Introduction to AMS2018
Getting started

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

Tsinghua University 22+23 October 2018
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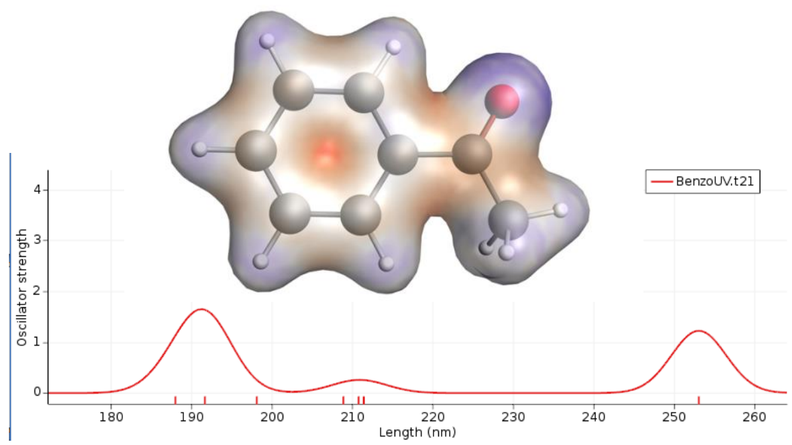
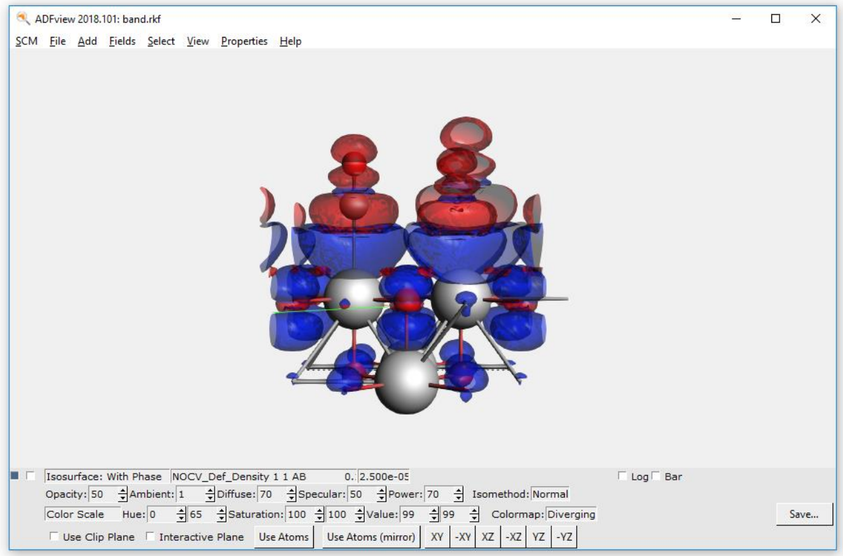
FermiTech support: wiki, support@fermitech.com.cn

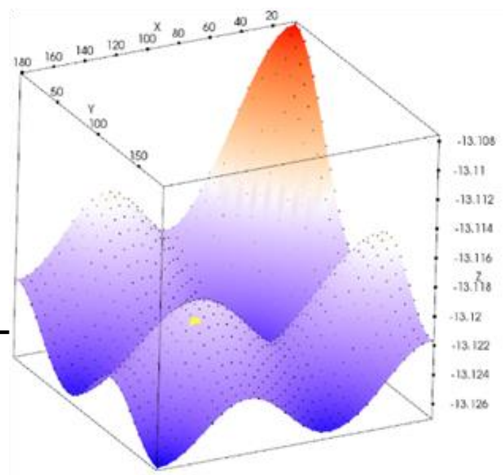
Making Computational Chemistry Work for You

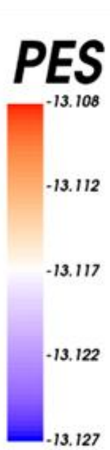
Program

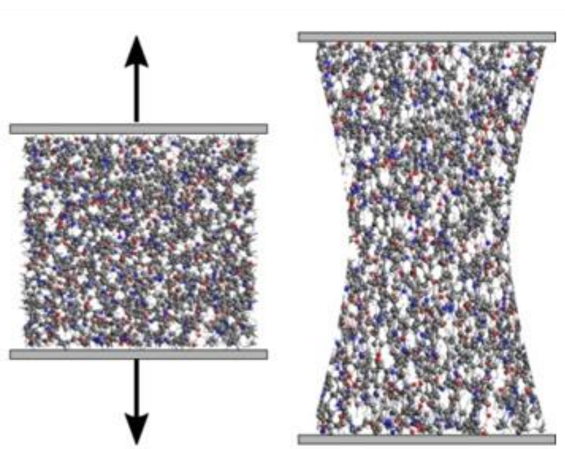
- Introduction
  - SCM & AMS
  - Computational chemistry& materials science
- Molecules: builder, database, import SMILES, xyz
  - Spectroscopy
  - Advanced: bonding analysis, charge transfer, SOCME
- Periodic structures: database, cif, surfaces
  - Advanced: bonding analyses (PEDA-NOCV, COOP)
- COSMO-RS: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

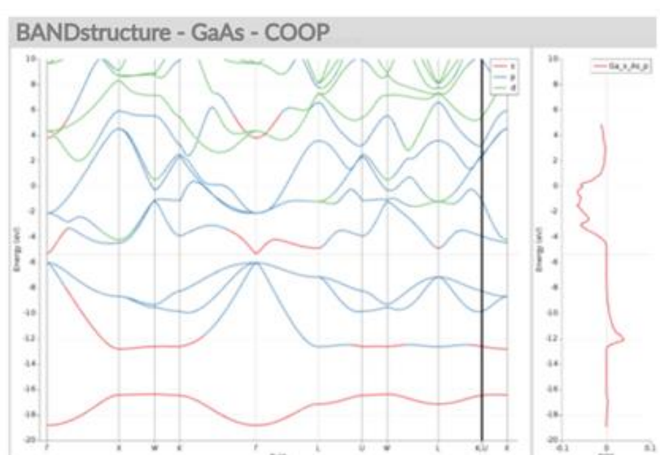






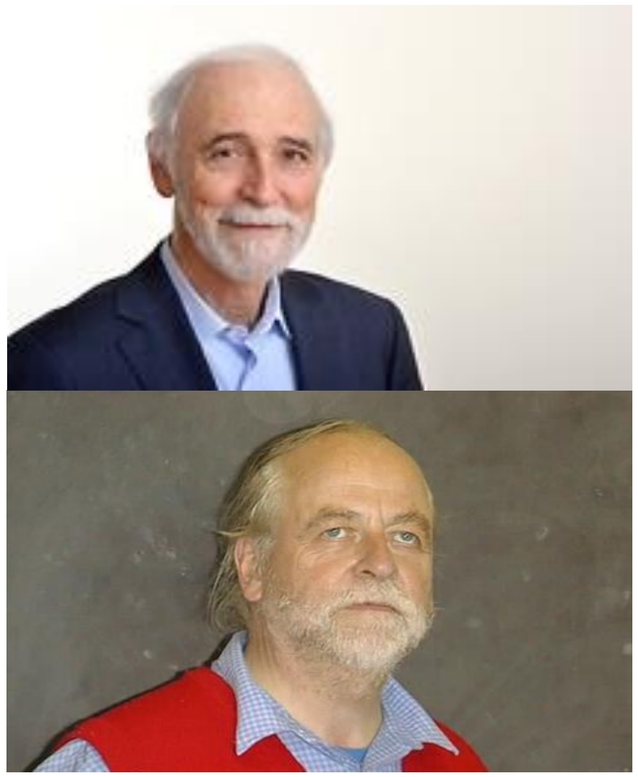


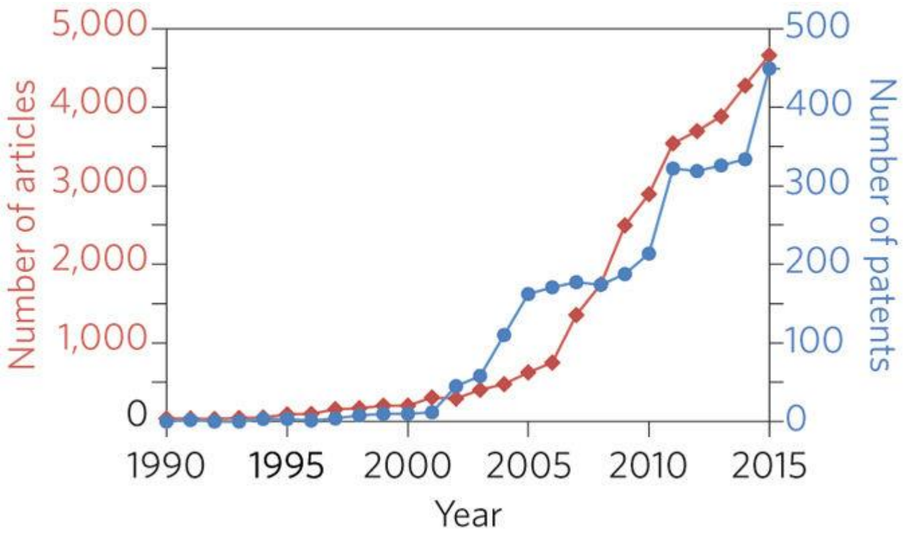




Background: SCM & ADF

- 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 & <u>support</u>



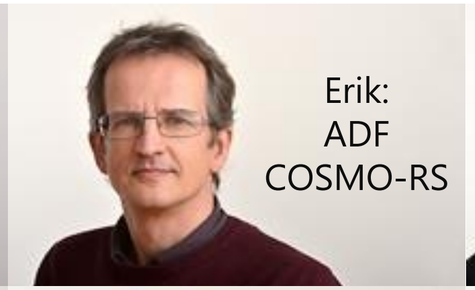


articles &patents in materials science with "density functional theory", Nat. Mat. 4619

The SCM team

Olivier:
GUI

Alexei:
ADF
ReaxFF


Erik:
ADF
COSMO-RS

Pier:
BAND

Mirko:
ADF
BAND

Hans:
Linux
GPU
Python

Thomas:
DFTB
Scripting

Laurens:
GUI

Ole: Support
Scientist

Evert Jan:
Adviser

Michal:
python
scripting

Robert:
DFTB

Anna:
ReaxFF

Nick:
COSMO-RS

Tomas:
ReaxFF

Stan:
CEO

Fedor:
Marketing

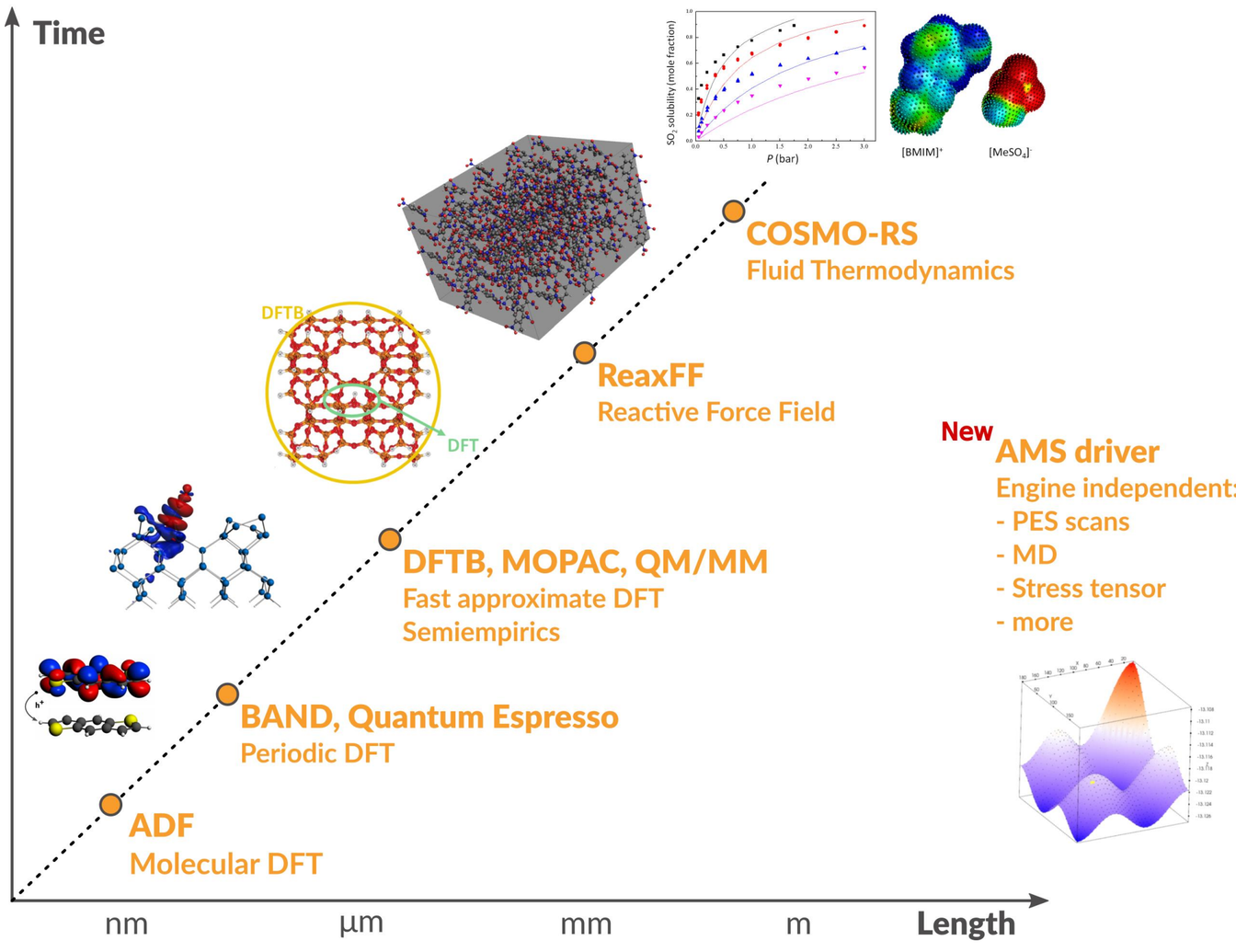
Sergio:
Collaborations

Frieda:
Invoices
Licenses

Kitty:
Finance

Amsterdam Modeling Suite

- ADF: powerful molecular DFT
  - Spectroscopy: NMR, EPR, VCD, UV, XAS
  - Advanced solvation / environments
- 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

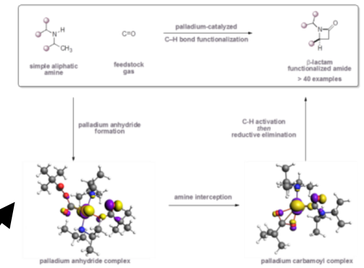


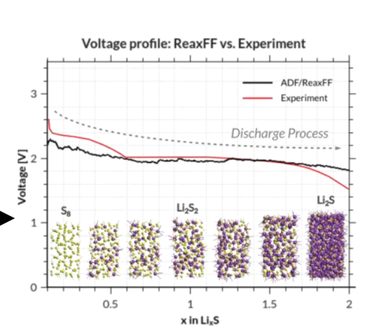
Why bother with calculations?

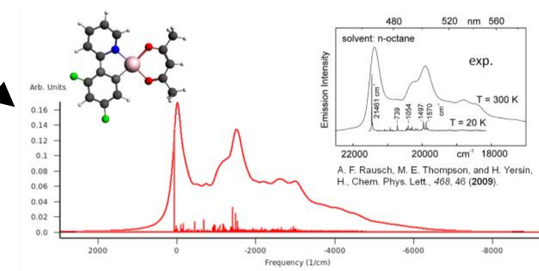
Computational chemistry & materials modeling

- 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

???

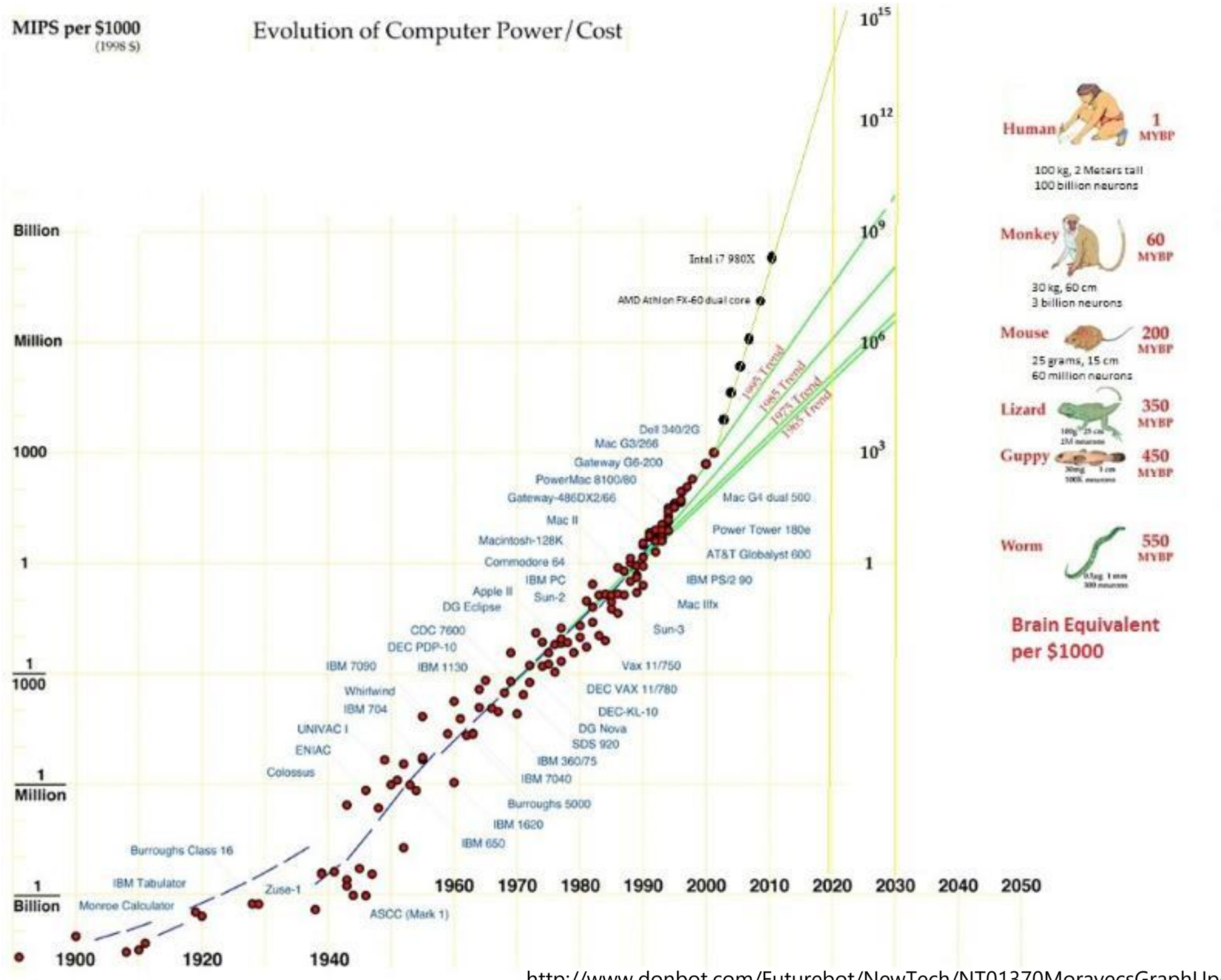






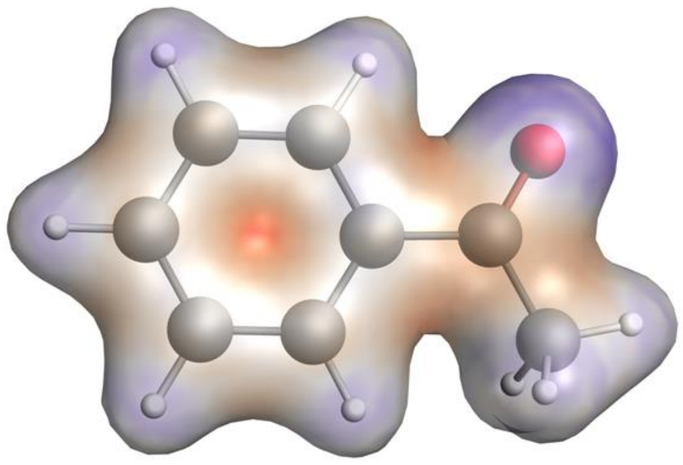
Best catalyst? => mechanism? lowest E_a ? best ligand? side reactions?
Best battery? => discharge? voltage? interaction with electrolyte?
Best OLED? => charge & exciton mobility? emission speed & color?

Compute power (r)evolution

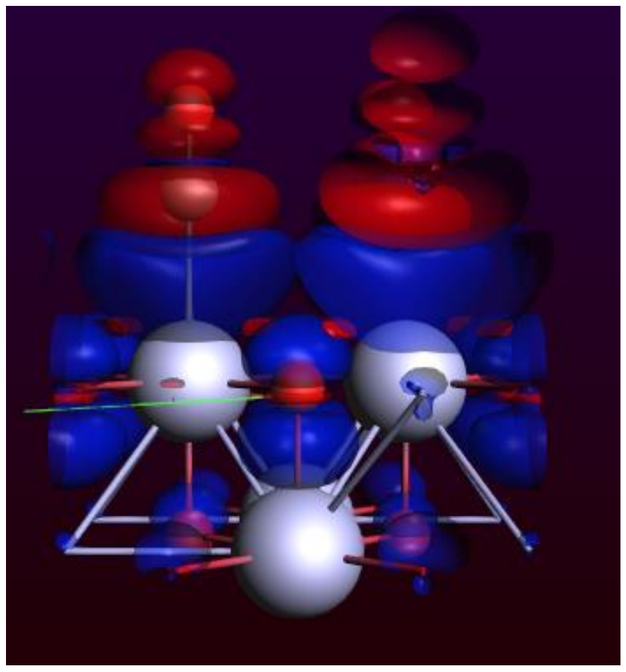


http://www.donbot.com/Futurebot/NewTech/NT01370MoravecsGraphUpdated2020.html

Computational Chemistry & Materials



$$H\psi = E\psi$$

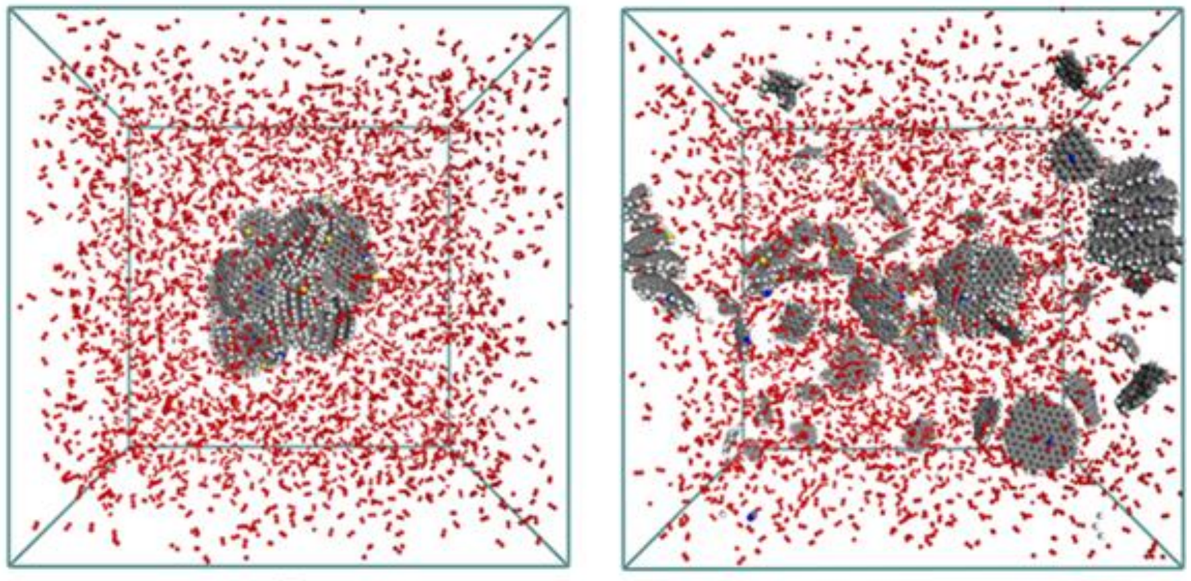


Electronic structure methods: Schrödinger equation
Electrons in molecules & materials
Expand ψ: atomic orbitals / plane waves
Solve self-consistently
Pragmatic: DFT

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

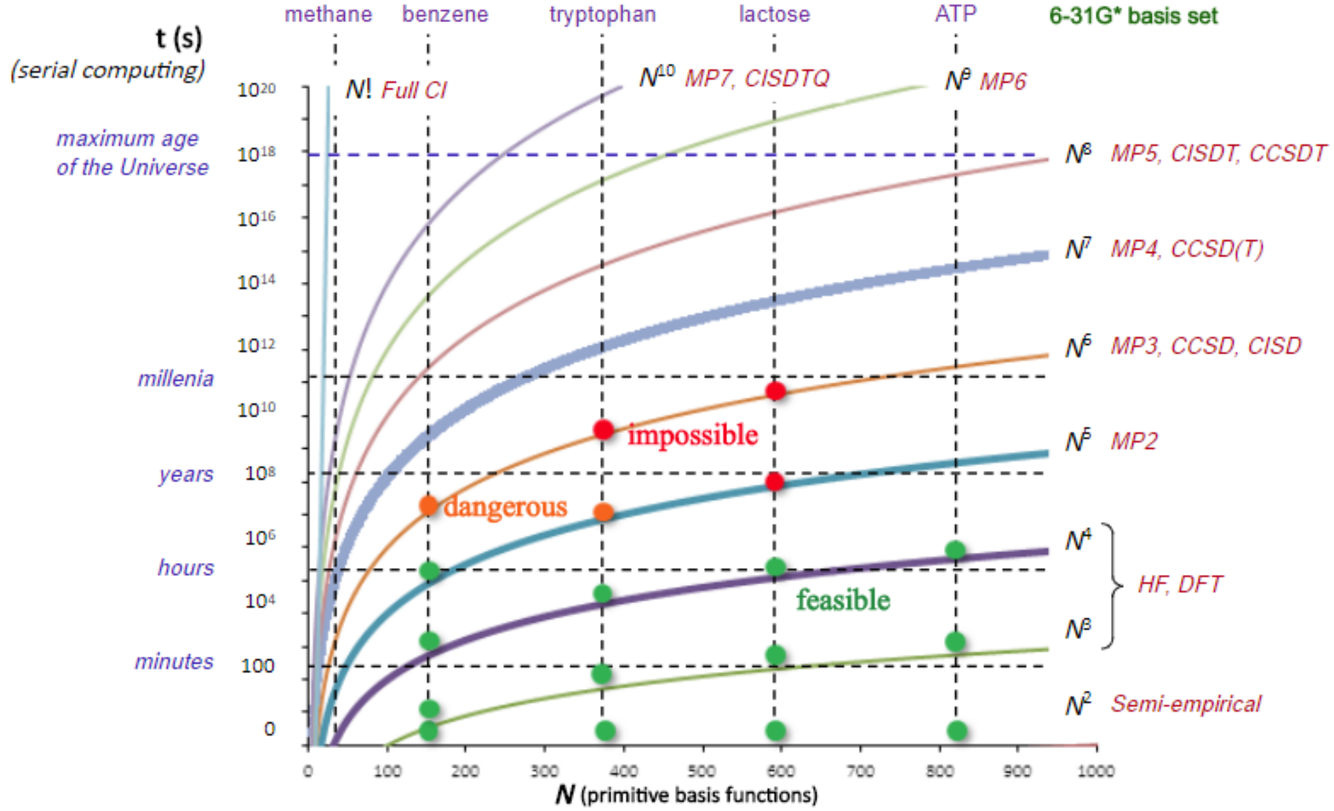
Movement of atoms: solve numerically + propagate,

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!

$$\phi_i(\mathbf{r}) = \sum_j c_{ij}\chi_j(\mathbf{r})$$

orbital — expansion coefficients — basis functions

$$\left(-\frac{1}{2}\nabla^2 + V_{\text{nuc}}(\mathbf{r}) + V_{\text{C}}[\rho,\mathbf{r}] + V_{\text{XC}}[\rho,\mathbf{r}]\right)\phi_i(\mathbf{r}) = \epsilon_i\phi_i(\mathbf{r}) \qquad \rho = \sum_i |\phi_i(\mathbf{r})|^2$$

Kinetic energy

Electrostatic potential due to nuclei

$$V_{\text{nuc}}(\mathbf{r}) = \sum_{I\in\text{nuclei}} \frac{-Z_I}{|\mathbf{r}-\mathbf{R}_I|}$$

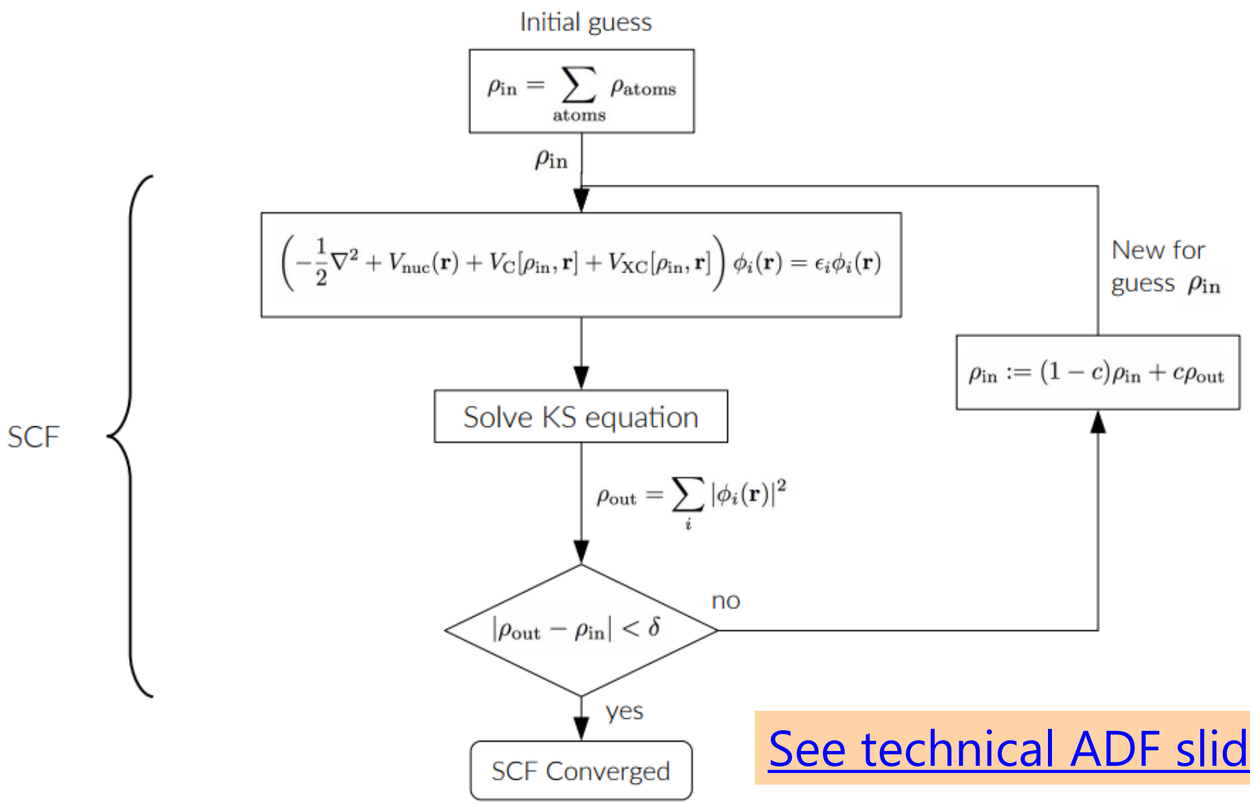
Electrostatic potential due to electrons

$$V_{\text{C}}[\rho,\mathbf{r}] = \int \frac{\rho(\mathbf{r}')}{|\mathbf{r}'-\mathbf{r}|}d\mathbf{r}'$$

Exchange-correlation Potential (*e.g.* PBE)

$$V_{\text{XC}}[\rho,\mathbf{r}] \propto \rho(\mathbf{r})^{\frac{1}{3}}$$

More general: v_{ext} can include external field

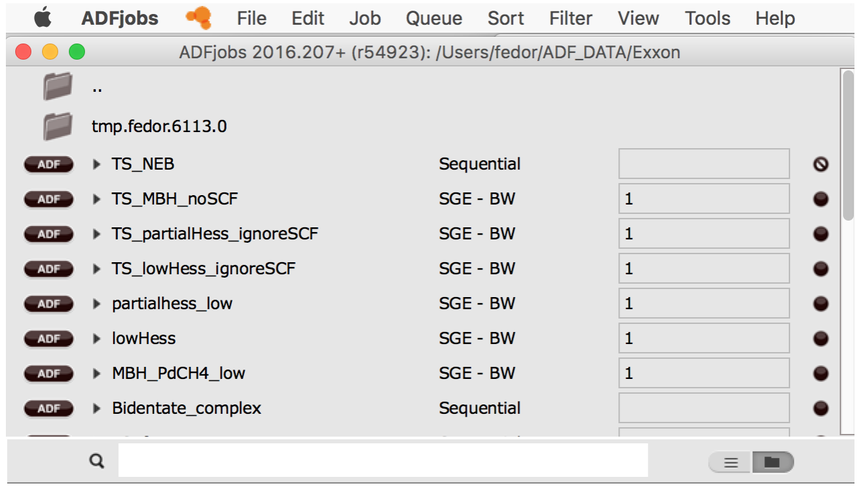


[See technical ADF slides]

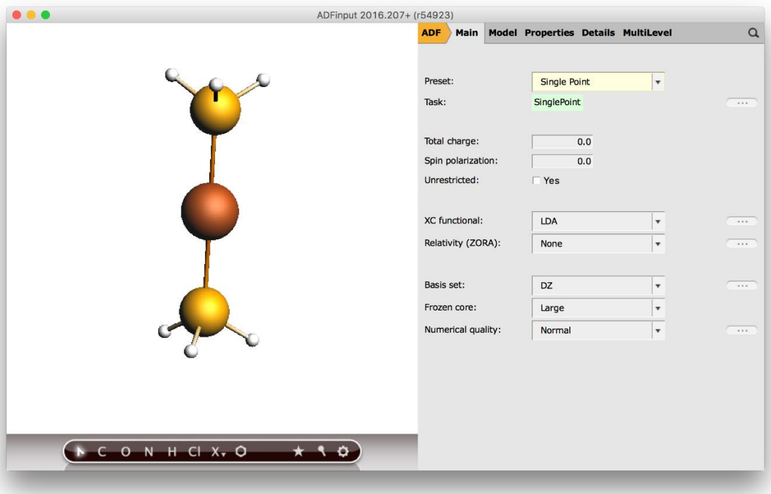
Getting started with the GUI

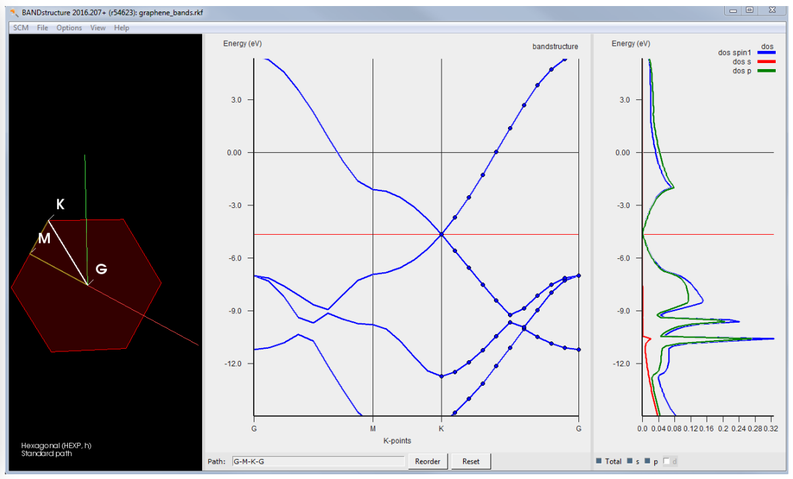
Starting ADFjobs: job bookkeeping tool

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

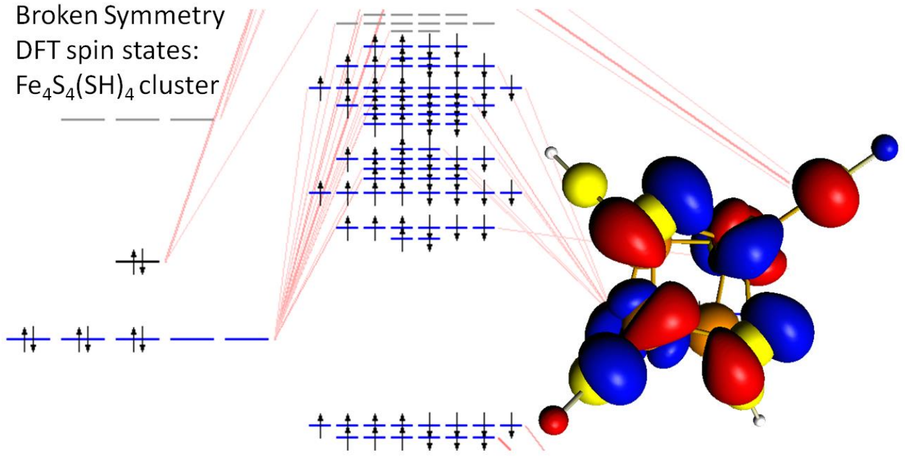


- Other GUI modules: (Input, View, Levels, Movie, Spectra, Band Structure, COSMO-RS, …)
  - Can be opened by dbl-clicking '.exe' (Win) or opening e.g. '$ADFBIN/adfinput'

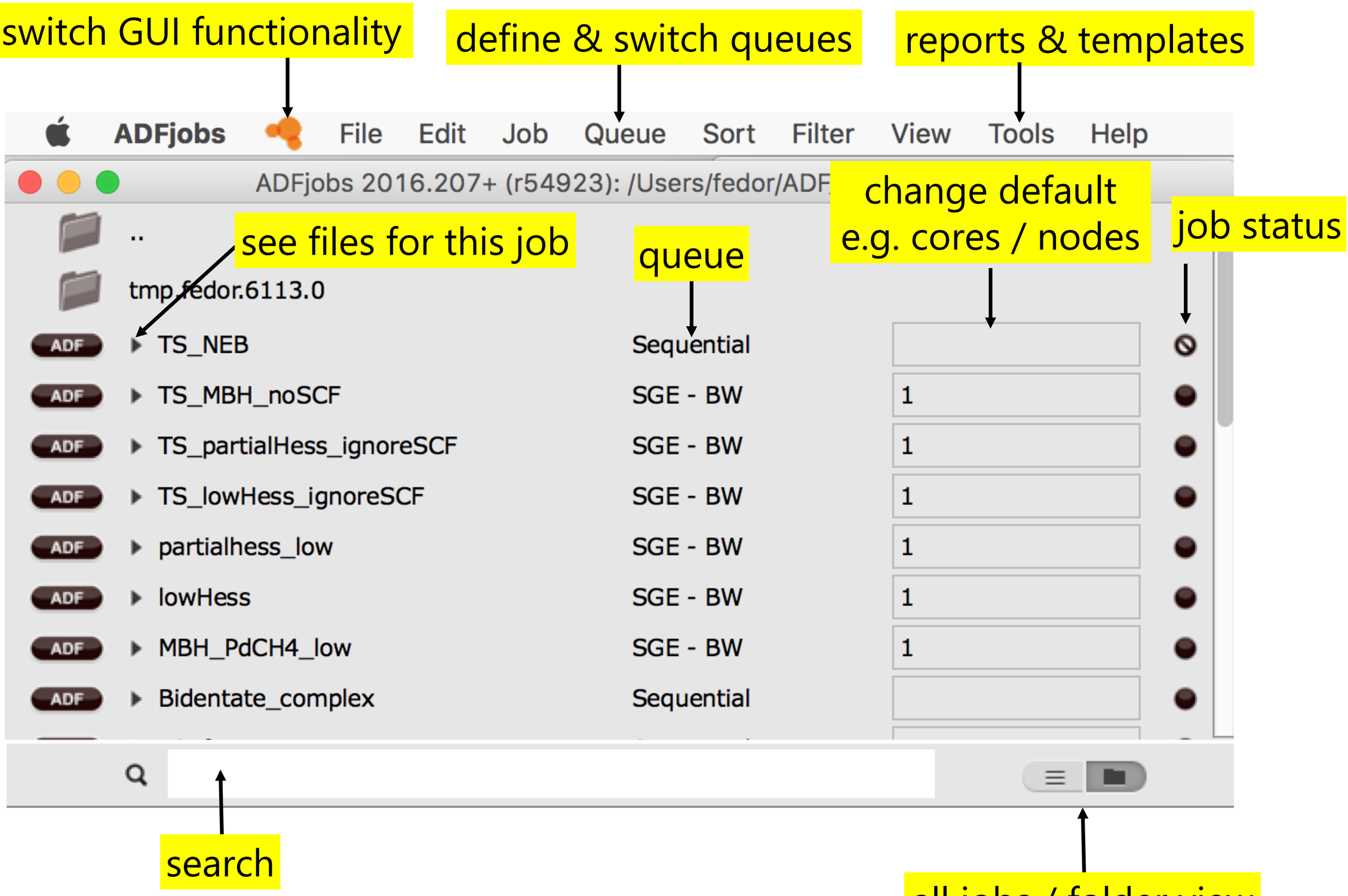




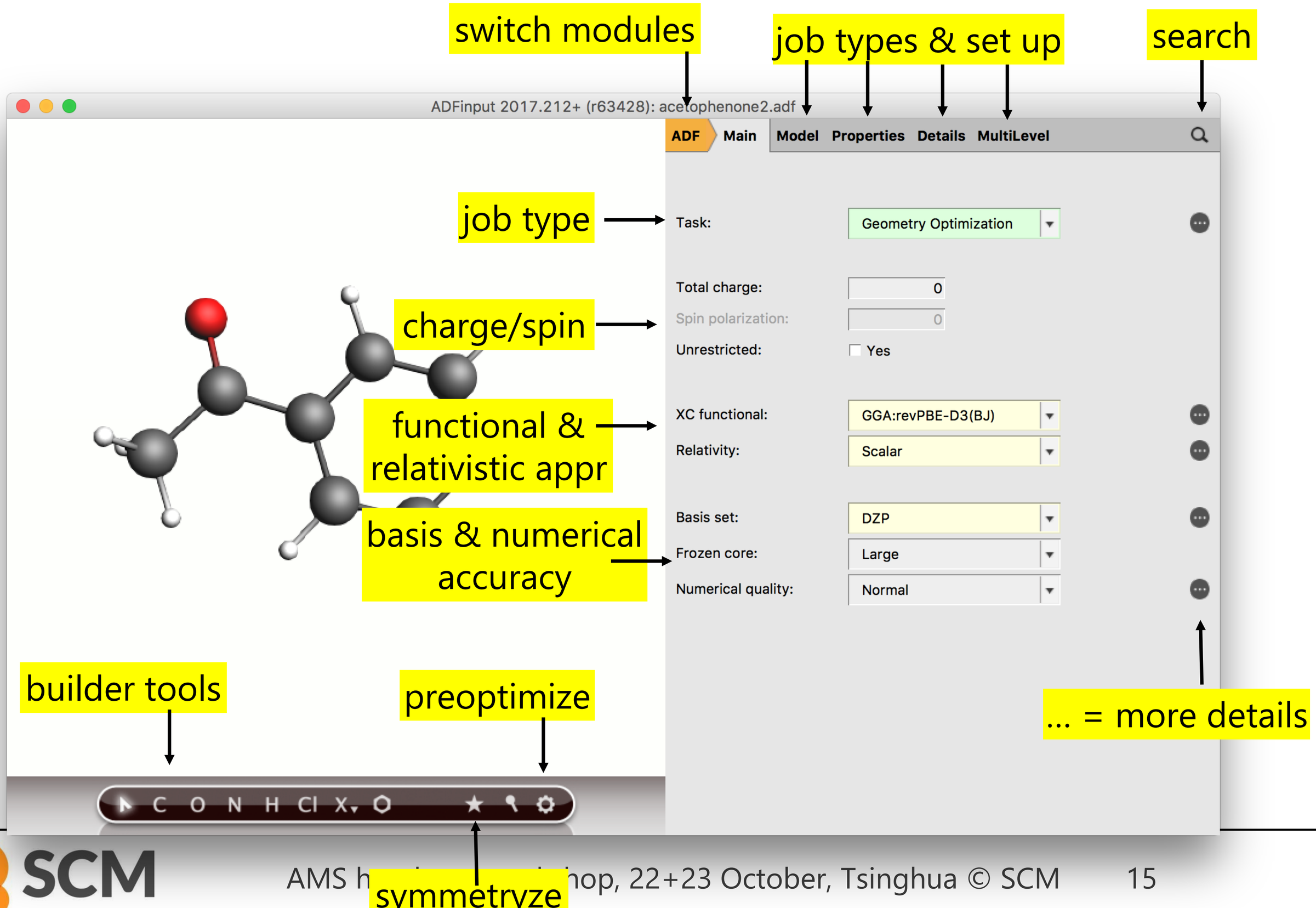
Broken Symmetry DFT spin states: $Fe_4S_4(SH)_4$ cluster



ADFjobs: job bookkeeping



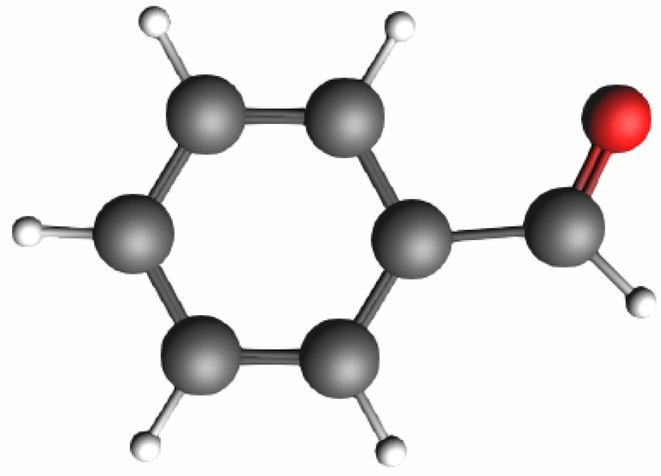
Basic calculations & settings



Building molecules

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

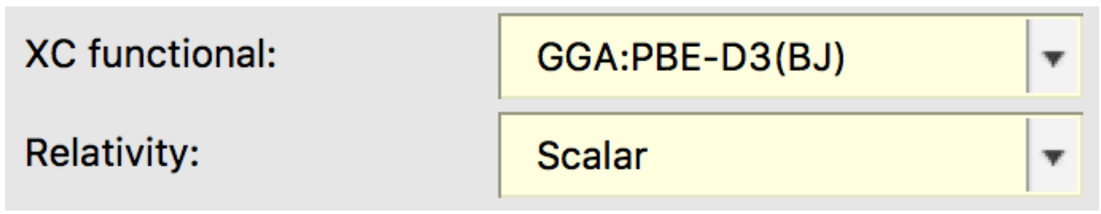
- NB: tutorials also offline with your ADF!
- Import: SMILES, xyz, cif, pdb, …



- Included library + building

- **Excercise 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

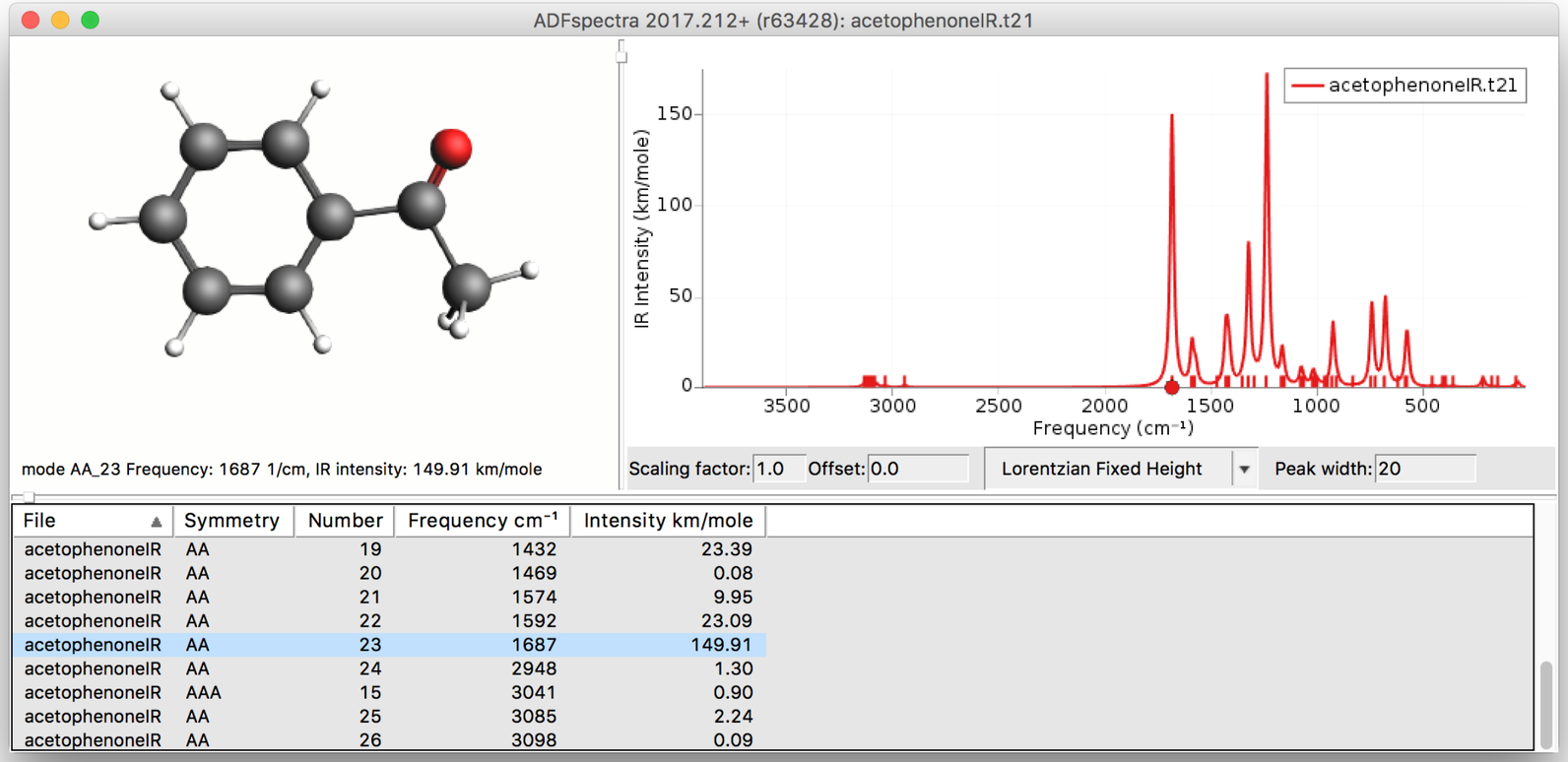


Spectra: IR

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

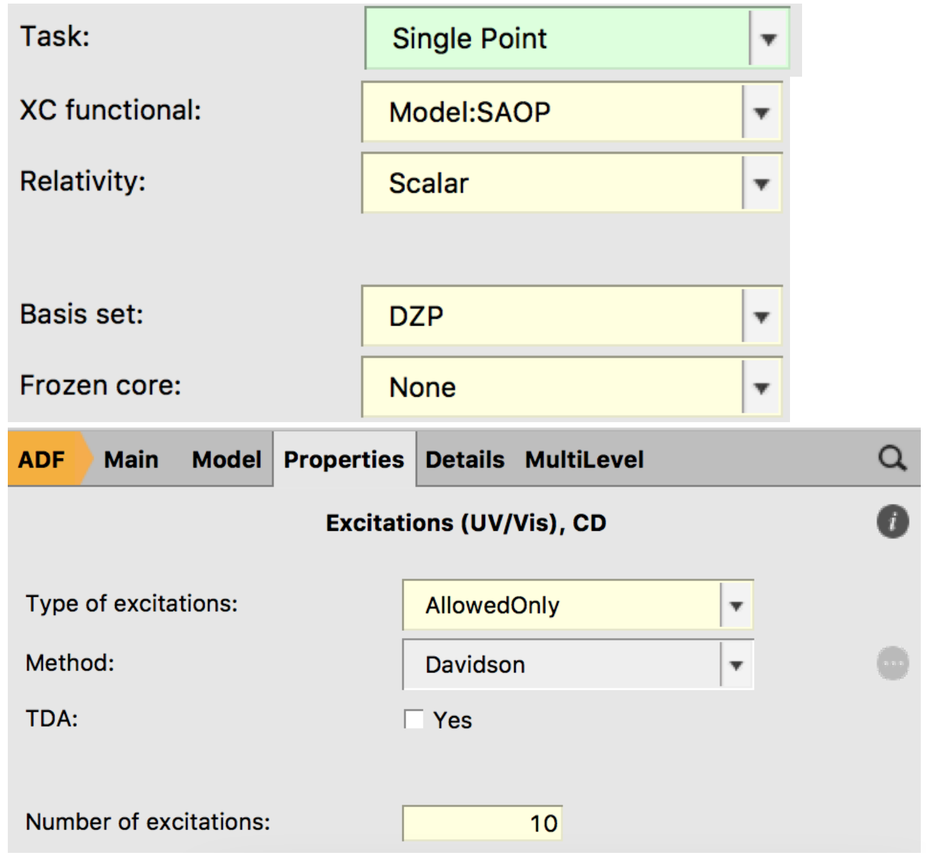
- **Excercise 3:** Calculate & visualize frequencies

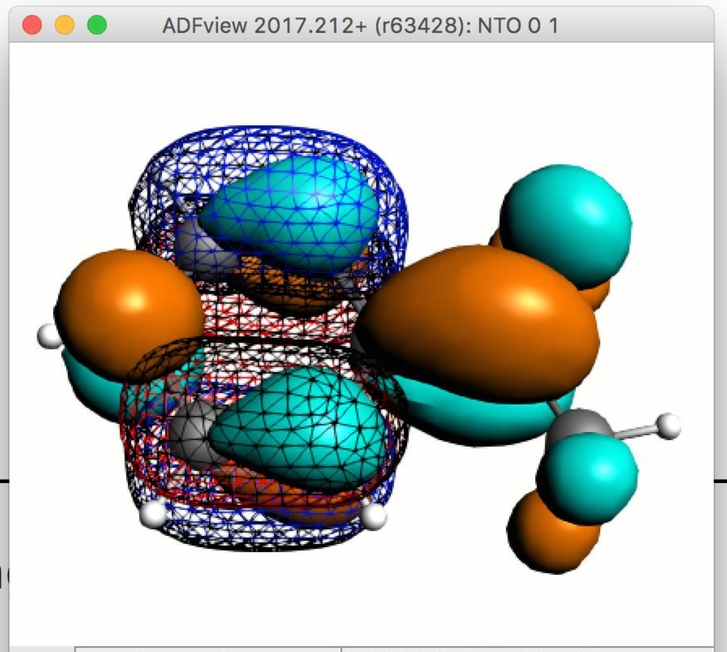
  - NB analytical frequencies available for most GGAs, not for hybrids
  - Go to spectra, visualize the CO stretch at ~1690cm^{-1}
  - Increase the line width to ~20
  - Compare to NIST data



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

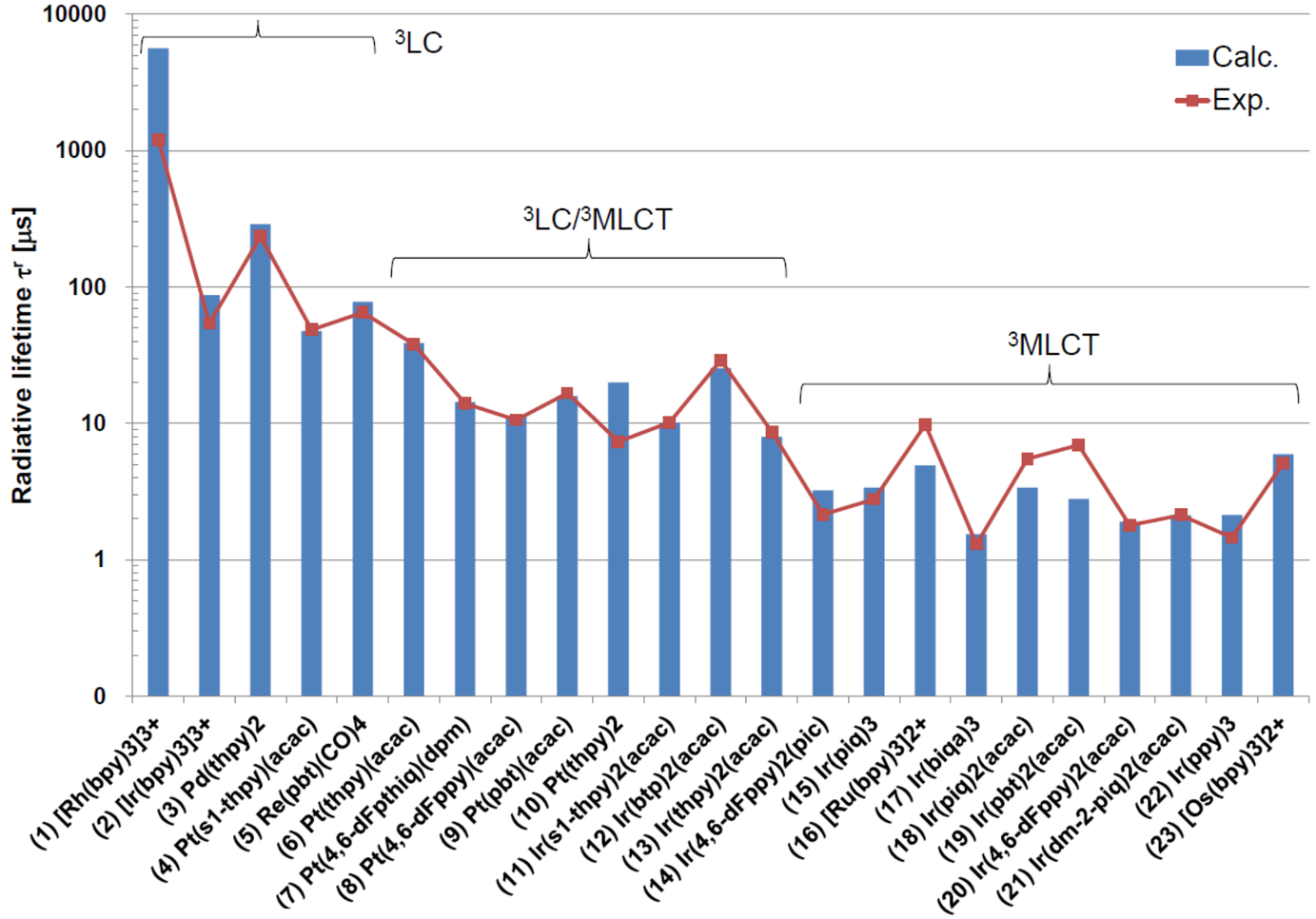


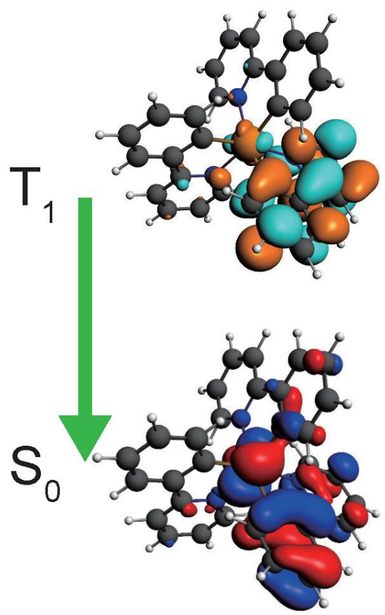


Phosphorescent OLED emitters

- 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



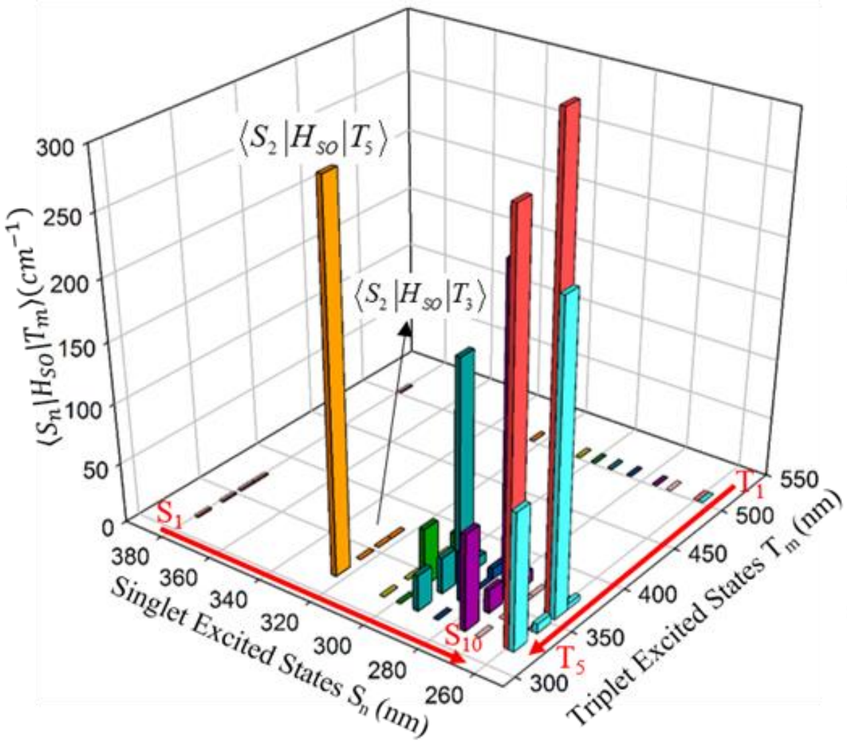


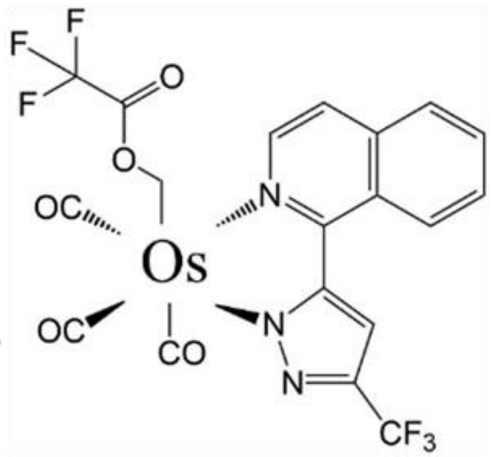
23 Ir, Rh, Ru, Os, Pt, Re complexes

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

ADF tutorial online

Intersystem crossing: spin-orbit coupling

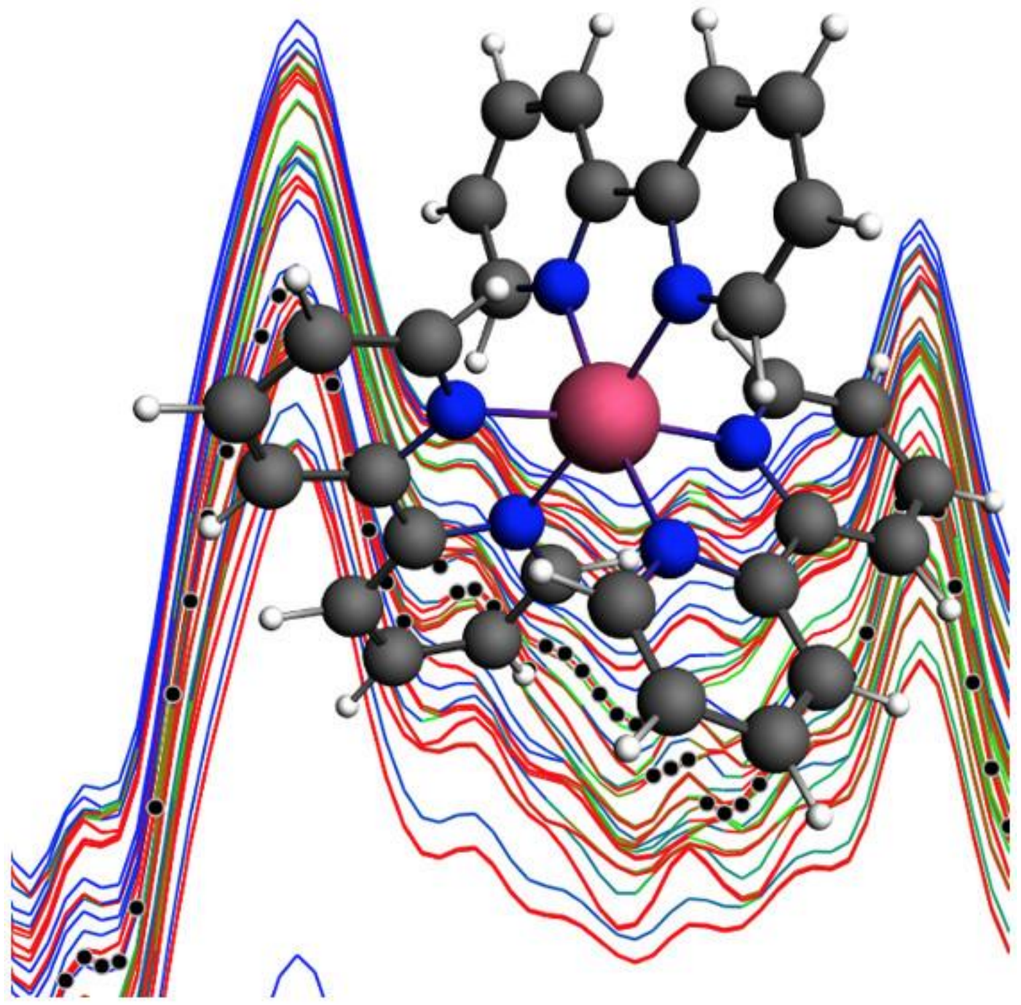




El-Sayed for organometallics:
SOC is largest when:
- both S (^{1}dπ*) and T (^{3}d'π*) are MLCT
- different d-orbitals are involved (d ≠ d').

λ_{exc}-dependent quantum yield
SOCME negligible for S_1-T_n
ISC from higher S_n states

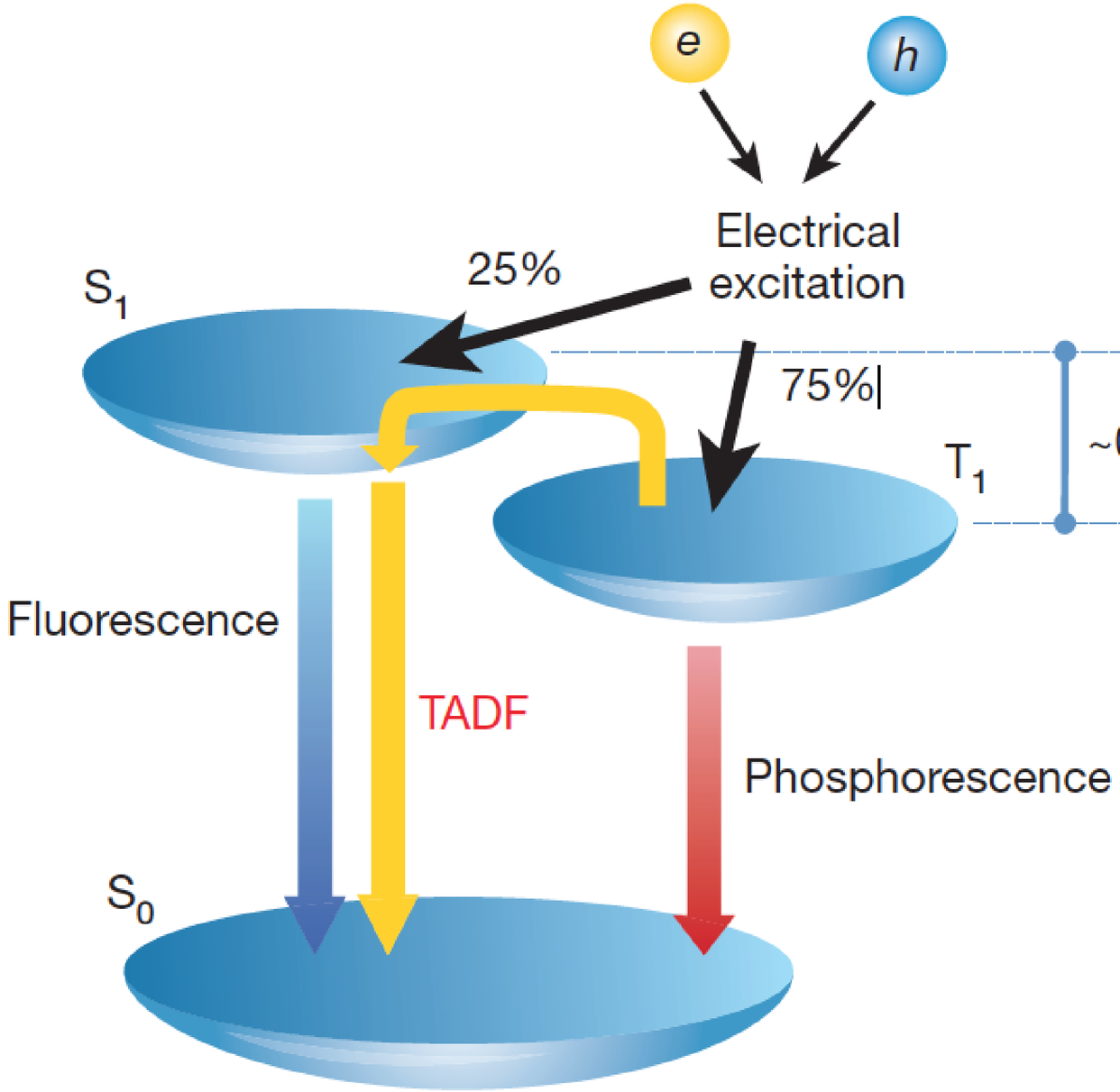
Phys. Chem. Chem. Phys. **16**, 26184-26192 (2014)
NB: See also full k_{ISC} Paul et al. JPCL, 2017, **8**, 4893



Surface-Hopping Dynamics $Ru(bpy)_3^{2+}$
- 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 S1-T1 gap
- Maximize SOC
- Maximize k_{phos} & k_{TADF}

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

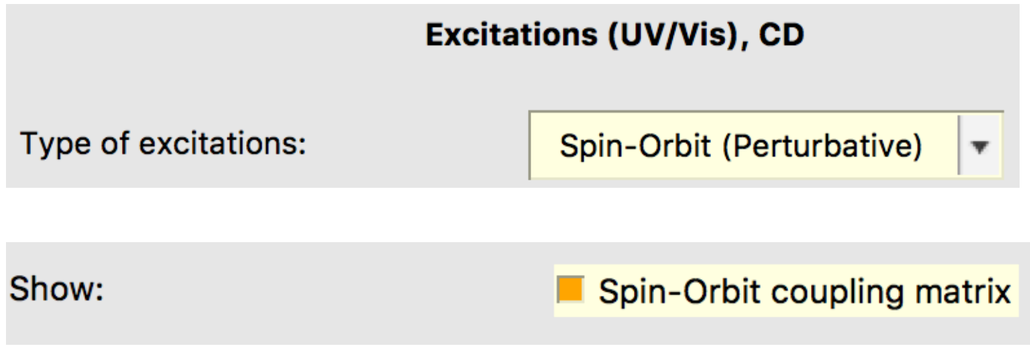
$$\rho_{\mathrm{FC}} = \frac{1}{\sqrt{4\pi\lambda_{\mathrm{M}}k_{\mathrm{B}}T}}\sum_{n=0}^{\infty}\exp(-S)\,\frac{S^n}{n!}\exp\left[-\frac{(\Delta E_{\mathrm{ST}} + n\hbar\omega_{\mathrm{eff}} + \lambda_{\mathrm{M}})^2}{4\lambda_{\mathrm{M}}k_{\mathrm{B}}T}\right]$$

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)



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

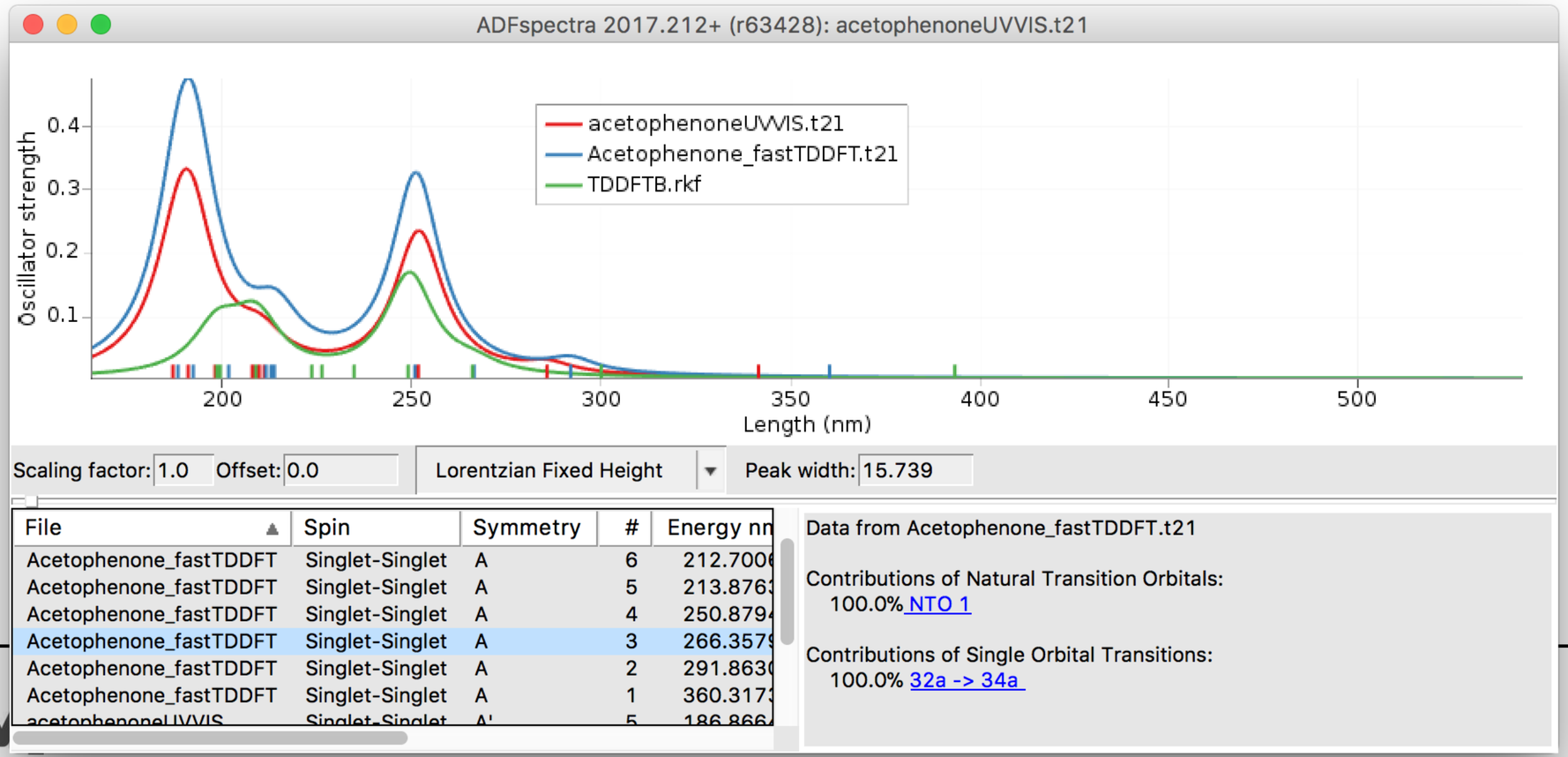
<S|Hso|T>	T1	T2	T3	T4	T5	T6
S1:	0.38	21.60	3.45	3.87	0.33	0.72
S2:	3.41	0.01	0.00	0.08	5.84	0.00
S3:	0.06	0.60	1.61	5.22	0.09	19.20
S4:	16.09	0.00	0.02	0.01	2.28	0.08
S5:	14.92	3.35	1.66	0.72	0.00	0.19
S6:	1.83	0.09	0.04	0.01	19.21	0.00
S7:	3.03	0.96	0.38	1.07	0.04	0.50
S8:	12.59	6.59	1.87	1.36	0.08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

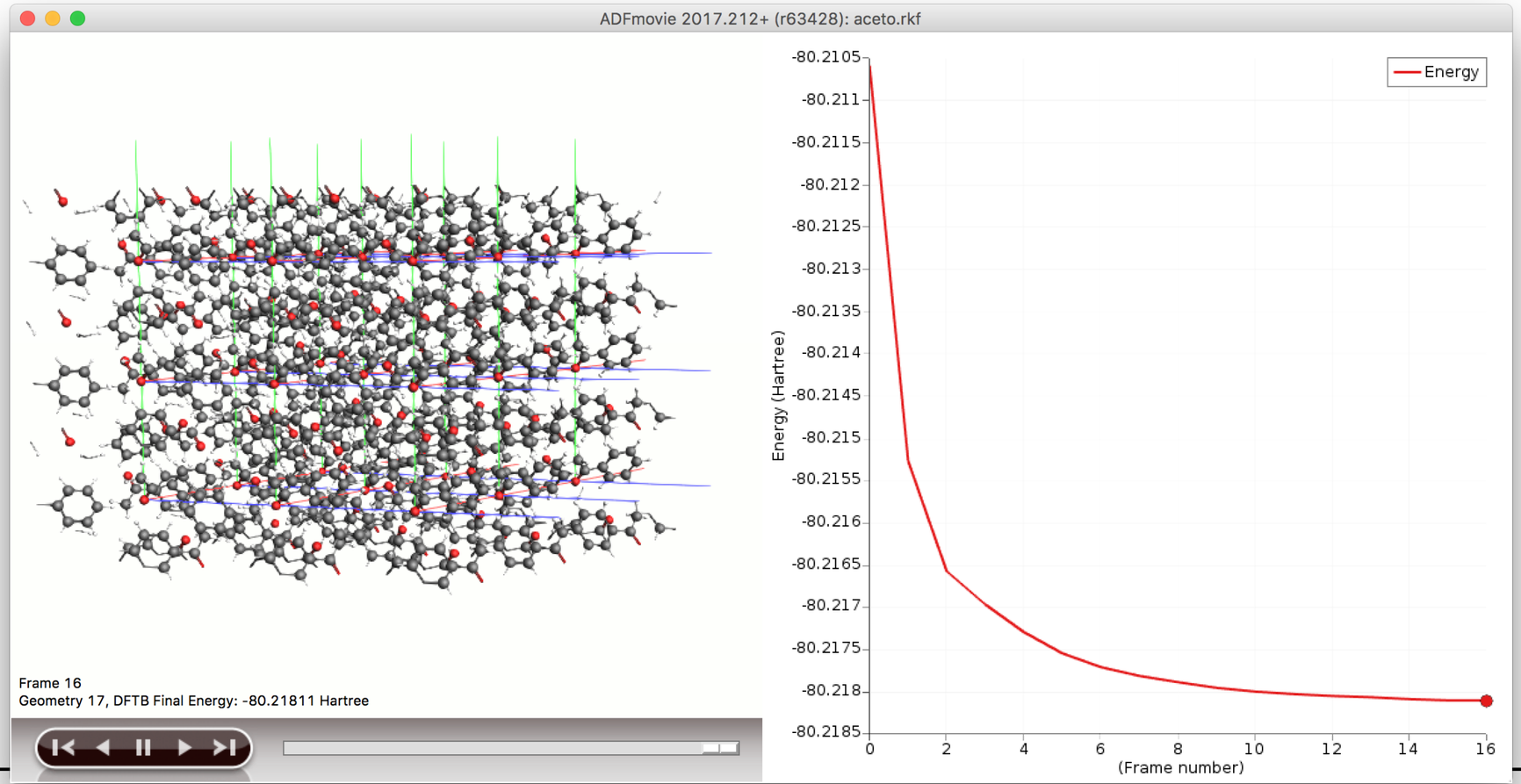
www.scm.com/doc/Tutorials/DFTB/DFTB-GUI_tutorials.html

- 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 !



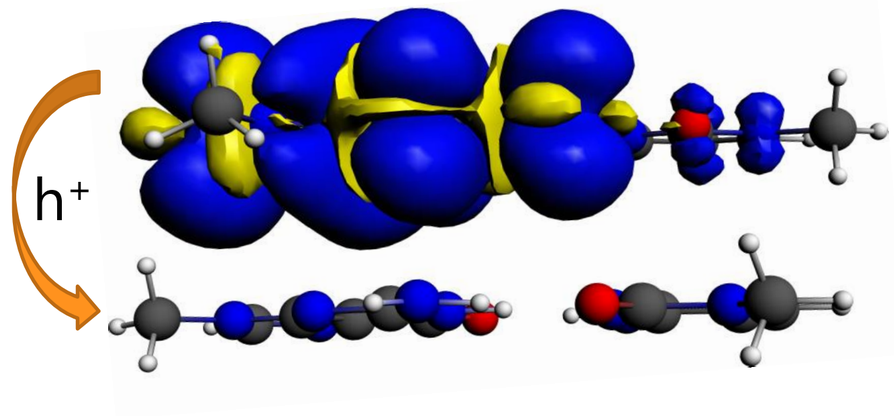
Going periodic with DFTB

- 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

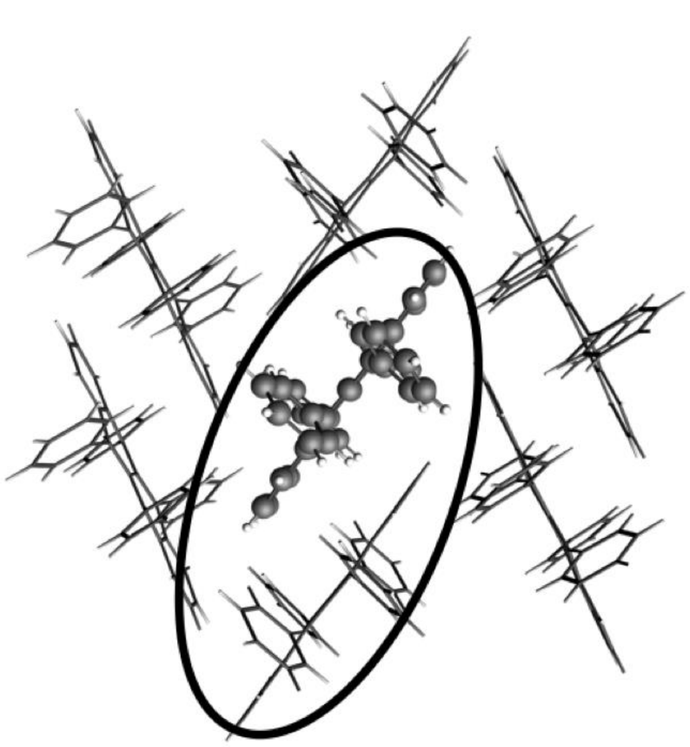
- Hopping transport:
  - Charge transfer integrals (FO) - easy
  - Electronic couplings from FDE

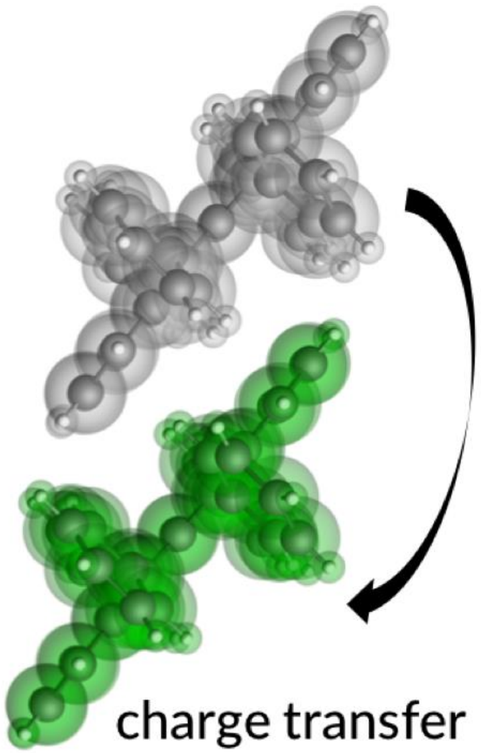


- Band transport: effective mass tensors in BAND
  - AMS2018: for any k-point & also for DFTB
  - Simulating excited state: create a core hole

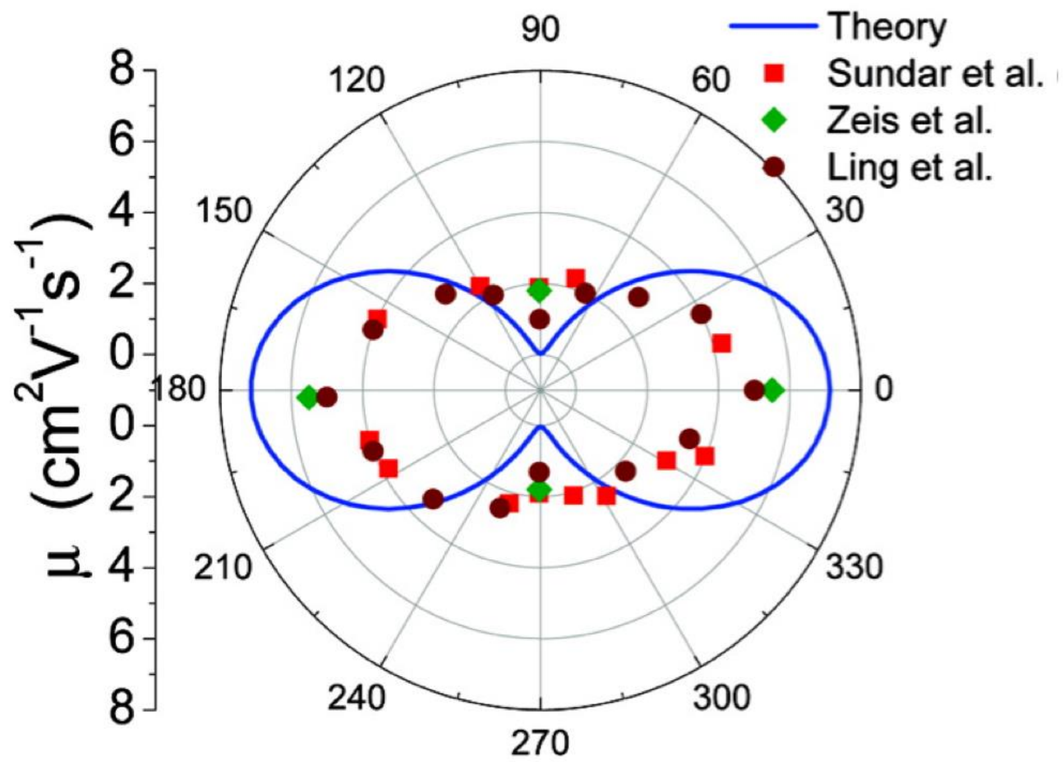
- Non-equilibrium Green's Function (NEGF)
  - transmission probabilities for single-molecule junctions
  - quick calculation: wide-band limit
  - also in BAND (periodic structures, fully self-consistent, bias) and in DFTB
    - See online tutorials

Effective transfer integral J_{eff} = electronic coupling V





extract dimers



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

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

Anisotropic mobility:

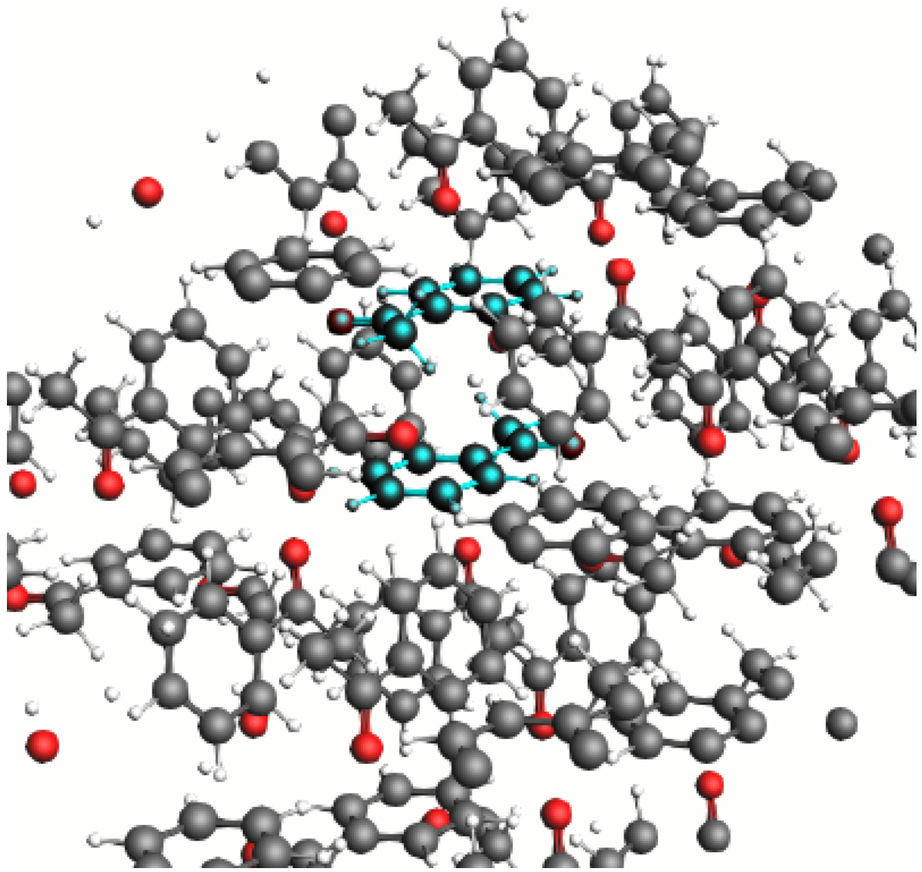
$$\mu_\Phi = \frac{e}{2k_B T} \sum_i W_i r_i^2 P_i \cos^2\gamma_i \cos^2(\theta_i - \Phi)$$

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

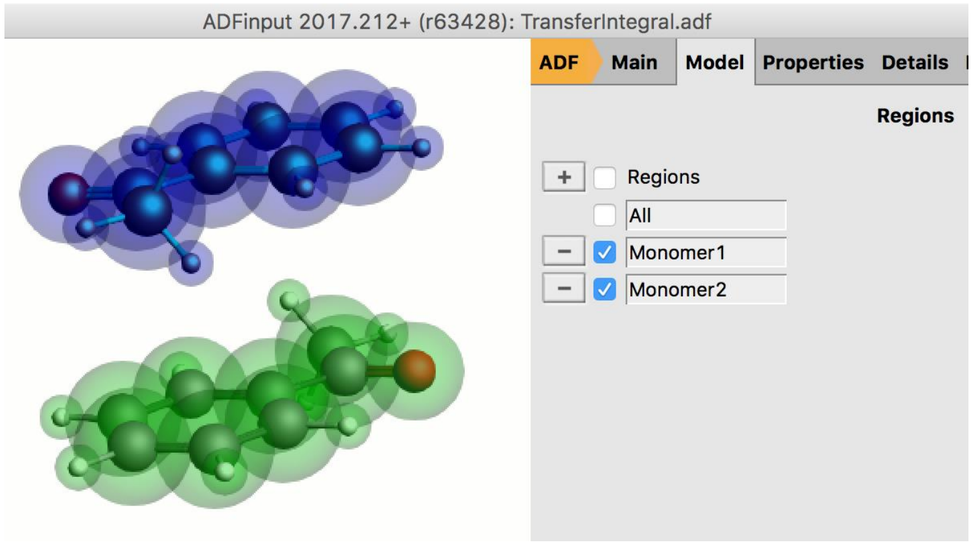
Charge transfer integrals & recombination

- 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

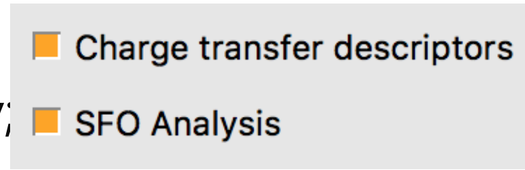
ADFoutput 2018.105: CT_aceto.out

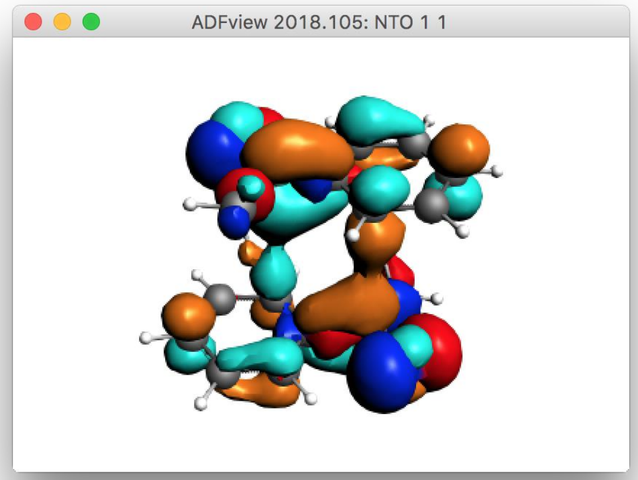
Charge transfer integrals relevant for hole or electron mobility calculations

```
Electronic coupling V (also known as effective (generalized) transfer integrals J_eff)
V = (J-S(e1+e2)/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

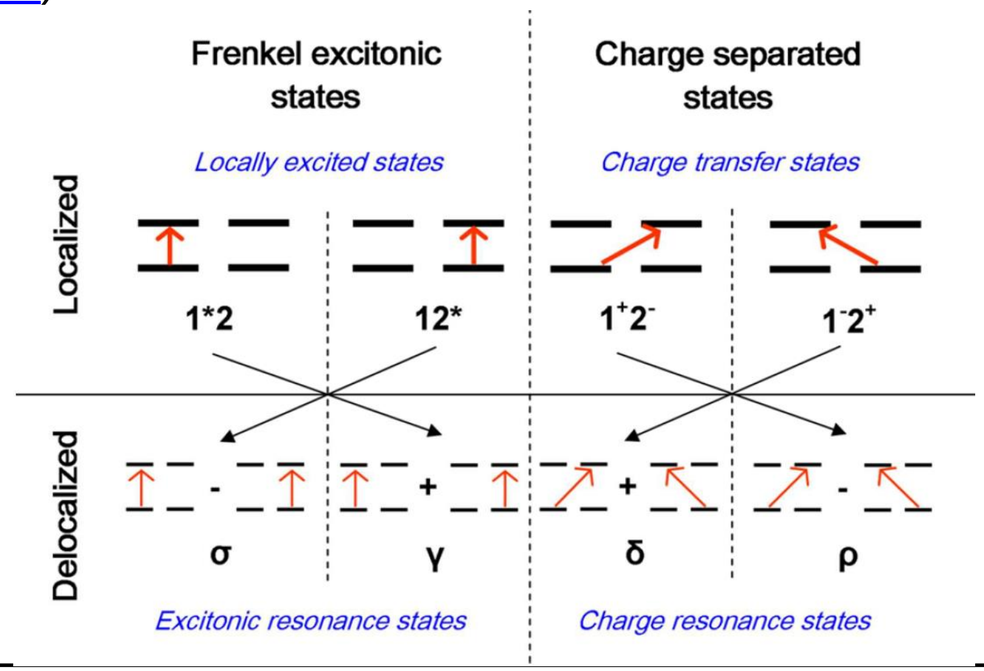
- Exercise 9: Calculate the excitations with SFO analysis + CT descriptors
  - Untick charge transfer integrals
  - Properties -> Excitations: select Allowed only;



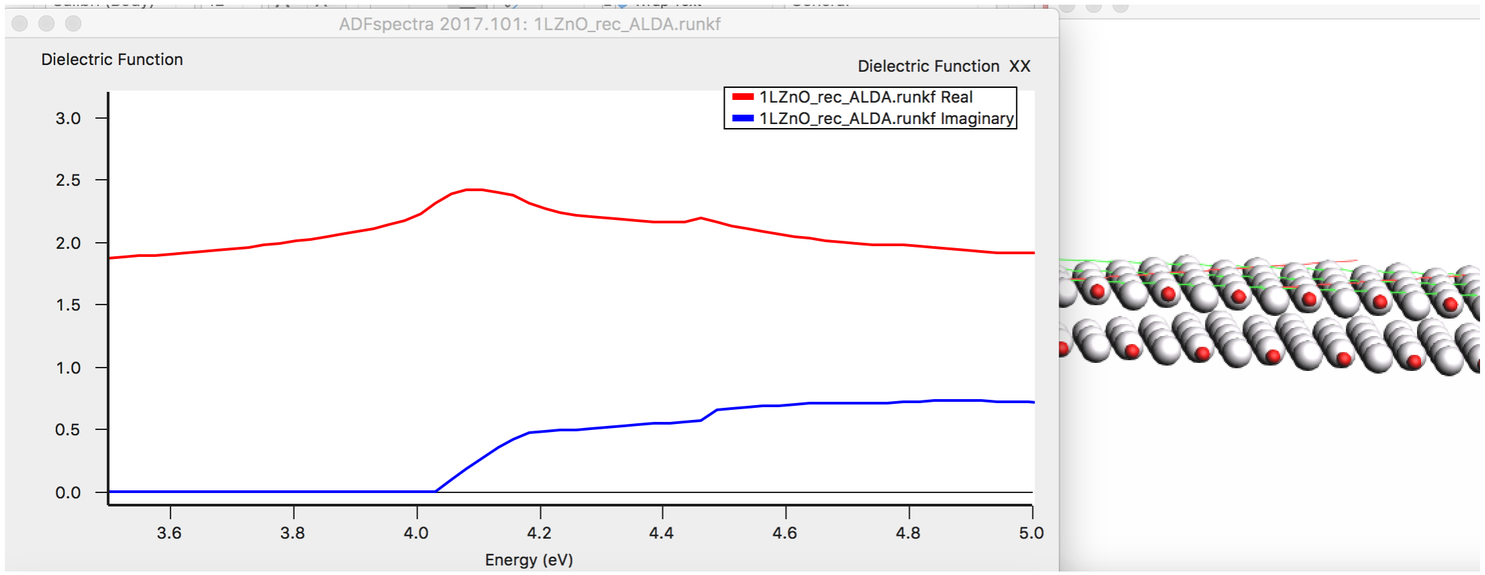


  - Tick SFO Analysis + CT descriptors
  - Save as a different file & run
  - Visualize the spectrum and NTOs of two lowest states (CT)
  - In output search for Plasser (see paper with Lischka)
  - CT = 1 & POS = 1.5 and CTNET = 0 => Charge resonance
  - Very small exciton splitting
  - LAMBDA = 0.4655 => perhaps use hybrid or RSH (Tozer)

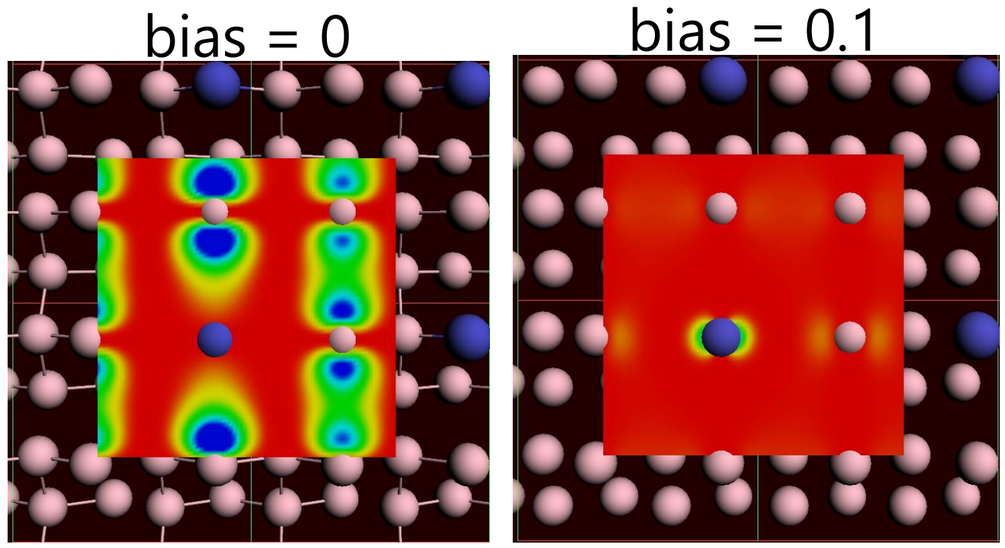
```
Descriptors (based on Plasser, Lischka, et al.)
  CT_AT =     0.9524     R_HE  =     4.8449
  CT    =     0.8778     PR    =     1.9530     COH =     1.2649
  POS   =     1.4898     CTNET =     0.1539
Descriptors (Peach, Tozer, et al.)
 LAMBDA =     0.4655     R_HE  =     0.1334

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
```



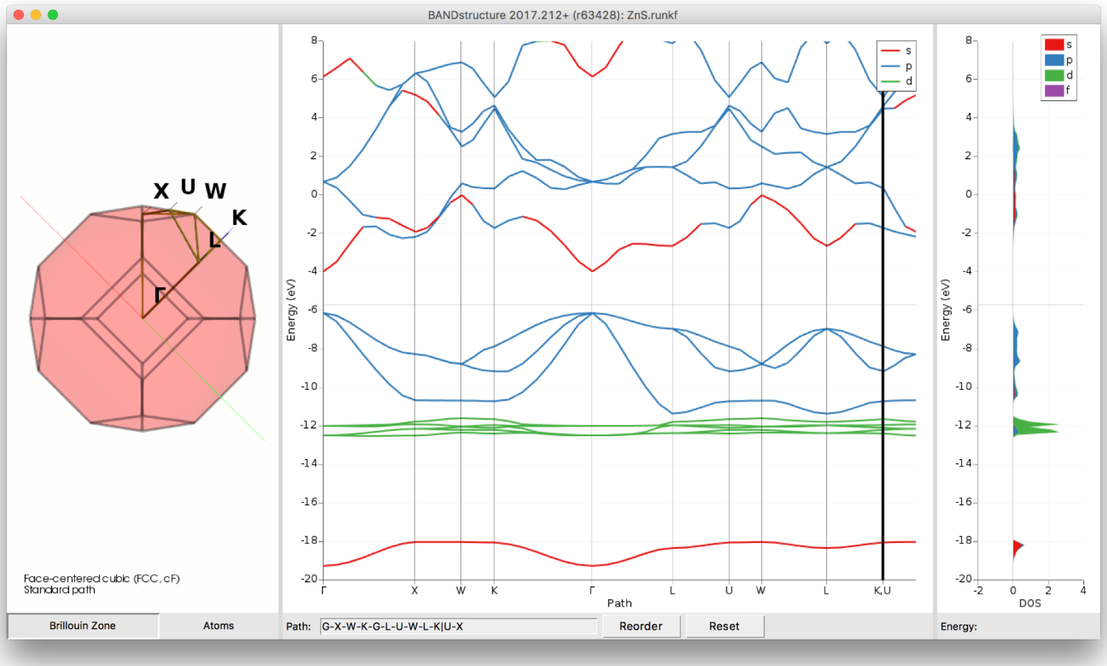
BAND & QE : Periodic DFT



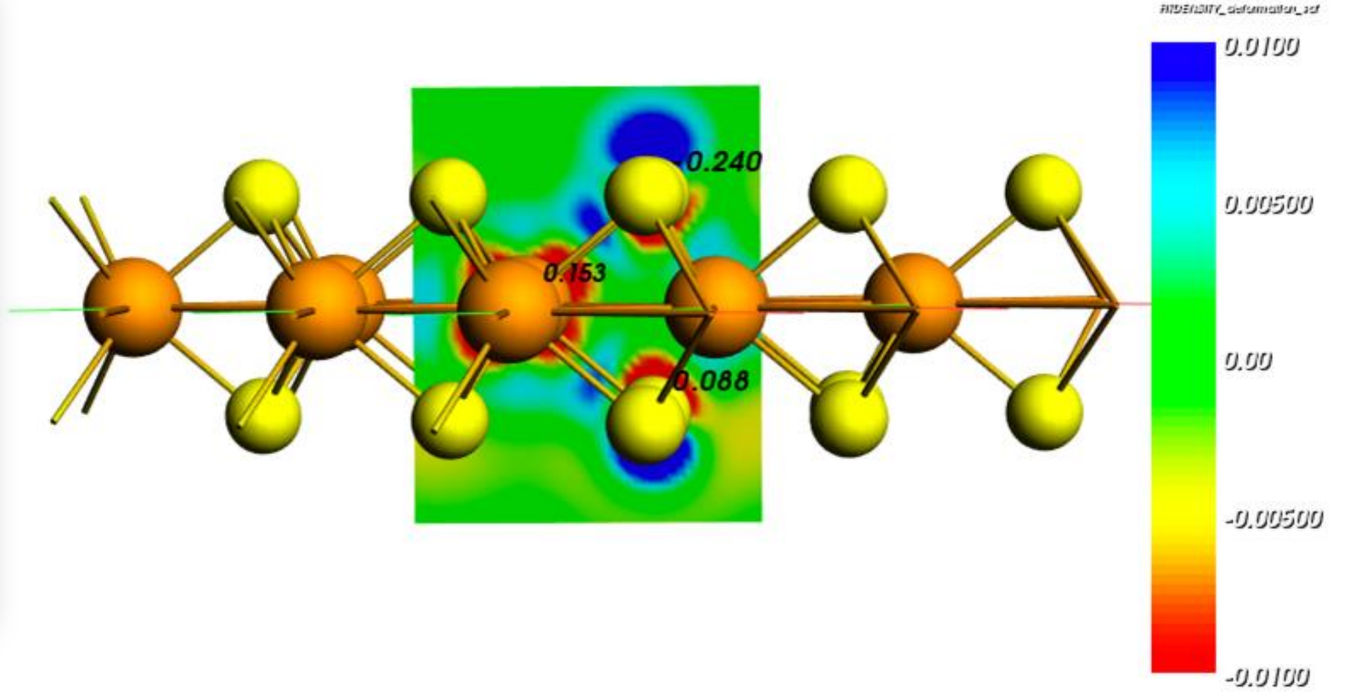
Dielectric function ML ZnO



STM PtGe(100)



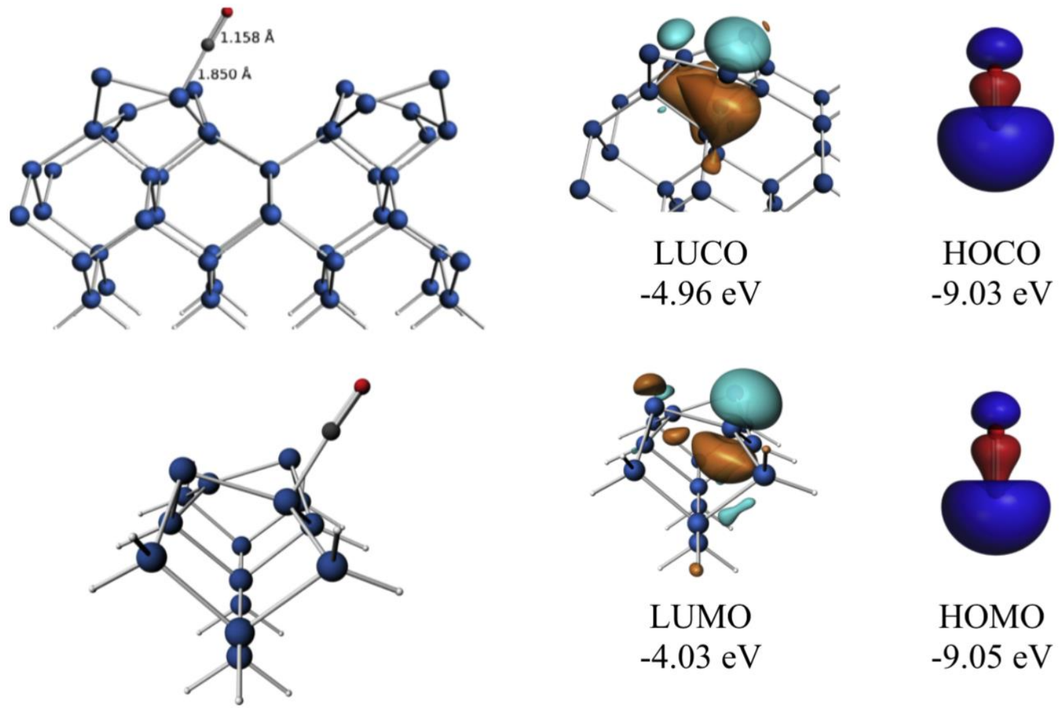
Band structure, pDOS, fat bands ZnS



Polarizing MoS_2 with an electric field

BAND vs. Plane Wave codes (QE)

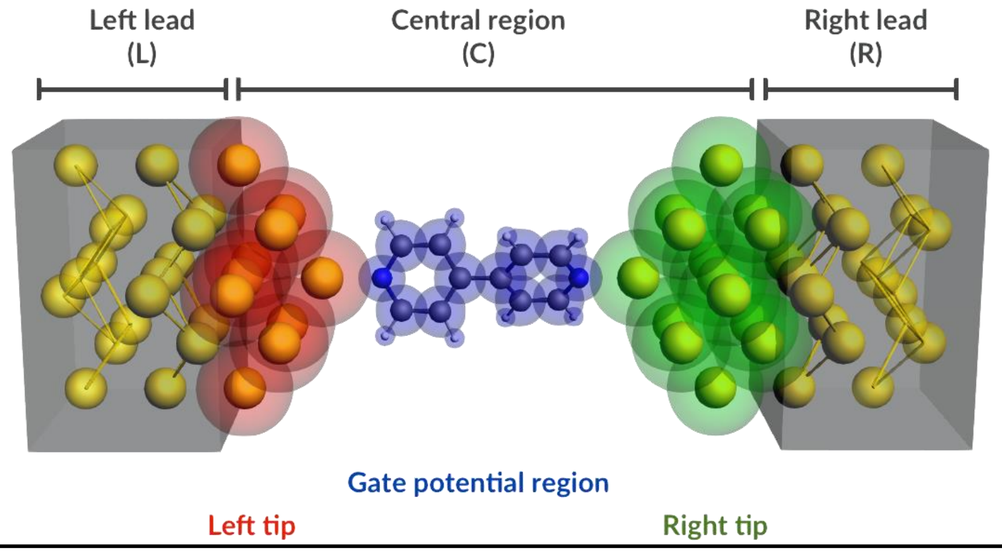
- Atom centered basis functions, STO or NAO
  - Compare cluster with periodic
  - No pseudopotentials, all elements
  - Core spectroscopy (core holes)
  - Easy (orbital, density) analysis with GUI
  - Fast for empty (1D, 2D, porous)
  - xc: SCAN, MN15-L, HSE06, GLLB-sc, D3(BJ), …
  - Self-consistent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



- True 2D surfaces, 1D polymers
  - Het. catalysis: polarization, COSMO
  - 2D electronics (homogeneous E field)
  - Nanotubes

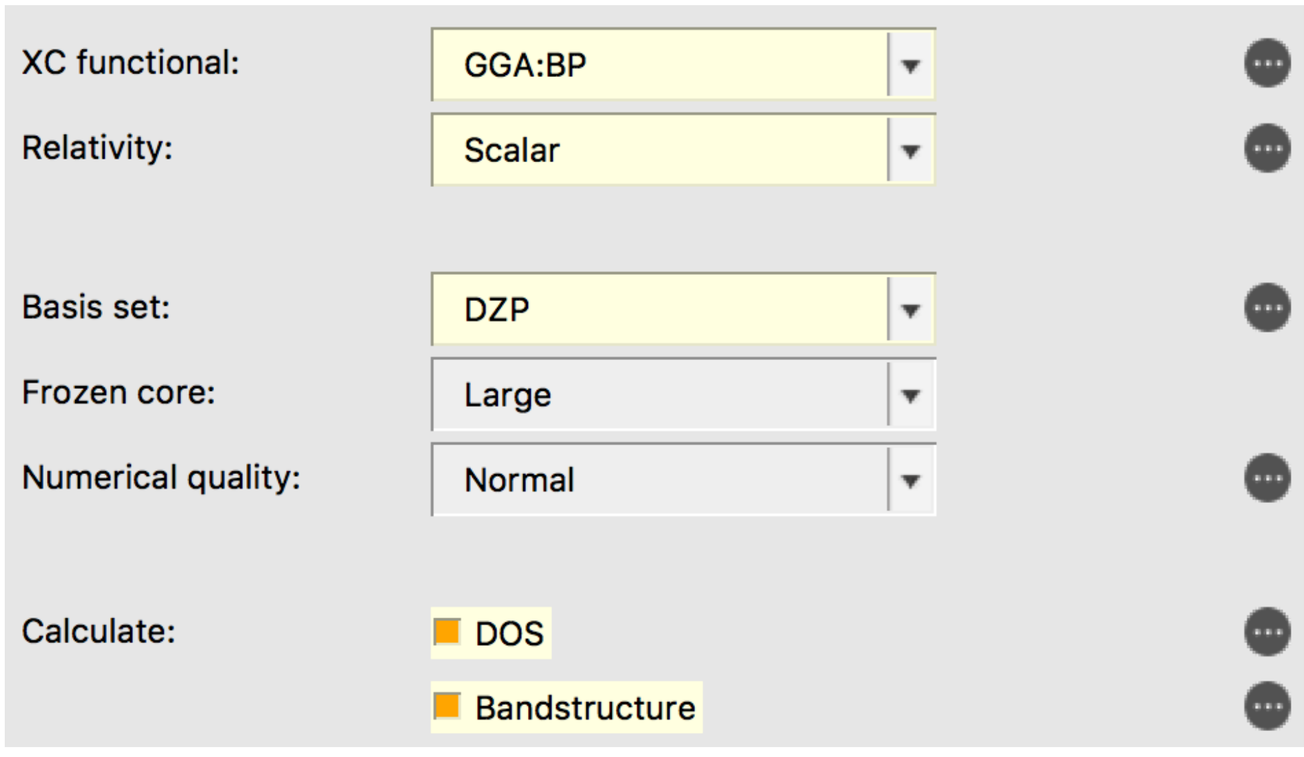
- Integrated Graphical Interface:
  - Easy set up & analysis
  - Switch: ADF, BAND & Quantum Espresso

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



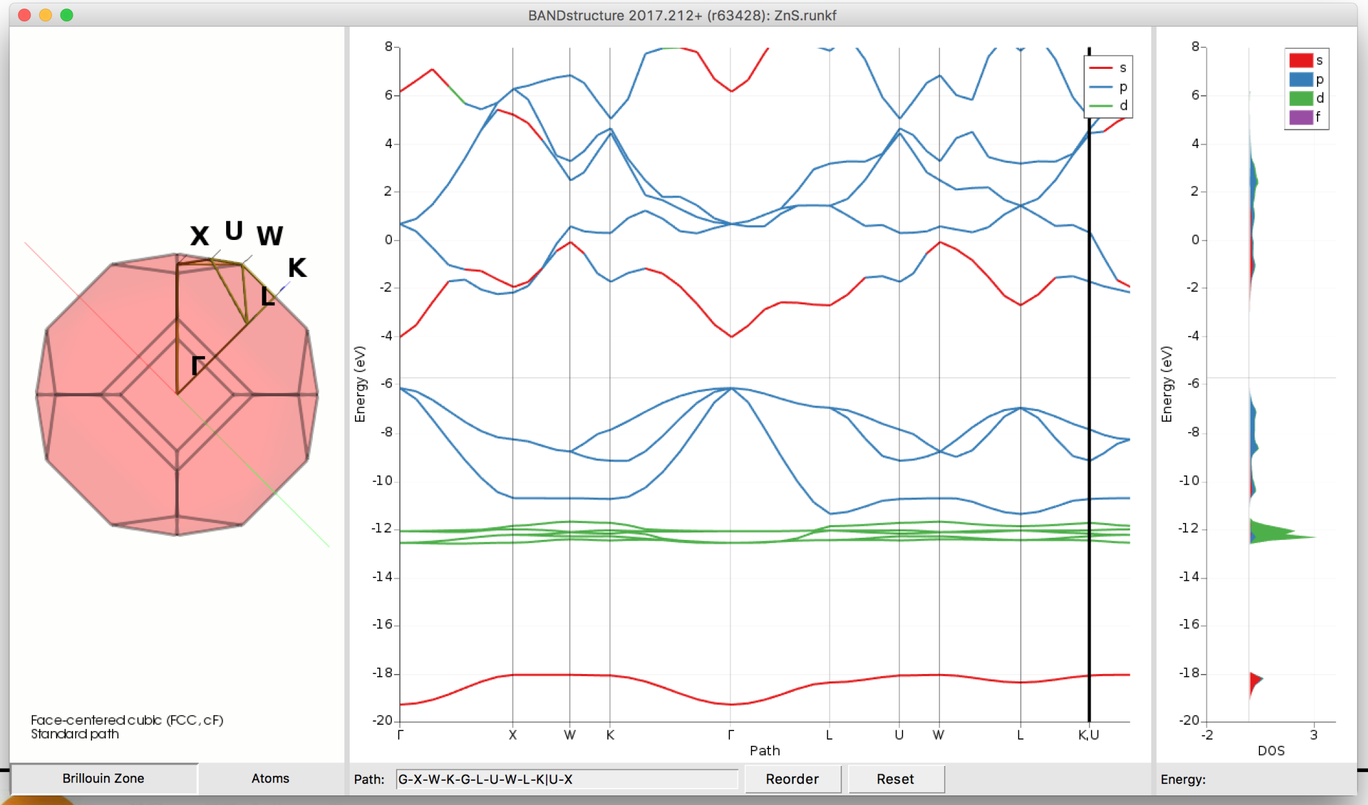
Band structure, pDOS, fat bands, COOP

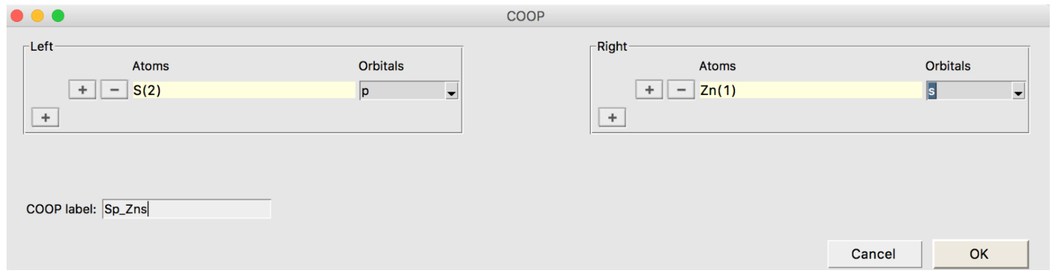
- Exercise 10: ZnS bulk
  - New input, go to BAND
  - click on the ‘crystal’ builder tool in the bottom
  - select cubic -> Zincblende and accept the default
  - Settings: BP, SR-ZORA, and DZP
  - Select DOS and Bandstructure (default interpolation)
  - Run it!



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

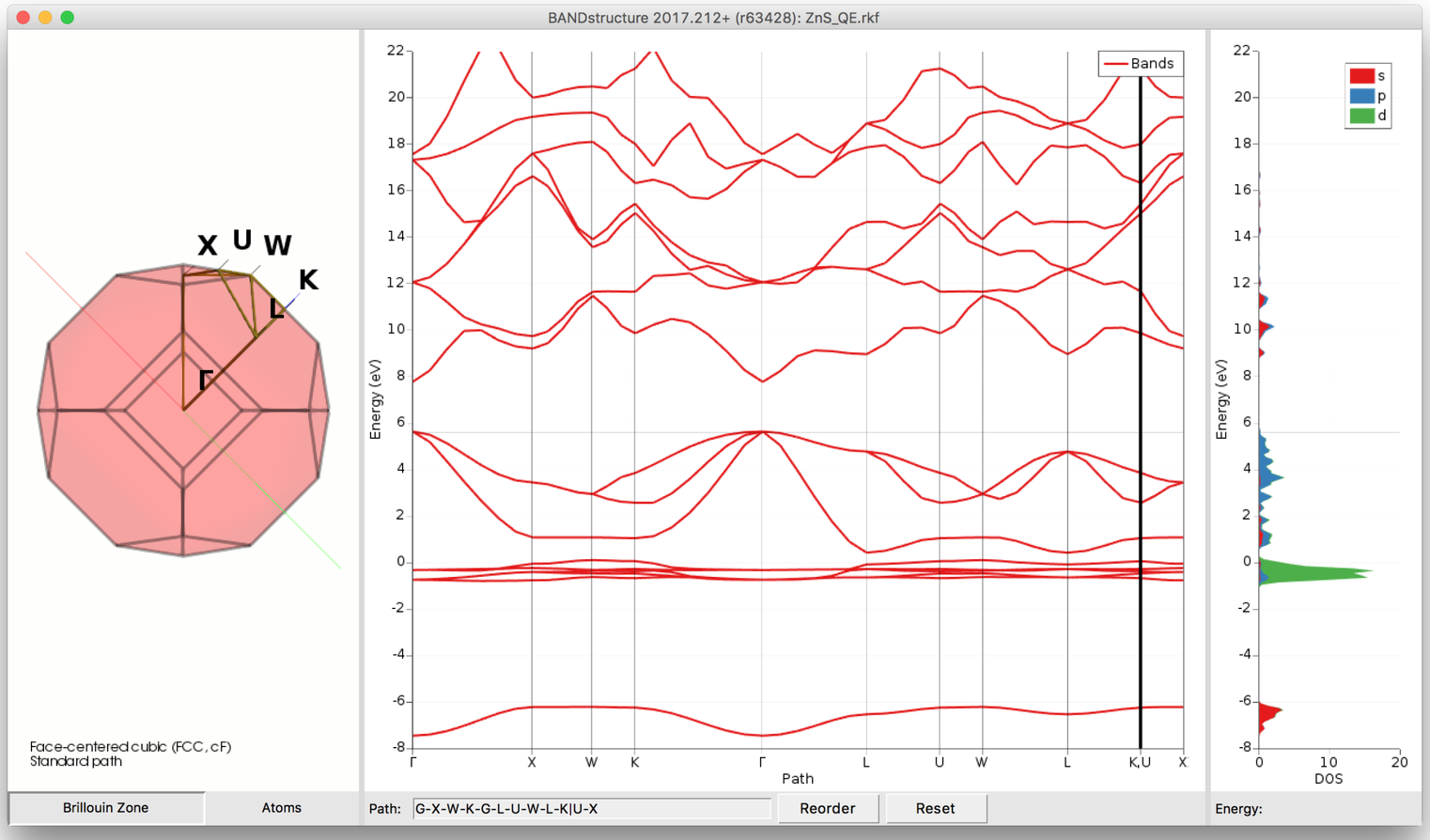




recent JACS study by Hoffmann: COOP in perovskites (tutorial)

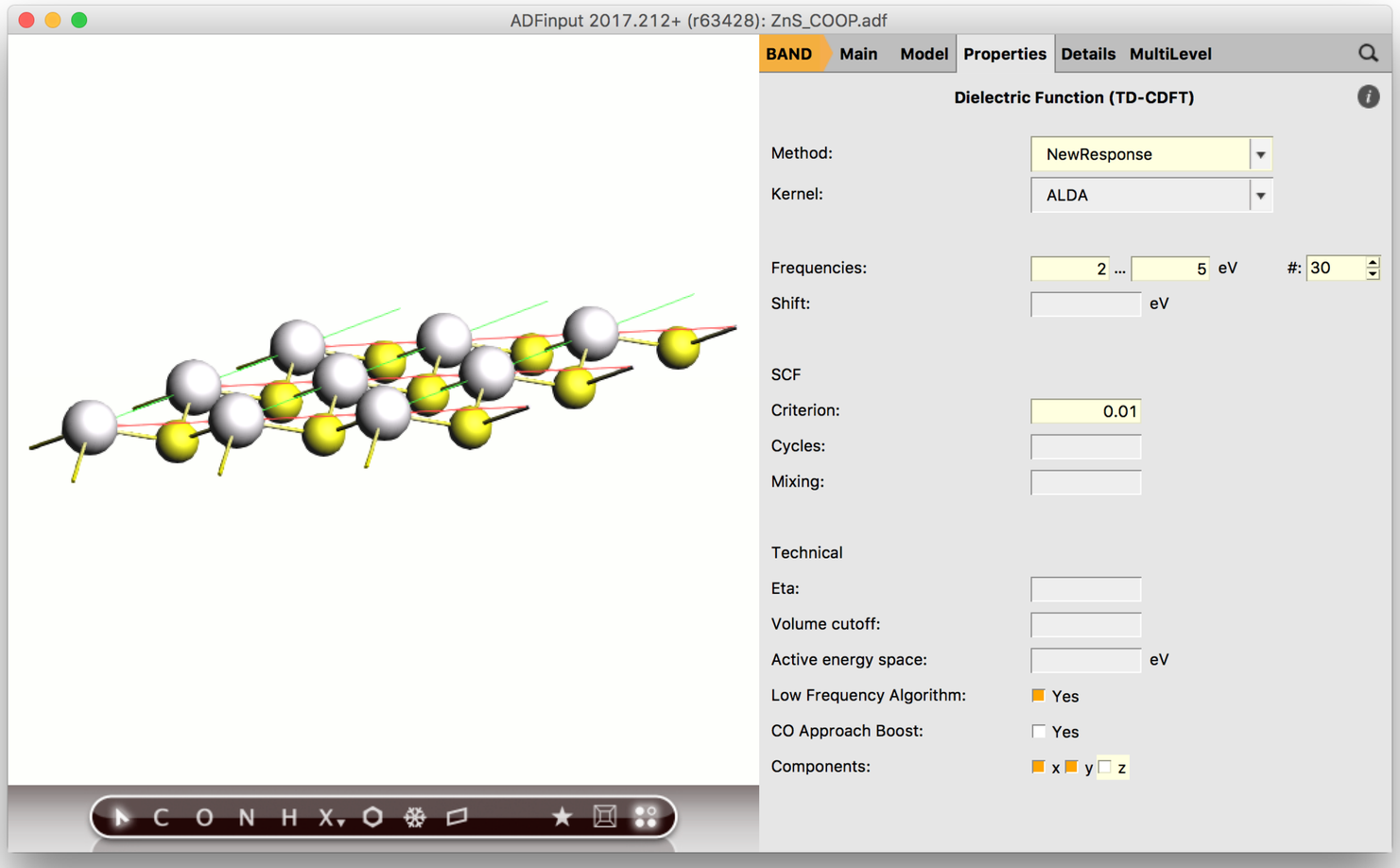
Band structure, pDOS with QE

- 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



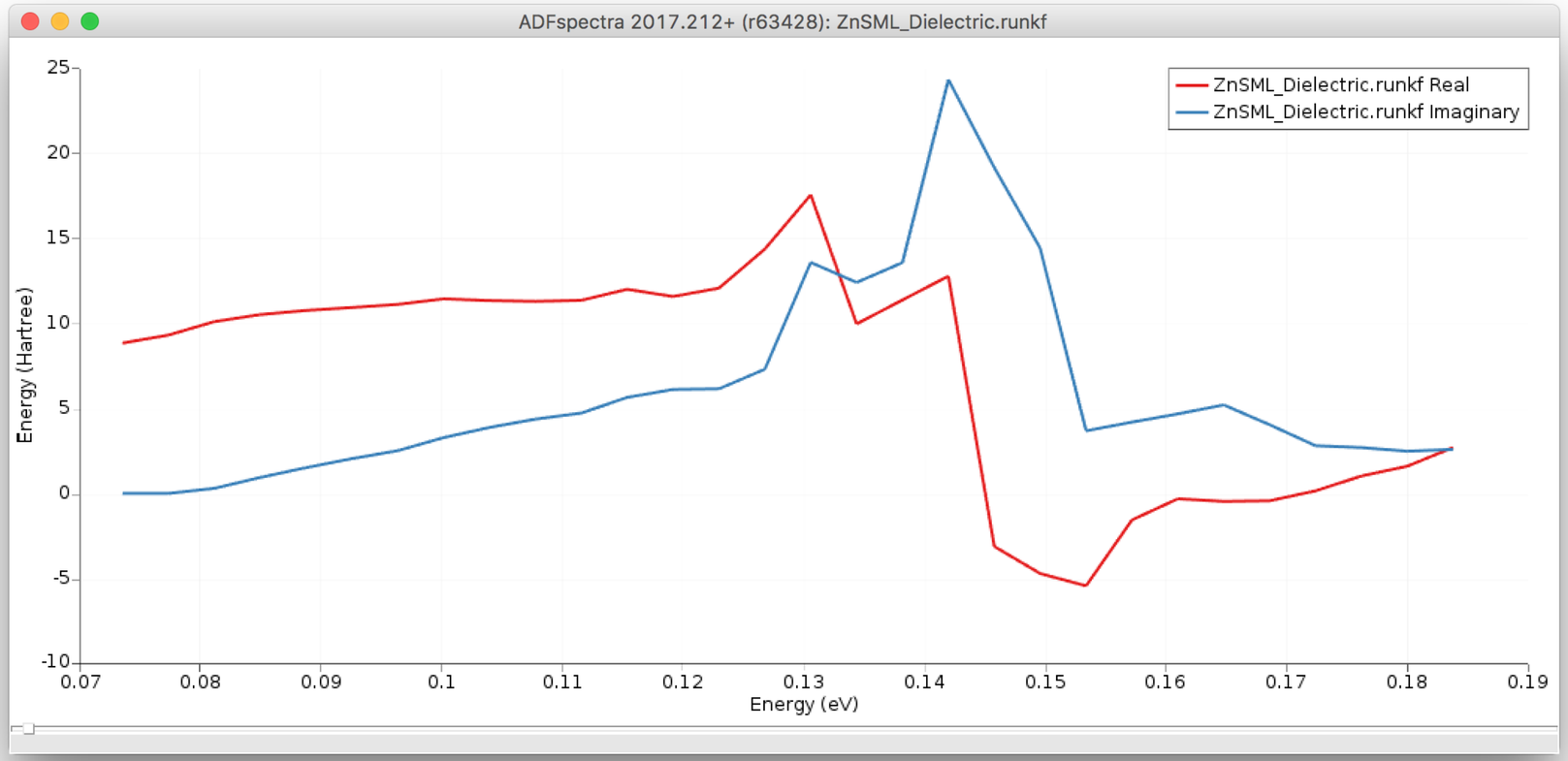
Surfaces, dielectric function

- 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 ?!



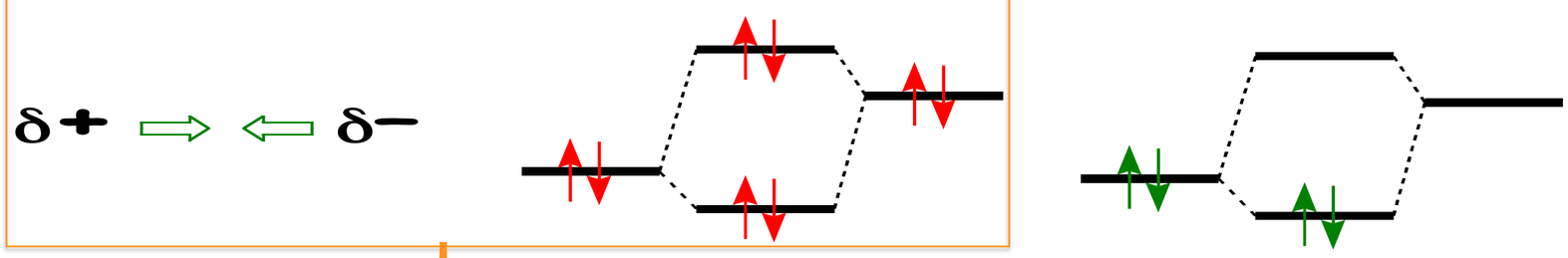
Energy decomposition analysis

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

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

- ΔE_{prep} = geometry 'deformation' energy

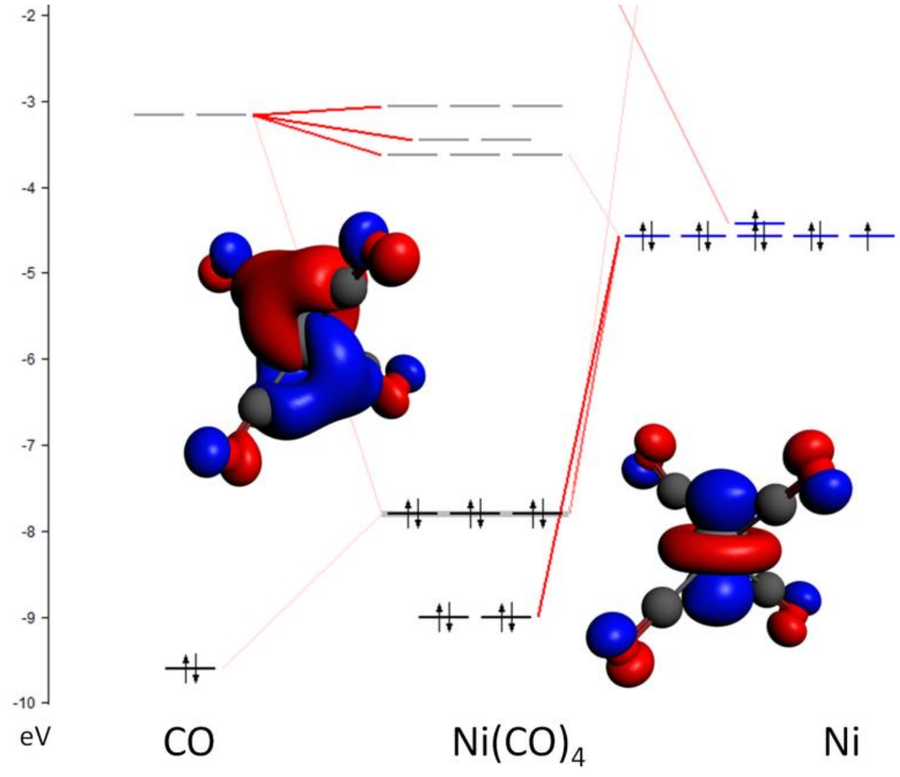
$$\Delta V_{elstat} + \Delta E_{Pauli} + \Delta E_{oi} + \Delta E_{disp}$$



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

Extensions:

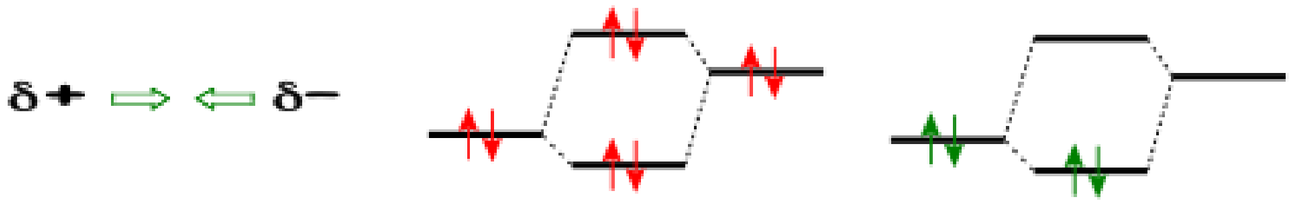
- Periodic EDA: M. Raupach & R. Tonner, J. Chem. Phys. 142, 194105 (2015)): molecule-surface interactions
- Ziegler, Michalak, Mitoraj: ETS-NOCV



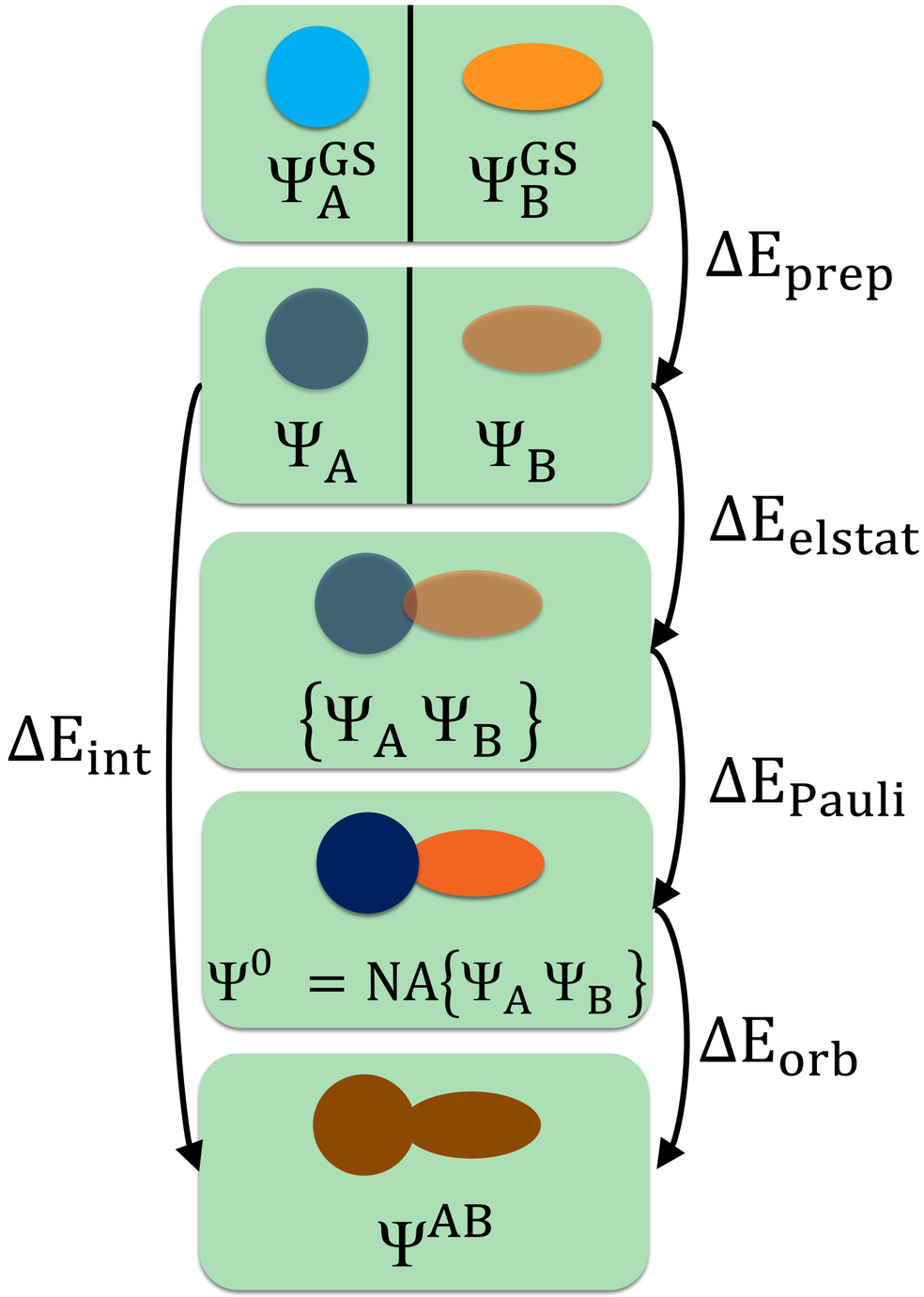
EDA/ETS-NOCV: bond & density decomposition

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

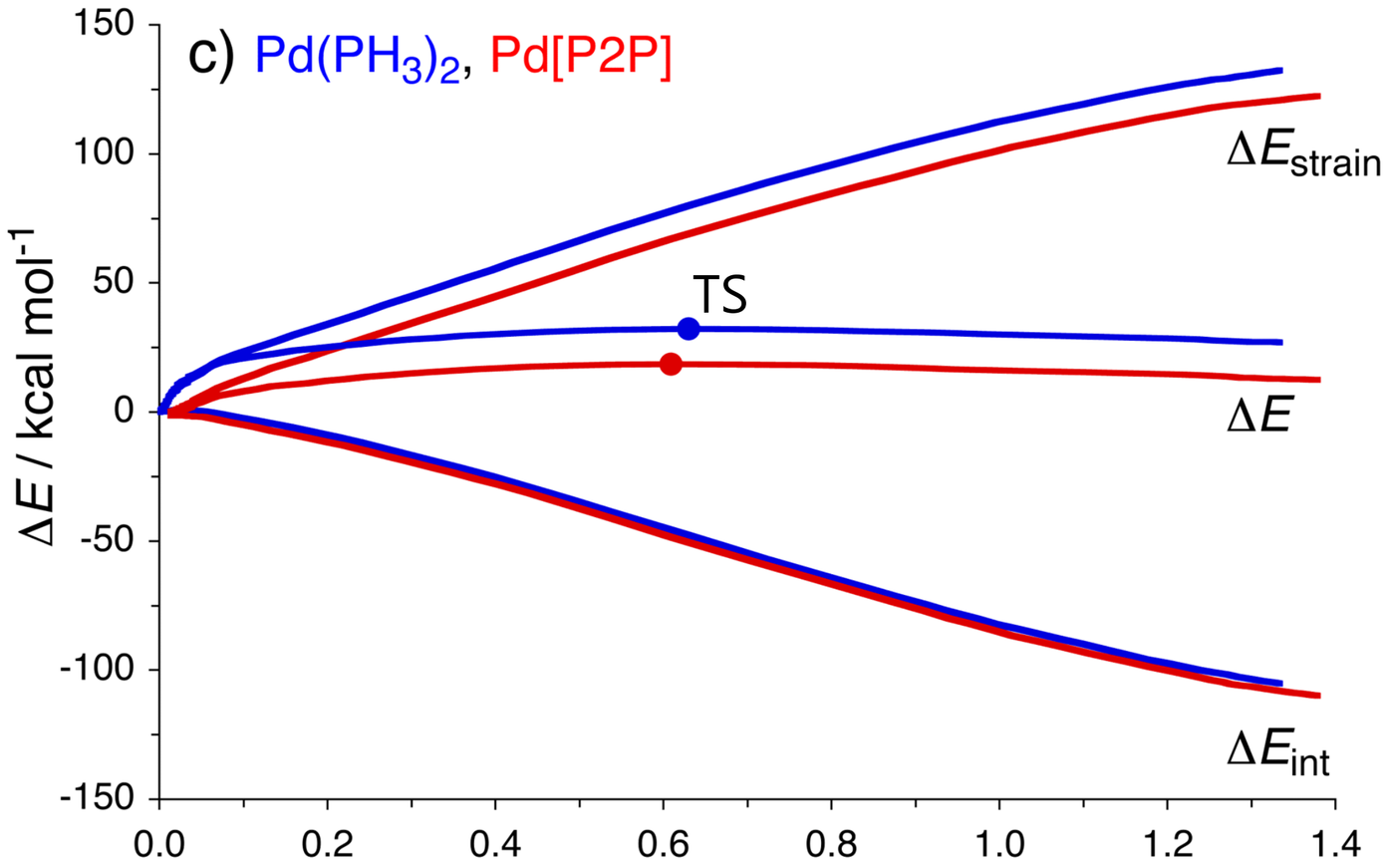
$$\Delta V_{elstat} + \Delta E_{Pauli} + \Delta E_{oi}$$

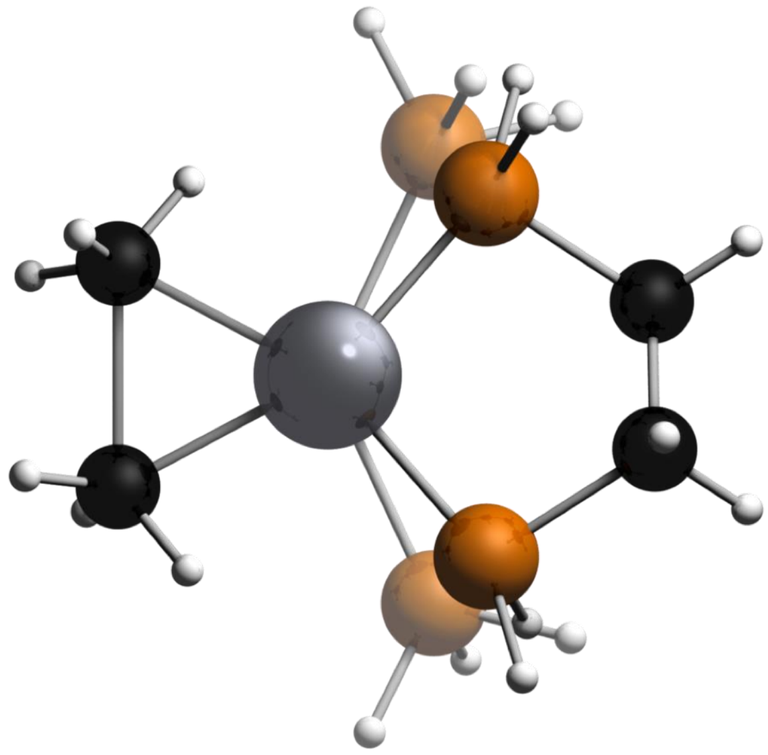


- Combine with NOCV (webinar)
  - Orbital interactions / charge transfer
- Also periodic 1D, 2D, 3D (tutorials)
  - (Ad)sorption nanotbues, surfaces, MOFs etc.
  - Raupach &Tonner, J. Chem. Phys. 142, 194105 (2015)



Catalyst design: activation strain model





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

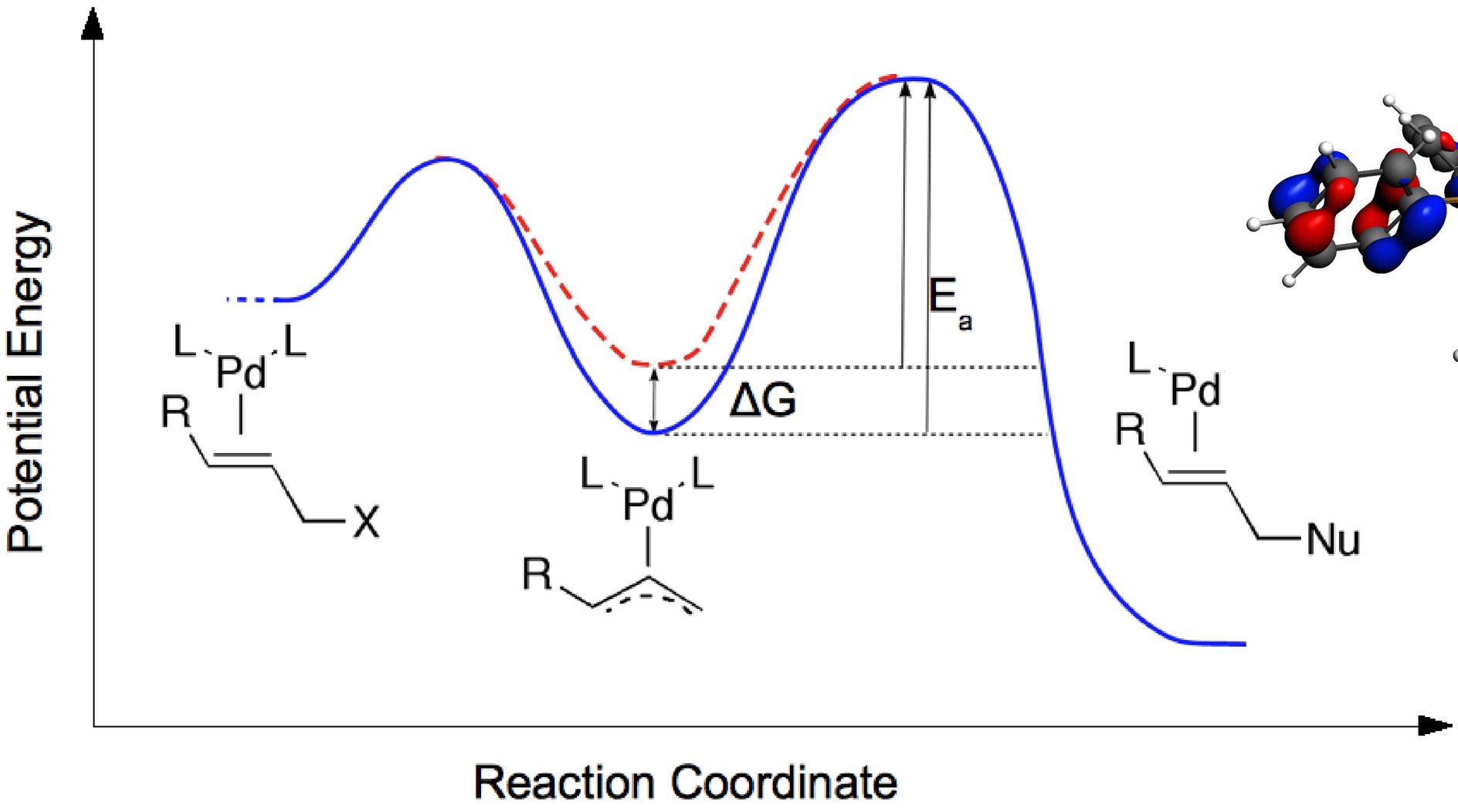
Latest reviews:
Chem. Soc. Rev. 2014, 43, 4953
WIRES Comput. Mol. Sci. 2015, 5, 324

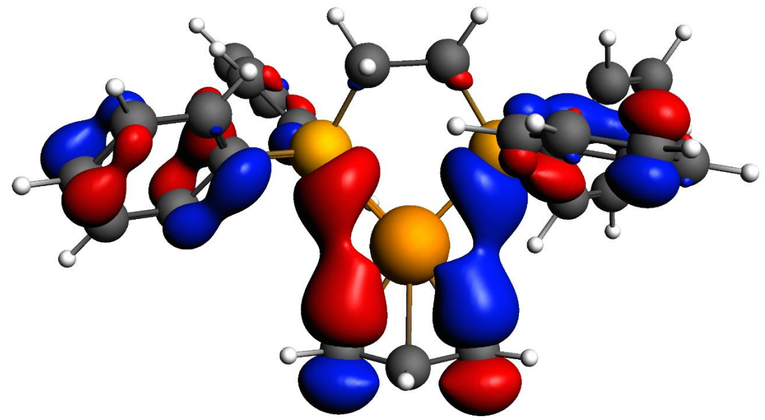
EDA along the reaction path
Bite-Angle Effect: Activation Strain analyses:
- HOMO–LUMO interaction marginally improved
- But: strain reduced by building it into catalyst

Catalyst natural selection: survival of the weakest

Increased bite angle dppe → dppb

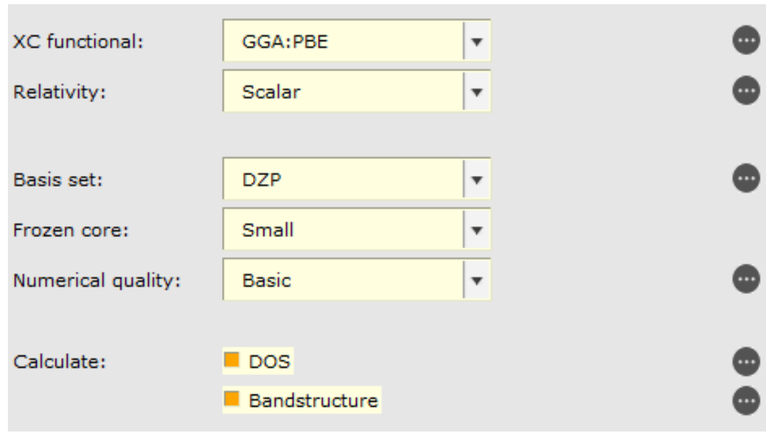
- Improved electronic interaction <u>and</u> larger repulsive strain
- Strain outweighs electronic interactions → dppb most destabilized → best catalyst





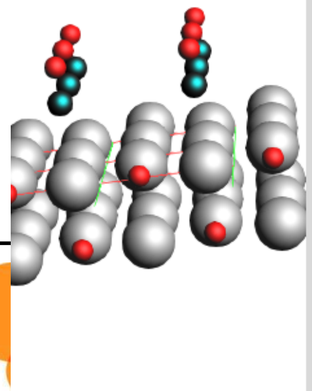
J. Wassenaar, et al. ***Catalyst selection based on intermediate stability measured by mass spectrometry.*** Nature Chem. 2, 417 (2010)

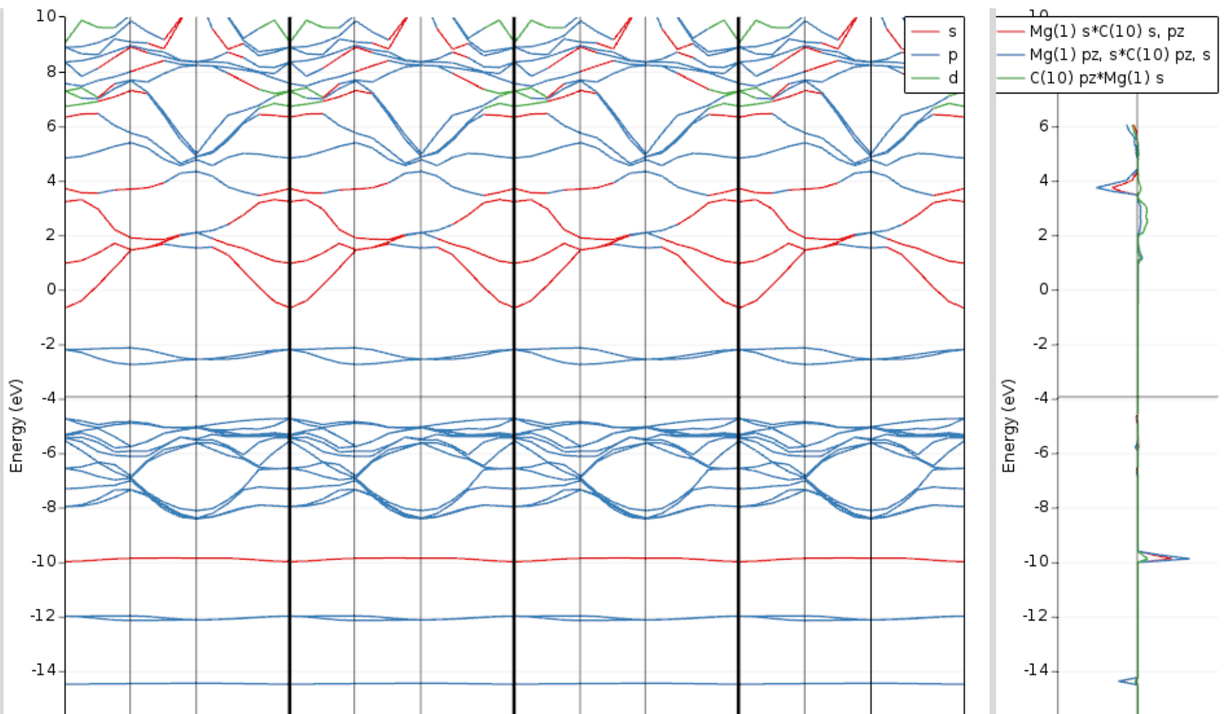
CO on MgO: COOP



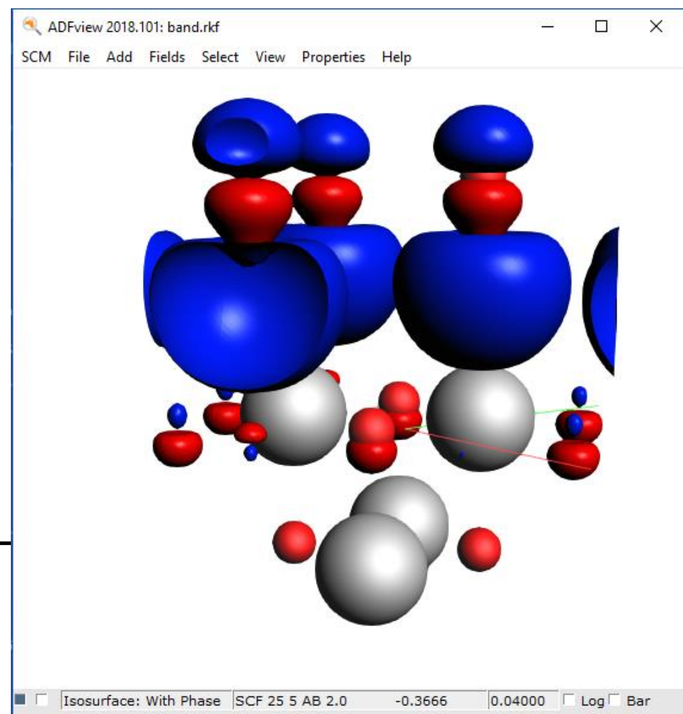
- **Exercise 13**: First do the [PEDA-NOCV tutorial]
- New input with same coordinates
- Scalar, PBE, DZP/small, basic, DOS, BandStructure
  - DOS details (…) => COOP, -20 to + 20eV
- Visualize the band structure and various COOPs
  - DOS-> COOP… Try different Mg (s) + Mg (p_z) and C (p_z) + C (s) combo's
  - 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





r, Tsinghua



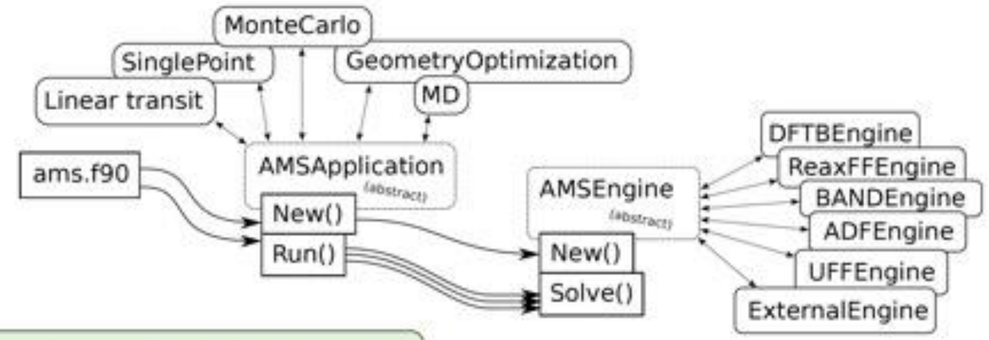
AMS: Powerful driver

- 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

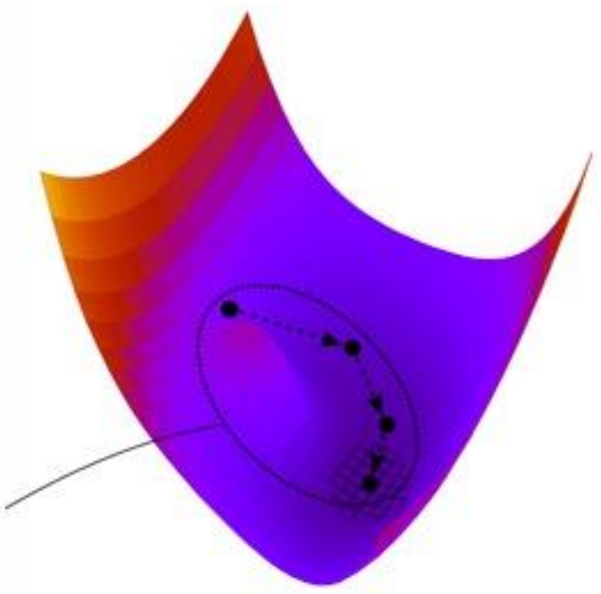
- Task farming (double parallelization)
  - Elastic tensors, phonons, frequencies




```
Task GeometryOptimization

Properties
   NormalModes true
End

GeometryOptimization
   Converge grad=1.0e-6
End

System
   Atoms
      H   0.0   0.0   0.0
      H   0.8   0.0   0.0
   End
End

Engine DFTB
   Model DFTB3
   ResourcesDir DFTB.org/3ob-3-1
EndEngine
```

AMS input

Engine input

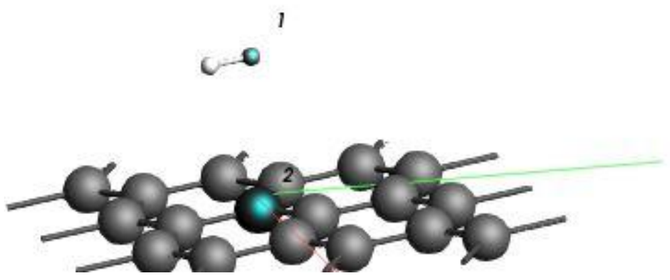


AMS: PES scan & TS search

- Exercise 14: H_2 on graphene
  - Find graphite (or build it), slice a 1L 001 surface & remove top layer to get graphene
  - Create 3x3 super cell and build H_2 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 H_2 from 0.74-1.4 (7 points)
    - Set SC-2 both H-C coordinates from 2.4-1.8 (7 points)



Number of scan points for coordinate SC-1: 7 SC-2: 7

Results for all PES points: Save

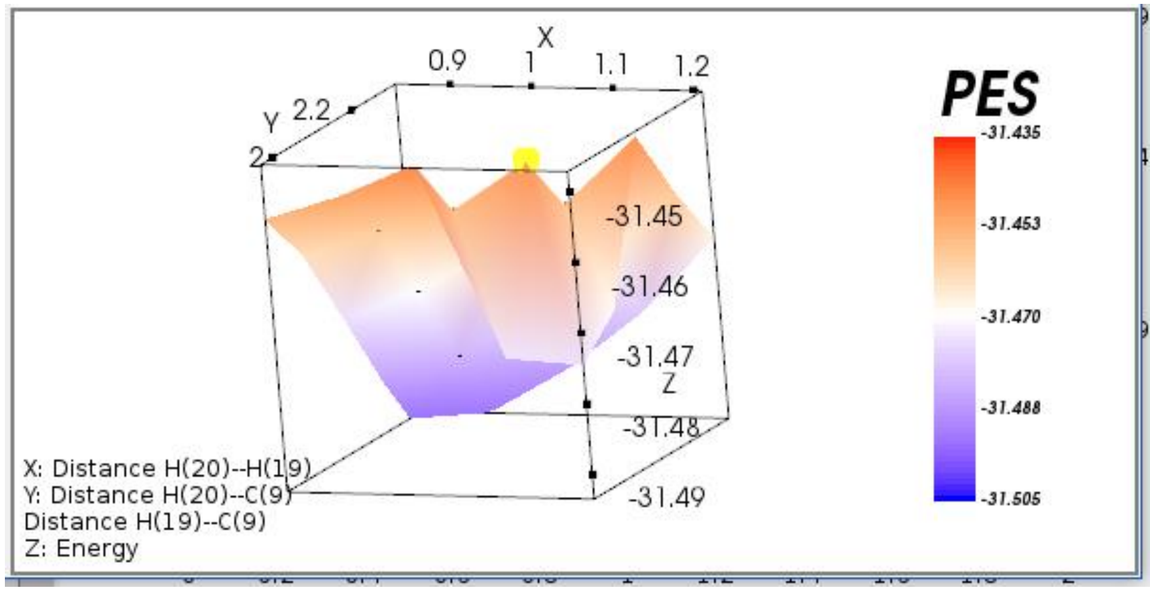
− H(20) H(19)	0.74	1.4	Å	SC- 1
− H(20) C(9)	2.4	1.8	Å	SC- 2
− H(19) C(9)	2.4	1.8	Å	SC- 2

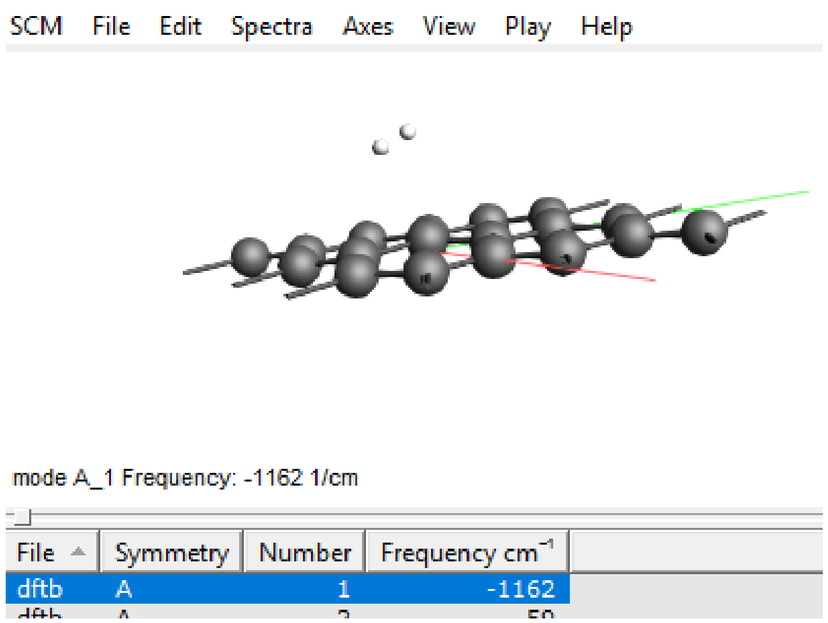
  - Lower convergence criteria in Details -> Geometry Optimization
  - Save & Run

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

AMS: PES scan & TS search

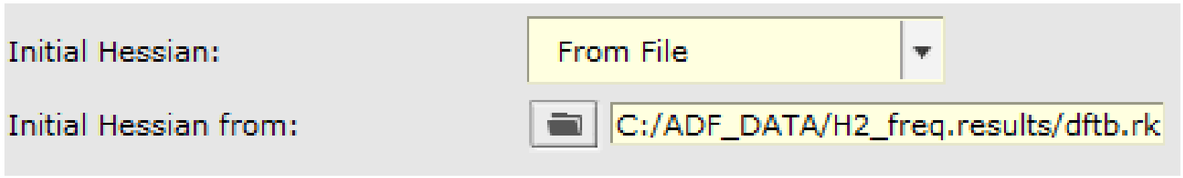
- Exercise 14: Explore the 2D PES
  - When Finished: SCM -> Movie
  - Find a plausible TS start point (x=1.18, y = 2.0)
  - File -> Save Geometry
  - Make a New input & import that geometry
  - Now we calculate the Hessian:
  - Go to DFTB, choose DFTB3-D3BJ/3ob-3-1
    - Task: Single point, followed by frequencies
  - Save & Run
  - Visualize the Spectra and check that there is 1 large imaginary mode



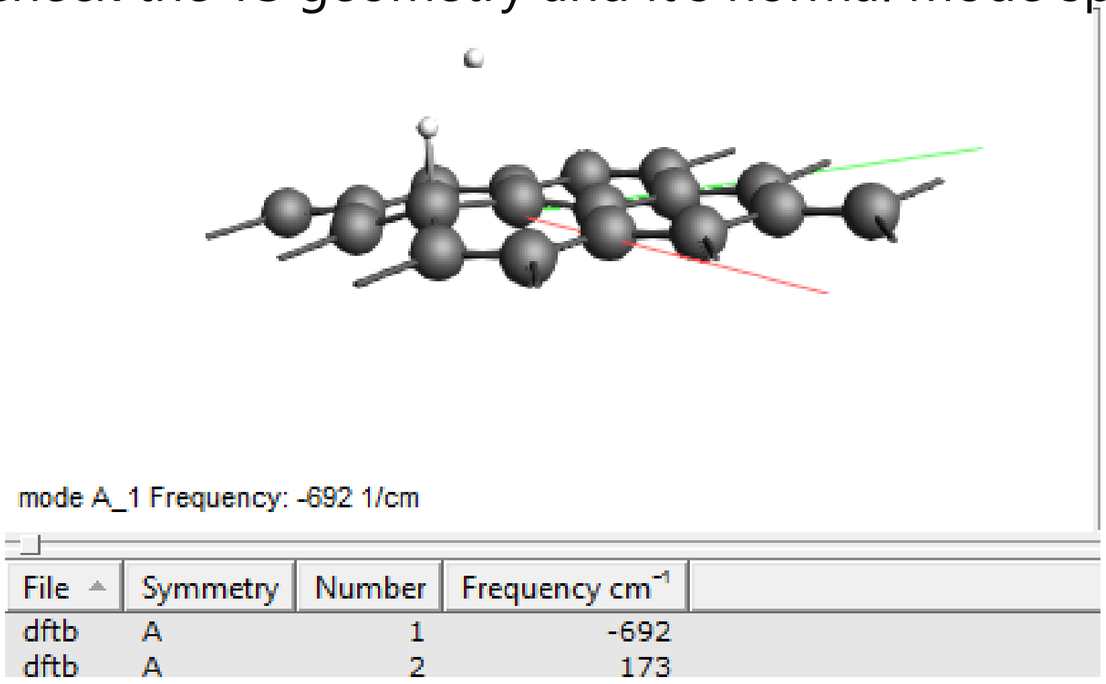


AMS: PES scan & TS search

- 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 it's normal mode spectrum



  - Calculate the activation energy as E(TS) – E (graphene + H_2) (you can put H_2 at 50A)