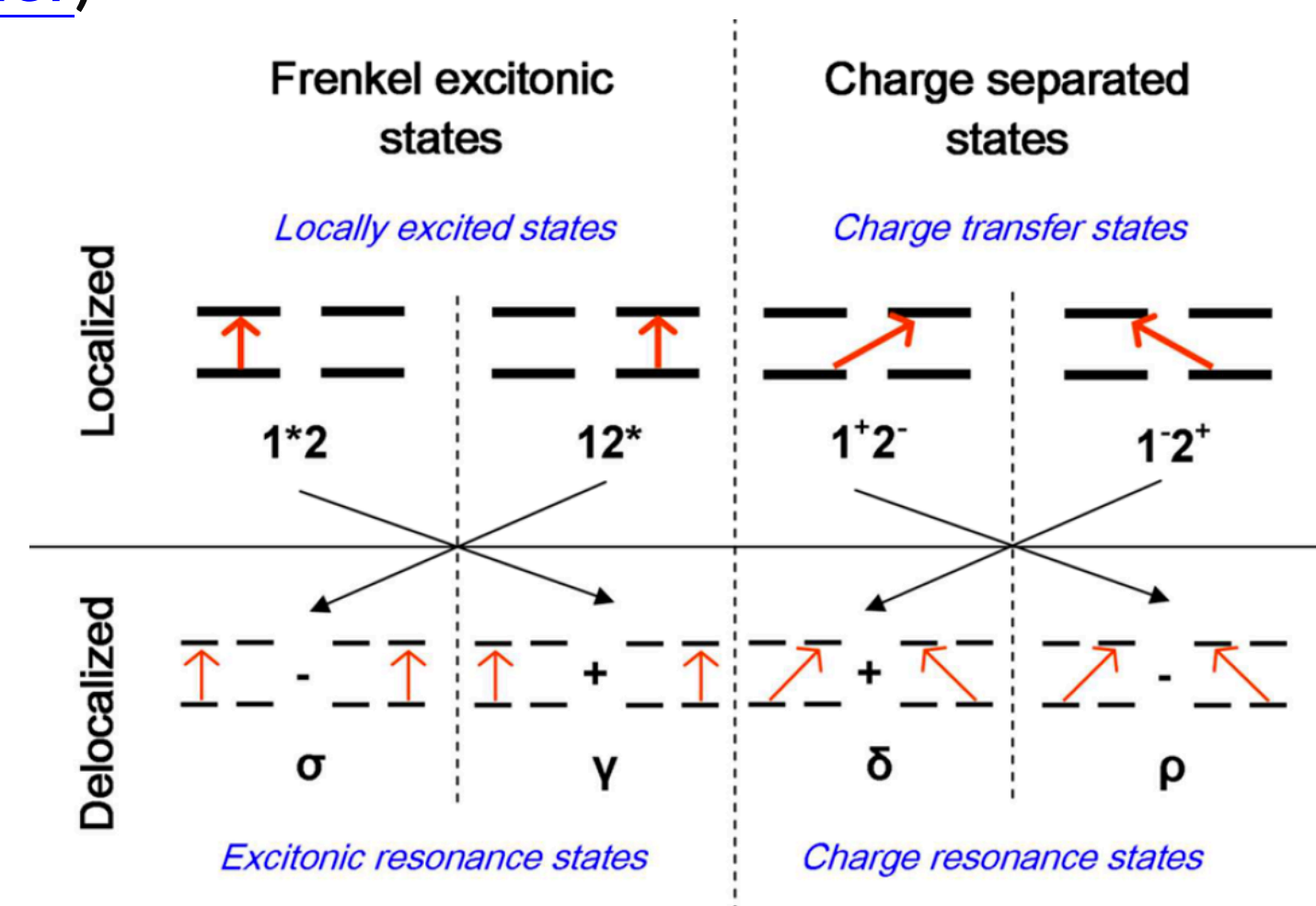
☒ Charge transfer descriptors
☒ SFO Analysis



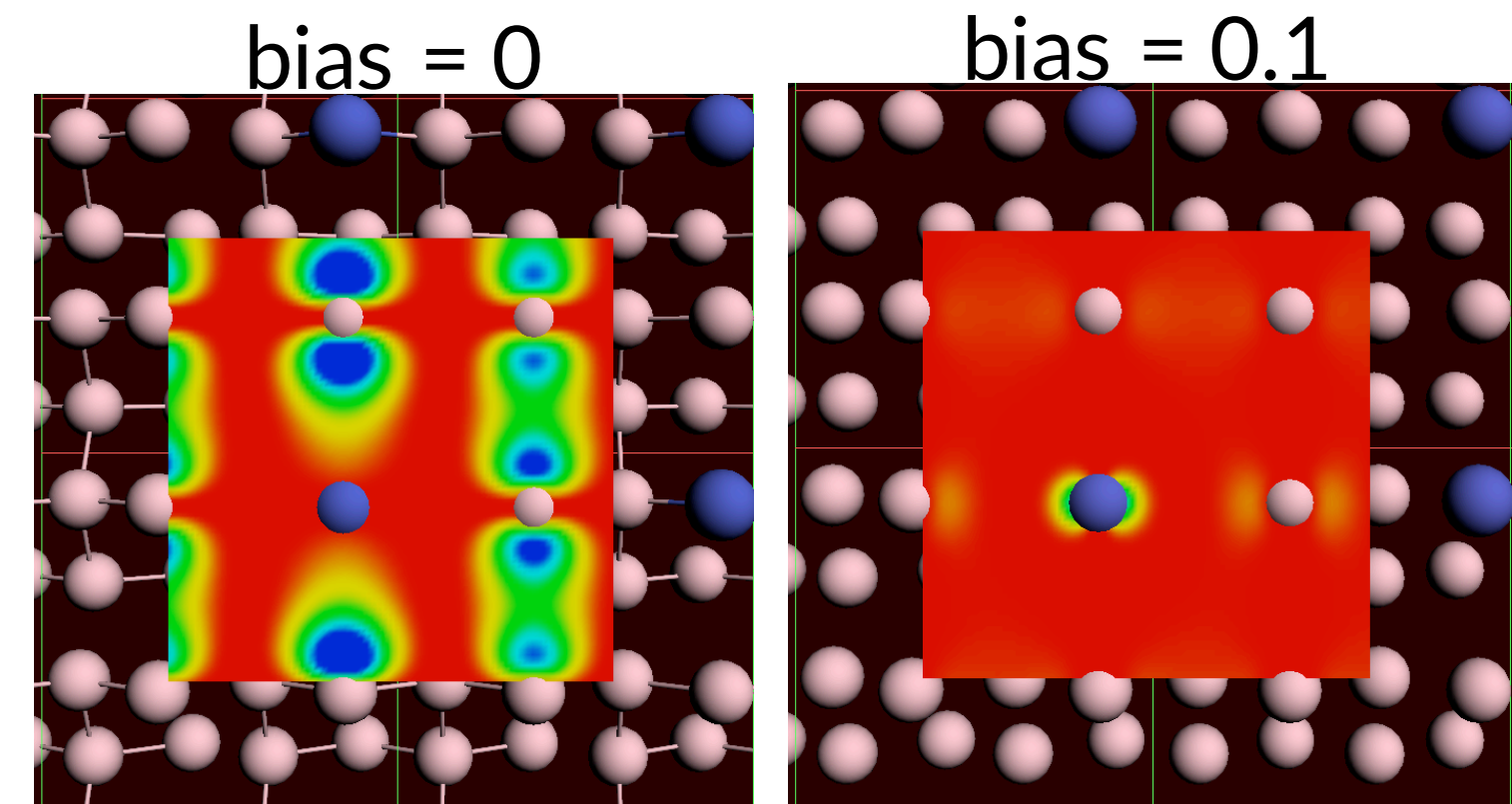
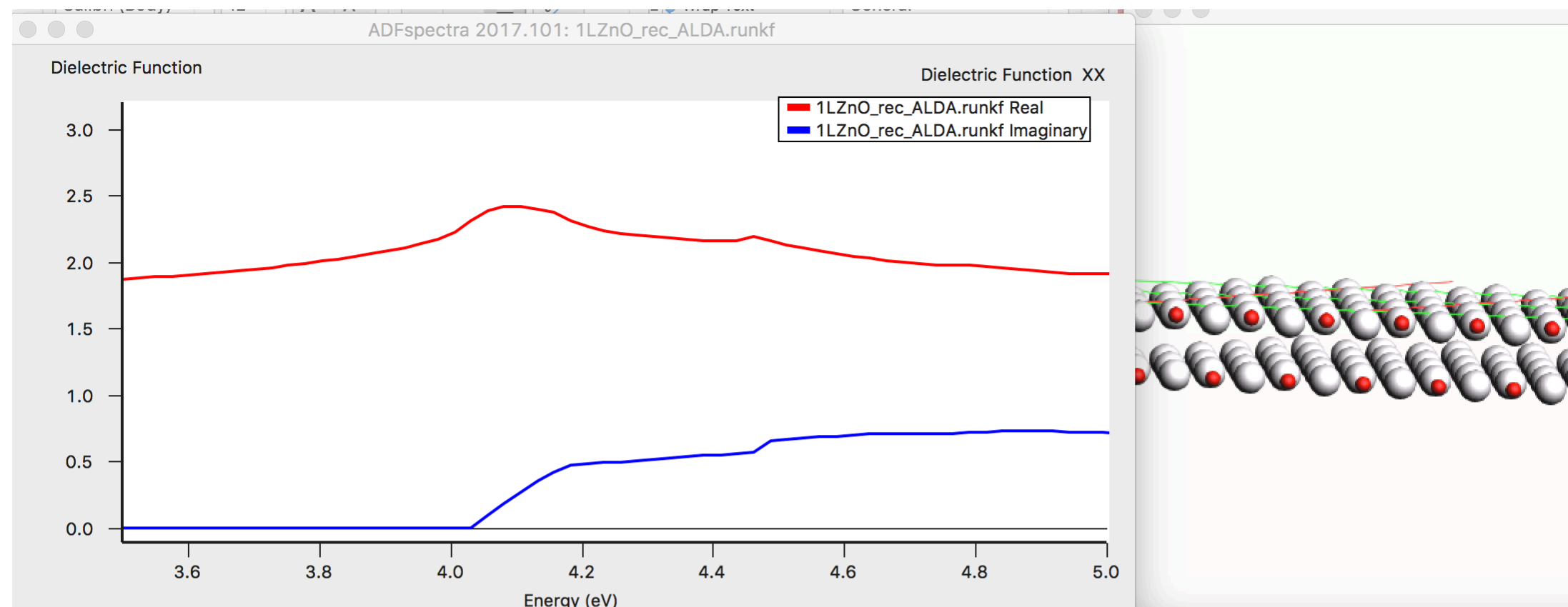
Descriptors (based on [Plasser](#), Lischka, et al.)
 CT_AT = 0.9524 R_HE = 4.8449
 CT = 0.8778 PR = 1.9530 COH = 1.2649
 POS = 1.4898 CTNET = 0.1539
 Descriptors (Peach, Tozer, et al.)
 LAMBDA = 0.4655 R_HE = 0.1334

FRAGMENT -> FRAGMENT ANALYSIS BASED on SFOs

Frag -> Frag	weight	mu(x)	mu(y)	mu(z)
1 -> 1	0.0698	0.0247	-0.0011	-0.0072
2 -> 2	0.0501	0.0199	-0.0157	-0.0011
1 -> 2	0.5172	-0.0082	0.0182	-0.0066
2 -> 1	0.3630	-0.0089	0.0099	-0.0036
All -> All	1.0000	0.0275	0.0114	-0.0186

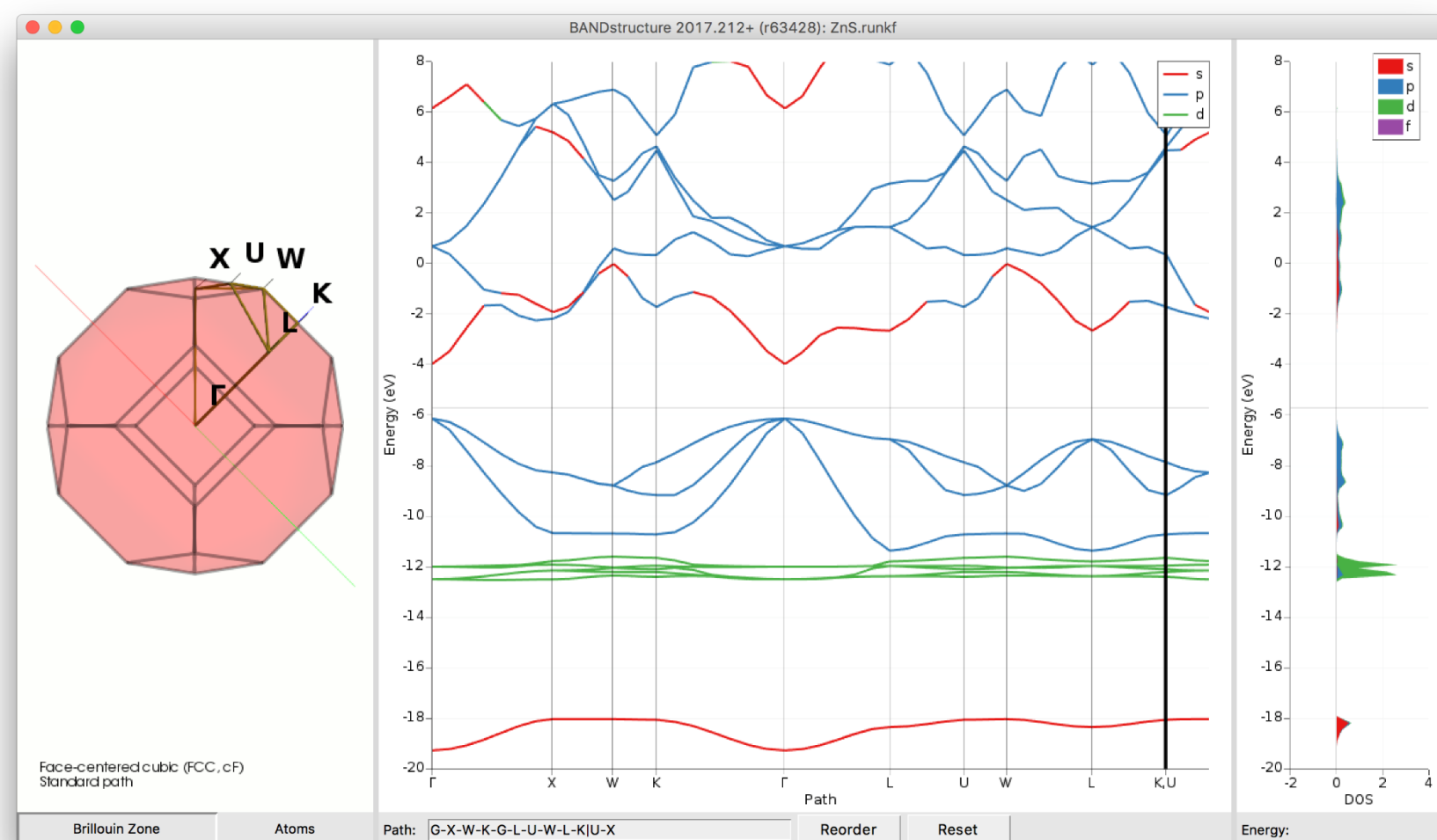


BAND & QE : Periodic DFT

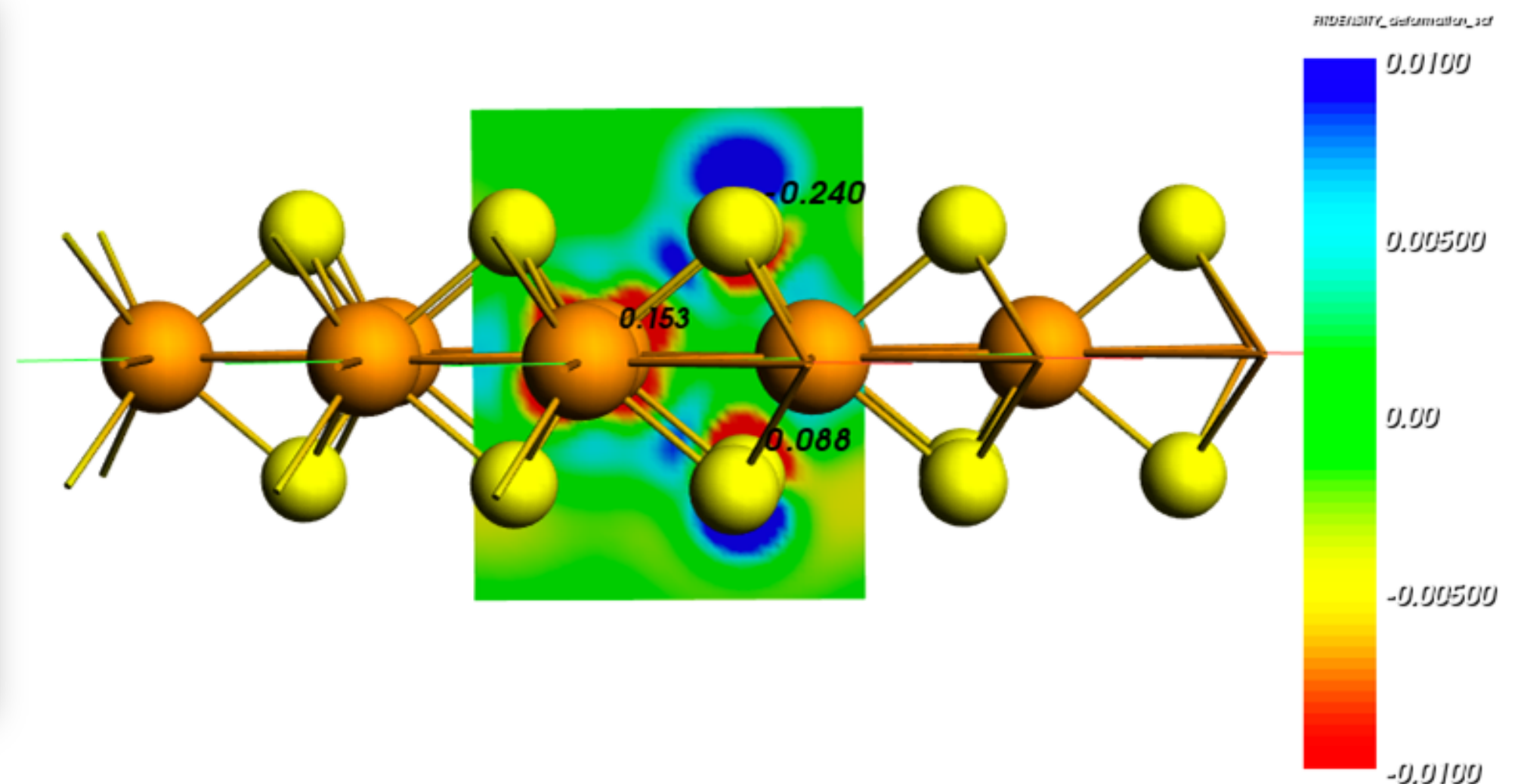


Dielectric function ML ZnO

STM PtGe(100)



Band structure, pDOS, fat bands ZnS

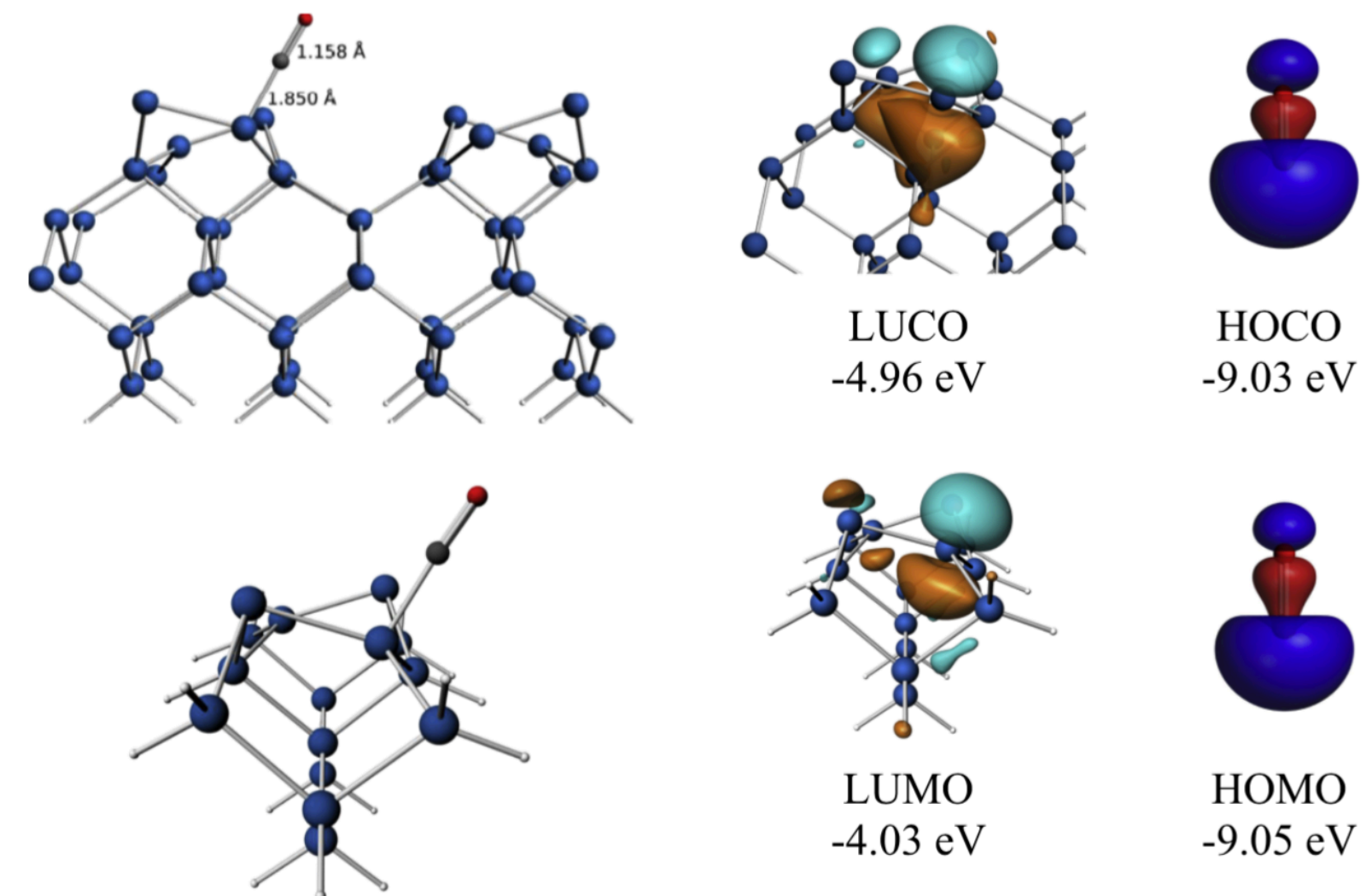


Polarizing MoS₂ with an electric field

BAND vs. Plane Wave codes (QE)

- Atom centered basis functions, STO or NAO

- Compare cluster with periodic
- No pseudopotentials, all elements
- Core spectroscopy (core holes)
- Easy (orbital, density) analysis with GUI
- Fast for empty (1D, 2D, porous)
- xc: SCAN, MN15-L, HSE06, GLLB-sc, D3(BJ), ...
- Self-consistent NEGF
 - Gate & bias potential
 - Spin transport



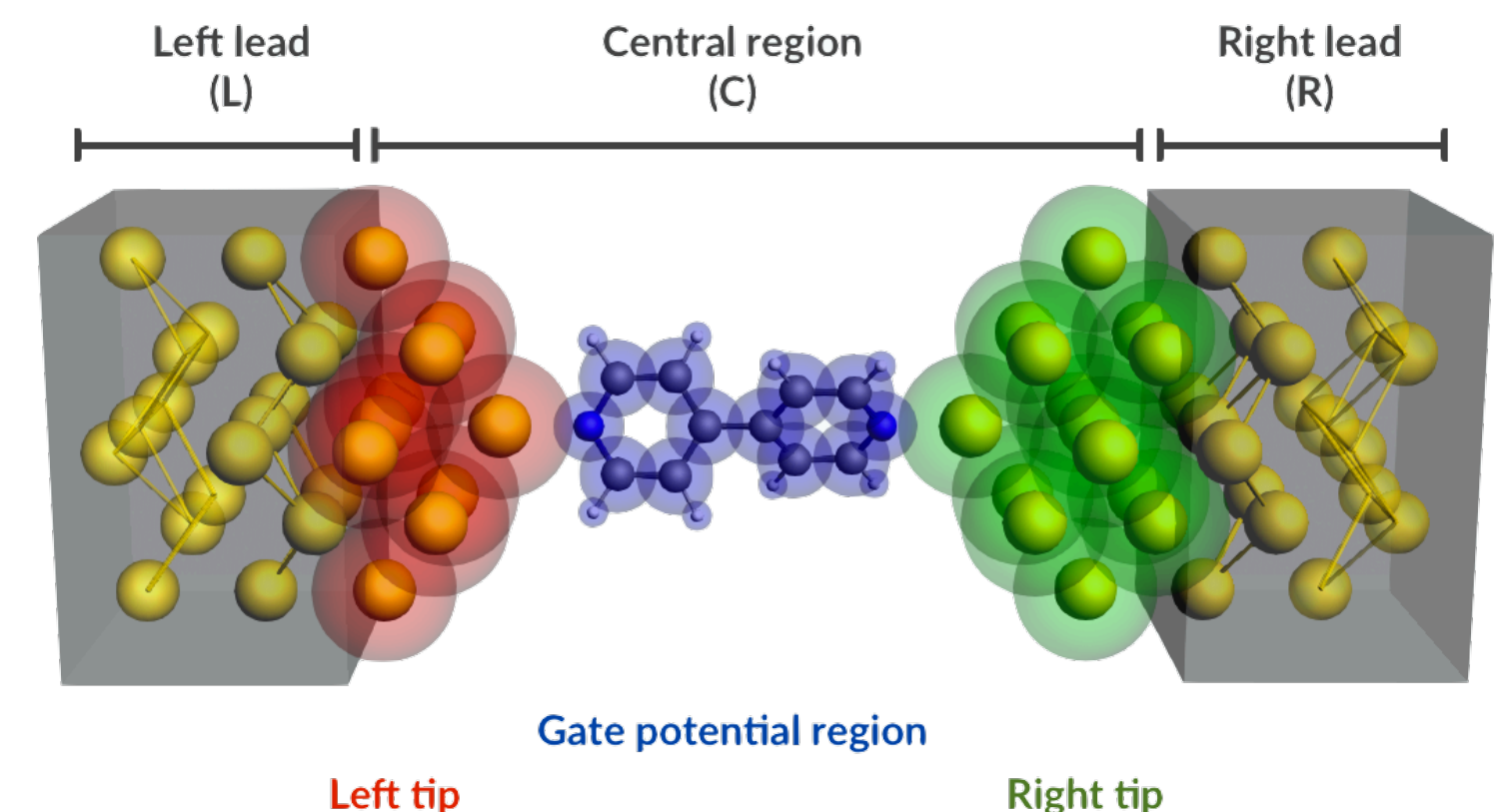
- True 2D surfaces, 1D polymers

- Het. catalysis: polarization, COSMO
- 2D electronics (homogeneous E field)
- Nanotubes

- Integrated Graphical Interface:

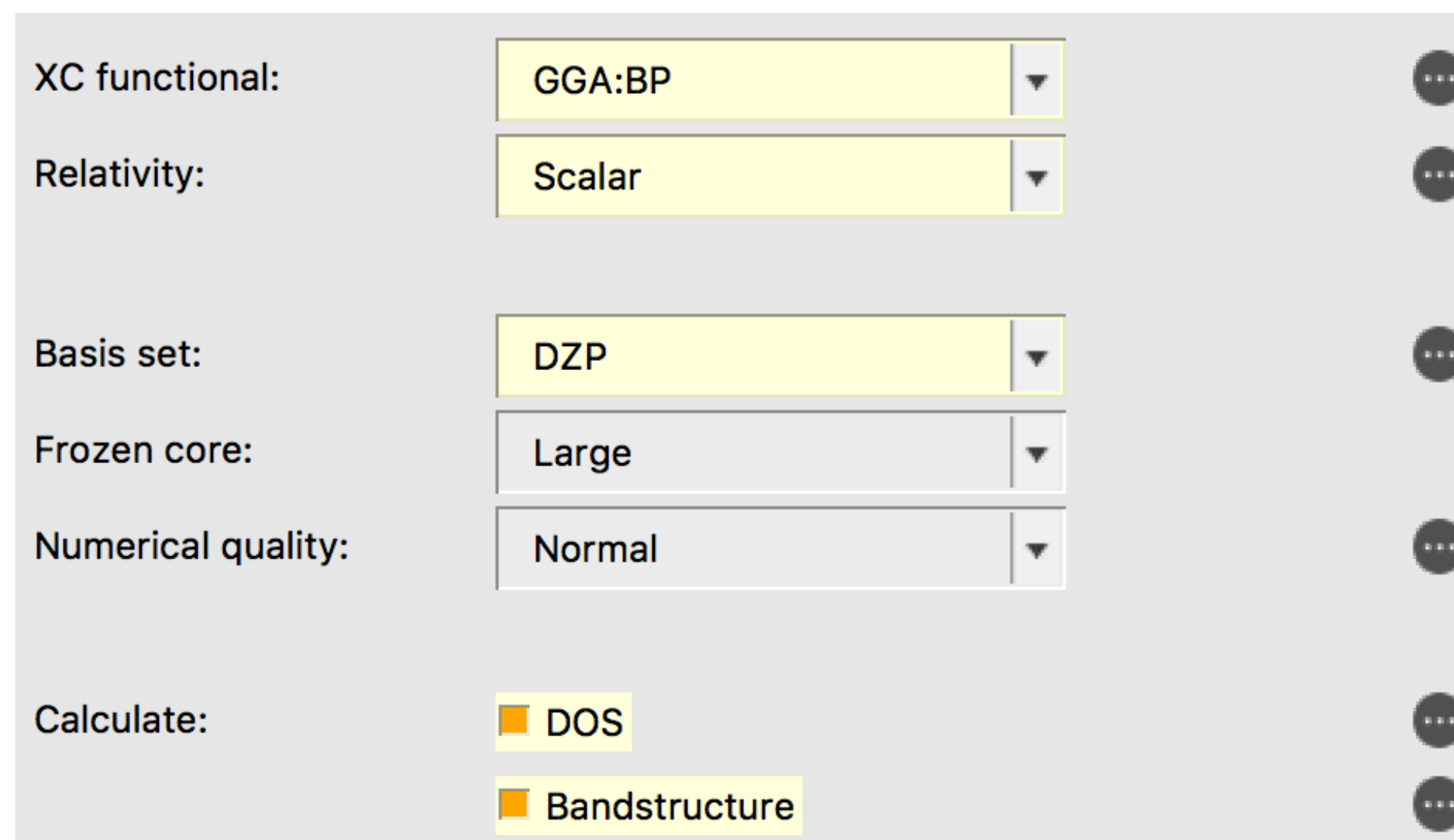
- Easy set up & analysis
- Switch: ADF, BAND & Quantum Espresso

crystal orbitals, periodic energy decomposition analysis
M. Raupach and M. Tonner, [J. Chem. Phys. 142, 194105 \(2015\)](#)



Band structure, pDOS, fat bands, COOP

- Exercise 10: ZnS bulk
 - New input, go to BAND
 - click on the 'crystal' builder tool in the bottom
 - select cubic -> Zincblende and accept the default
 - Settings: BP, SR-ZORA, and DZP
 - Select DOS and Bandstructure (default interpolation)
 - Run it!



The screenshot displays a settings panel with the following configuration:

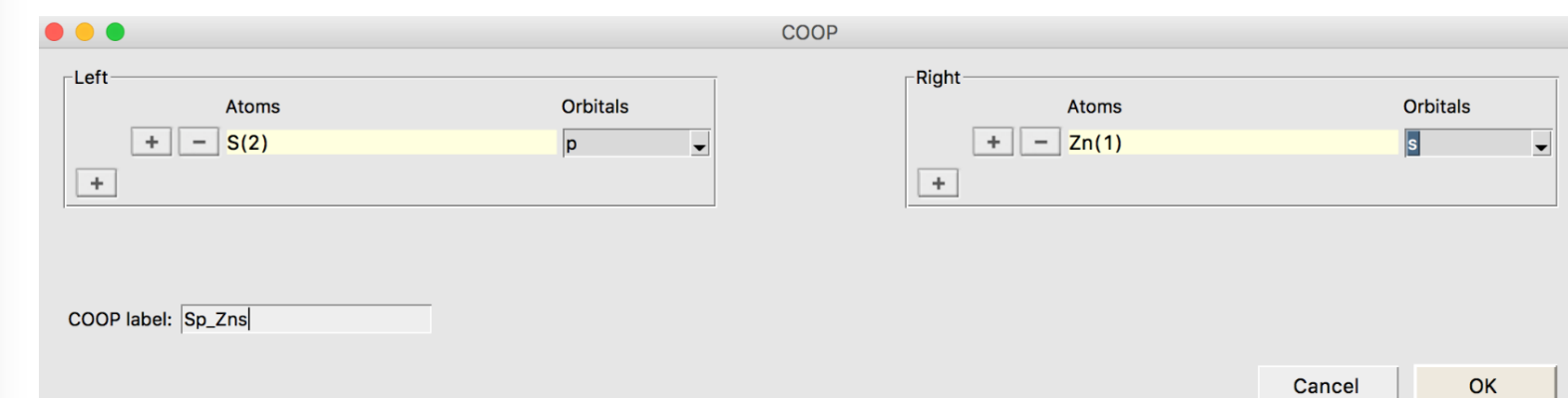
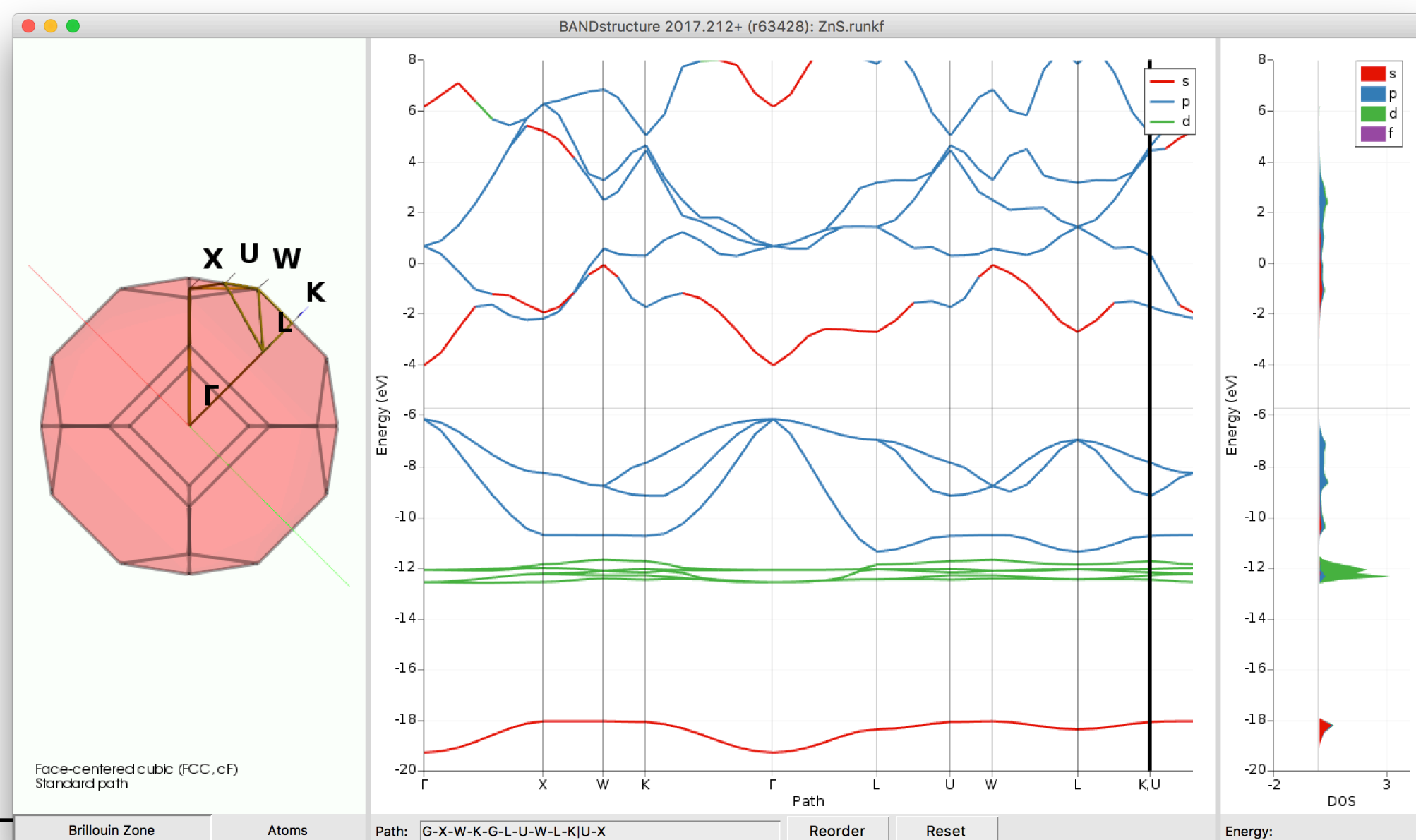
- XC functional:** GGA:BP
- Relativity:** Scalar
- Basis set:** DZP
- Frozen core:** Large
- Numerical quality:** Normal
- Calculate:** ☒ DOS, ☒ Bandstructure

Each parameter row has a dropdown arrow on the right, and a vertical column of three dots (⋮) is present on the far right of the panel.

Band structure, pDOS, fat bands, COOP

- Exercise 10: ZnS bulk

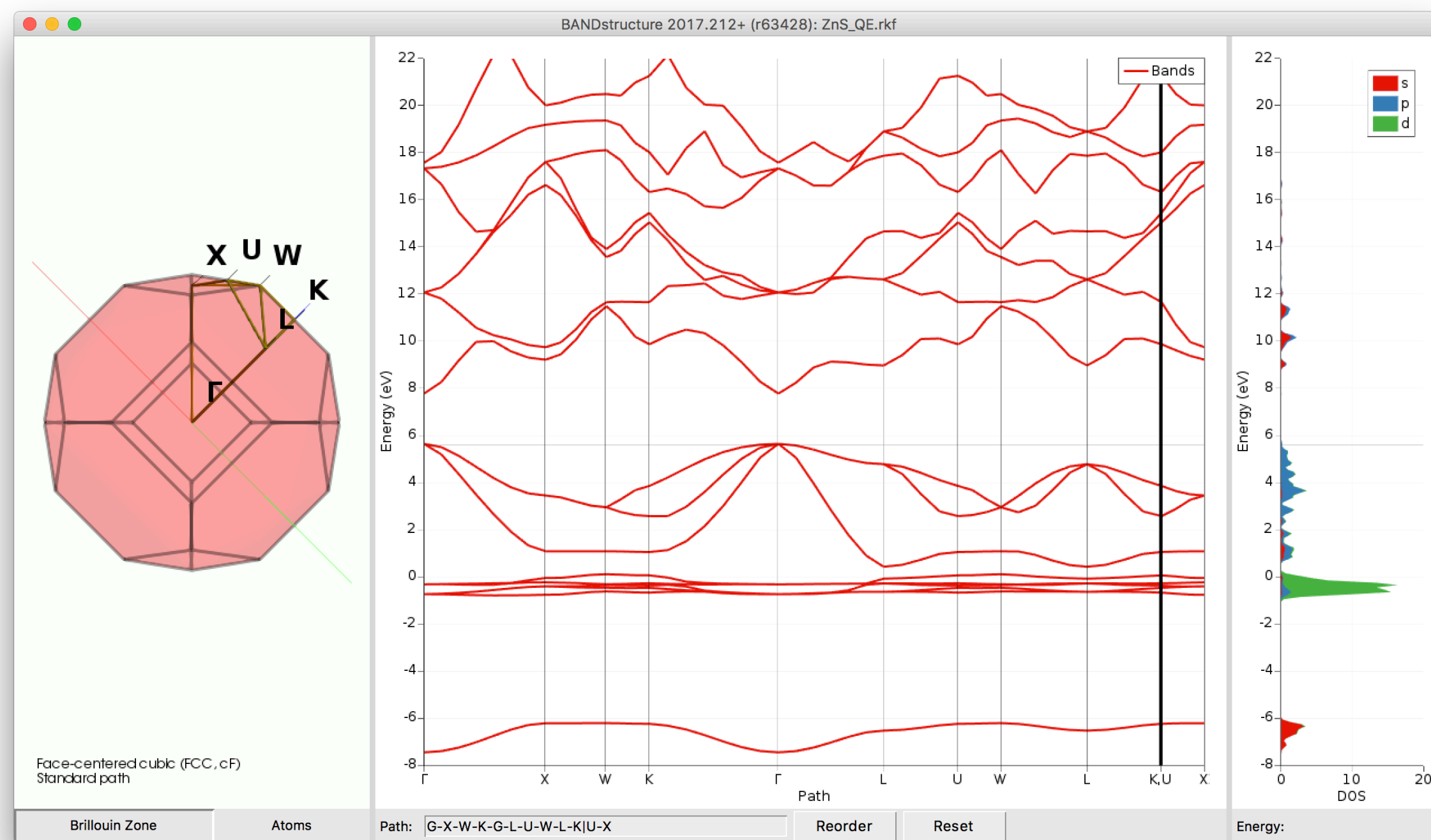
- Visualize the band structure (SCM Menu). You will automatically see the pDOS and 'fat bands'
- ZnS is a direct band gap semiconductor (p-s transition)
 - Check the logfile and output for band gap info and kmesh
 - Low band gap: try model potentials (TB-mBJ, GLLB-sc) and HSE06? [see benchmark study](#).
 - Should also be converged wrt kpoints, basis, etc.
- Restart the calculation from SCF and in the DOS details tick 'COOP'
 - Visualize the crystal orbital overlap population between the Zn s and S p orbitals



recent [JACS study by Hoffmann](#): COOP in perovskites ([tutorial](#))

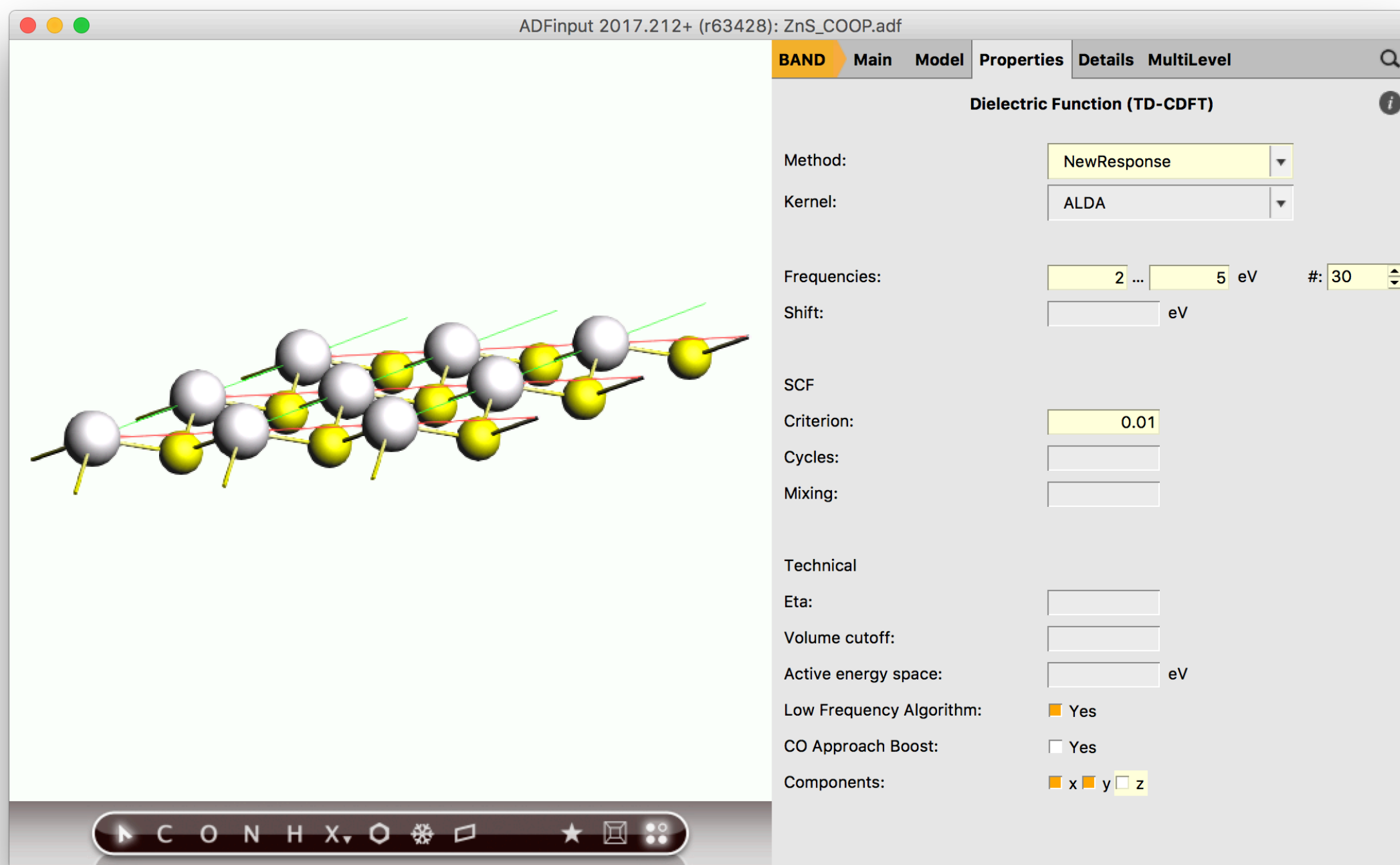
Band structure, pDOS with QE

- Exercise 10: ZnS bulk with QE
 - Switch from BAND to Quantum ESPRESSO
 - Choose the same k-mesh (5x5x5), functional and Vanderbilt pseudopotentials
 - You will see a similar band structure, but they aren't colored according to character
 - DOS can be projected by QE



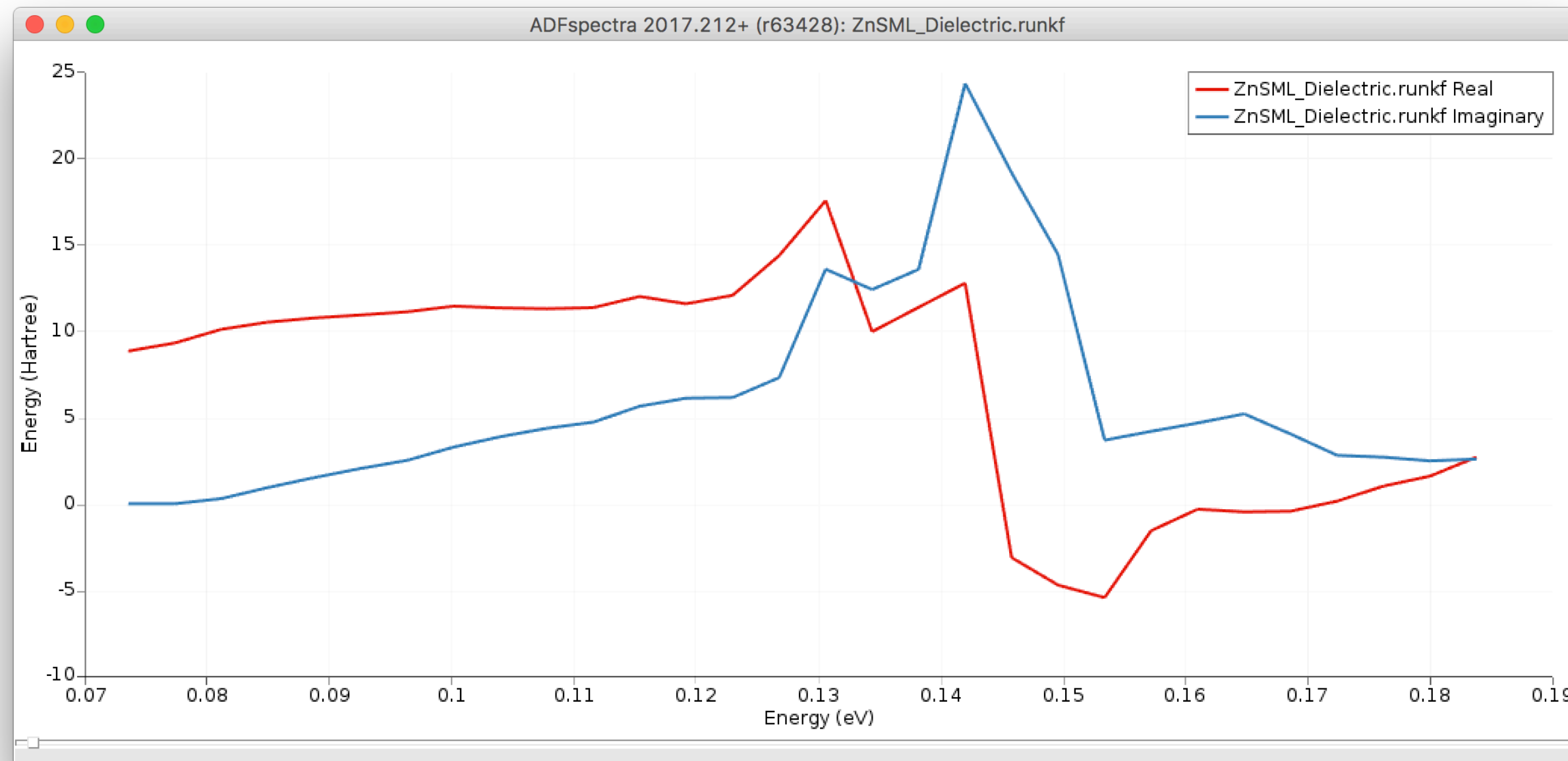
Surfaces, dielectric function

- Exercise 11: ZnS monolayer: 2D-TDCDFT
 - Cut the 111 surface with the slicer tool, and choose 1 layer
 - From properties -> dielectric function choose NewResponse
 - Calculate 30 frequencies between 2-5 eV
 - Set the SCF convergence criterion to 0.01 and switch off the z-component
 - Run it (you will prompted Nosymm is used)



Surfaces, dielectric function

- Exercise 11: ZnS monolayer: 2D-TDCDFT
 - SCM -> Spectra will show the averaged dielectric function
 - Look at the susceptibility, polarizability and refractive index in Spectra->TDCDFT
 - You could use a 'scissor' shift to upshift the virtuals
 - Converge with respect to k-points!
 - Geometry of the ions should be optimized, this will effect electronic properties
 - For free-standing ML, also optimize lattice ?!

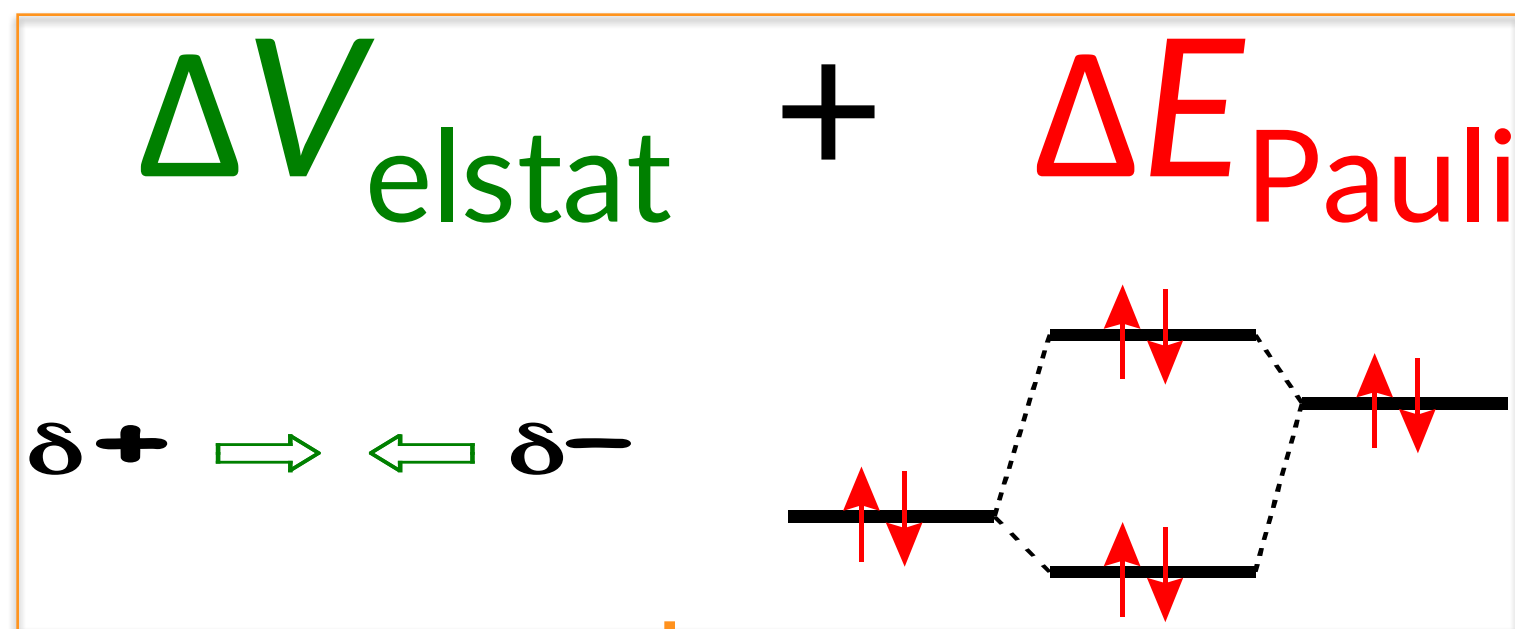


Energy decomposition analysis

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

Chem. Soc. Rev. 2014, 43, 4953;
WIRES Comput. Mol. Sci. 2015, 5, 324
Online tutorial & teaching materials

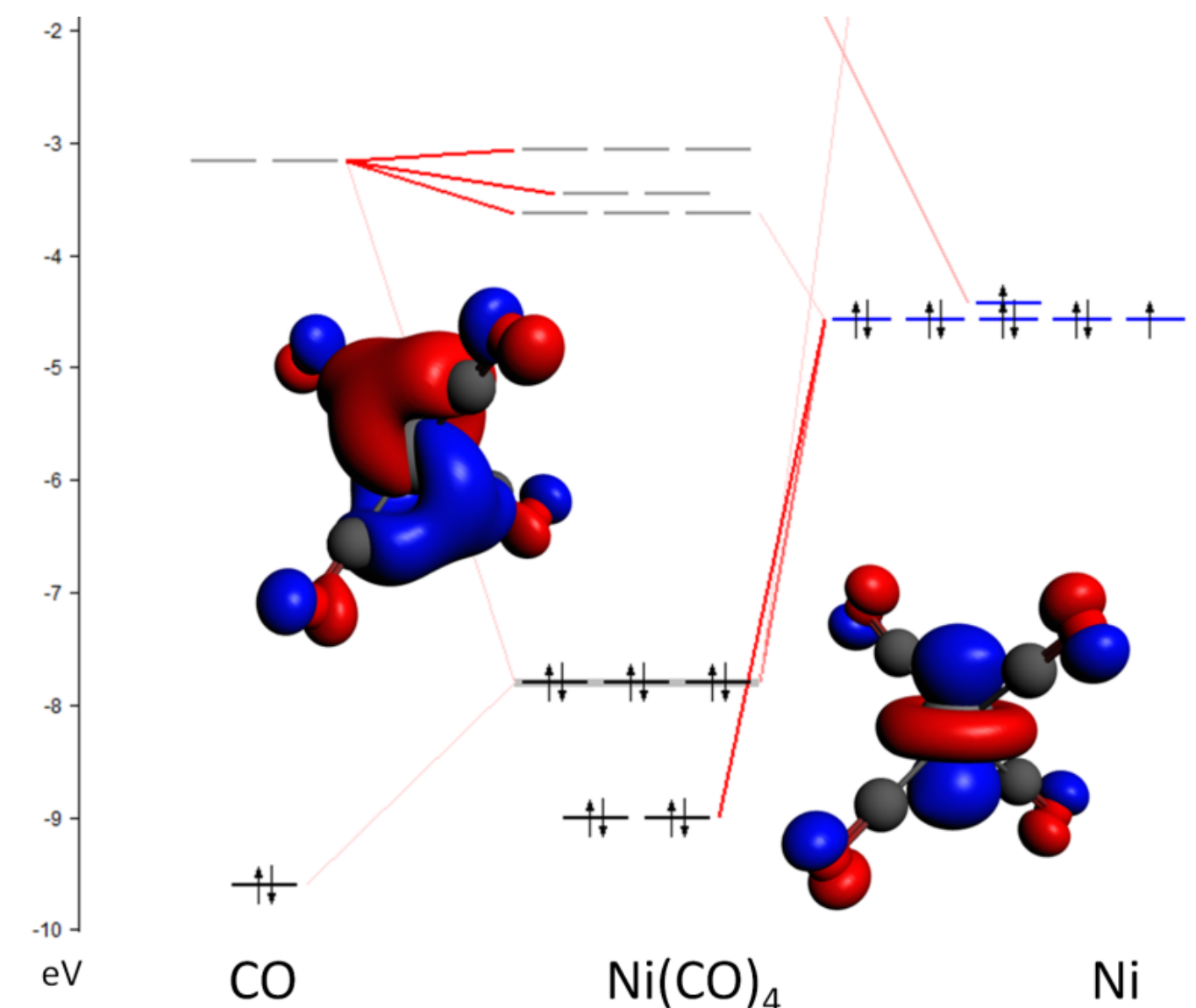
- ΔE_{prep} = geometry 'deformation' energy



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

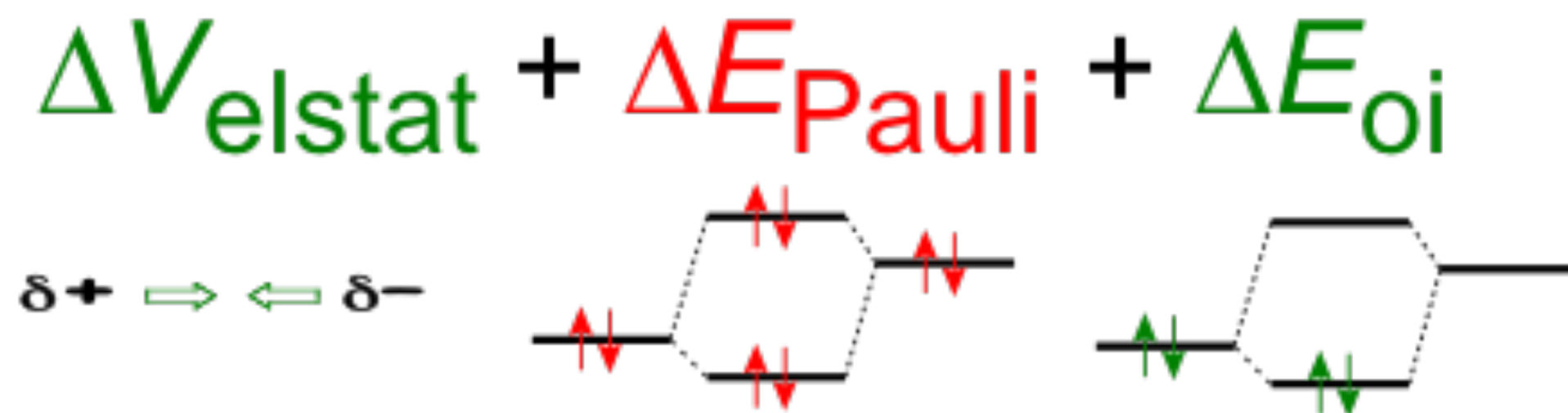
Extensions:

- Periodic EDA: M. Raupach & R. Tonner, J. Chem. Phys. 142, 194105 (2015): molecule-surface interactions
- Ziegler, Michalak, Mitoraj: ETS-NOCV

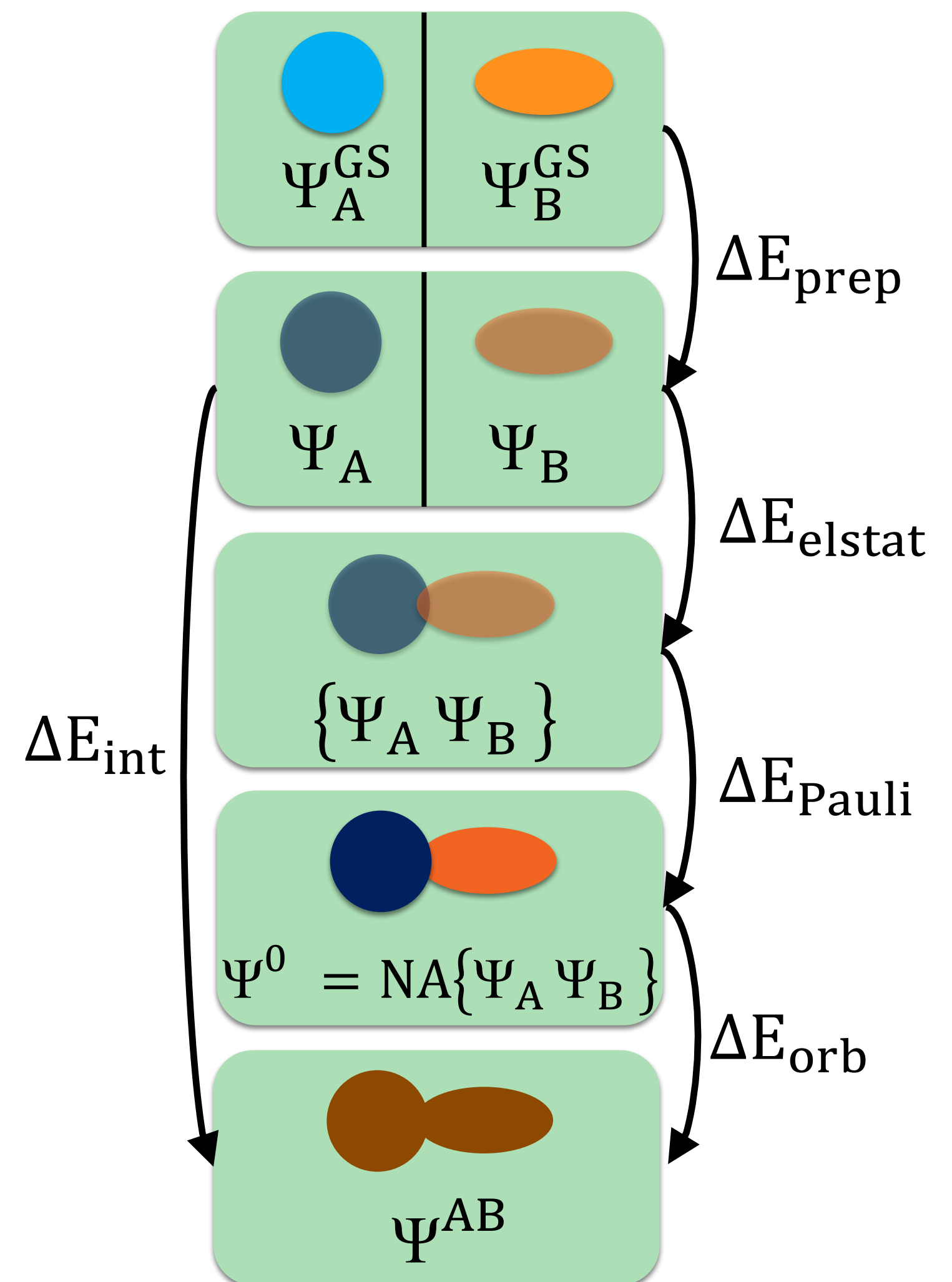


EDA/ETS-NOCV: bond & density decomposition

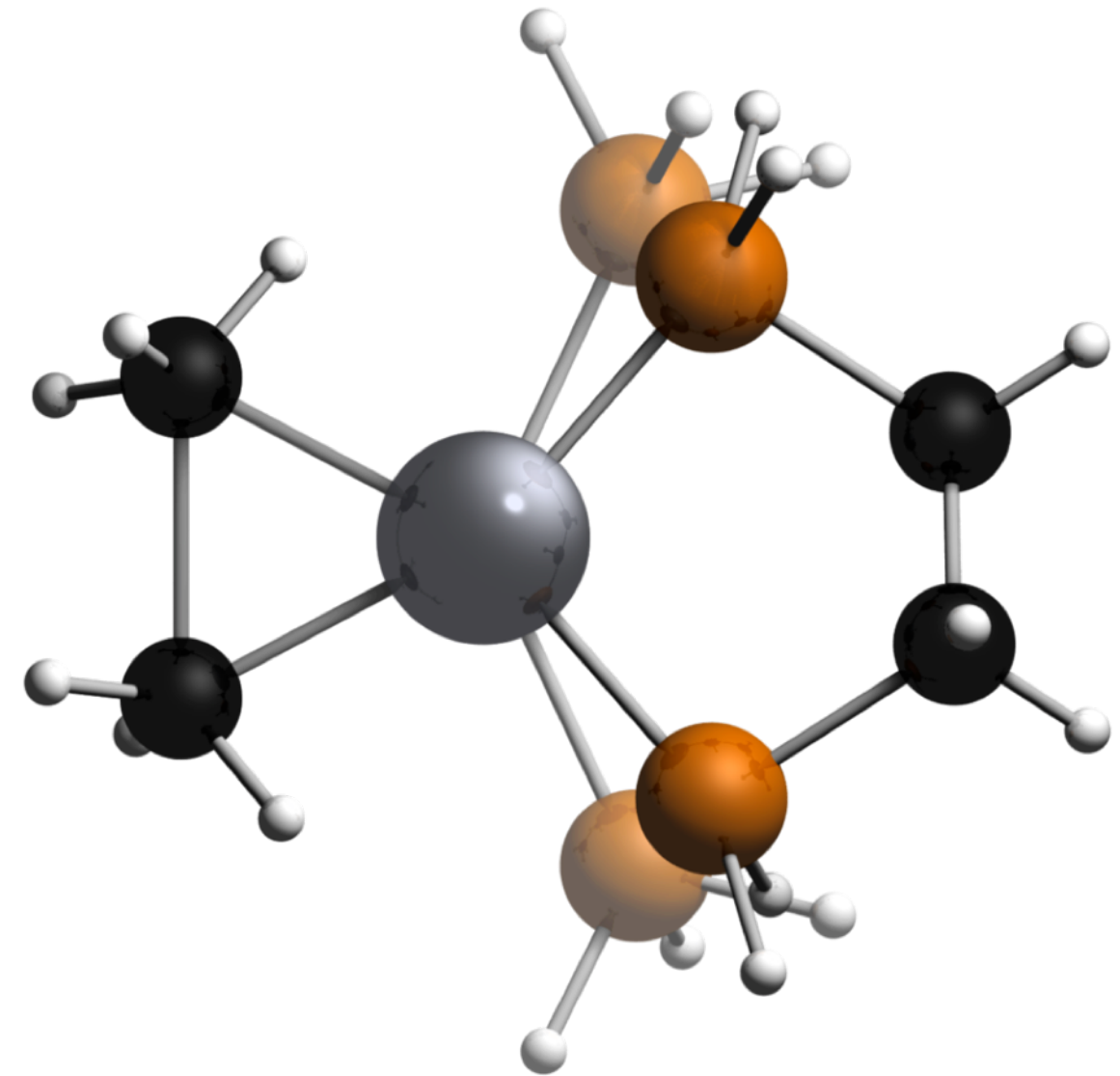
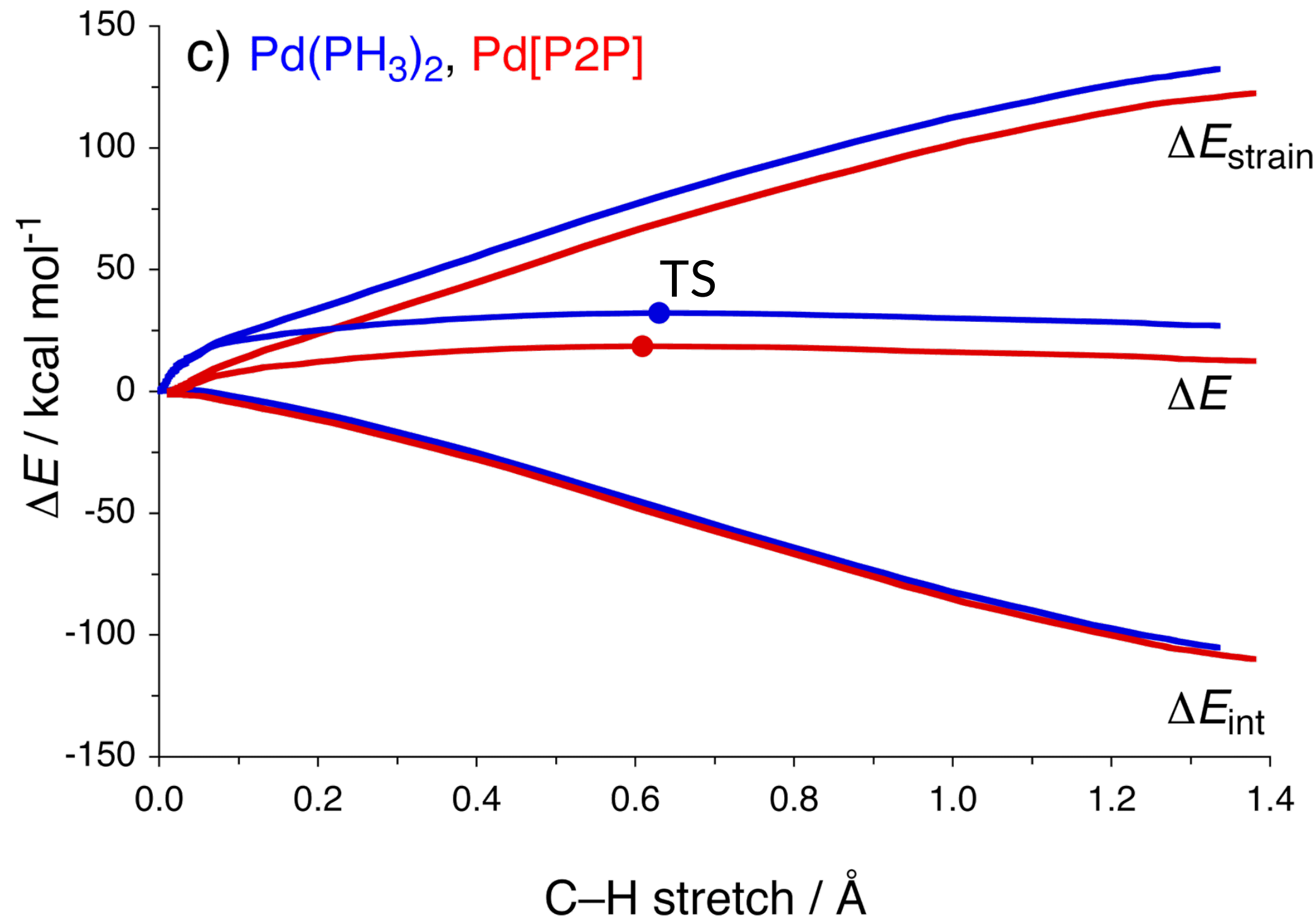
- Molecule built from fragments
- Bond analysis with meaningful terms:



- Combine with NOCV ([webinar](#))
 - Orbital interactions / charge transfer
- Also periodic 1D, 2D, 3D ([tutorials](#))
 - (Ad)sorption nanotubes, surfaces, MOFs etc.
 - Raupach & Tonner, [J. Chem. Phys. 142, 194105 \(2015\)](#)



Catalyst design: activation strain model



Chem. Eur. J. (communication) 2009, 15, 6112
 Org. Biomol. Chem. 2010, 8, 3118
 Nature Chem. 2010, 2, 417

Latest reviews:

Chem. Soc. Rev. 2014, 43, 4953
 WIREs Comput. Mol. Sci. 2015, 5, 324

EDA along the reaction path

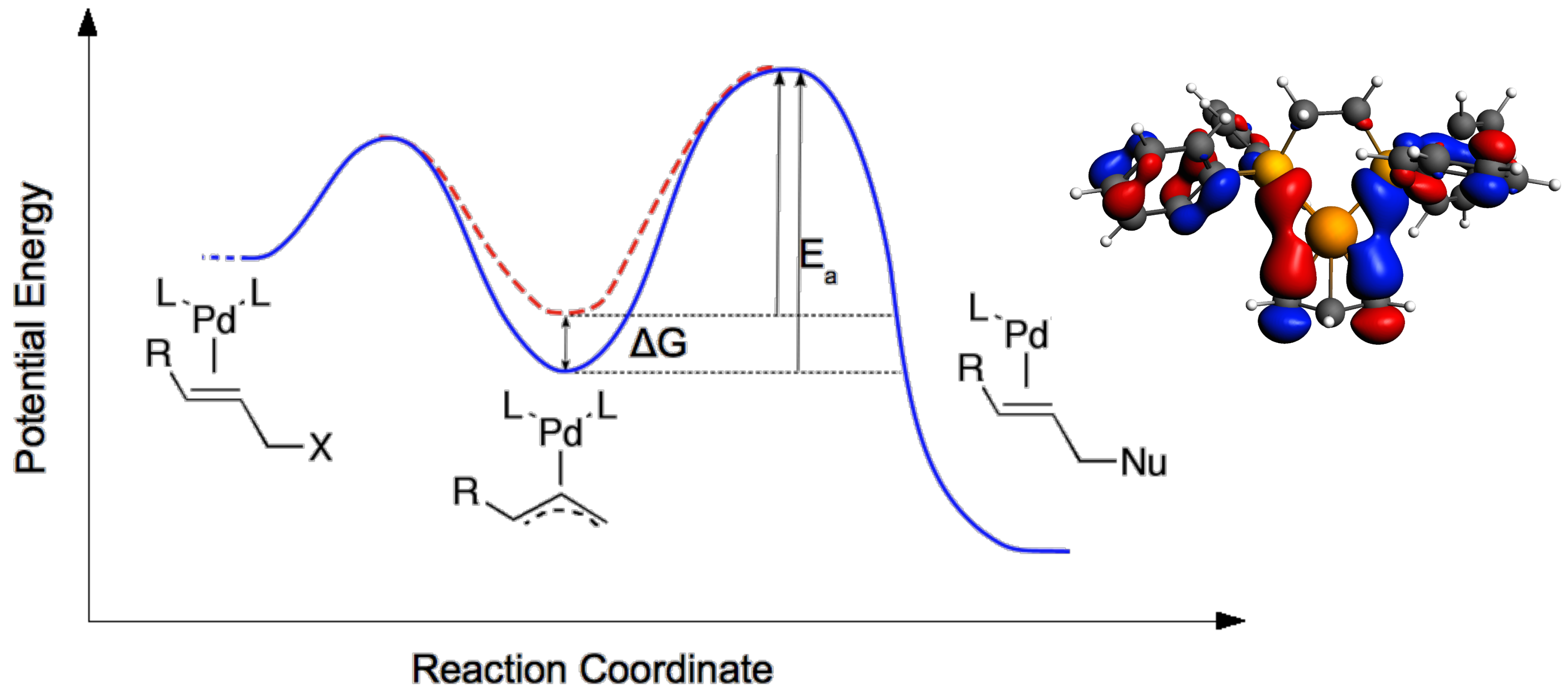
Bite-Angle Effect: Activation Strain analyses:

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

Catalyst natural selection: survival of the weakest

Increased bite angle dppe \rightarrow dppb

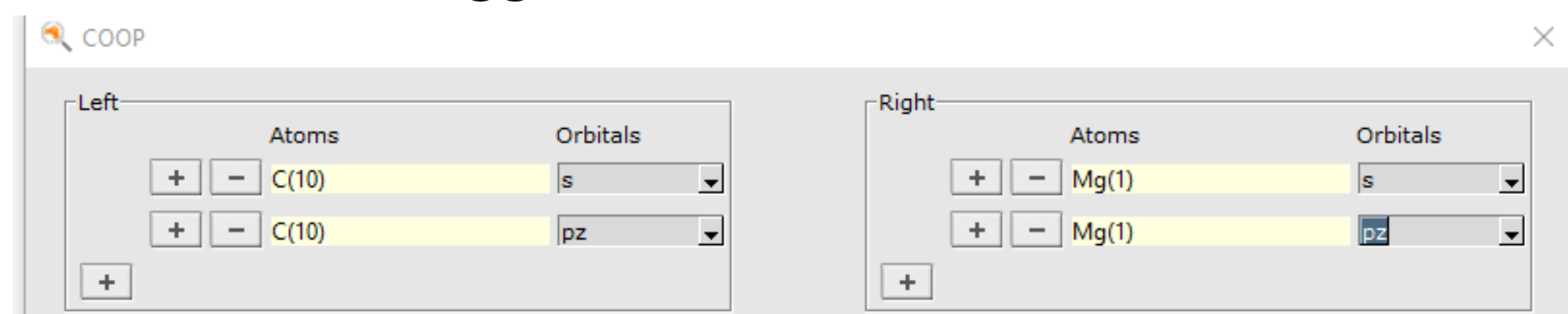
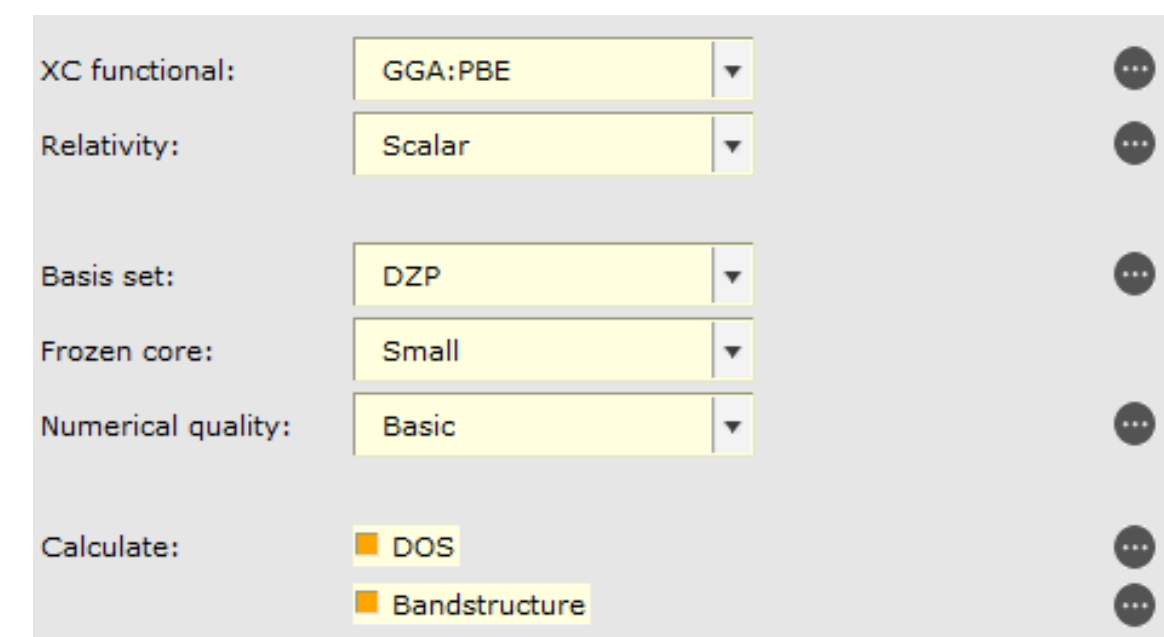
- Improved electronic interaction and larger repulsive strain
- Strain outweighs electronic interactions \rightarrow dppb most destabilized \rightarrow best catalyst



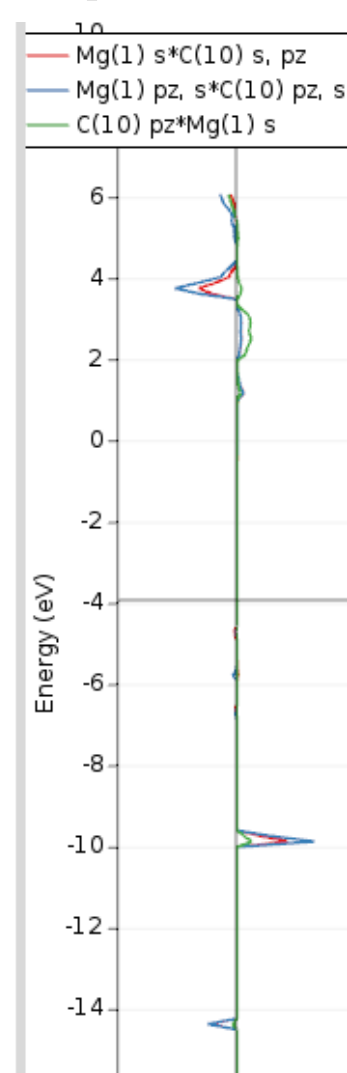
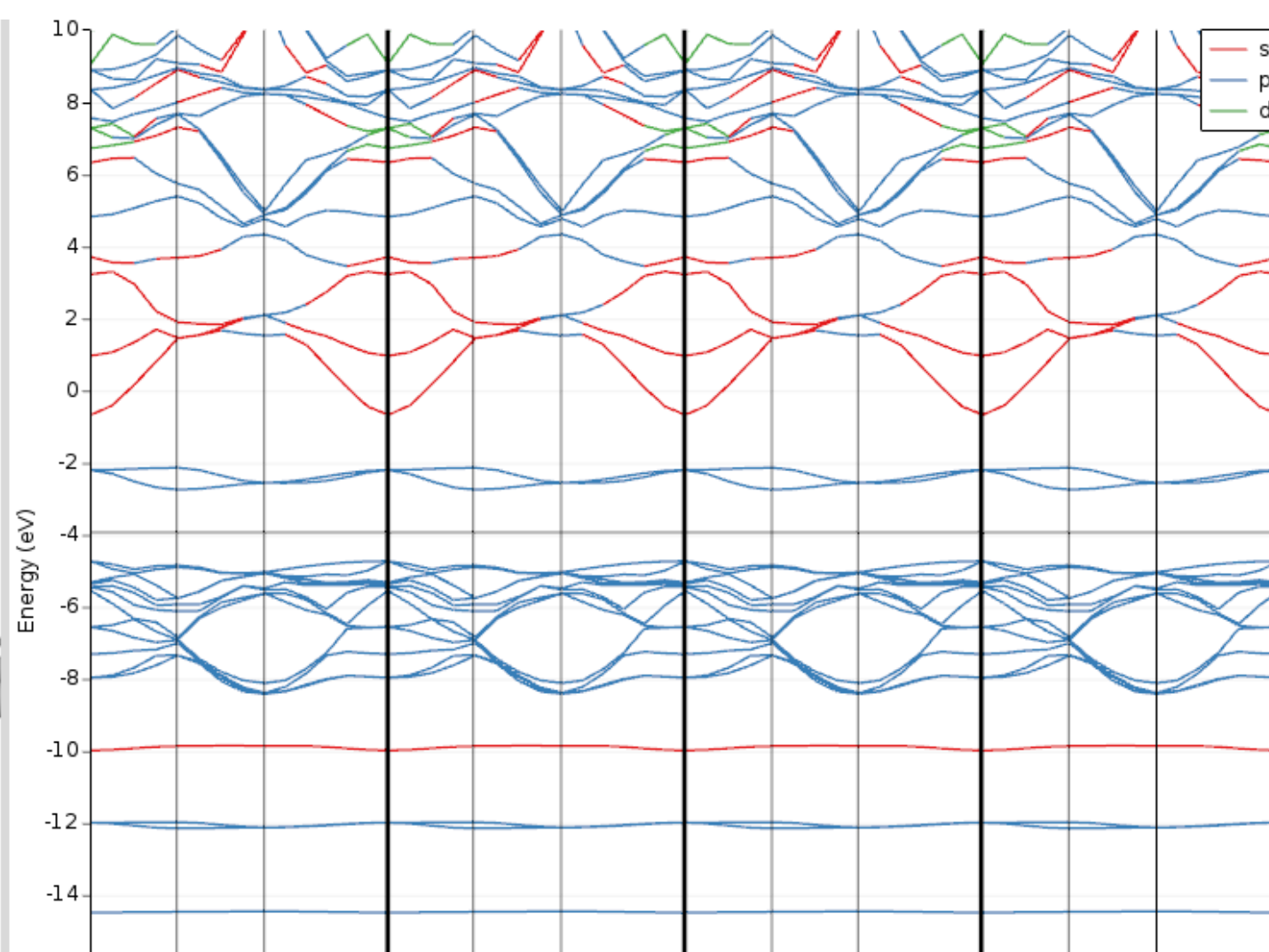
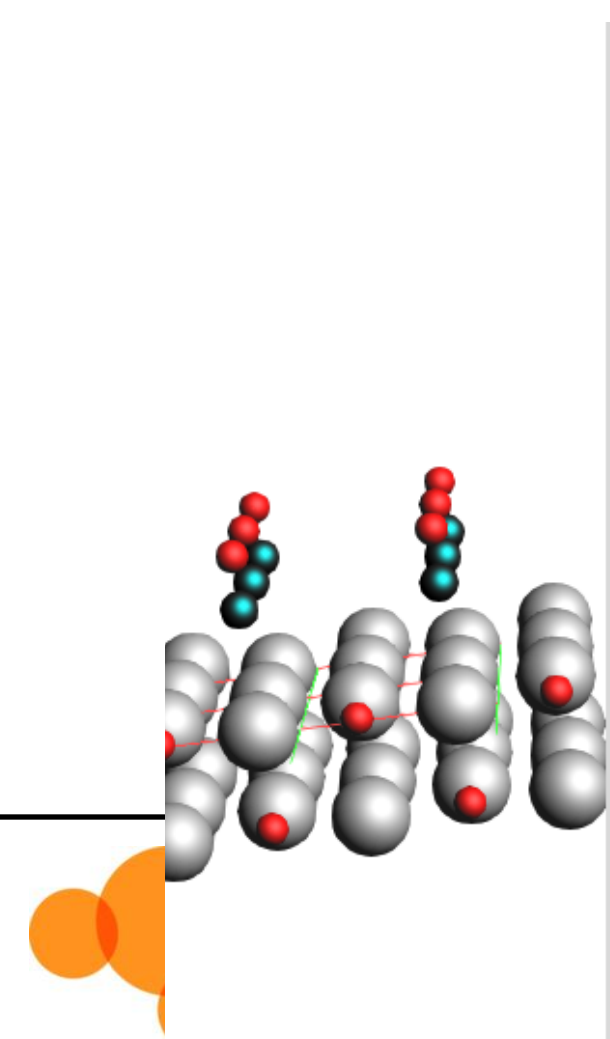
J. Wassenaar, et al. *Catalyst selection based on intermediate stability measured by mass spectrometry*. [Nature Chem. 2, 417 \(2010\)](#)

CO on MgO: COOP

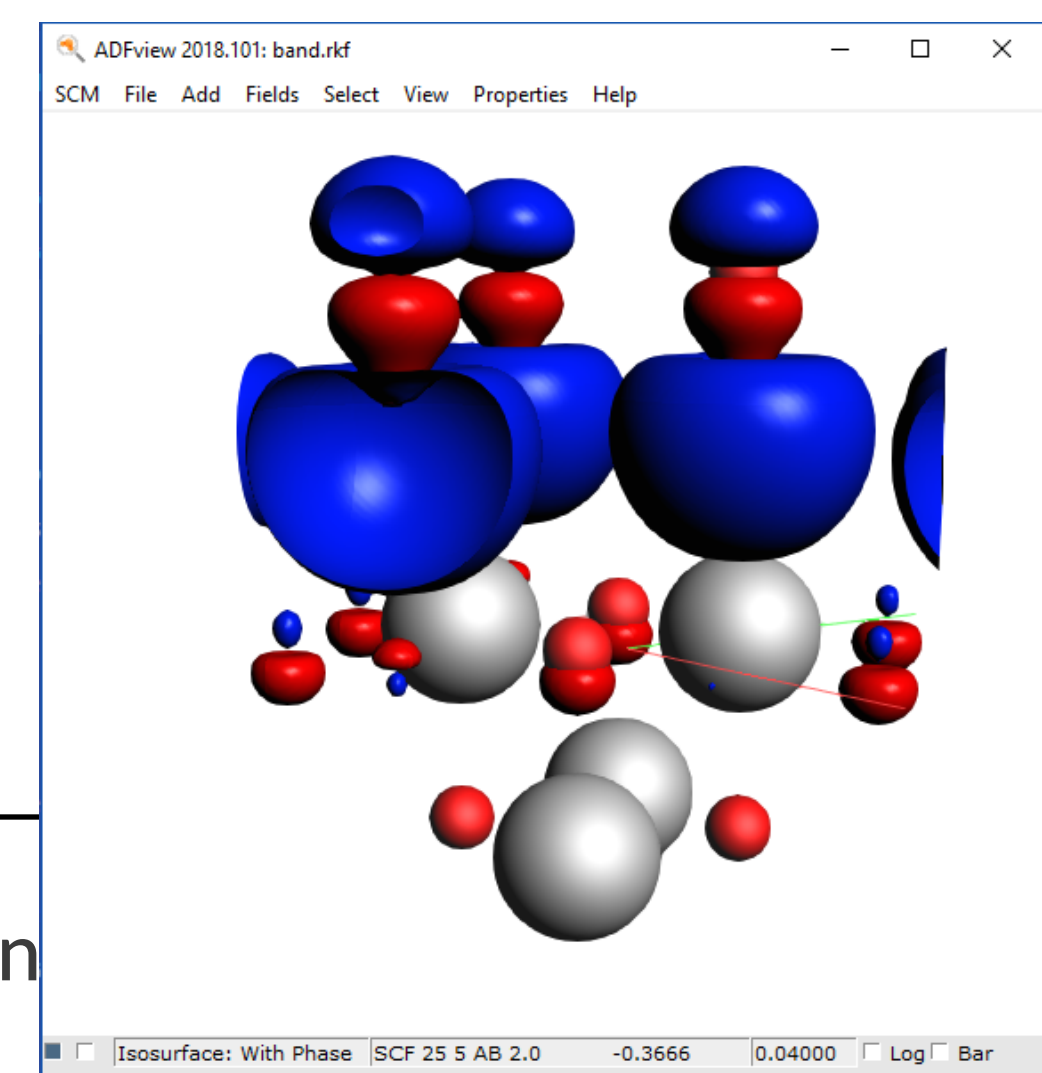
- **Exercise 13:** First do the [PEDA-NOCV tutorial](#)
- New input with same coordinates
- Scalar, PBE, DZP/small, basic, DOS, BandStructure
 - DOS details (...) => COOP, -20 to + 20eV
- Visualize the band structure and various COOPs
 - DOS-> COOP... Try different Mg (s) + Mg (p_z) and C (p_z) + C (s) combo's
 - What is the biggest contribution to the -10 eV band? Mg(s)+C(s- p_z); Mg's p_z helps a bit



- Show MO of that band with ADFview, improve grid & tweak cut-off

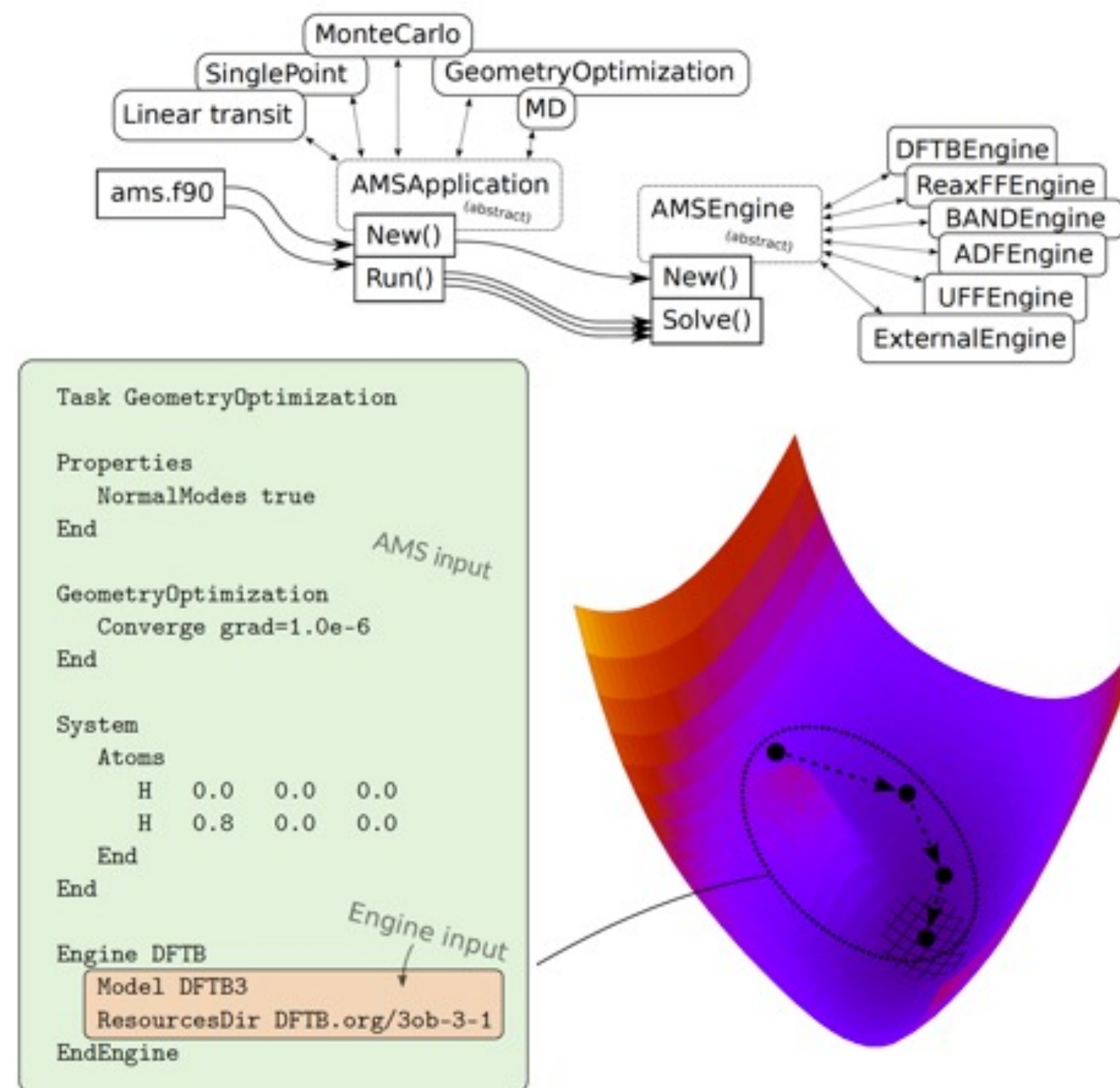


ber, Dalian



AMS: Powerful driver

- Scan multiple coordinates for any periodicity
 - Works with ADF, BAND, DFTB, MOPAC, UFF, ReaxFF
 - Can be extended/interfaced with other codes
- Advanced MD barostats and thermostats
 - Also with DFT(B): AIMD
 - Other 'ReaxFF' functionality to be ported:
 - fbMC, CVHD, Molecule Gun, GCMC
- Reuse PES information
- Task farming (double parallelization)
 - Elastic tensors, phonons, frequencies



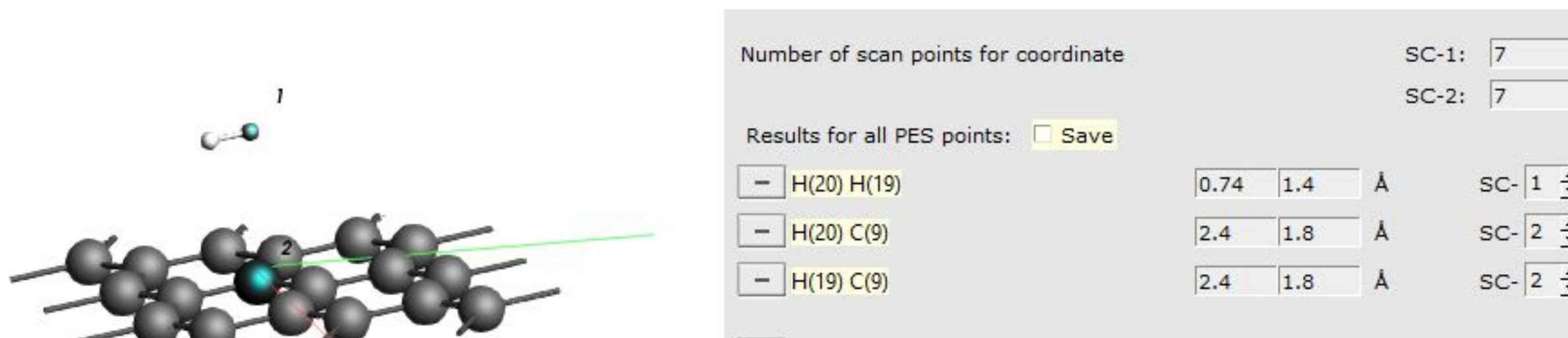
AMS: PES scan & TS search

- Exercise 14: H₂ on graphene

- Find graphite (or build it), slice a 1L 001 surface & remove top layer to get graphene
- Create 3x3 super cell and build H₂ somewhere in the input window
- Adjust Model -> Coordinates to put it atop, 2.4 above surface

H(19)	0.0	0.37	2.4
H(20)	0.0	-0.37	2.4

- Go to DFTB, choose DFTB3-D3BJ/3ob-3-1 and set Task: PES Scan, click ‘...’
- In the PES Scan panel set the Scan coordinates by selecting atoms and clicking +:
 - Set SC-1 to H₂ from 0.74-1.4 (7 points)
 - Set SC-2 both H-C coordinates from 2.4-1.8 (7 points)



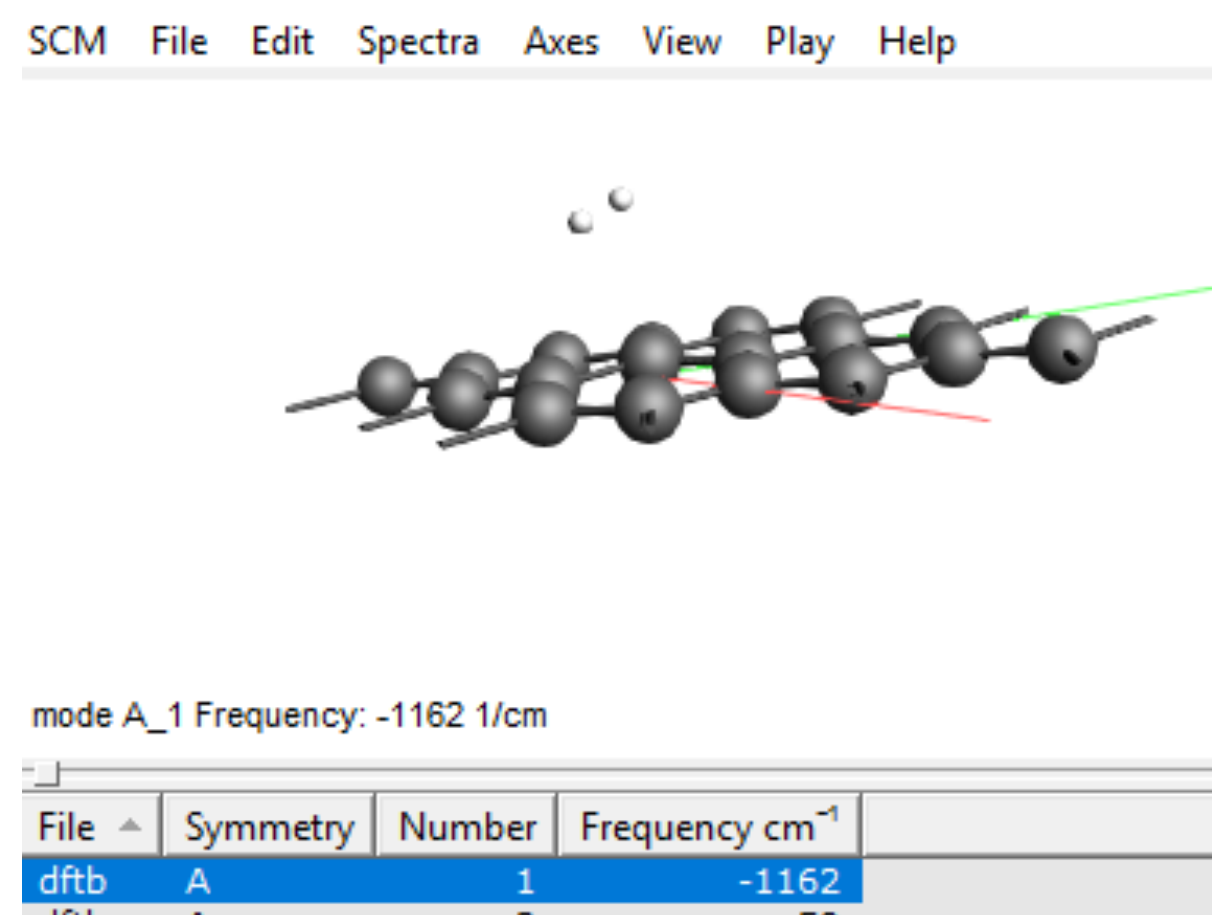
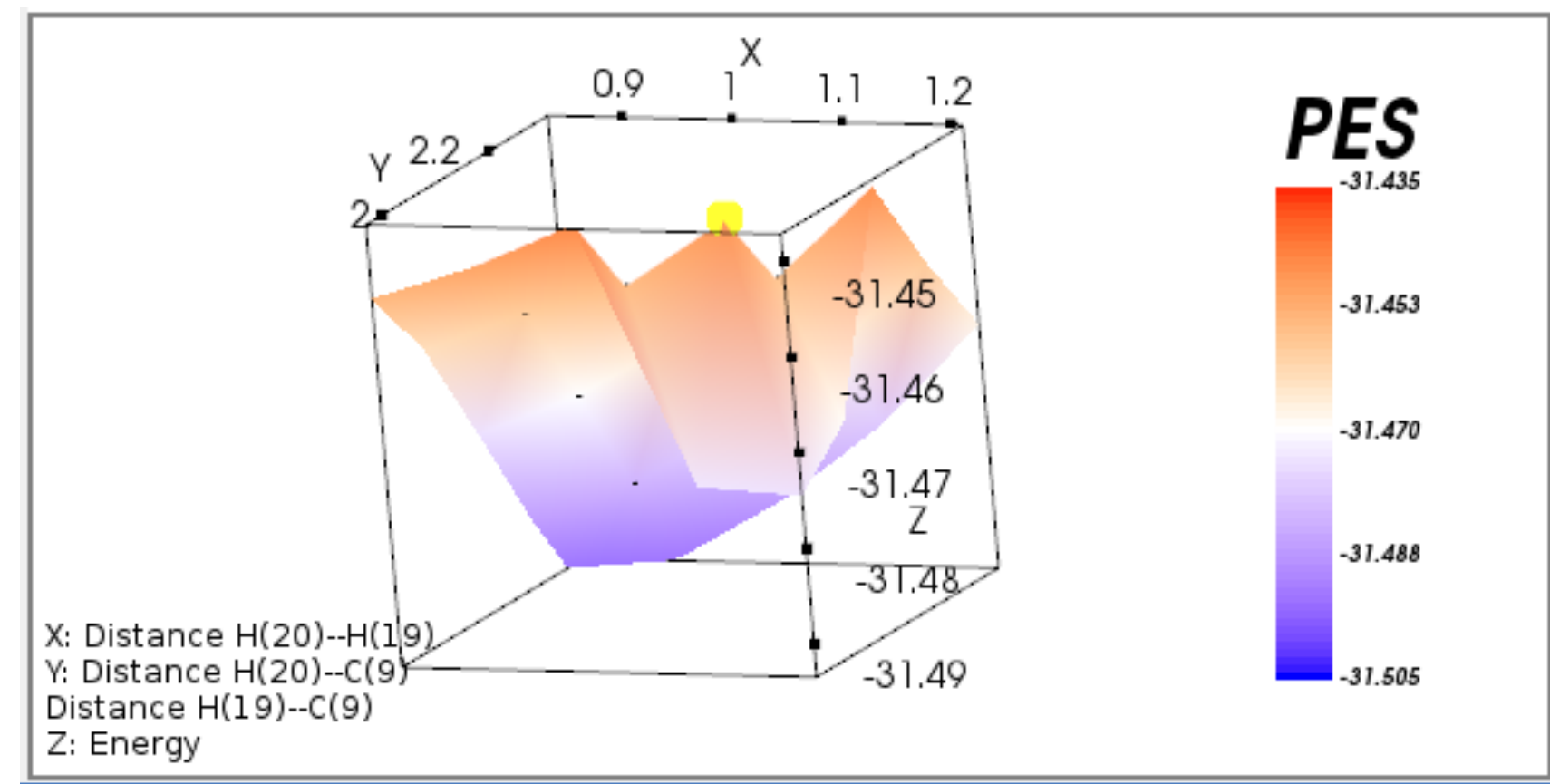
- Lower convergence criteria in Details -> Geometry Optimization
- Save & Run

Gradient convergence:	1.0e-2	Hartree/Å
Energy convergence:	1.0e-4	Hartree
Step convergence:	1.0e-2	Å

AMS: PES scan & TS search

- Exercise 14: Explore the 2D PES

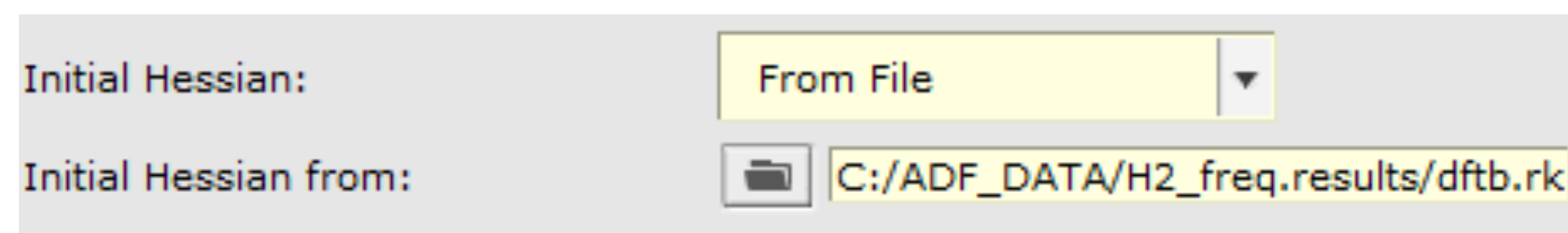
- When Finished: SCM -> Movie
- Find a plausible TS start point (x=1.18, y = 2.0)
- File -> Save Geometry
- Make a New input & import that geometry
- Now we calculate the Hessian:
- Go to DFTB, choose DFTB3-D3BJ/3ob-3-1
 - Task: Single point, followed by frequencies
- Save & Run
- Visualize the Spectra and check that there is 1 large imaginary mode



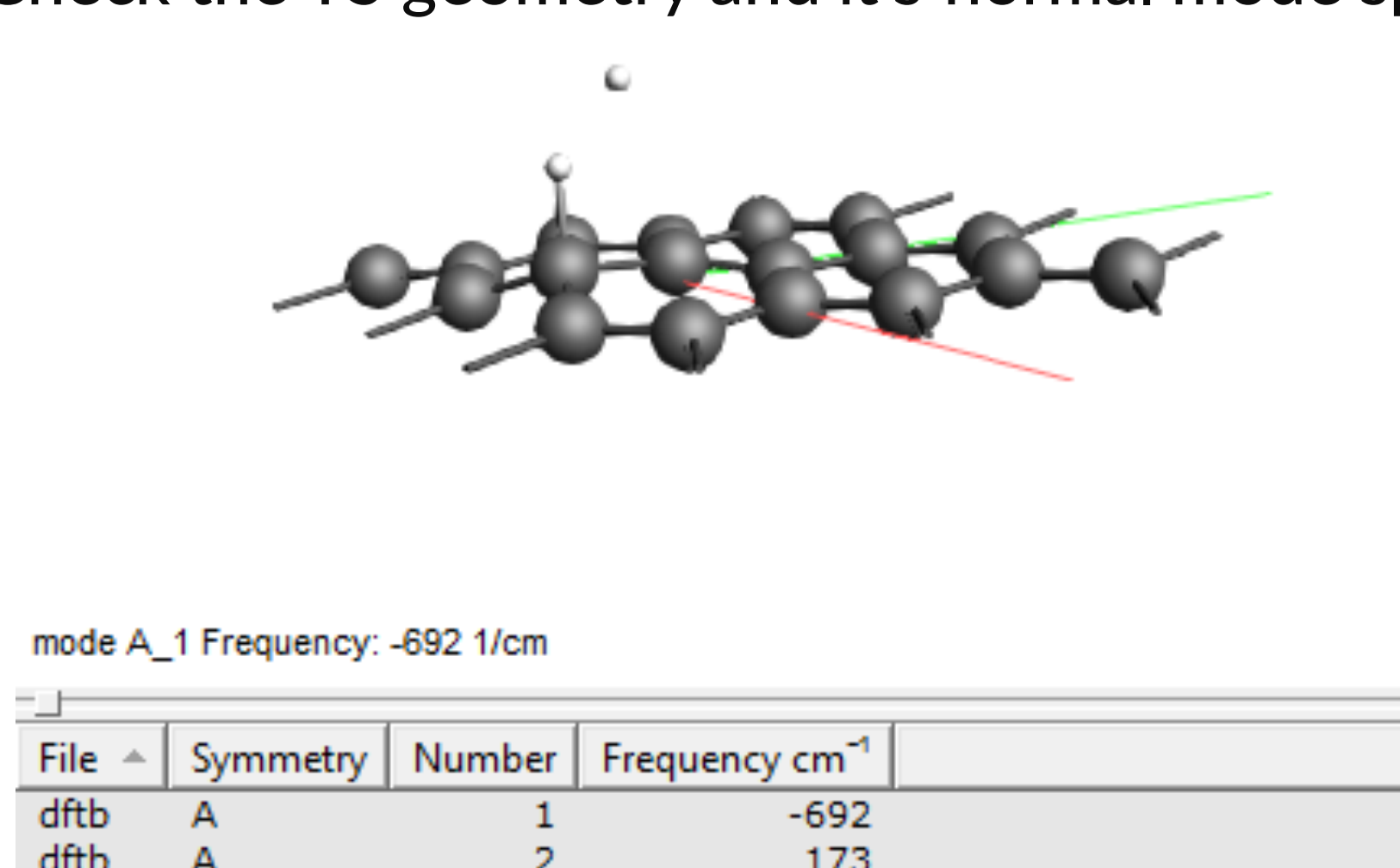
AMS: PES scan & TS search

- Exercise 14: Find the TS

- Change Task to Transition State
- In Details -> Geometry Optimization: Initial Hessian -> From file -> find dftb.rkf



- Save as a different file & Run
- Check the TS geometry and its normal mode spectrum



- Calculate the activation energy as $E(\text{TS}) - E(\text{graphene} + \text{H}_2)$ (you can put H_2 at 50Å)