chemistry & materials
with the
ADF modeling suite 2014

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Outline

- Background, history of Amsterdam Density Functional

- ADF: Strong points & unique features
  - Spectroscopic properties
  - Organic Electronics
  - Solvation / environments
  - Bonding analysis
- BAND: periodic extension of ADF
- DFTB: fast approximate DFT
- ReaxFF: reactive molecular dynamics
- COSMO-RS: fluid thermodynamics

- GUI demonstration / hands-on workshop @ ANU

Scientific Computing & Modelling

time (s)

(My) 10^{12}

(s) 10^{0}

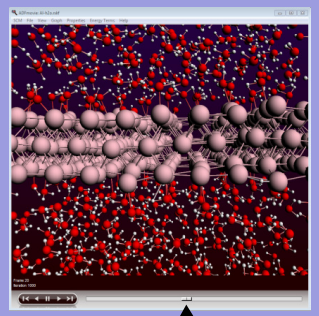
(ms) 10^{-3}

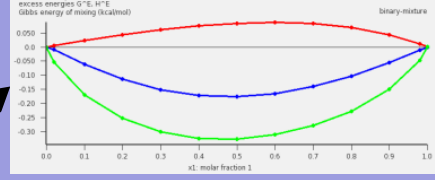
(μs) 10^{-6}

(ns) 10^{-9}

(ps) 10^{-12}

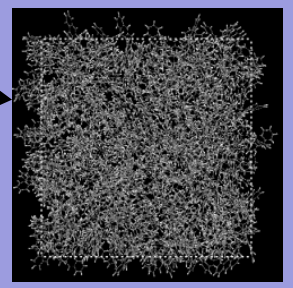
(fs) 10^{-15}





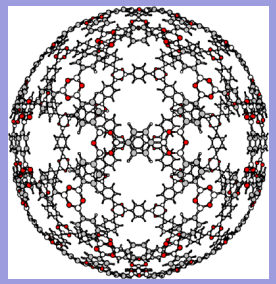
continuum methods
COSMO-RS

mesoscale
methods



molecular dynamics
kinetic Monte Carlo
ReaxFF

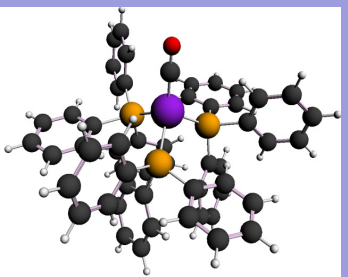
MOPAC
DFTB
QM/MM

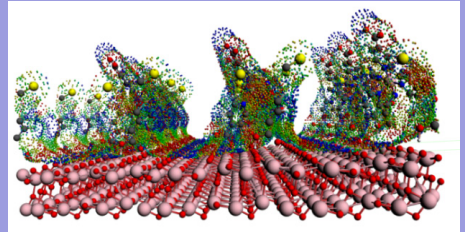


ADF:
DFT

BAND: periodic DFT

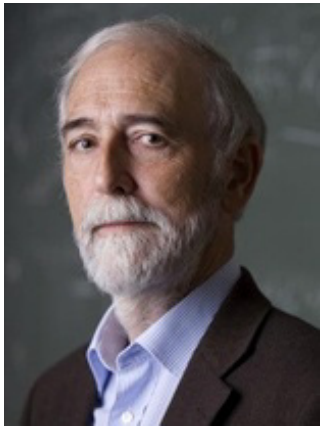
(nm) 10^{-9} (μm) 10^{-6} (mm) 10^{-3} (m) 10^{0} … (AU) 10^{9}





Amsterdam Density Functional development

- Baerends group VU, Amsterdam (>1973)
- Ziegler group, Calgary (>1975)
- SCM: Spin-out VU, 1995
- Many academic groups worldwide
- Currently 12 people (8 senior PhD's) + advisors
- Many academic collaborators
  - Development, testing, debugging, optimizing, porting, documentation, support, ..
  - Implement what users want
- Collaboration in EU networks:
  - 2010-2017: 1 IPP, 1 EID, 1 multi-ITN, 1 FOFF
  - 3 PhDs + 1 PD
  - 2 more ITNs approved last month (MOFs, OPVs)



Evert-Jan Baerends

Tom Ziegler

ADF modeling suite 2014 authors

E.J. Baerends, T. Ziegler, J. Autschbach, D. Bashford, A. Bérces, J.A. Berger, F.M. Bickelhaupt, C. Bo, P.L. de Boeij, P.M. Boerrigter, S. Borini, R. E. Bulo, L. Cavallo, D.P. Chong, L. Deng, R.M. Dickson, A. C. T. van Duin, D.E. Ellis, M. van Faassen, L. Fan, T.H. Fischer, C. Fonseca Guerra, M. Franchini, A. Ghysels, A. Giammona, S.J.A. van Gisbergen, M. Gorbani Asl, A.W. Götz, J.A. Groeneveld, O.V. Gritsenko, M. Grüning, S. Gusarov, F.E. Harris, T. Heine, P. van den Hoek, C.R. Jacob, H. Jacobsen, L. Jensen, E.S. Kadantsev, J.W. Kaminski, G. van Kessel, R. Klooster, F. Kootstra, A. Kovalenko, M.V. Krykunov, E. van Lenthe, J.N. Louwen, D.A. McCormack, E. S. McGarrity, A. Michalak, M. Mitoraj, S.M. Morton, J. Neugebauer, V.P. Nicu, L. Noodleman, V. P. Osinga, S. Patchkovskii, M. Pavanello, P.H.T. Philipsen, D. Post, C.C. Pye, W. Ravenek, M. de Reus, J.I. Rodríguez, P. Romaniello, P. Ros, R. Rüger, P.R.T. Schipper, H. van Schoot, G. Schreckenbach, J.S. Seldenthuis, M. Seth, D.G. Skachkov, J.G. Snijders, M. Solà, M. Swart, D. Swerhone, G. te Velde, P. Vernooijs, L. Versluis, L. Visscher, O. Visser, F. Wang, T.A. Wesolowski, E.M. van Wezenbeek, G. Wiesenekker, S.K. Wolff, T.K. Woo, A.L. Yakovlev

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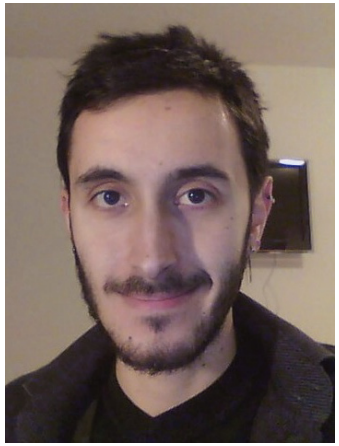
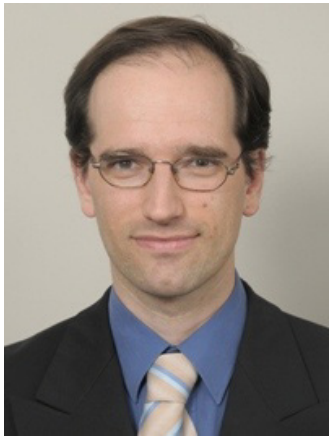
MSc. Hans van Schoot
ReaxFF, MD, GPUs



MSc. Mirko Franchini
ADF, BAND technical

SCM staff – office / management / business



Dr. Stan van Gisbergen
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License files, user interactions

Mrs. Kitty Kleinlein
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Bookkeeping, special projects

Mrs. Evelyn van Royen
EU subsidy expert
Consultancy

2 current EU projects: Propagate, MoWSeS

- PROPAGATE: 3 EID: Bremen-VU-SCM

  AIMD, BOMD, LvN (excited states) QM/MM development

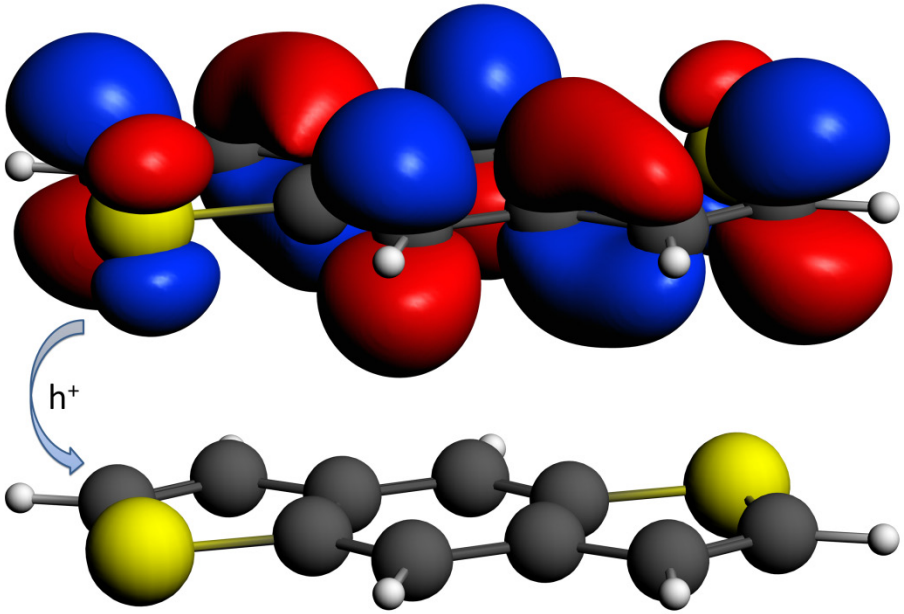
Michiel de Reus

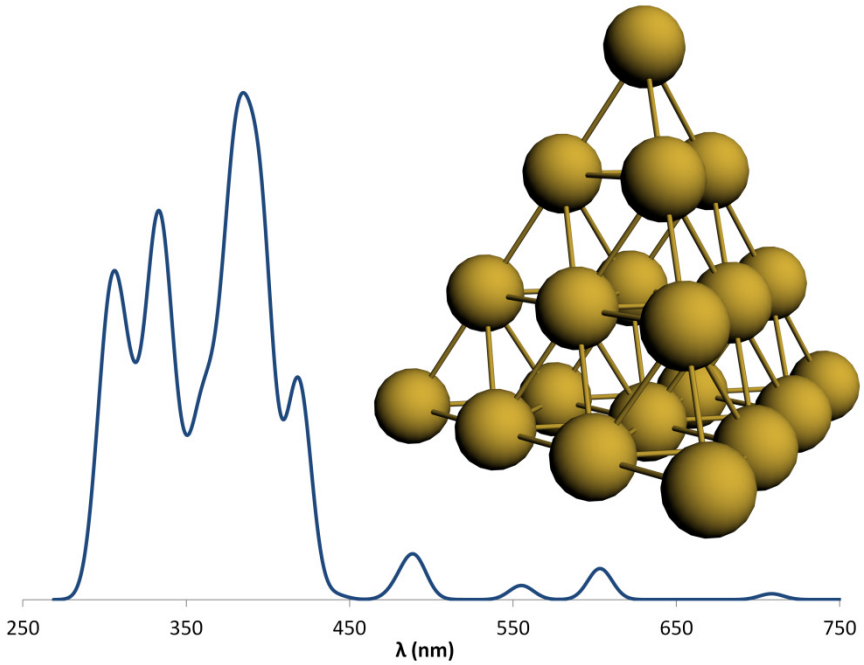
Robert Rüger

Michal Handzlik

- MoWSeS: multi-partner ITN
  - 2D systems: charge/heat transport
  - Soon: PD for 2D optical properties

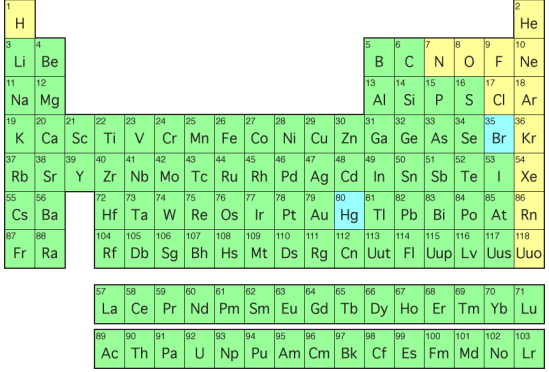
Dr. Wu Li





ADF – molecular DFT

ADF: strong points

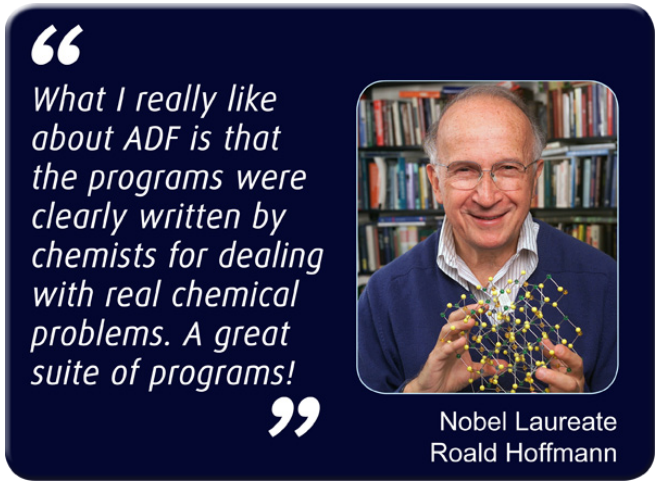


- Accurate & Efficient
  - Slater orbitals, all-electron, all elements
  - relativistic effects (ZORA): **indispensable** for heavy elements & TM
- Spectroscopy
  - Many properties: NMR, IR, Raman, UV/Vis, X-Ray, EPR, (V)CD, ROA, ….
  - Advanced environment effects: FDE, RISM, (QM/MM – FlexMD)
- Chemical analysis
  - Energy decomposition, ETS-NOCV, density properties, charge transfer
- Active developers worldwide
  - recent functionals, newest developments, user input
- User-friendly
  - Out-of-the-box parallel, integrated GUI, scientific support

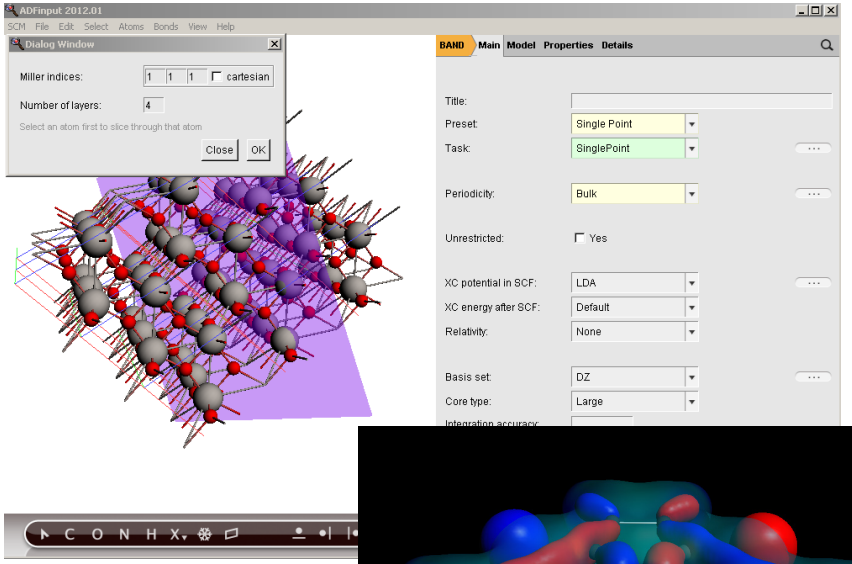
User-friendly

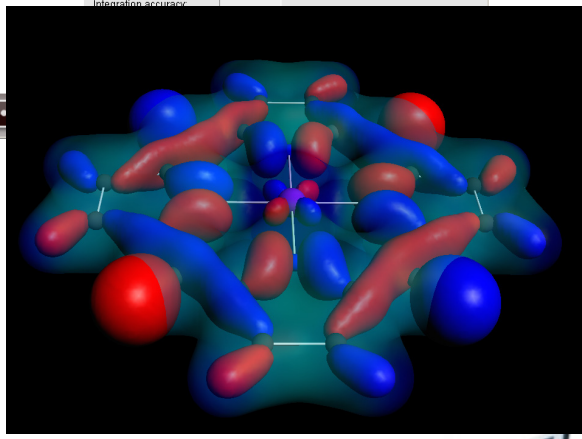
Out-of-the-box parallel binaries
Mac, Windows, Linux/Unix

Expert support team



Fully integrated GUI



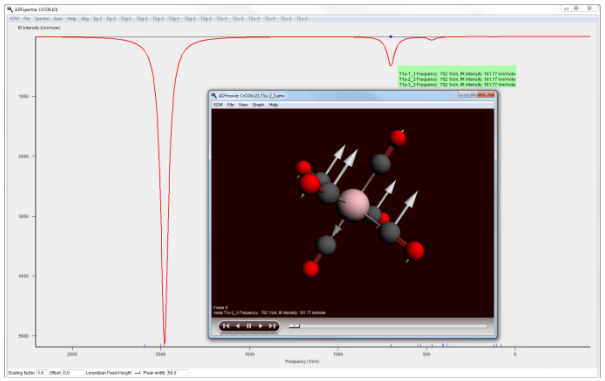


"The support at SCM is truly top notch."
Dr. K. Skinner, Top-10 US chemical company

"... I was very impressed by the quality of the support and their efficiency..."
R. David, Director HPC, University of Strasbourg

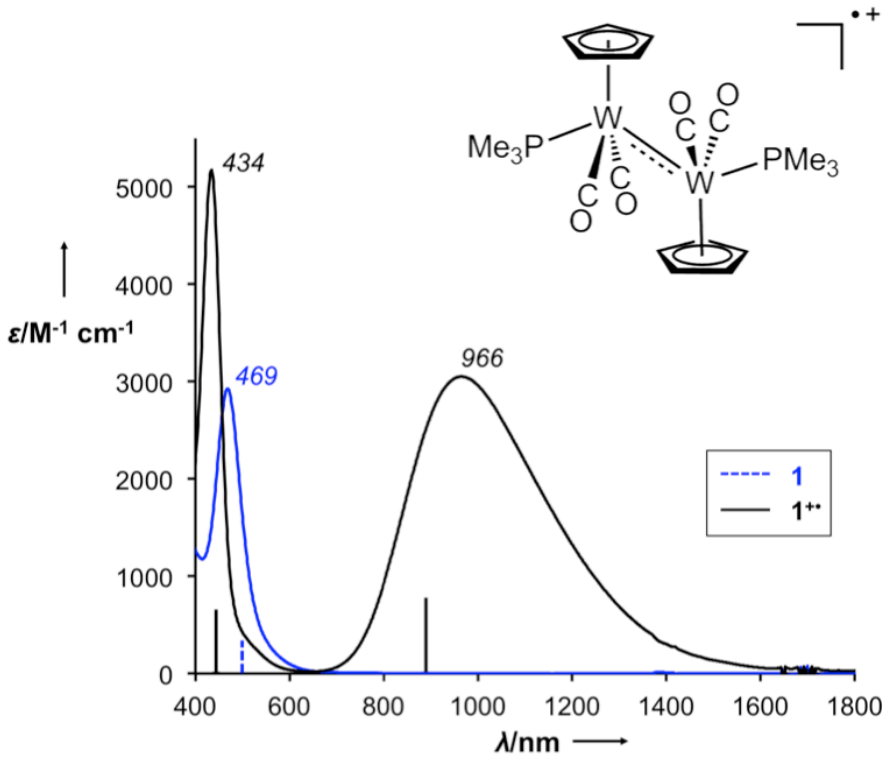
Many Spectroscopic Properties

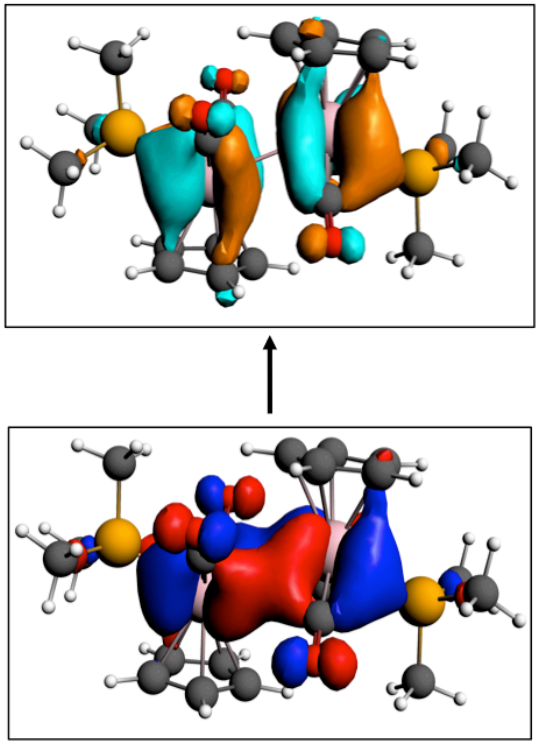
- IR frequencies and intensities, VCD
  - –analytical and numerical
- Time-Dependent DFT (+gradients and vibronic effects)
  - –Closed or open shell, **spin-orbit coupled** (also perturbatively)
  - –Frequency dependent (hyper-) polarizabilities (NLO)
  - –UV/Vis, X-ray absorption (NEXAFS/XANES)
  - – (resonance) Raman, SE(H)RS, V(R)ROA
  - –Circular dichroism (CD), optical rotation (ORD)
  - –Core excitations, state-selected excitations
  - –Lifetime effects, dispersion coefficients



- NMR
  - – chemical shifts, spin-spin couplings, finite nucleus, paramagnetic, hybrids, SOC
- ESR
  - –G-tensor, hyperfine interaction, D-tensor (SO part)
  - – MCD
- Nuclear-quadrupole interaction (EFG: Q-tensors, NRVS)

Insights in dinuclear metalloradical: VIS/NIR, EPR

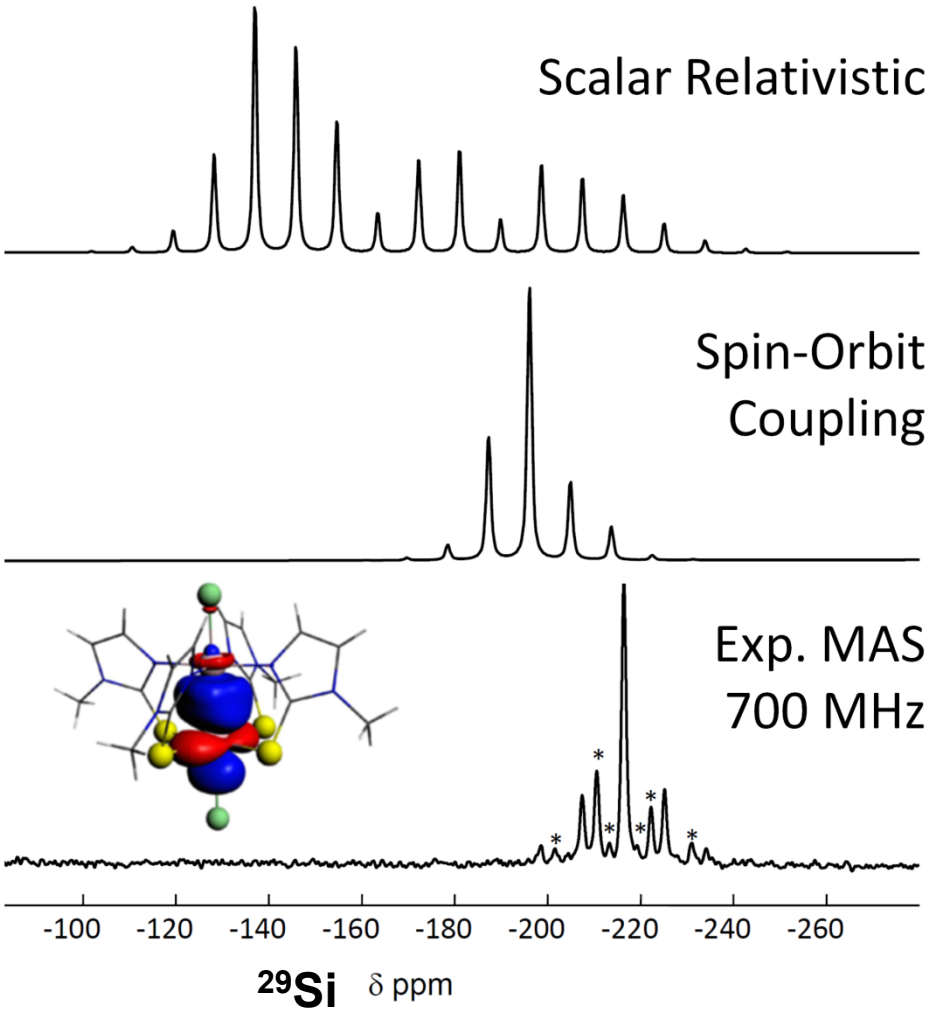




E. F. van der Eide, P. Yang, E. D. Walter, T. Liu, and R. M. Bullock, *Angew. Chem. Int. Ed.* **51**, 8361 (2012)

EPR	Exp.	Calc.
g_1	2.662	2.606
g_2	1.955	1.988
g_3	1.940	1.954

Accurate NMR: all-electron, STOs, and ZORA



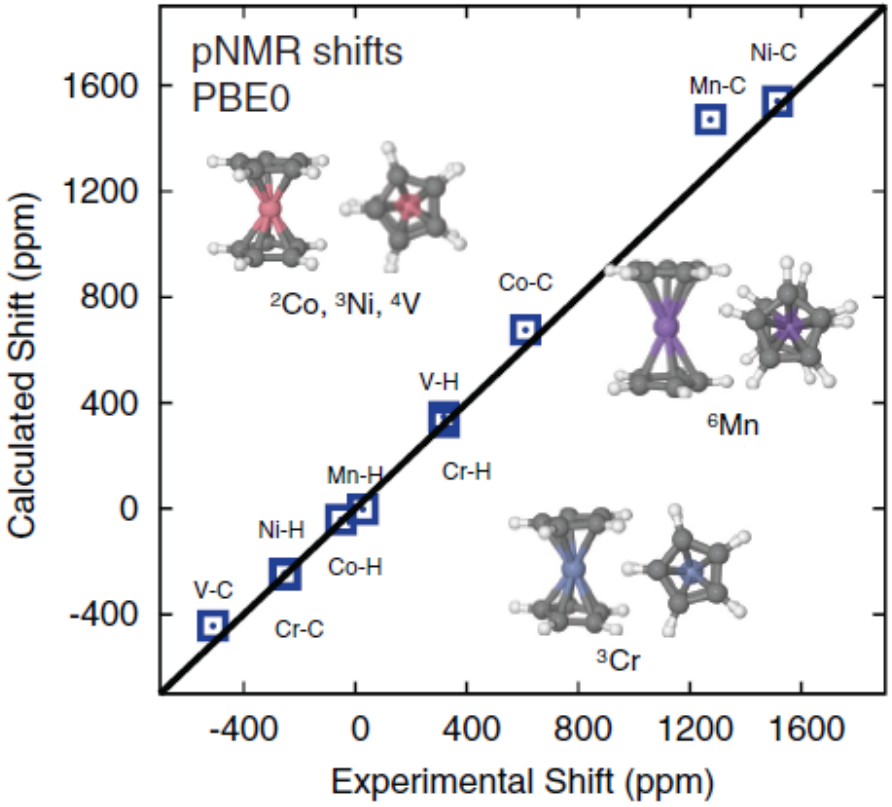
- Heavy Atom effect on Light Atom Pt→Si

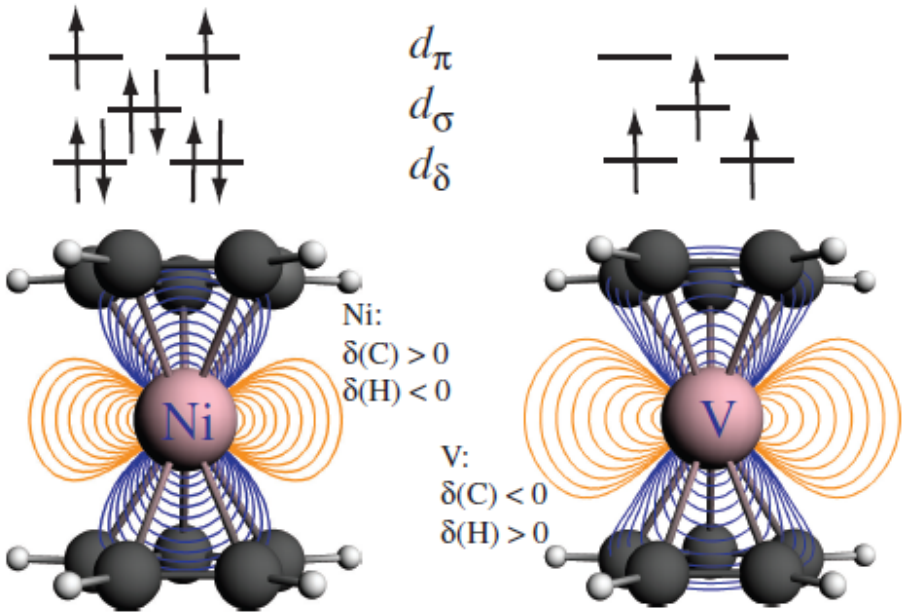
- Only Spin-Orbit Coupling gets NMR spectrum right

- NBO: dative, not covalent

L. A. Truflandier, E. Brendler, J. Wagler, J. Autschbach, *^{29}Si DFT/NMR Observation of Spin-Orbit Effect in Metallasilatrane Sheds Some Light on the Strength of the Metal→Silicon Interaction Alkyl Complexes* Angew. Chem. Int. Ed. 50, 255 (2011)

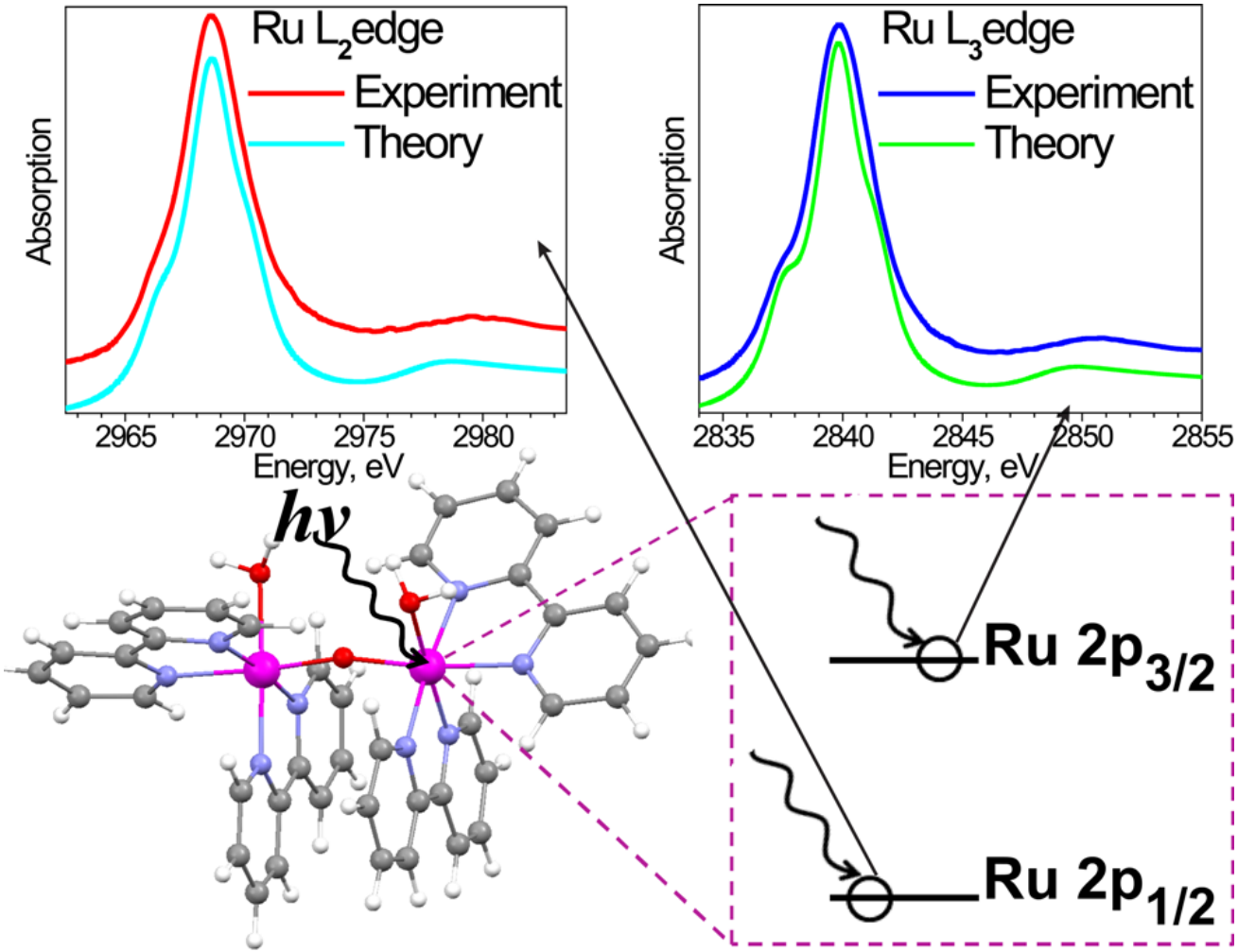
pNMR shifts of 3*d* metallocenes, $M(Cp)_2$:





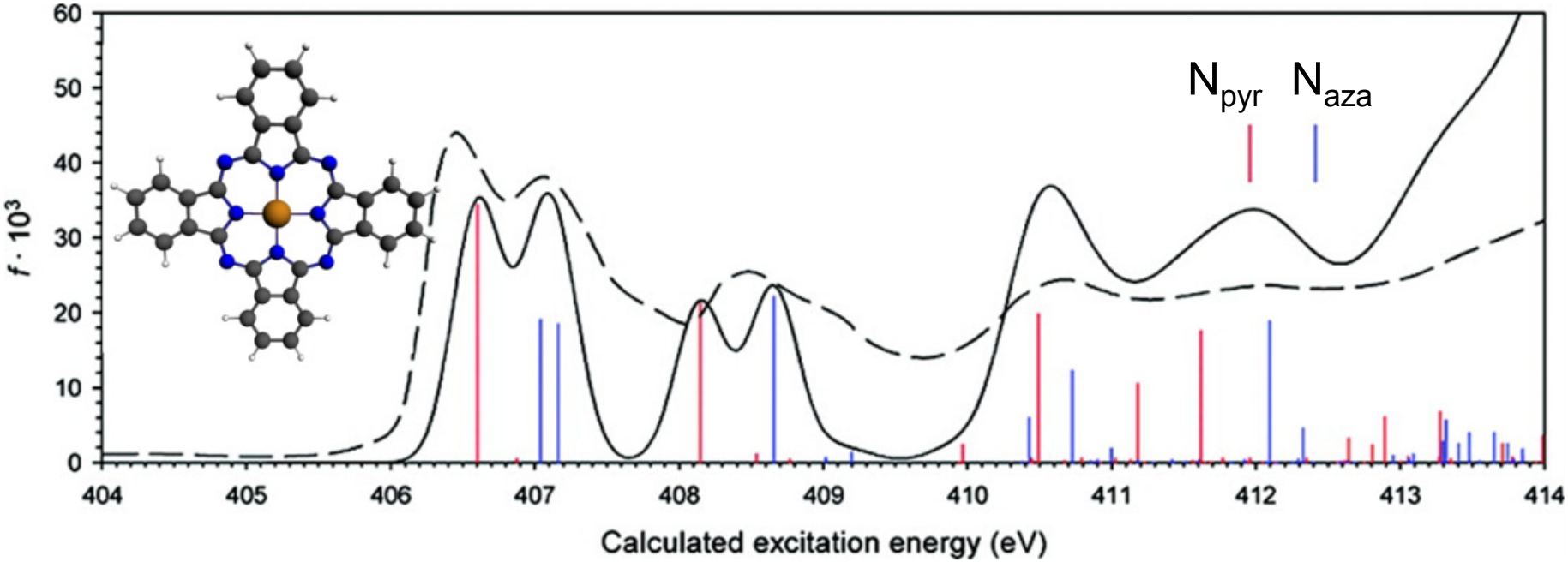
JCTC 8 (2012), 598.

XANES (SO-TDDFT) Ru water-splitting cat.



I. Alperovich, G. Smolentsev, D. Moonshiram, J.W. Jurss, J.J. Concepcion, T.J. Meyer, A. Soldatov, Y. Pushkar *Understanding the Electronic Structure of 4d Metal Complexes: From Molecular Spinors to L-Edge Spectra of a di-Ru Catalyst* J. Am. Chem. Soc., **133** 15786-15794 (2011).

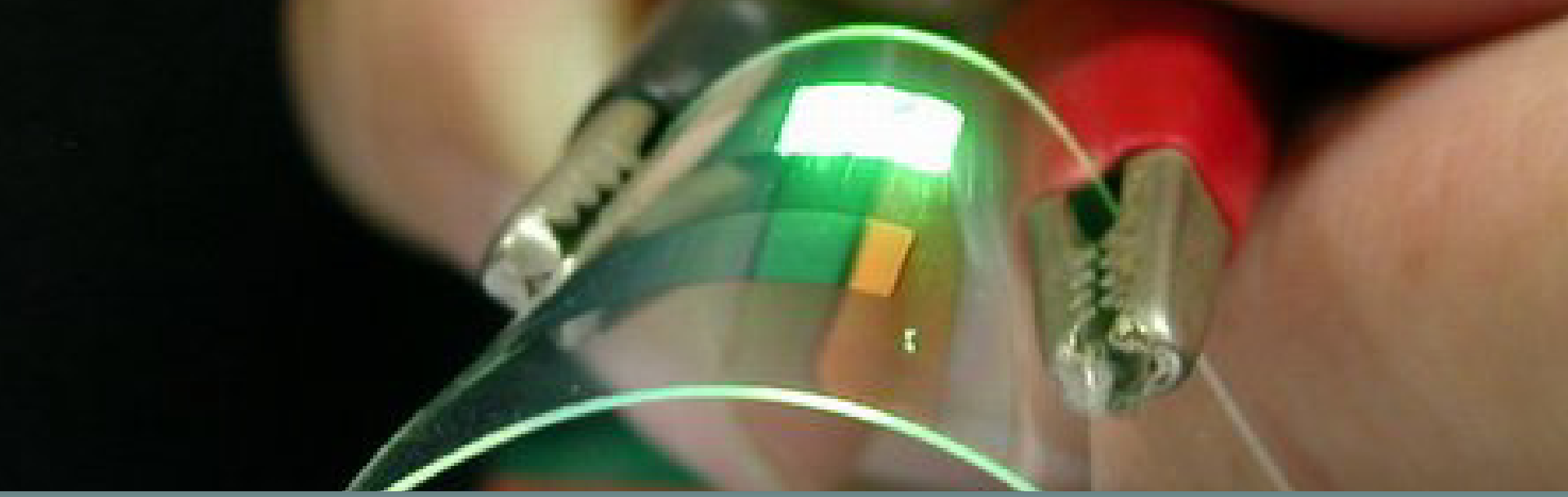
X-ray: NEXAFS (Slater-TS) M-Pc



——— calc

- - - - - - exp.

R. De Francesco, M. Stener, and G. Fronzoni, *Theoretical Study of Near-Edge X-ray Absorption Fine Structure Spectra of Metal Phthalocyanines at C and N K-Edges* J. Phys. Chem. A, **116** 2285-22894 (2012).



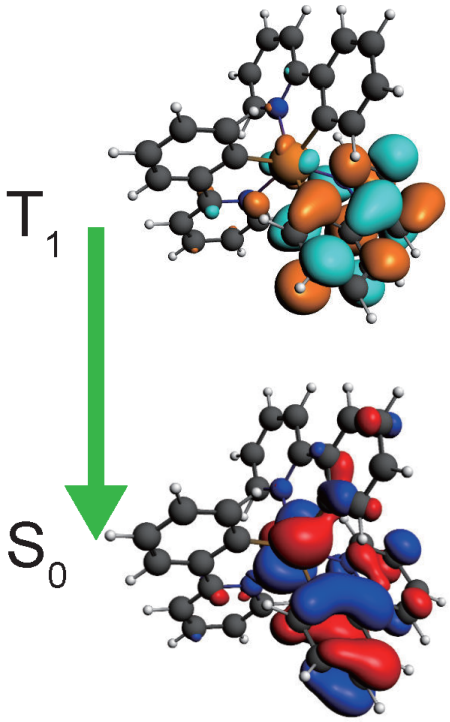
Modeling Organic Electronics with ADF

- Spin orbit coupling TDDFT:
  phosphorescence OLEDs, Dye spectra DSSCs

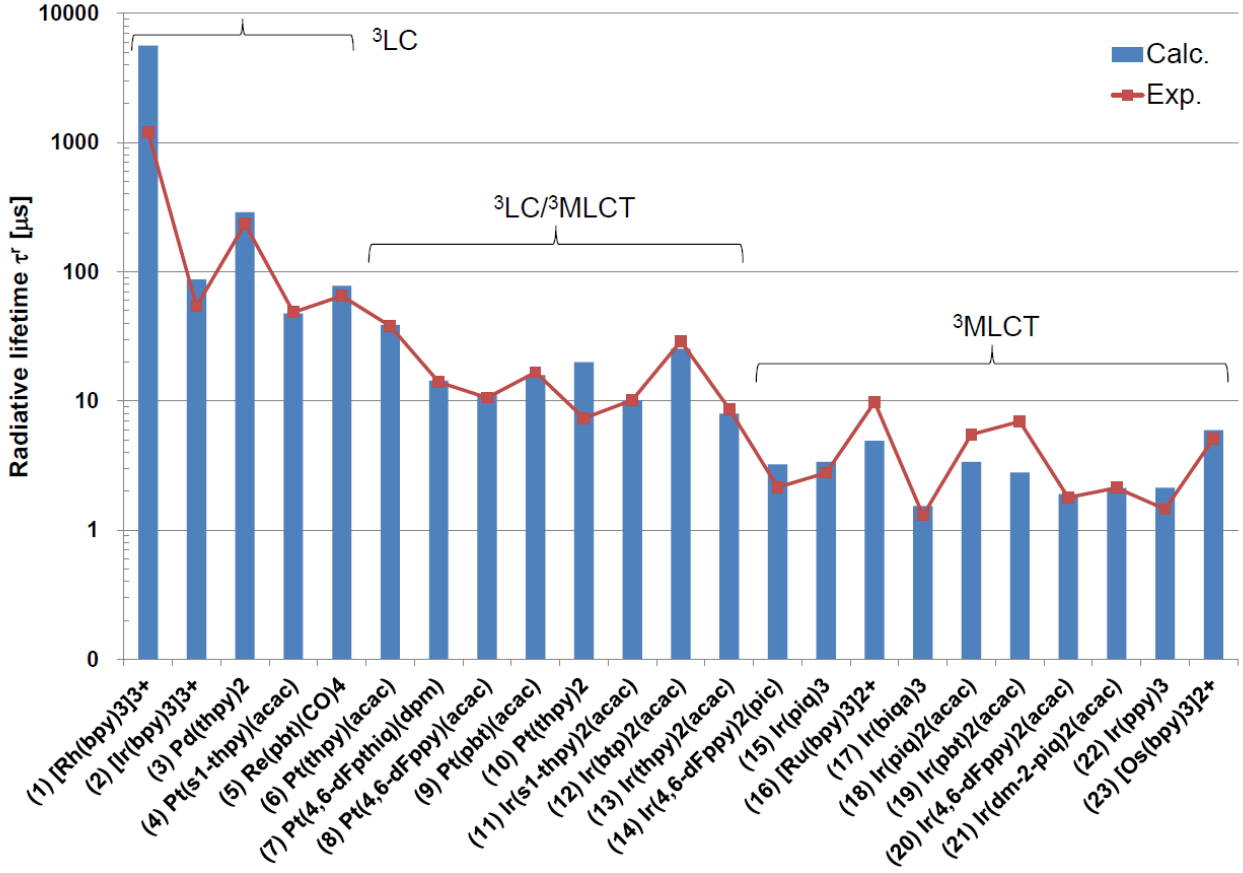
- Fragment-based approach:
  charge mobilities (OFETs), exciton coupling (OPVs)

Picture: Wikipe

Phosphorescent OLED emitters: SOC-TDDFT with solvation compares well with Expt.

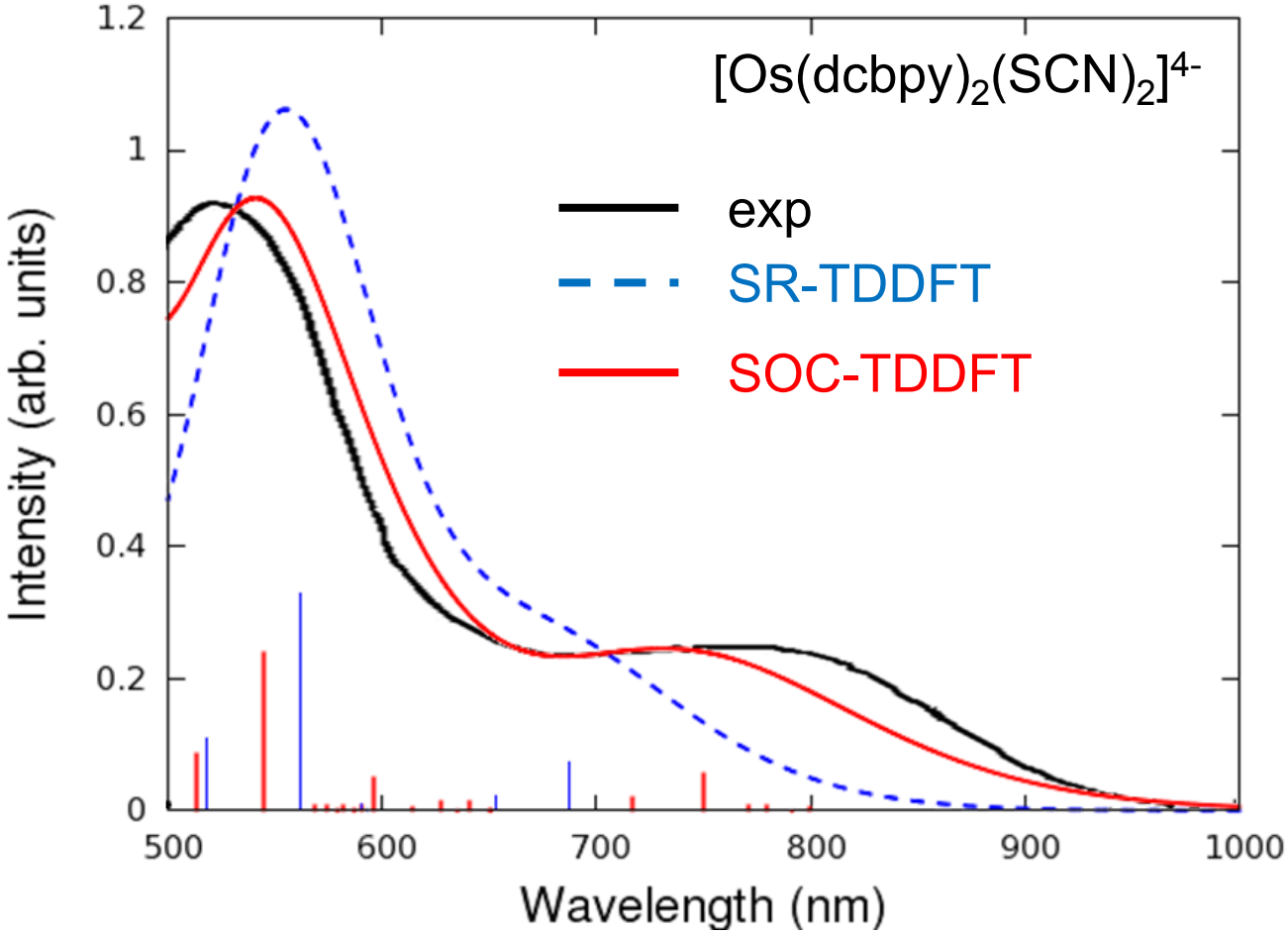


Phosphorescence



K. Mori et al., Phys. Chem. Chem. Phys 16, 14523 (2014).

Spin-orbit coupling increases dye efficiency



SOC indispensible to describe low-energy absorption bands of Os dyes

E. Ronca, F. de Angelis, and S. Fantacci, *TDDFT Modeling of Spin-Orbit Coupling in Ru and Os Solar Cell Sensitizers,* J. Phys. Chem. C, just accepted

Hole / electron mobilities

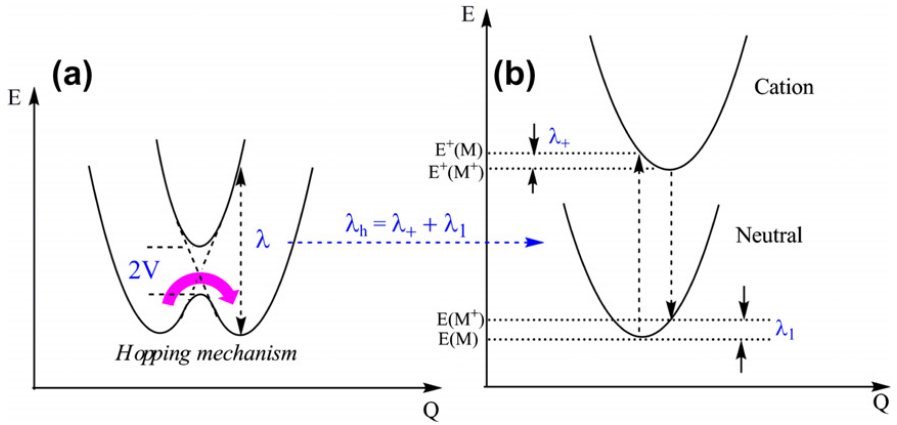
- Ordered crystals (low T) => band-like transport

$$\mu_{\alpha\beta} = e\tau\left(m^{-1}\right)_{\alpha\beta} \qquad \left(m^{-1}\right)_{\alpha\beta} = -\frac{1}{\hbar^2}\frac{\partial^2\varepsilon(\mathbf{k})}{\partial k_\alpha \partial k_\beta}$$

- Amorphous materials: incoherent **hopping**

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

$$\mu = \frac{e}{k_B T}D \quad D = \frac{1}{2n}\sum_i r^2 k_i P_i \quad P_i = \frac{k_i}{\sum_i k_i}$$



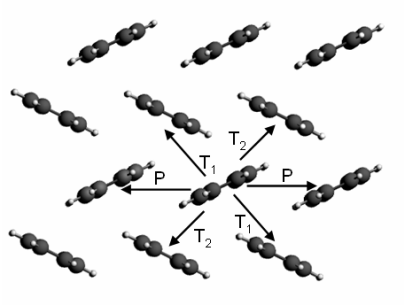
- Accoustic deformation potential

$$\mu = \frac{e\hbar^3 B L_{eff}}{\varepsilon_{ac}^2 (k_B T)(m_c m_d)}$$

m_c: the effective mass along the direction of transport
m_d: the density of states mass, $(m_a\, m_b)^{1/2}$
ε_{ac}: the acoustic deformation potential, V dE_{vbm}/dV
B: the elastic modulus
L_{eff}: the length of the π-bonded core of the molecule

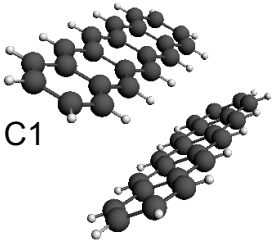
Effective transfer integral J_{eff} = electronic coupling V

- Definition of fragments



Molecular crystal of pentacene

extract dimer



Fragment C1

Fragment C2

- Matrix elements from ADF

(a) “transfer integral”

$$J_{\mathrm{RP}} = \left\langle \varphi^{\mathrm{C1}}_{\mathrm{HOMO}} \middle| h_{\mathrm{ks}} \middle| \varphi^{\mathrm{C2}}_{\mathrm{HOMO}} \right\rangle$$

(b) spatial overlap

$$S_{\mathrm{RP}} = \left\langle \varphi^{\mathrm{C1}}_{\mathrm{HOMO}} \middle| \varphi^{\mathrm{C2}}_{\mathrm{HOMO}} \right\rangle$$

(c) site energy

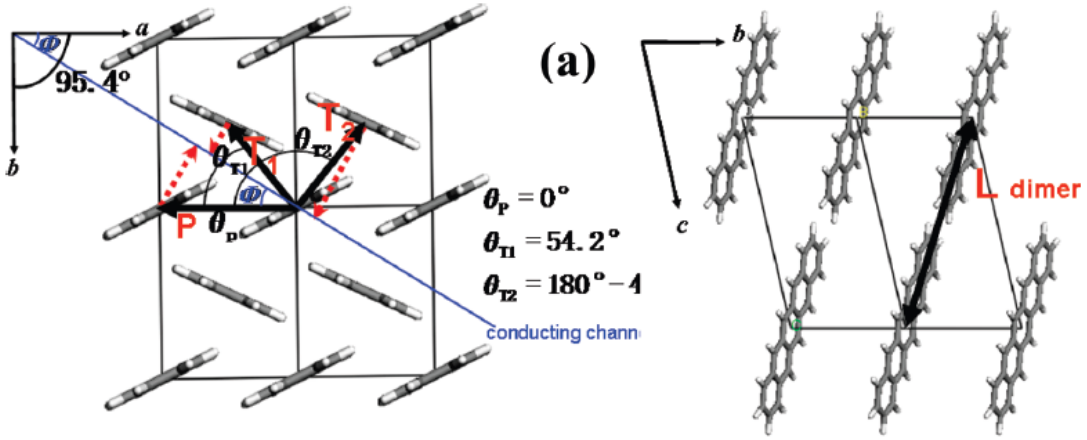
$$H_{\mathrm{RR}} = \left\langle \varphi^{\mathrm{C1}}_{\mathrm{HOMO}} \middle| h_{\mathrm{ks}} \middle| \varphi^{\mathrm{C1}}_{\mathrm{HOMO}} \right\rangle$$

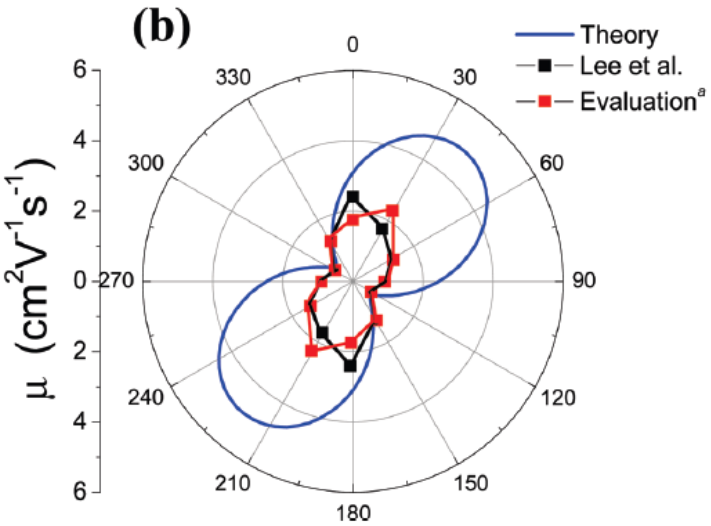
$$H_{\mathrm{PP}} = \left\langle \varphi^{\mathrm{C2}}_{\mathrm{HOMO}} \middle| h_{\mathrm{ks}} \middle| \varphi^{\mathrm{C2}}_{\mathrm{HOMO}} \right\rangle$$

orthogonalization

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

Anisotropic hole mobilities in pentacene



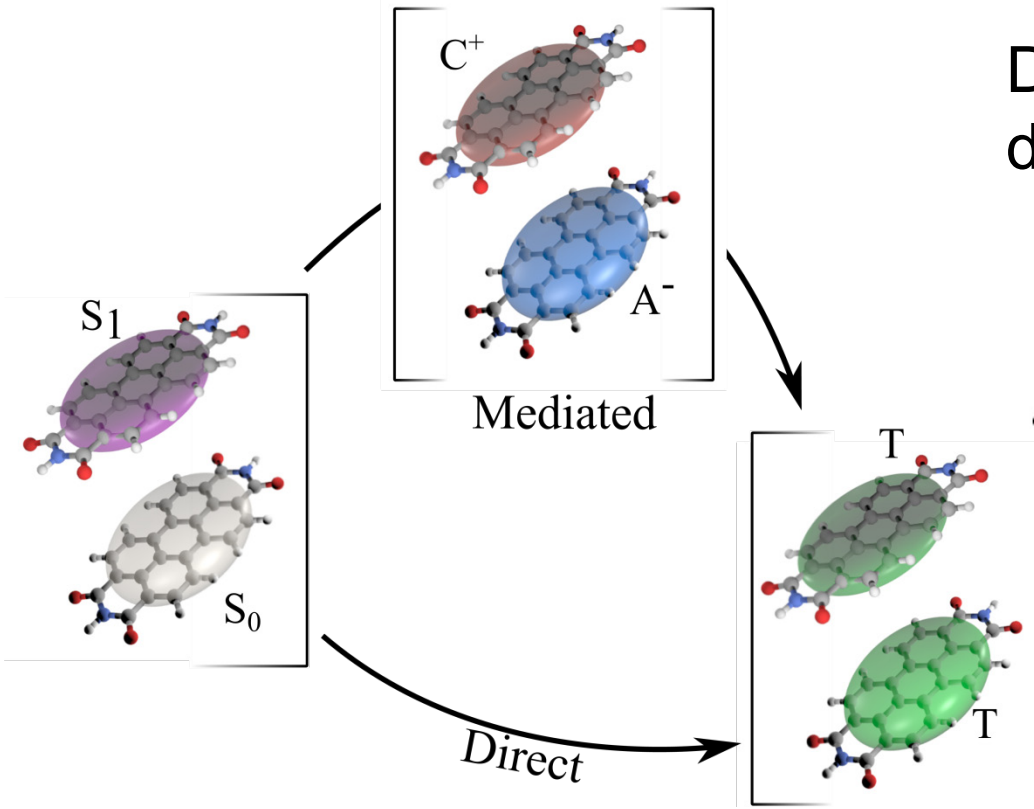


Anisotropic mobility :

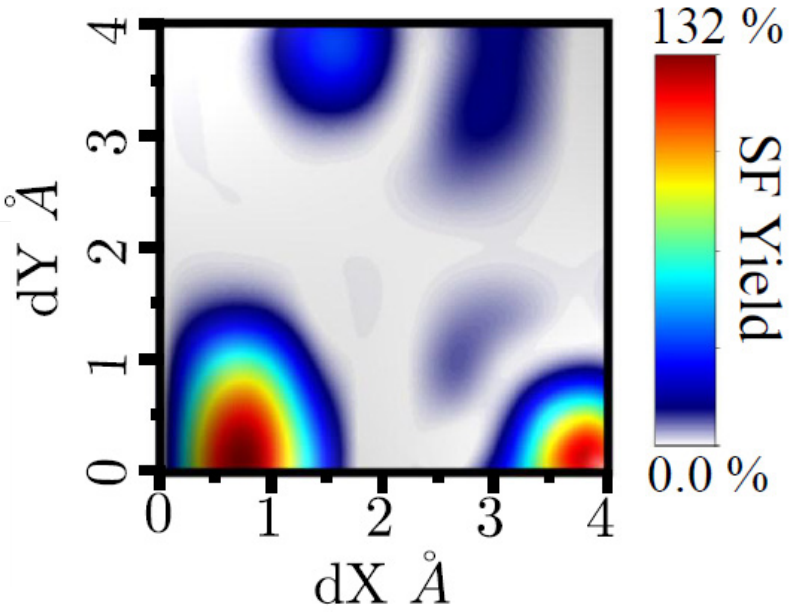
$$\mu_{\Phi} = \frac{e}{2k_B T} \sum_i W_i r_i^2 P_i \cos^2 \gamma_i \cos^2(\theta_i - \Phi)$$

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

Singlet Fission Yields in Organic Crystals:



Direct pathway dominates SF, depends on crystal packing



N. Renaud, P. A. Sherratt, and M. A. Ratner, *Mapping the Relation between Stacking Geometries and Singlet Fission Yield in a Class of Organic Crystals*, J. Phys. Chem. Lett., **4**, 1065-1069 (2013)

Advanced Solvation & Environments

- QM/MM & multi-layer

- Frozen-Density Embedding (subsystem DFT)

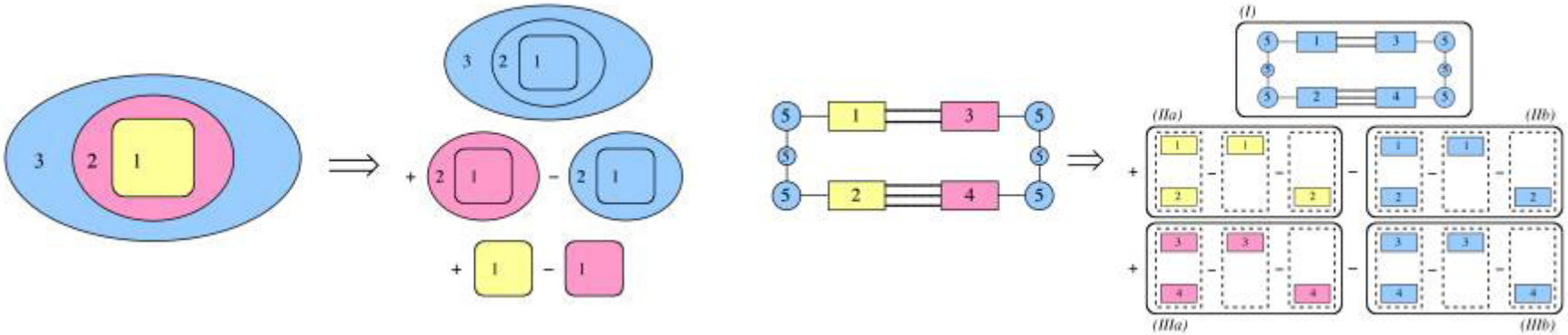
- Adaptive QM/MM, python tools

-DIM/QM: excitations of molecules on nanoparticles

QM/MM

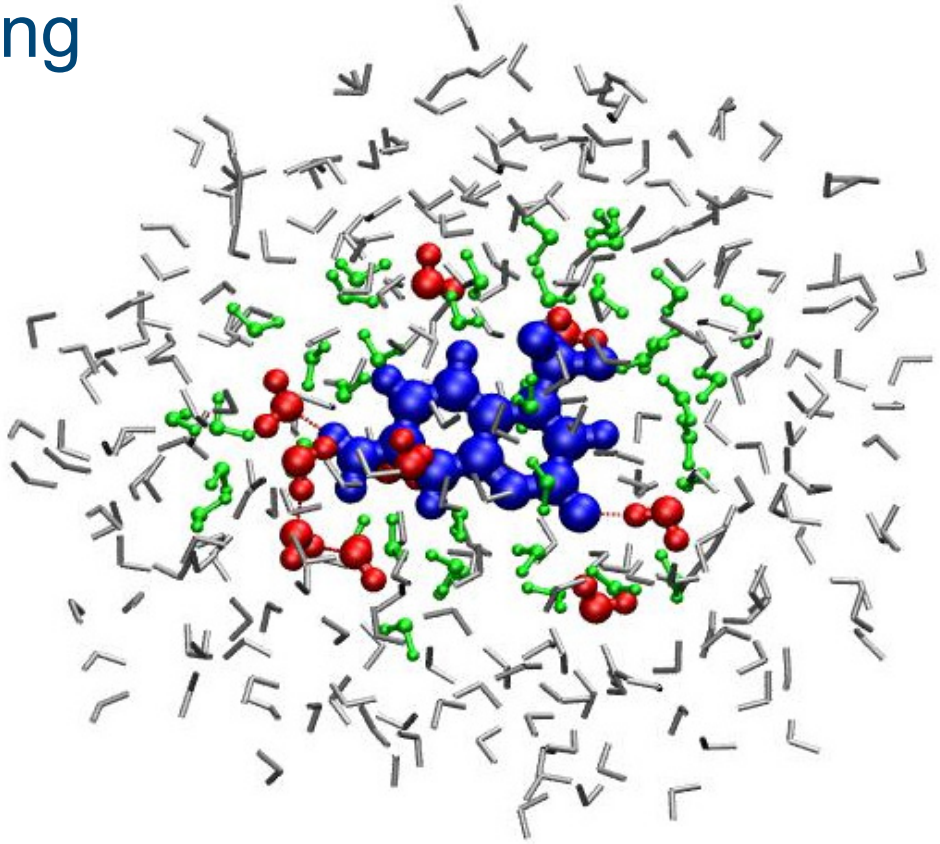
- Additive: fairly ‘standard’, not much developed since 2000
  - but: double link atoms, fractionally charged atoms possible

- Subtractive: QUILD (‘ONIOM’): highly flexible
  - QM, semi-empirical, MM, multiple regions



- QM/MM further developed in EU project
  - Automated tools, workflow for set up (python)

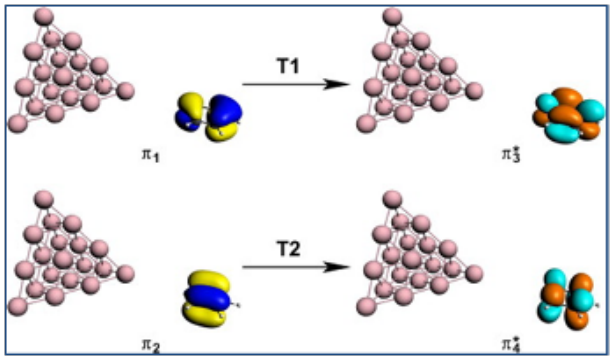
Frozen-density embedding

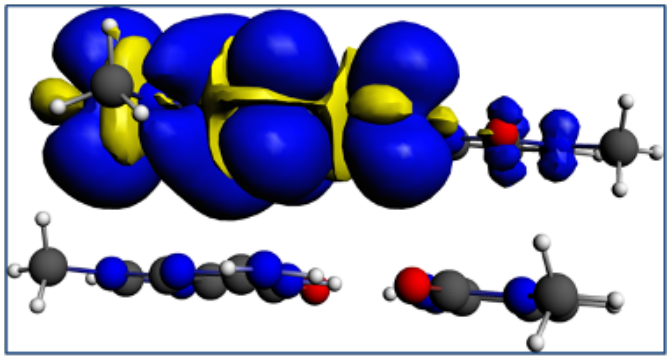


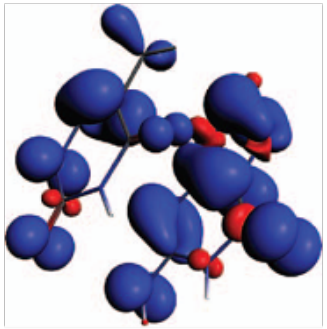
- "DFT in DFT", QM/QM
- Multiple layers defined
- Expt. solvent shift of 0.2 eV in aminocoumarin spectrum reproduced
- Many MD samples. A single 3D-RISM calc. also works!

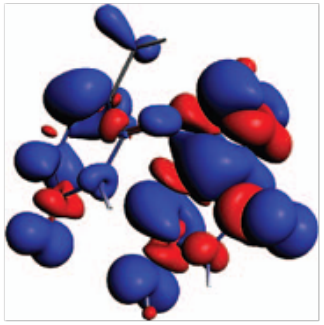
T.A. Wesolowski and A. Warshel, *Frozen Density Functional Approach for ab-initio Calculations of Solvated Molecules.* J. Phys. Chem. **97**, 8050 (1993)
J. Neugebauer, C.R. Jacob, T.A. Wesolowski and E.J. Baerends, *An Explicit Quantum Chemical Method for Modeling Large Solvation Shells Applied to Aminocoumarin C151.* J. Phys. Chem. A **109**, 7805 (2005)
C.R. Jacob, J. Neugebauer and L. Visscher, *A flexible implementation of frozen-density embedding for use in multilevel simulations.*J. of Comput. Chem. **29**, 1011 (2008)
Review Jacob & Neugebauer, WIRES:CMS **4**, 325 (2014)

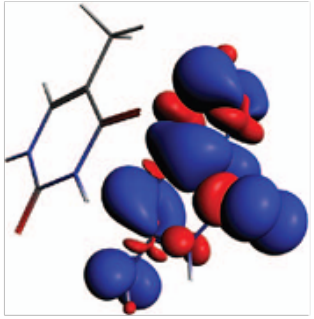
Frozen-density embedding developments:
State-Selective Excitations, Charge Transfer, Spin Densities

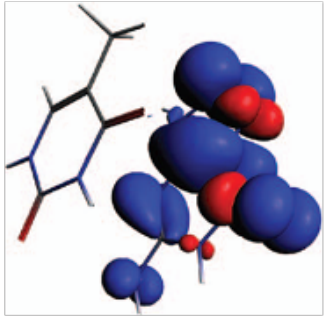





BP86

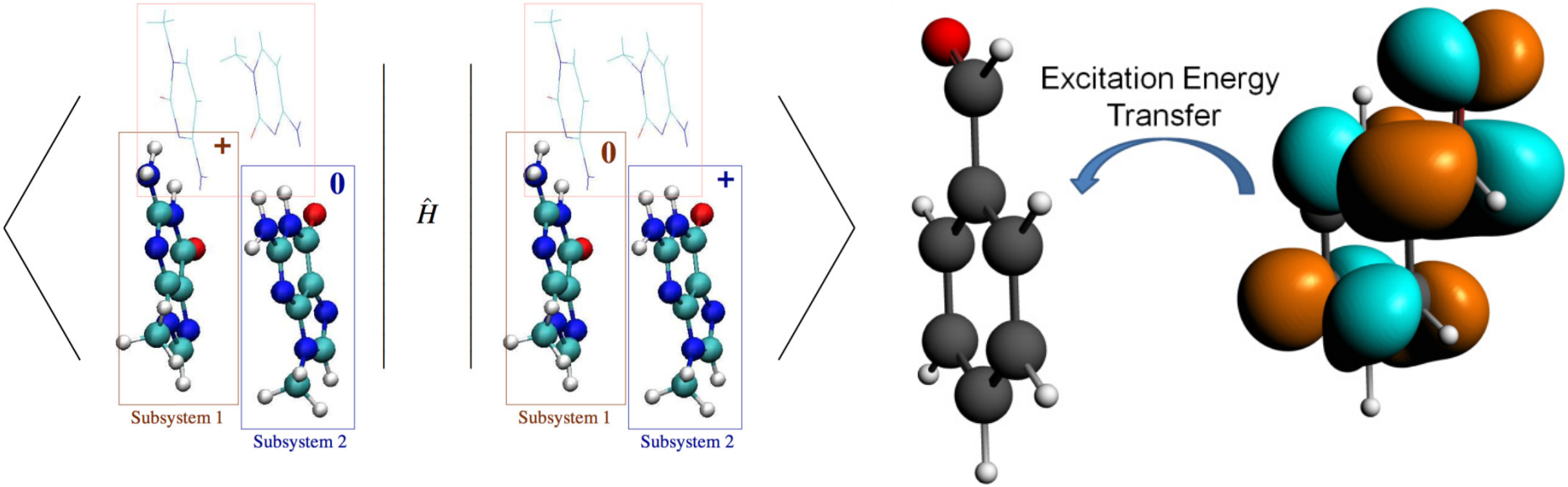

SIC-BP86


FDE


CASSCF

A. Kovyrshin and J. Neugebauer *Potential-energy surfaces of local excited states from subsystem- and selective Kohn-Sham-TDDFT.* Chem. Phys., **391**, 147-156 (2011); M. Pavanello and J. Neugebauer *Modelling charge transfer reactions with the frozen density embedding formalism.* J. Chem. Phys., **135**, 234103 (2011); A. Solovyeva, M. Pavanello, and J. Neugebauer *Spin densities from subsystem density-functional theory: Assessment and application to a photosynthetic reaction center complex model* J. Chem. Phys., **136**, 194014 (2012).

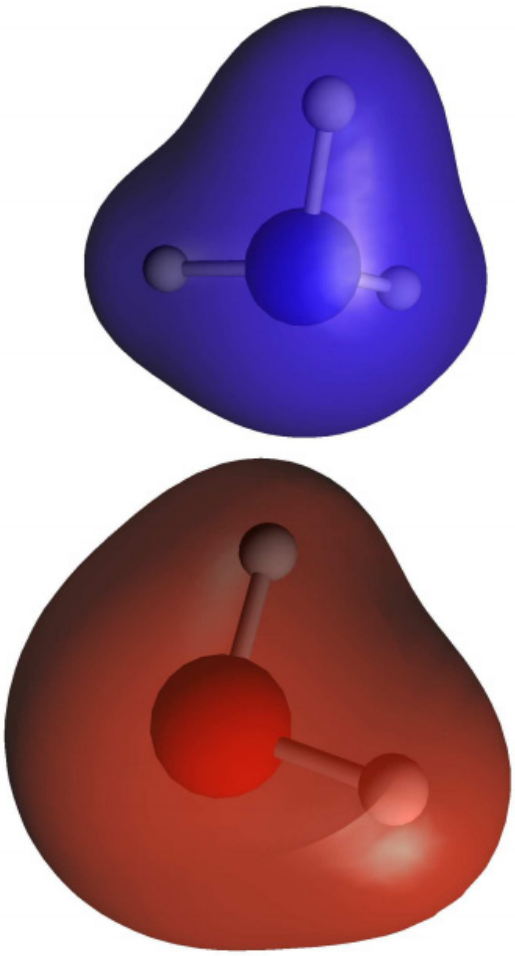
Electronic couplings + environment with FDE: charge transfer, exciton, charge separation



Linear scaling, environment response, constrain charge, excitation, spin, ...

Pavanello/Rutgers & Neugebauer/Muenster groups: *Excitons:* J. Chem. Phys. **138**, 034104 (2013), *long range charge separation*: J. Chem. Phys. **140**, 164103 (2014), *charge transfer*: J. Chem. Theory Comput. 2014, 10, 2546−2556

New in 2014: spin-spin couplings with FDE



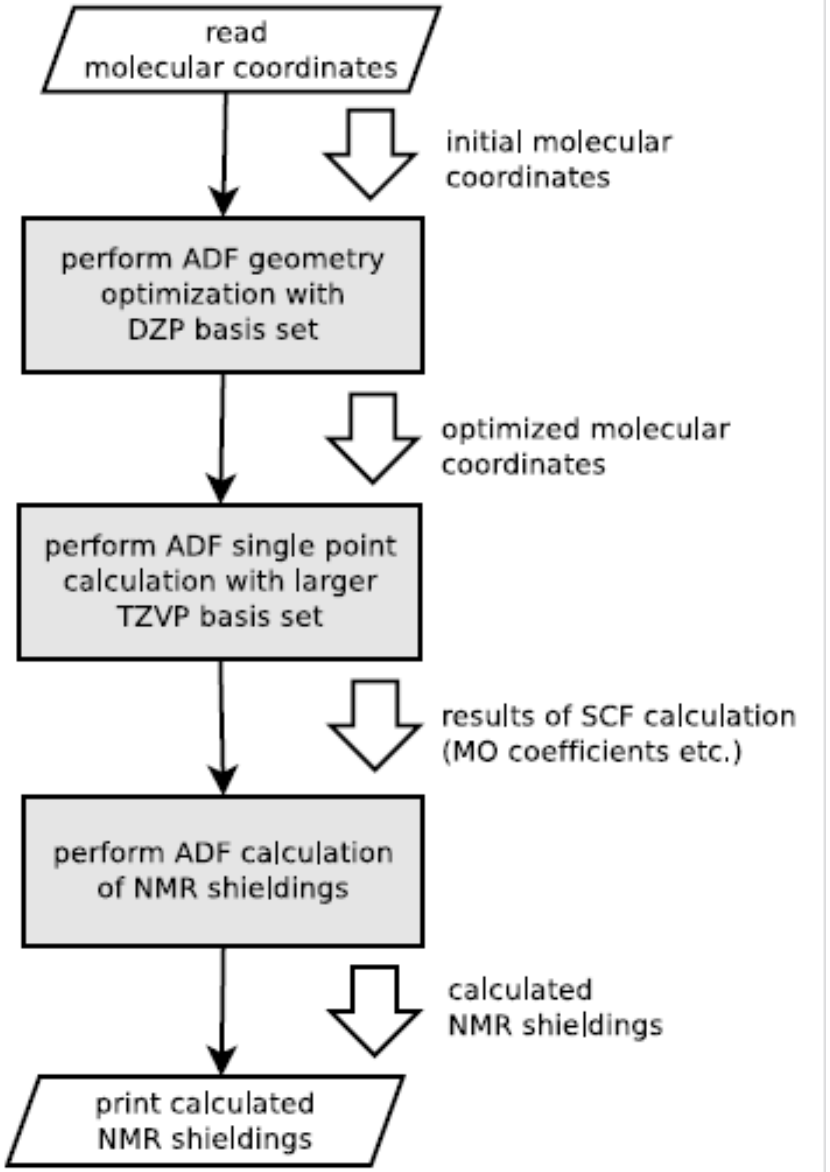
solvent-induced shifts of spin-spin coupling constants in AB dimers

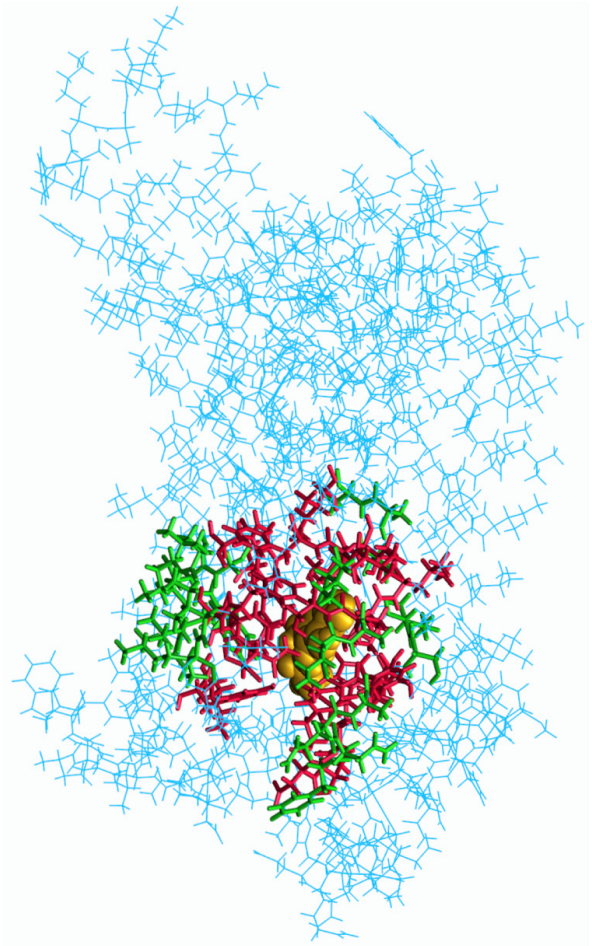
	HF–HF	NH_3–H_2O	H_2O–H_2O
	$\Delta^1 J$(F,H)	$\Delta^1 J$(O,H)	$\Delta^1 J$(O,H)
KS	17.9	−5.3	−4.1
FDE(m,0)	5.5	−4.9	−3.2
FDE(m,1)	9.9	−5.6	−3.7
FDE(m,3)	10.0	−5.6	−3.7
FDE(s,0)	12.3	−5.2	−3.5
FDE(s,1)	19.5	−6.3	−4.3
FDE(s,3)	19.7	−6.4	−4.4

J couplings in Hz

Götz, Autschbach, Visscher, J. Chem. Phys. **116**, 104107 (2014)

PyADF, PLAMS for QM/MM, QM/QM and workflow

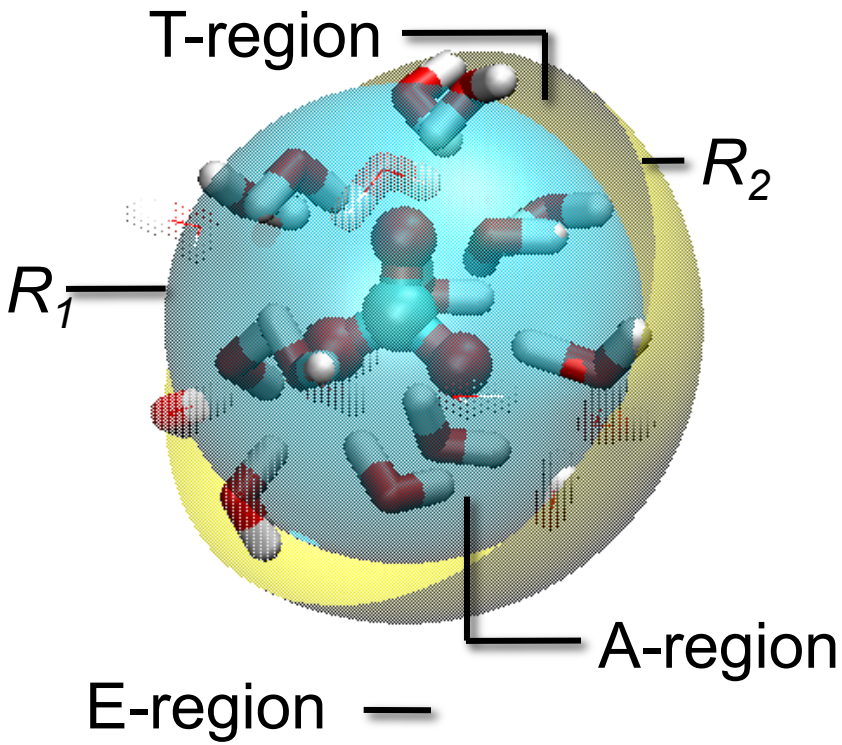




Example goal:
More accurate docking

Python tools for QM/MM: FlexMD (Plumed, ASE)

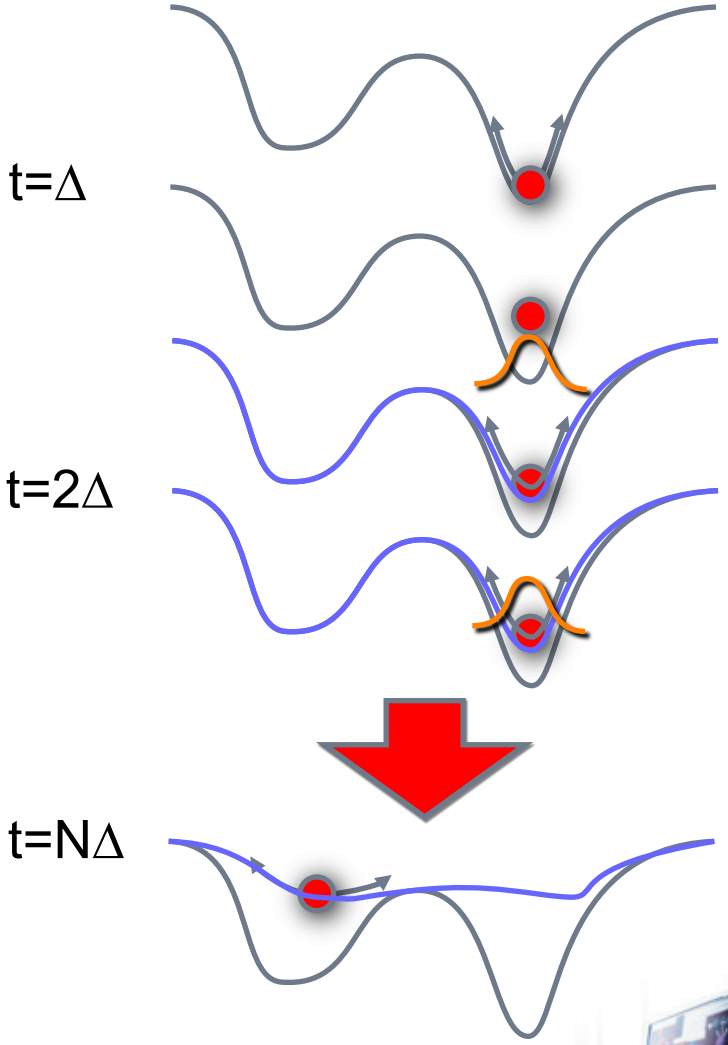
Adaptive QM/MM



Smooth QM↔MM transition

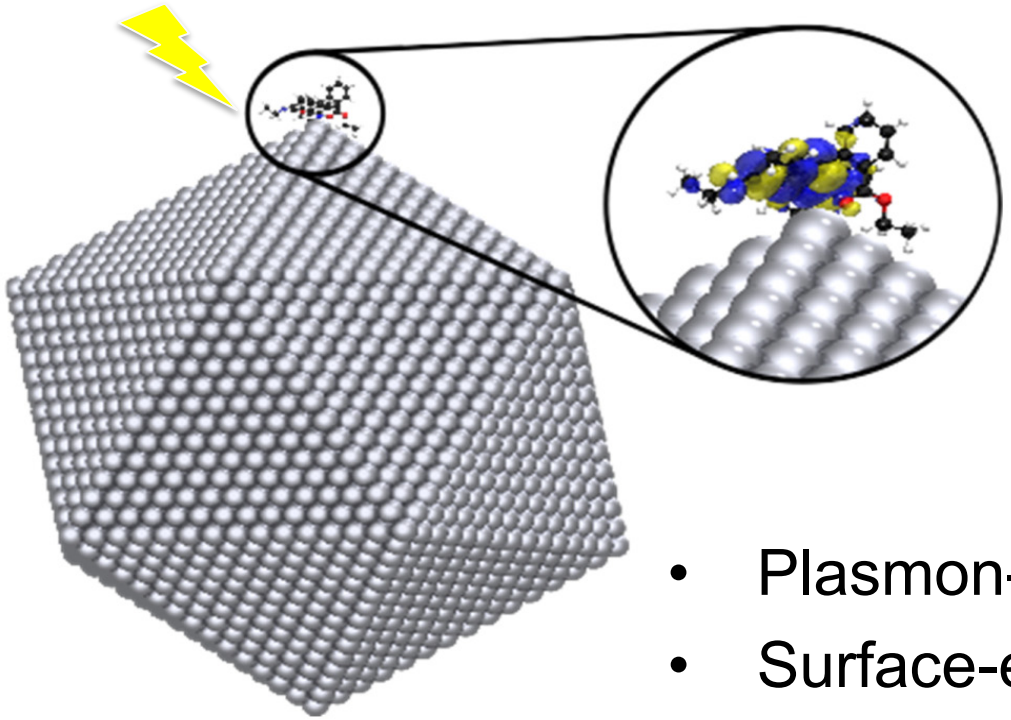
molecules passing the QM/MM boundary

Metadynamics



R. Bulo, C. Michel, P. Fleurat-Lessard, and P. Sautet, *Multiscale Modeling of Chemistry in Water: Are We There Yet?* J. Chem. Theor. Comput. **9**, 5567-5577 (2013)

coupled TDDFT – atomistic electrodynamics (DIM/QM)



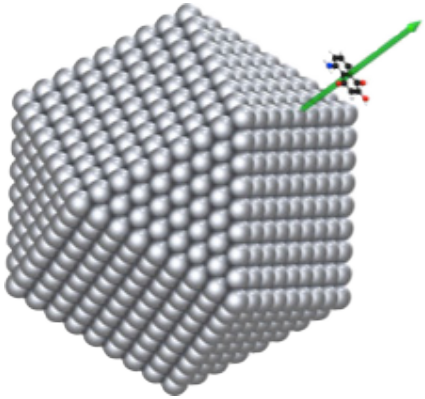
- Plasmon-exciton hybridization
- Surface-enhanced Raman scattering
- Plasmon enhanced photochemistry

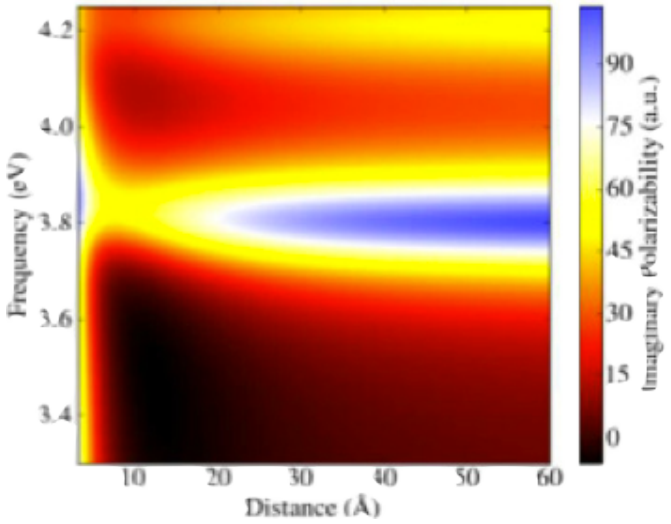
S. M. Morton and L. Jensen, *A discrete interaction model/quantum mechanical method to describe the interaction of metal nanoparticles and molecular absorption* J. Chem. Phys. 135, 134103 (2011), Gradients: J. Chem. Phys. **136**, 214103 (2012)

Recent review: *Acc. Chem. Res.* **47**, 88–99 (2014)

Enhanced Molecular Absorption

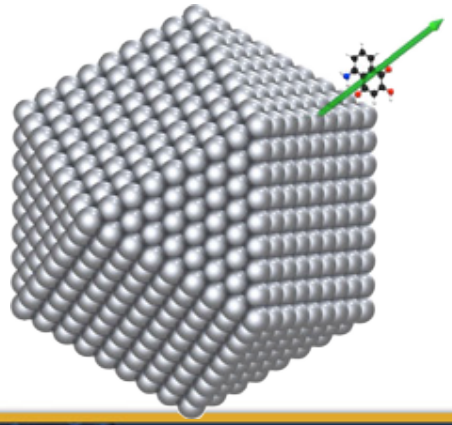
Flat - orientation

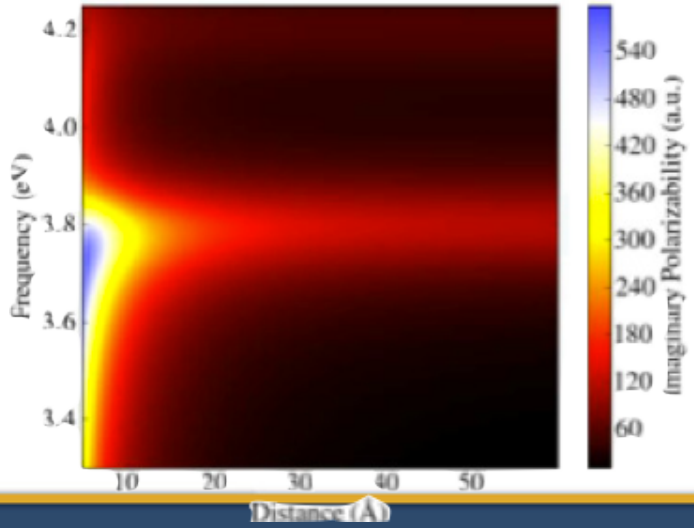




Reduced Absorption due to plasmon

Side - orientation





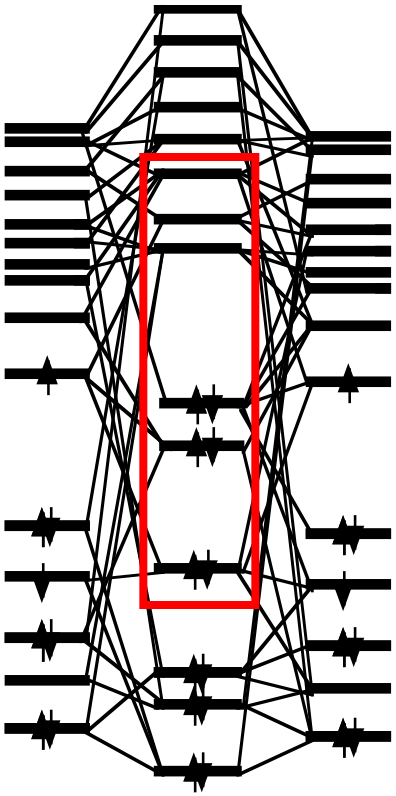
Enhanced Absorption due to plasmon

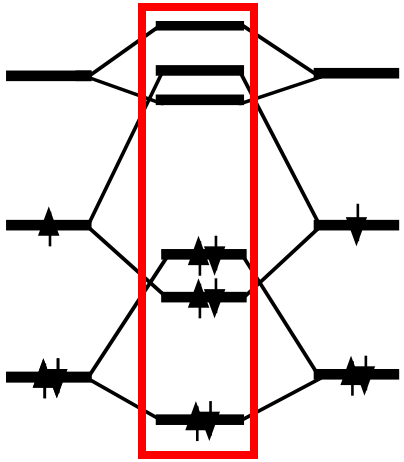
Morton, Jensen, J. Chem. Phys., 135, 134103, 2011

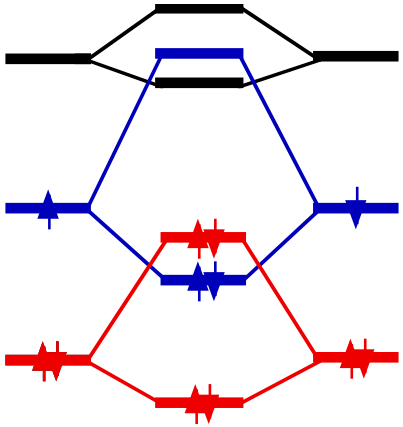
Chemical Analysis: Fragment Approach

$$AB + CD \rightarrow AB\text{–}CD$$

Rev. Comput. Chem. **2000**, *15*, 1.







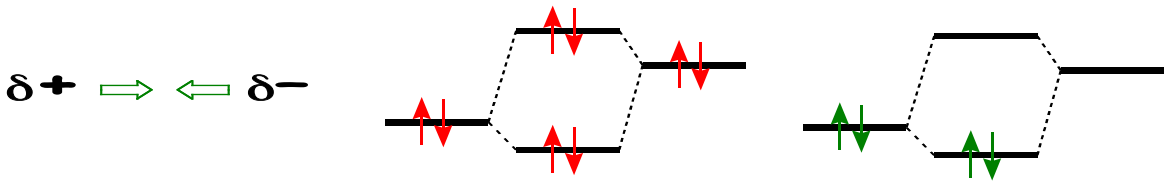
"local" bond in "delocalized" model

Analysis: Energy decomposition

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

Rev. Comput. Chem. **2000**, *15*, 1.

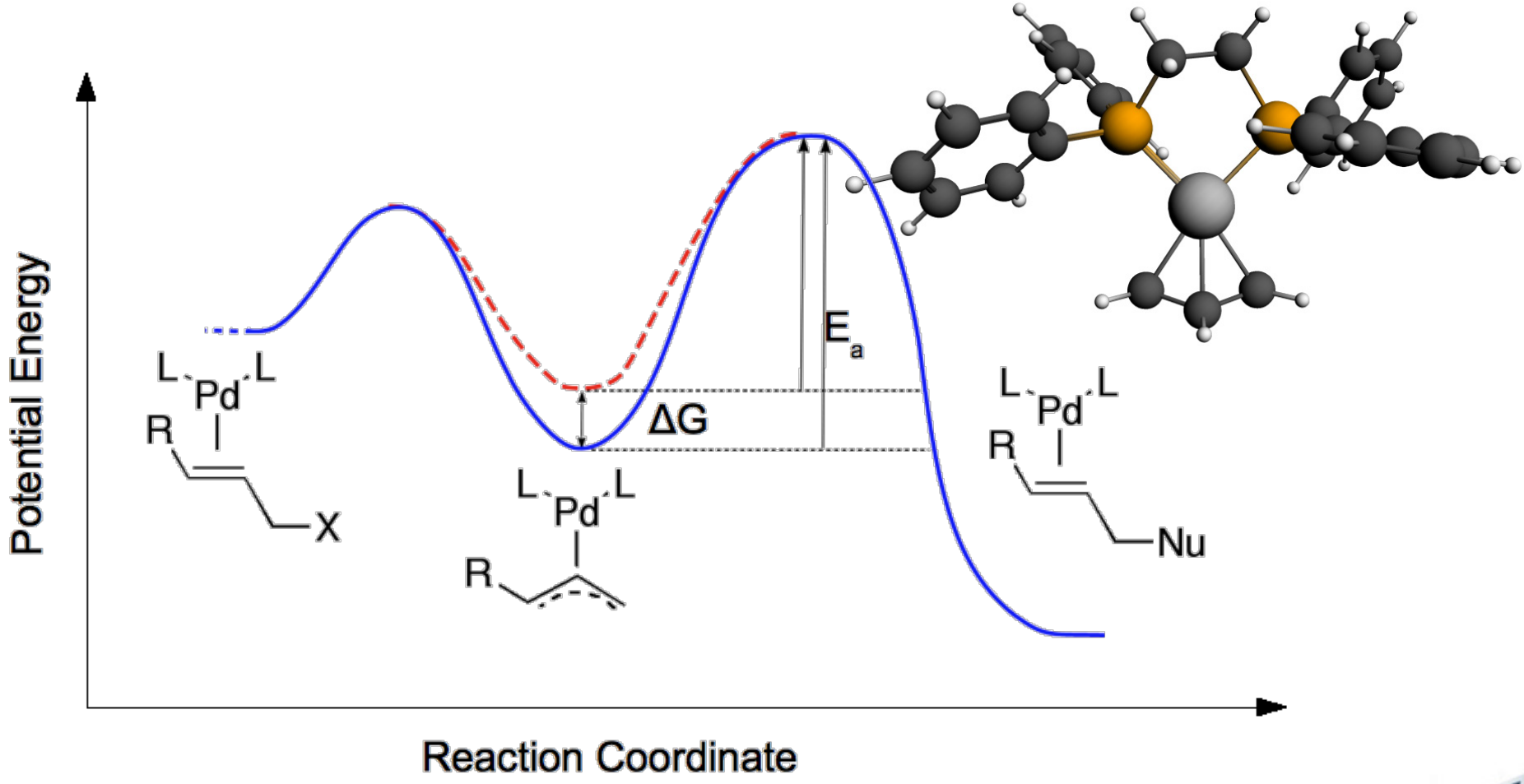
$$\Delta V_{elstat} + \Delta E_{Pauli} + \Delta E_{oi}$$



Extension: ETS-NOCV – energy decomposition + bonding analysis
M. Mitoraj, A. Michalak and T. Ziegler, J. Chem. Theor. Comput. **5**, 962 (2009)
See webinar by Mariusz on our website

Natural selection of catalysts: survival of the weakest

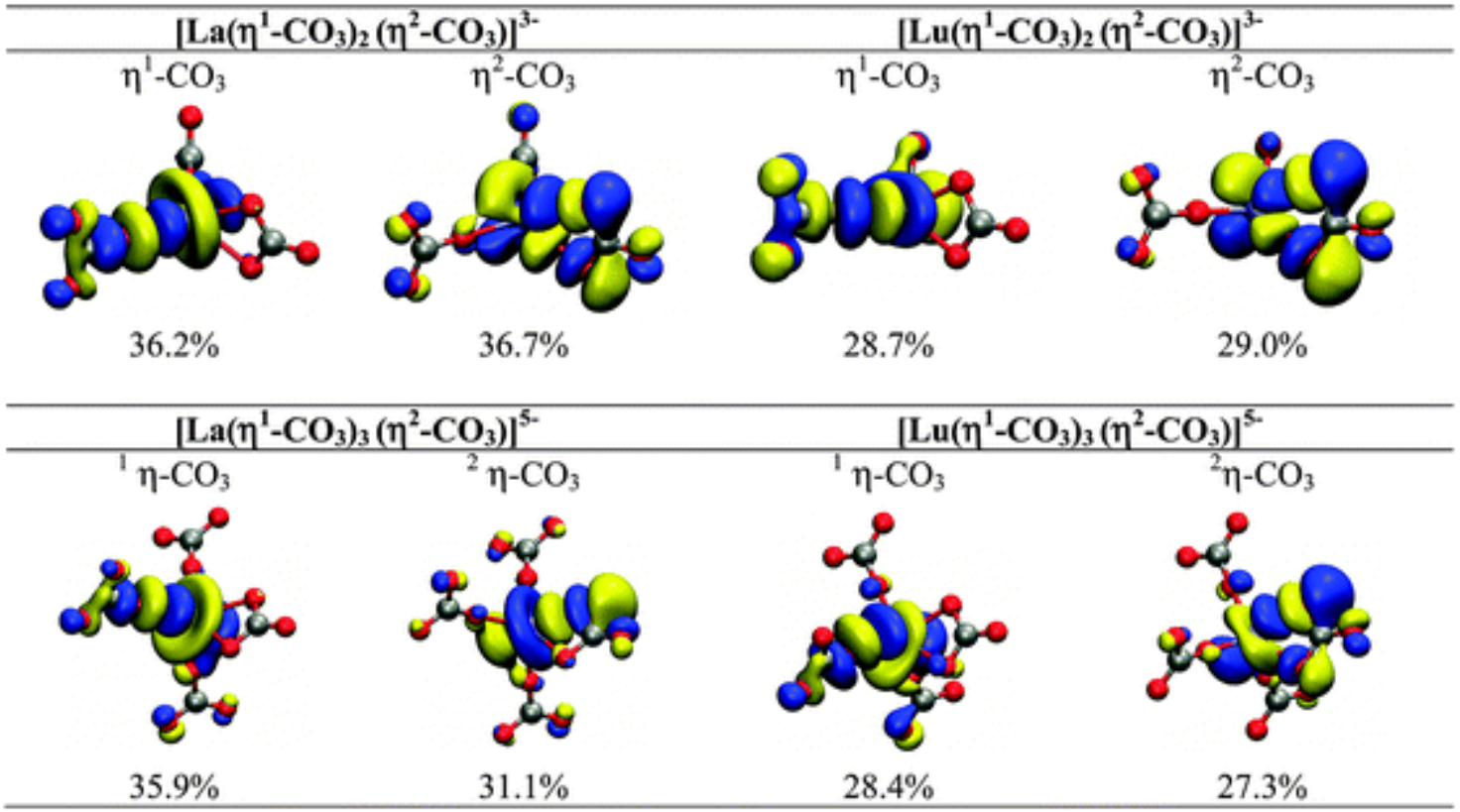
Bonding energy analysis: dppe → dppb increased bite angle:
improved electronic interaction, but larger strain in intermediate



J. Wassenaar, E. Jansen, W.-J. van Zeist, F. M. Bickelhaupt, M. A. Siegler, A. L. Spek, J. N. H. Reek *Nature Chem.* **2**, 417 (2010)

Natural orbitals for chemical valence: ETS-NOCV

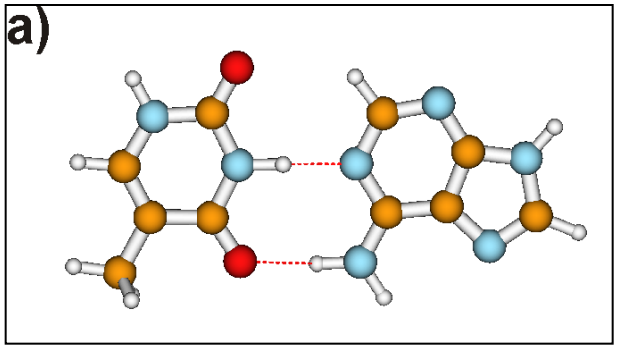
combined charge + bonding analysis:
deformation densities, specific orbital interactions



Electronic structure and bonding of lanthanoid(III) carbonates Y. Jeanvoine, P. Miró, F. Martelli, C. J. Cramer, and R. Spezia, *Electronic structure and bonding of lanthanoid(III) carbonates* Phys. Chem. Chem. Phys. **14**, 14822-14831 (2012)

ETS-NOCV analysis of bonding interactions

Adenine-Thymine

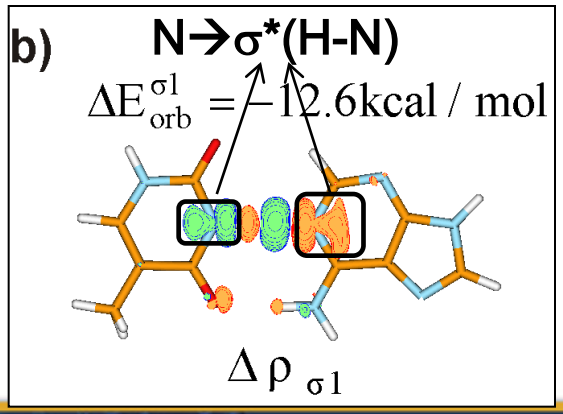


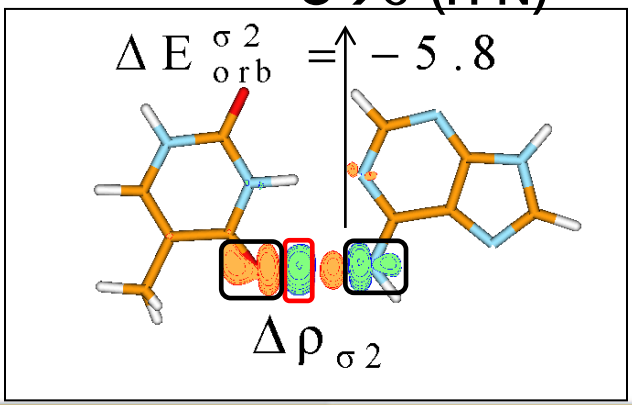
kcal/mol, (BP86/TZ2P)	A-T
ΔE_{int}	-13.0
ΔE_{orb}	**-22.0**
ΔE_{Pauli}	38.7
ΔE_{prep}	2.1
ΔE_{elstat}	-31.9
ΔE_{total}- experiment[99]	-12.1
ΔE_{total} – other theoretical results	-13.2

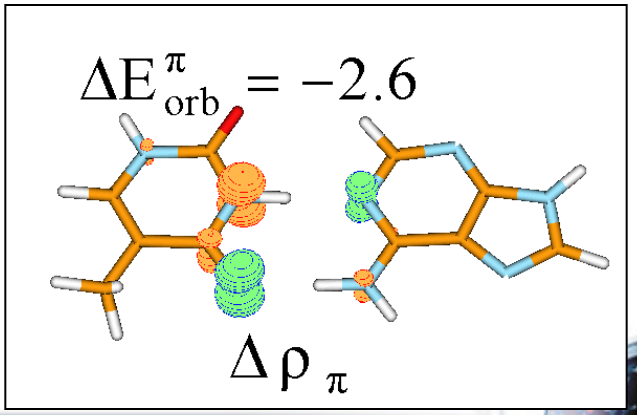
See ETS-NOCV Webinar (Mitoraj)

R. Kurczab, M. P. Mitoraj, A. Michalak,T. Ziegler *J. Phys. Chem. A,2010,* 114, 8581.

ΔE_{orb}=-22.0







Analysis: AIM critical points, bond paths

-Bader's Atoms in Molecules theory

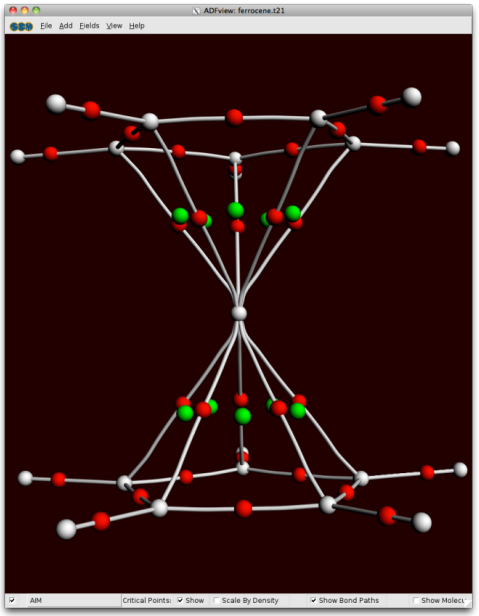
-Computation of properties (density, density gradient, Laplacian, etc.) along the bond paths

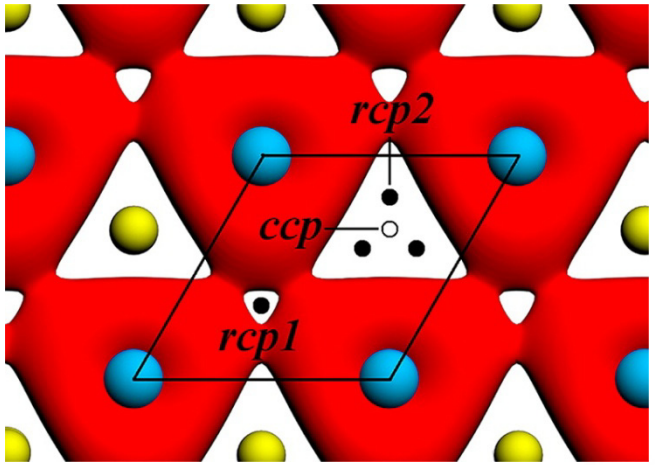
-Fast, iterative, grid-based methods

-Cross-platform, GUI support visualization

-Finds all critical points for large molecules

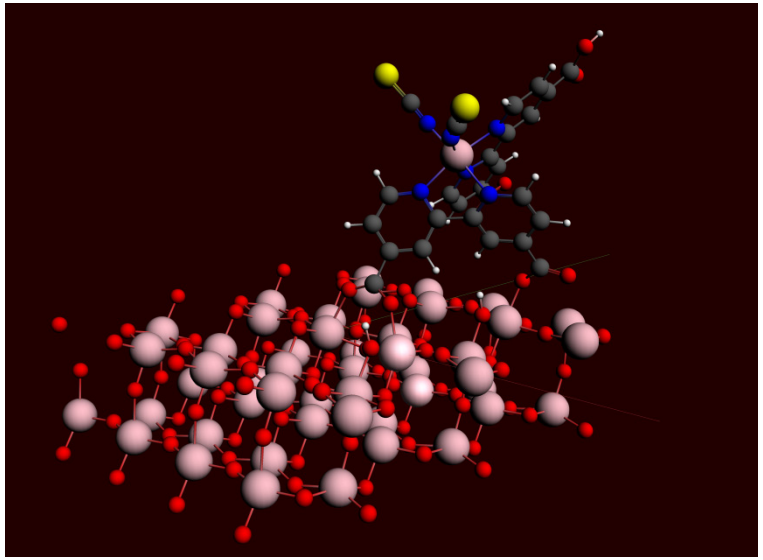
-Also in BAND and DFTB



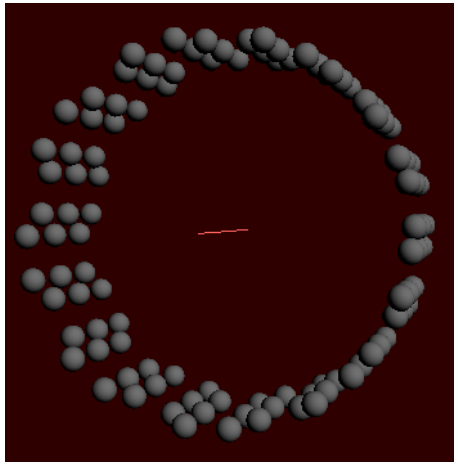


Transition from 2-D Semiconductor to 1-D Metal State and Electron Density Distribution in Nanolayered MoX_2 (X = S, Se, Te), J. Phys. Chem. C. **116**, 20651-20655 (2012)

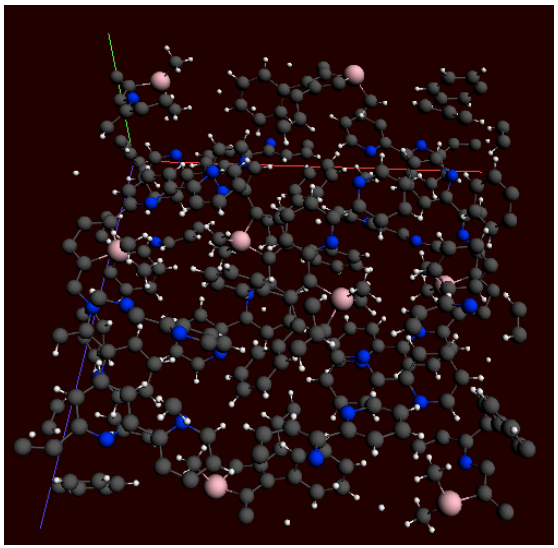
BAND: periodic DFT for 1-, 2, and 3D



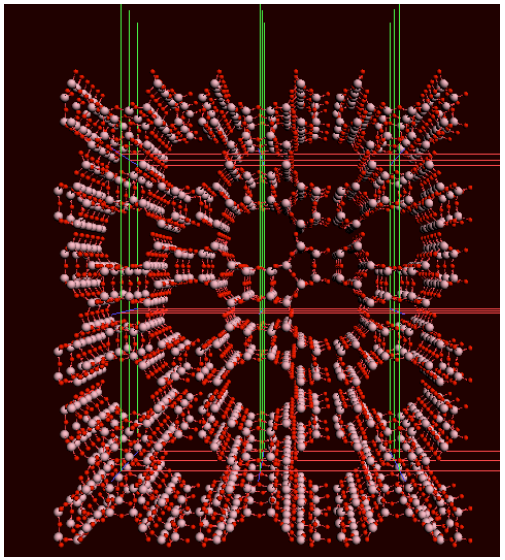
N3 on TiO_2 - surface



Nanotube
- chain



Solid - PyPySPyPy –
OLED material -
584 atoms in unit cell



Zeolite - solid

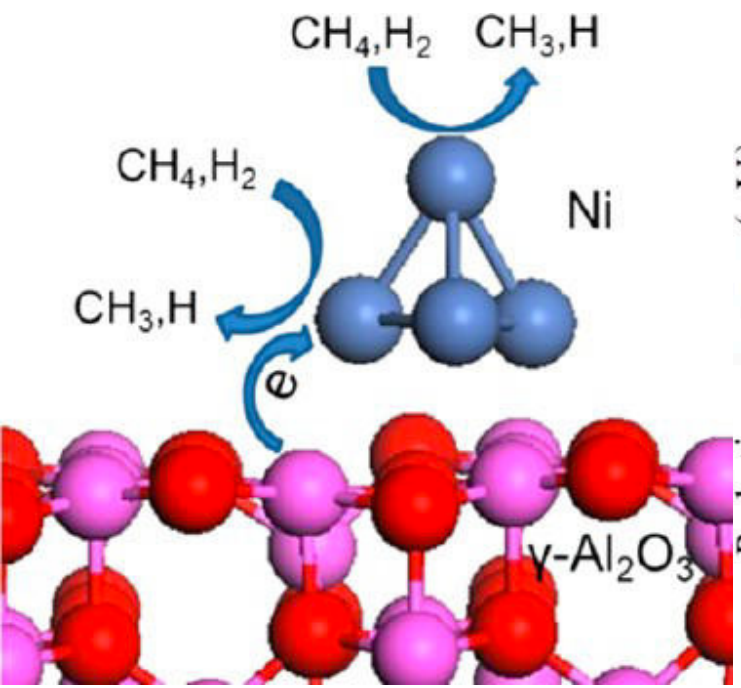
BAND vs. Plane Wave codes

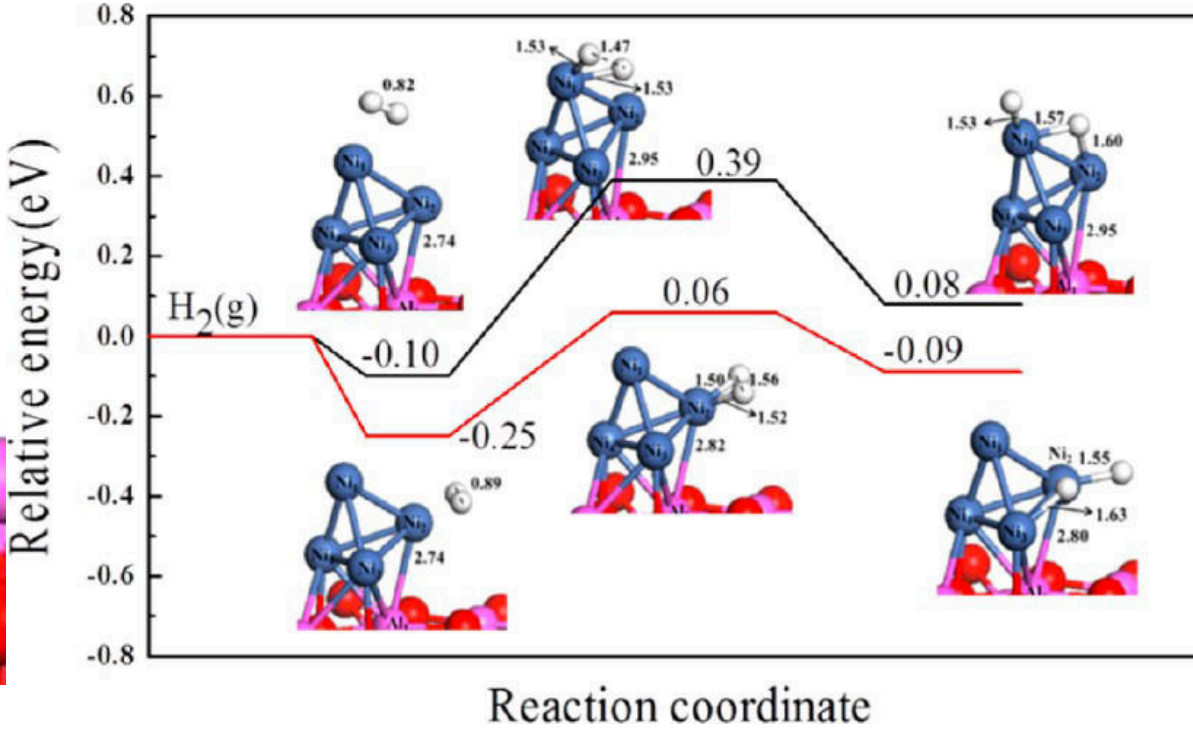
- True comparison molecular and periodic systems
  - same basis, Hamiltonian, xc functional
- Atom centered basis functions, STO or NAO
- No pseudopotential approximation
- Distance cut-offs => fast for “empty”, 1D and 2D
- Real 1D and 2D (no repetition artifacts)
- COSMO solvation model
- Homogeneous electric field
- Many spectroscopic properties (incl. core)
- Analysis options, orbital populations
- Molecular electronics: NEGF, eff. mass, 2D TD-DFT

* Latest XC: revTPSS, GGA-D3, TB-mBJ, GGA+U

CH_4 and H_2 dissociation on Ni/γ-Al_2O_3

- Dissociation at interface preferred
- Aluminum acts as electron donor

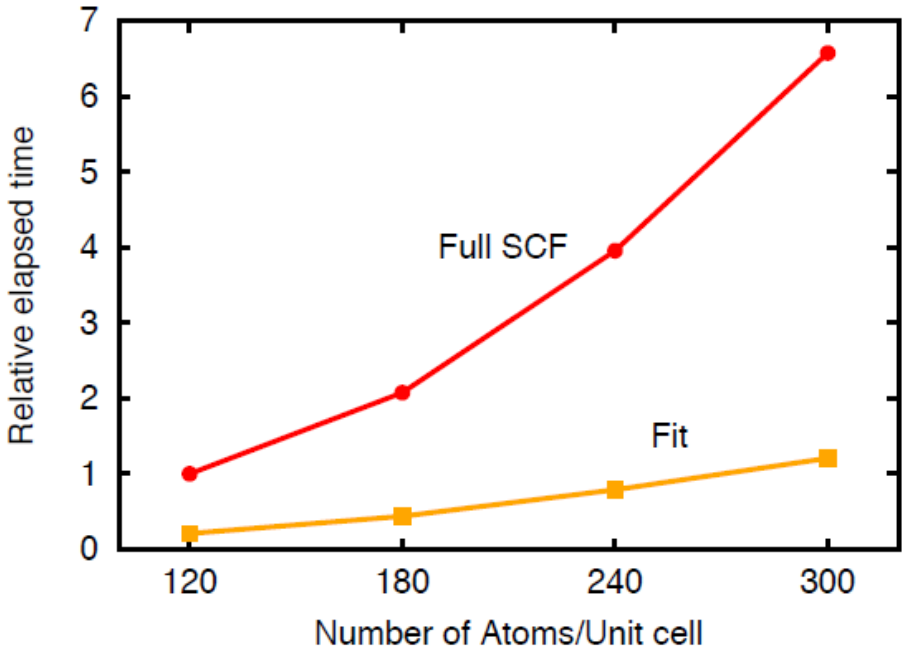


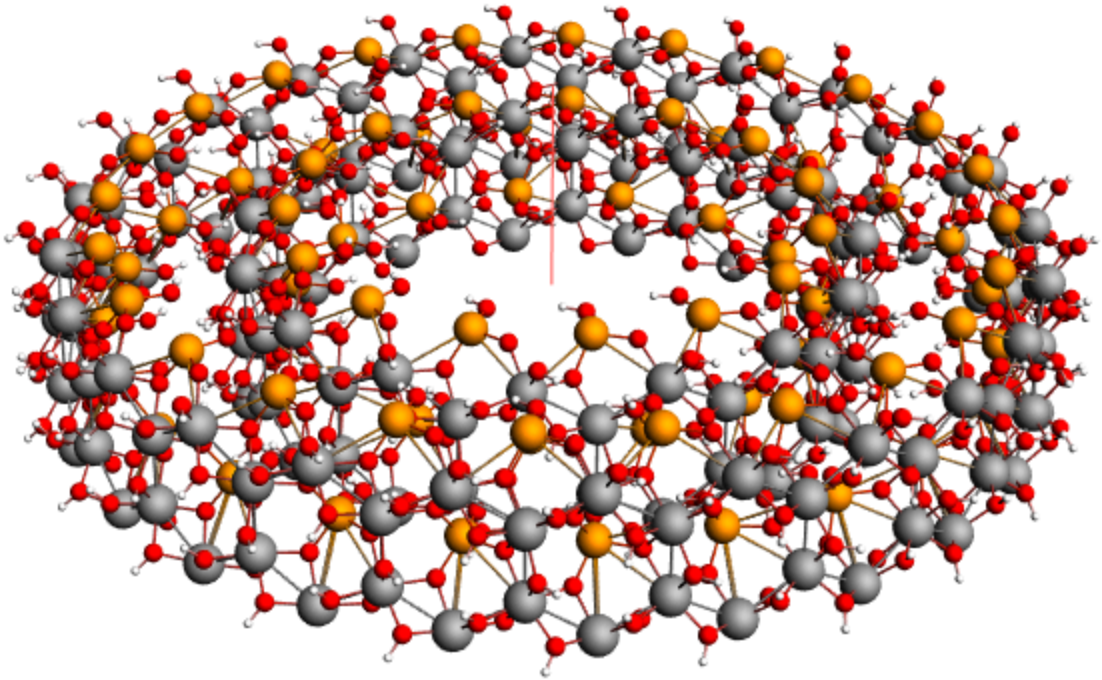


Li, Croiset, Ricardez-Sandoval, *J. Phys. Chem. C* **2013**, *117*, 16907

Current focus: speed & robustness:

Z_{lm} fit in BAND
- Near-linear scaling (N)
- Tunable, reliable, fast

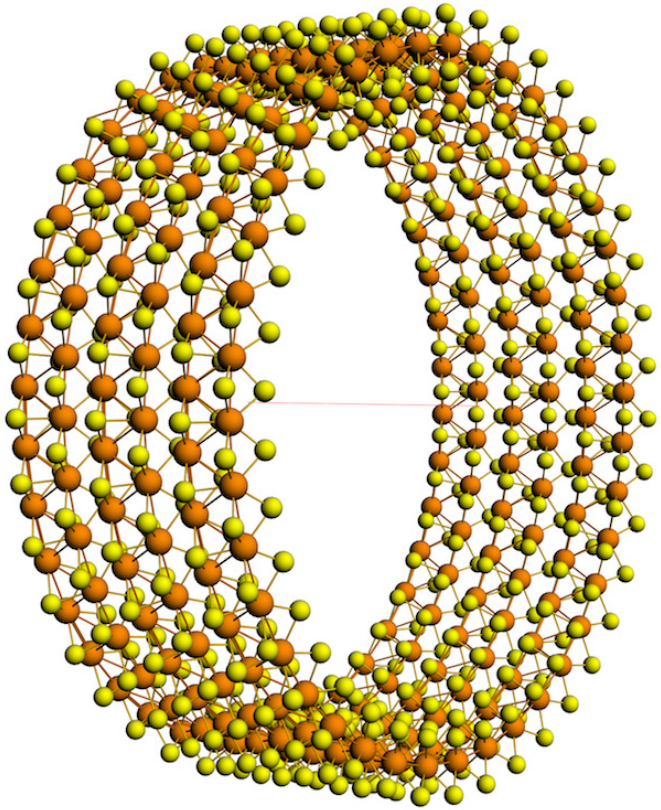


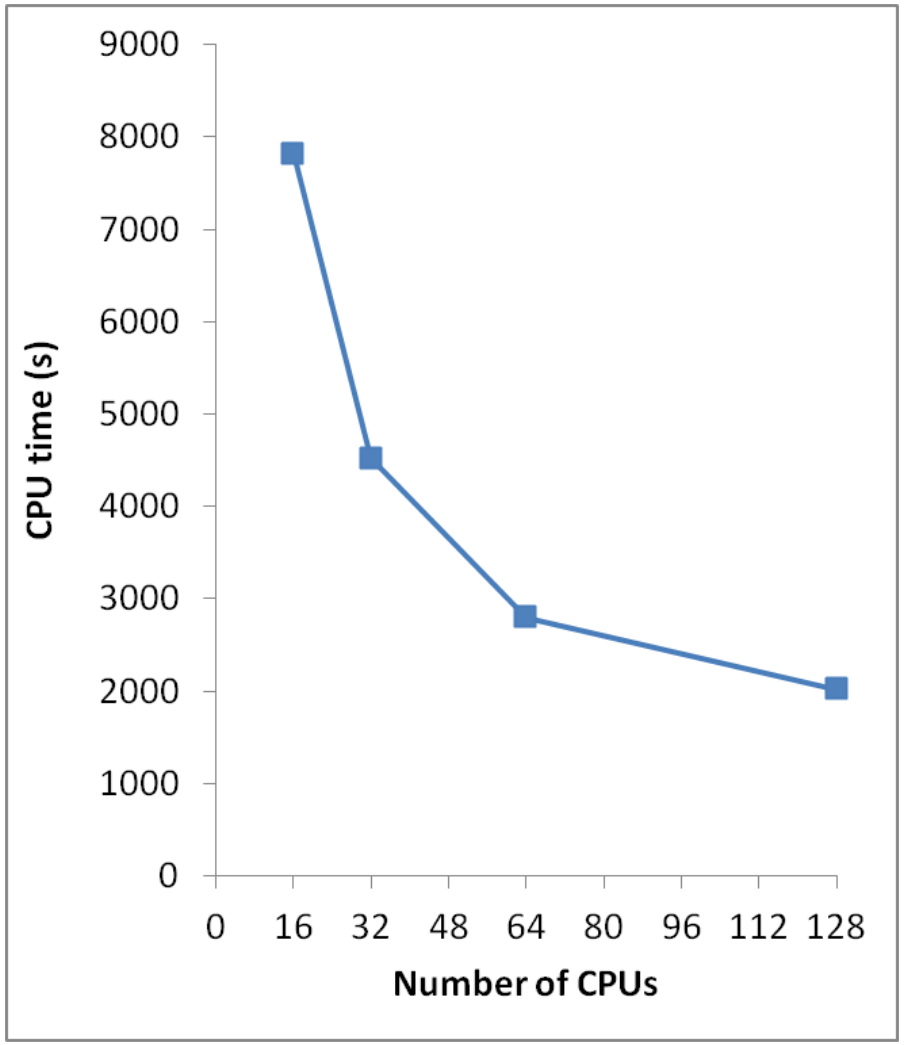


Recent application:

1D, 1 *k-point*
xc=PBE
1000 atoms
7000 basis functions
Geometry optimization
10 steps, 10 hours
4 nodes x 16 cores

Parallel scaling BAND



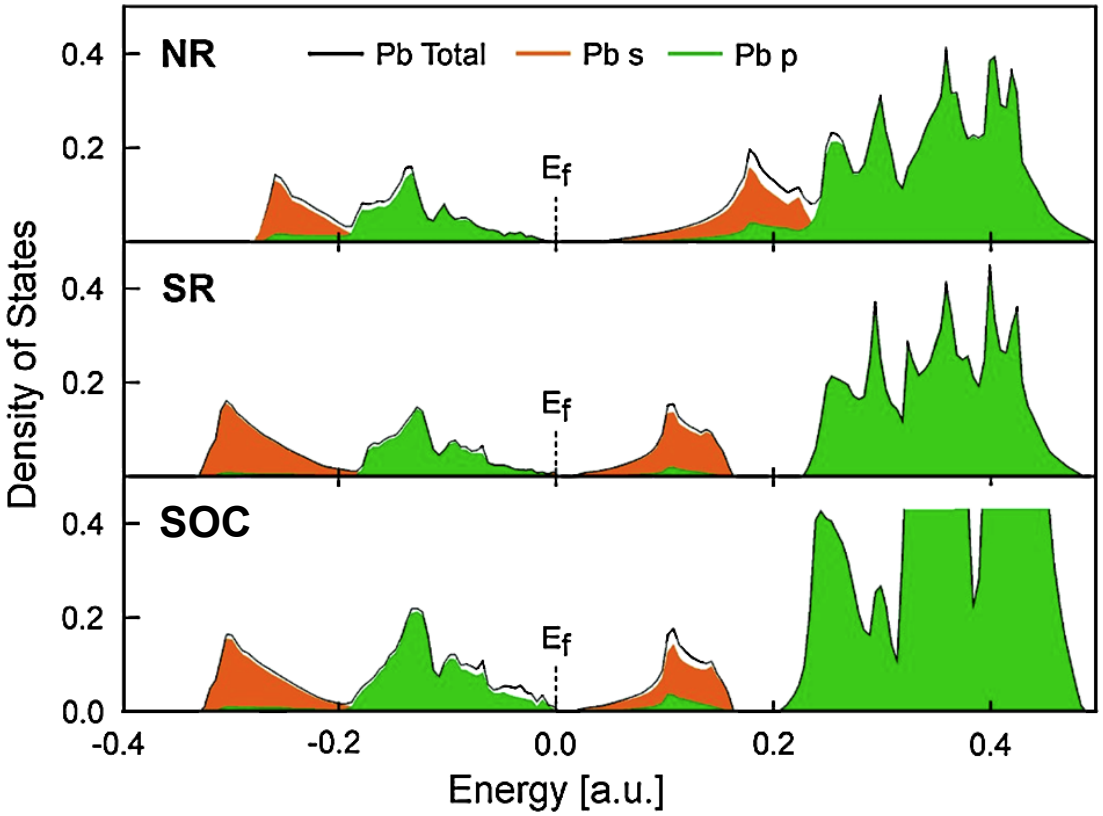


Recent application:

240 atoms, 1D, 3 k-points, nosym, TZP

1 full SCF @ 2.60GHz 16 cores Intel Xeon /w 64 GB RAM

Relativity makes your car start



- Total and partial density of states (DOS) of lead in Lead (IV) oxide

- Strong relativistic shift in both occupied and unoccupied Pb 6s states.

- Without relativity, 12V battery would be 2.4V!

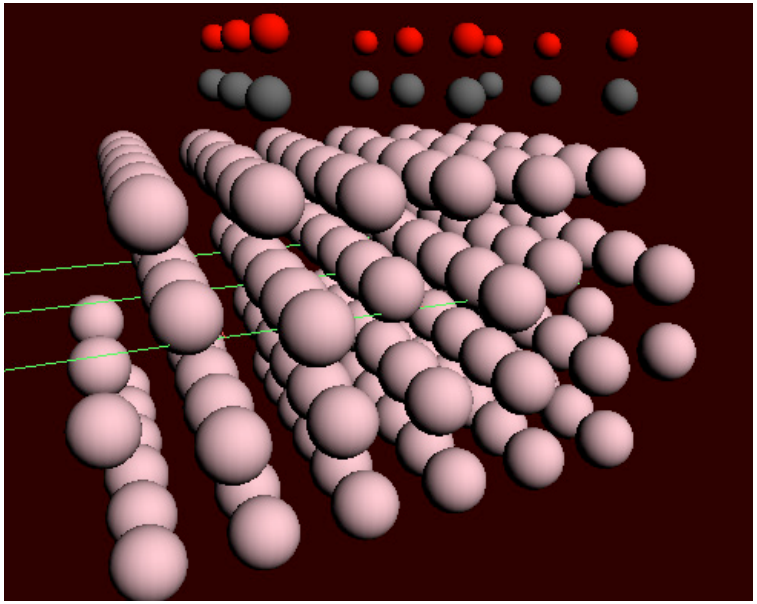
Orange = lead 6s states, Green = lead 6p states.
NR = nonrelativistic, SR = scalar relativistic, SOC = 2c w spin orbit coupling

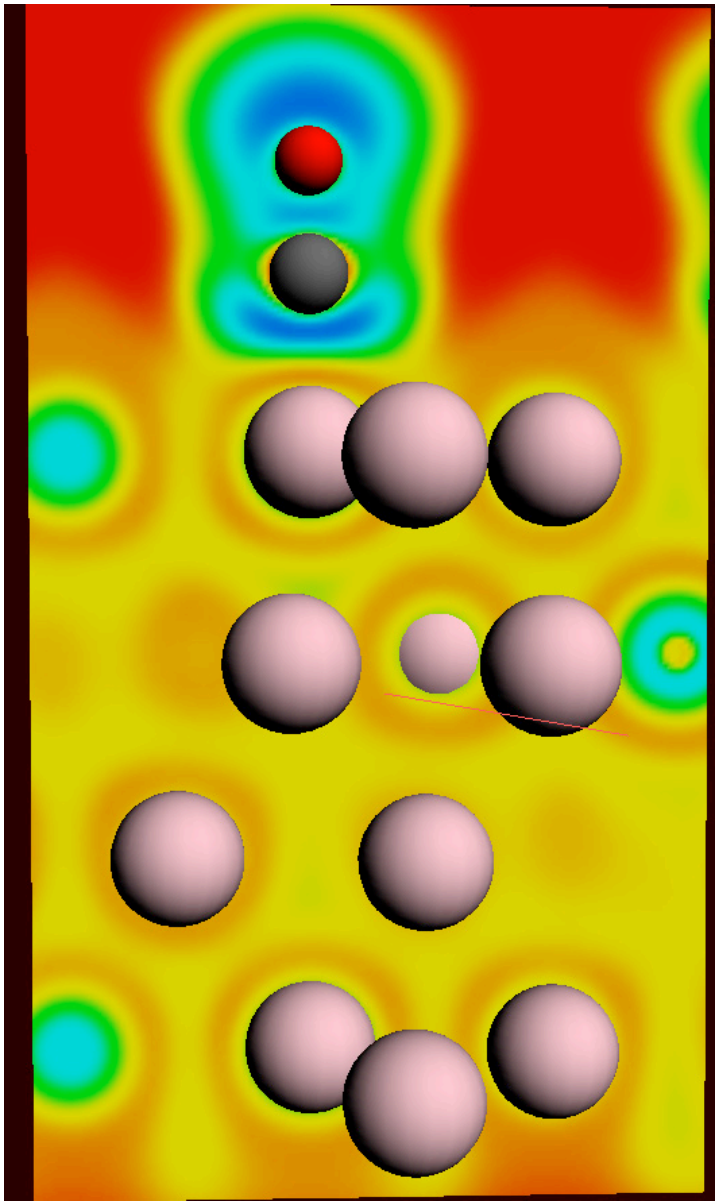
R. Ahuja, A. Blomqvist, P. Larsson, P. Pyykkö, and P. Zaleski-Ejgierd, Phys. Rev. Lett. **106**, 018301 (2011)

Visualization ELF

- Electron Localization Function

CO on Cu(100)



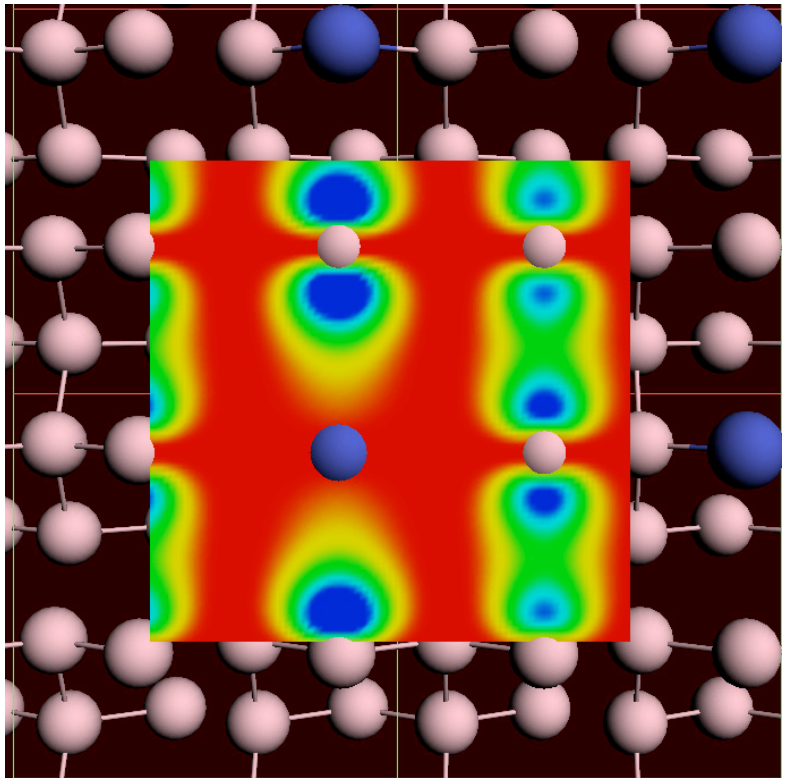


STM visualization with/without bias

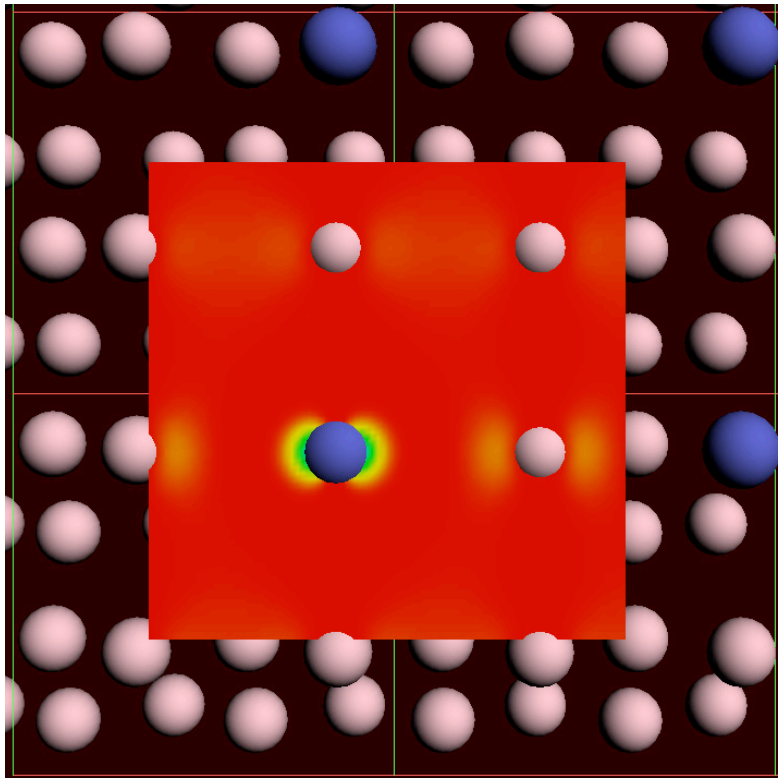
- STM images (Tersoff-Hamann)

Pt Ge(100)

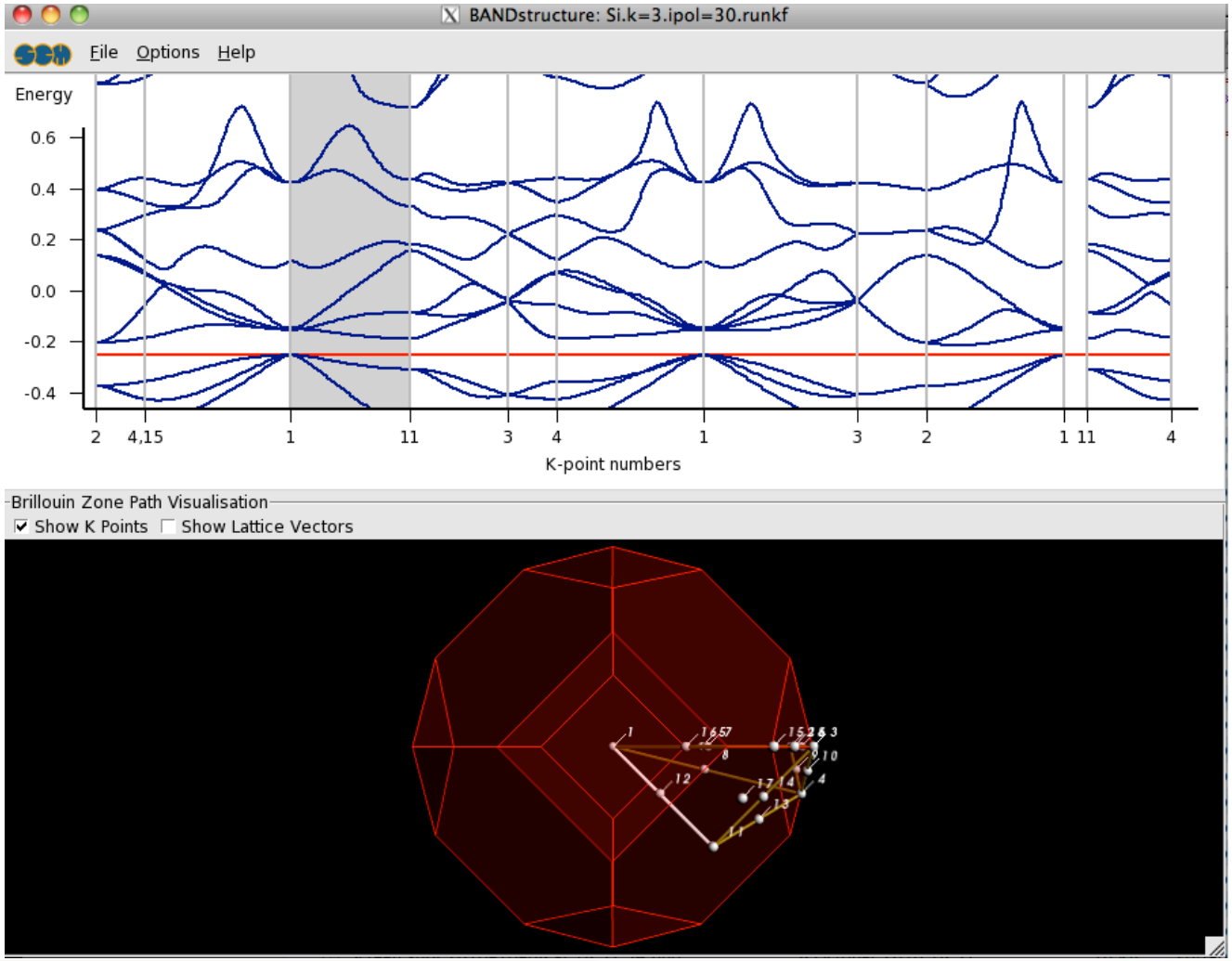
bias = 0



bias = 0.1



Smooth band structure with interpolation points



revTPSS: meta-GGA for physics & chemistry, surface science

- Most xc functionals are good for molecules (PBE, TPSS) OR for solids (AM05, PBEsol)
- revTPSS improves TPSS to treat both right.
- offers prospects for accurate surface chemistry

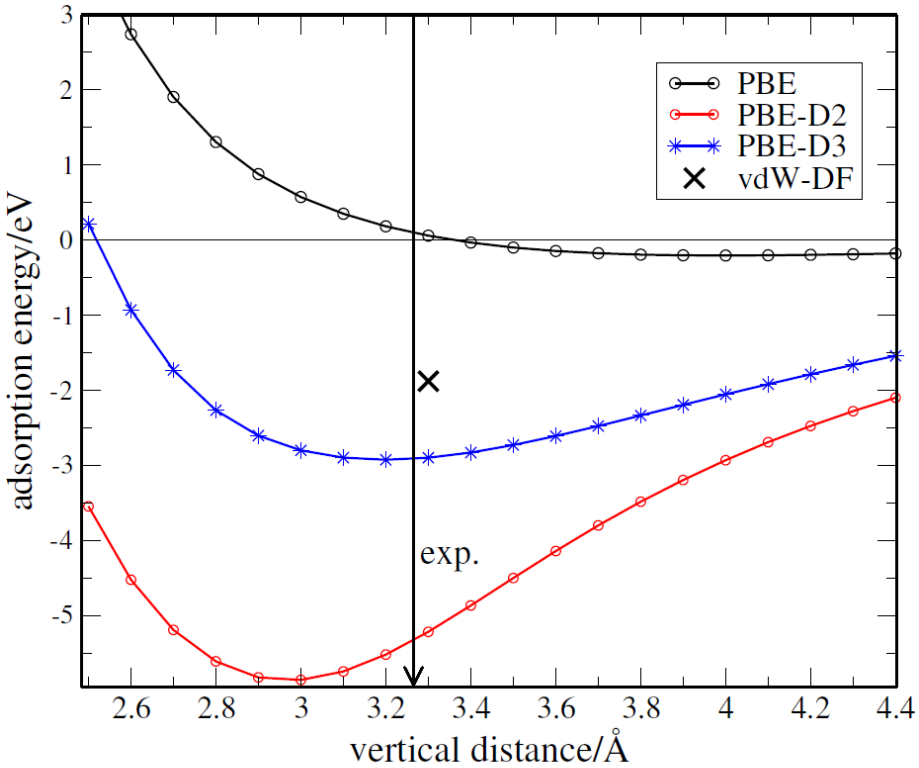
XC func.	LSDA	PBE	TPSS	AM05	PBEsol	revTPSS
Atomization energies[1]	77.4	15.5	5.9	38.7	35.9	5.9
Lattice constants[2]	0.079	0.065	0.047	0.039	0.038	0.036

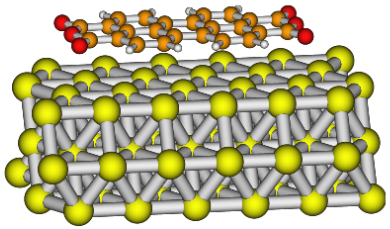
1: MAE in kcal/mol, AE6 molecules 2: 21 solids calculated with BAND, MAE in Angstrom

J.P. Perdew, A. Ruzsinszky, G.I. Csonka, L.A. Constantin, and J. Sun, *Phys. Rev. Lett*. **103**, 026403 (2009).

DFT-D3 XC functionals in ADF&BAND

- Less empirical than earlier DFT-D
- Asymptotically correct
- Available for elements Z = 1-94
- Dispersion coefficients and cutoff radii computed explicitly
- Dispersion coefficients independent of connectivity
- Similar or better accuracy for light elements, better for heavy ones
- Soon also: Steinmann / Corminboeuf xc functional





PTCDA on Au(111)
periodic DFT,
three layers of gold

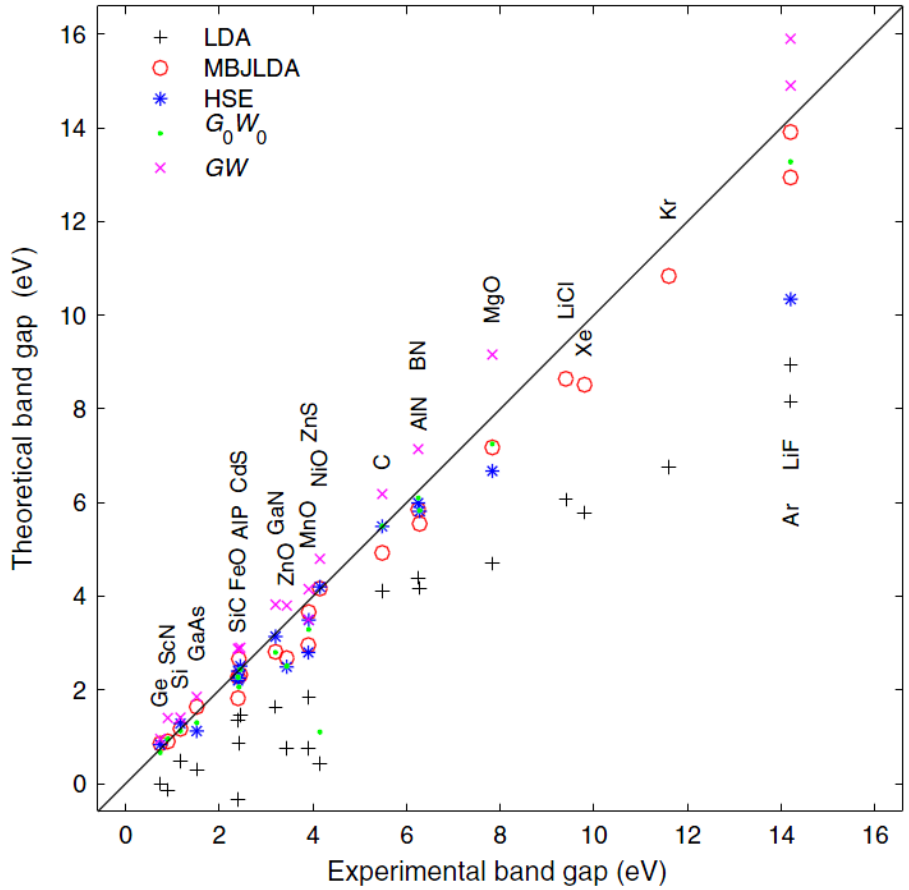
S.Grimme, J. Antony, S. Ehrlich, and H. Krieg: J. Chem. Phys. **132**, 154104 (2010).

Fixing the band gap 'problem' in DFT

Kohn-Sham gap ≠ fundamental gap
=> DFT underestimates band gap
- underlying problem: integer derivative discontinuity in v_{xc}
- $E_{gap} = I - A + \Delta_{xc}$

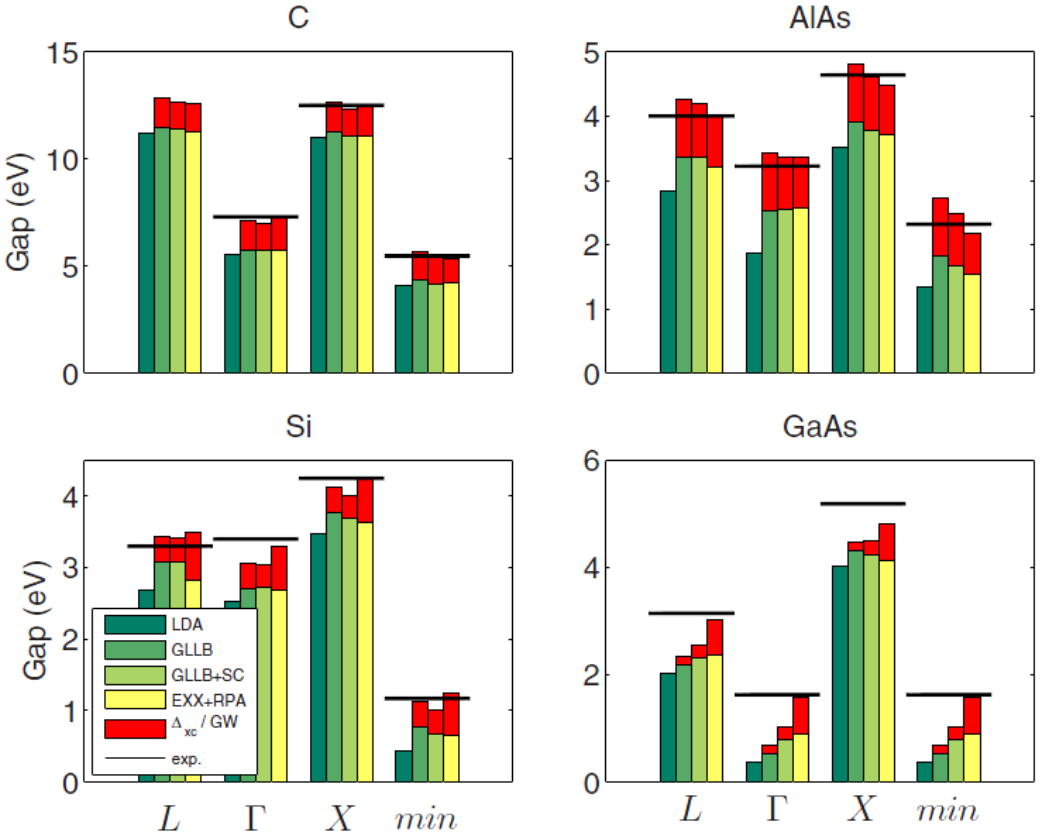
Possible 'solutions'
- many-body perturbation (GW)
- (screened) hybrids
- **LDA/GGA + *U*** (localize d, f electrons in TMO)
- OEP-like exchange:
    - **TB-mBJ** (fitted to band gaps, needs trick for 2D)
    - **GLLB-sc** (includes explicit Δ_{xc} – also applicable to 2D

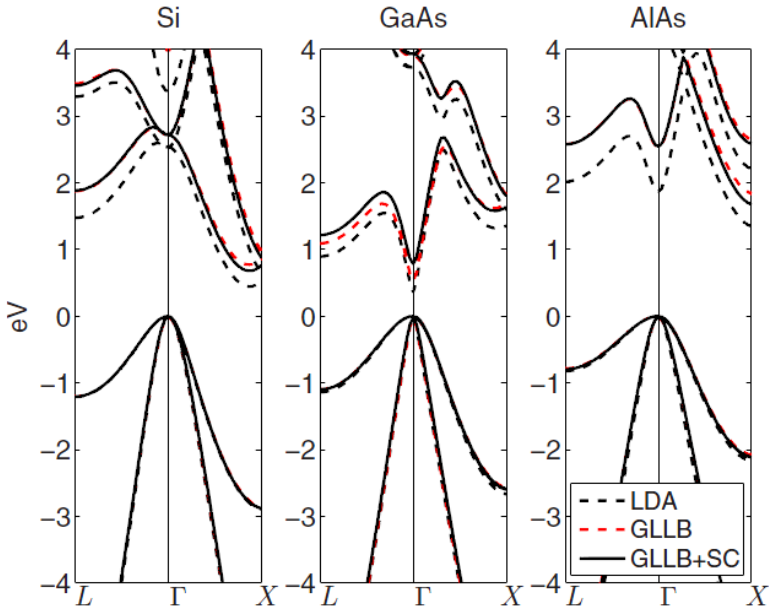
Tran & Blaha's modified Becke-Johnson (TB-mBJ)



Accurate Band Gaps of Semiconductors and Insulators with a Semilocal Exchange-Correlation Potential *Phys. Rev. Lett.* **102**, 226401 (2009).

GLLB-sc: good band gaps for the ‘right reason’?





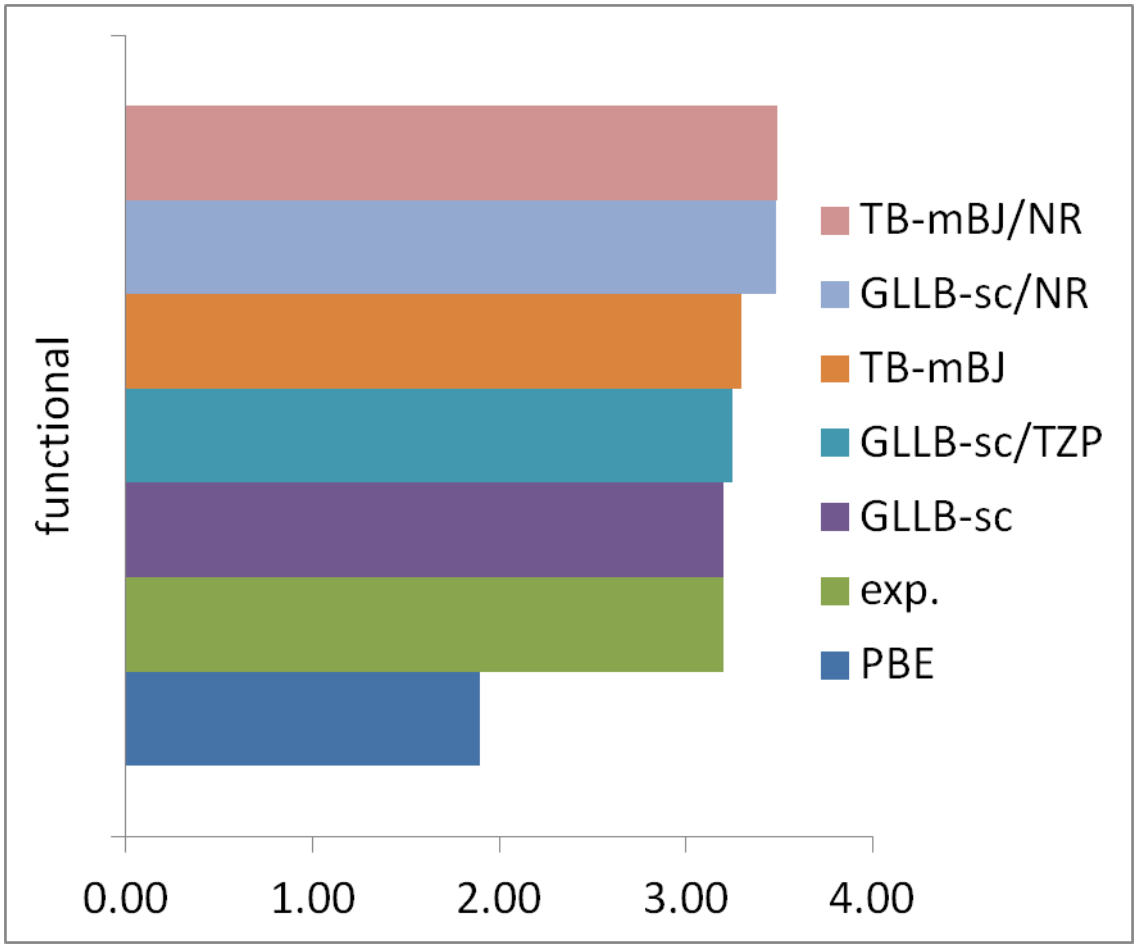
Kohn-Sham potential with discontinuity for band gap materials

M. Kuisma, J. Ojanen, J. Enkovaara, & T. T. Rantala Phys. Rev. B **82,** 115106 (2010)

GLLB-sc can also be applied to 2D, 1D

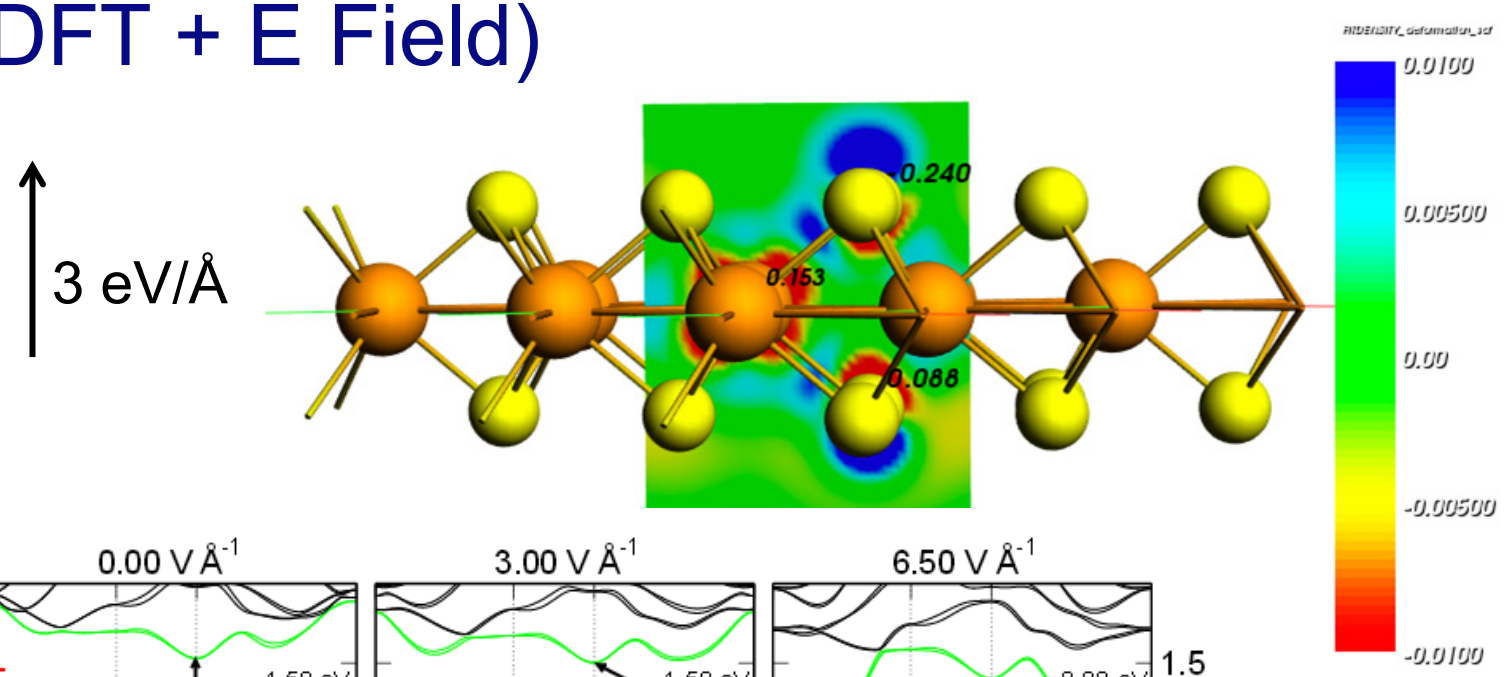
GaN in BAND: band gap

PBE	1.898
GLLB-sc	3.201 (Δ_{xc} = 0.92)
TB-mBJ	3.296
Non-relativistic:	
TB-mBJ/NR	3.494
GLLB-sc/NR	3.487
Smaller basis:	
GLLB-sc/TZP	3.253
Exp:	3.2 eV



(SR-TZ2P-AE, k=5 (75 k-points), acc=5)

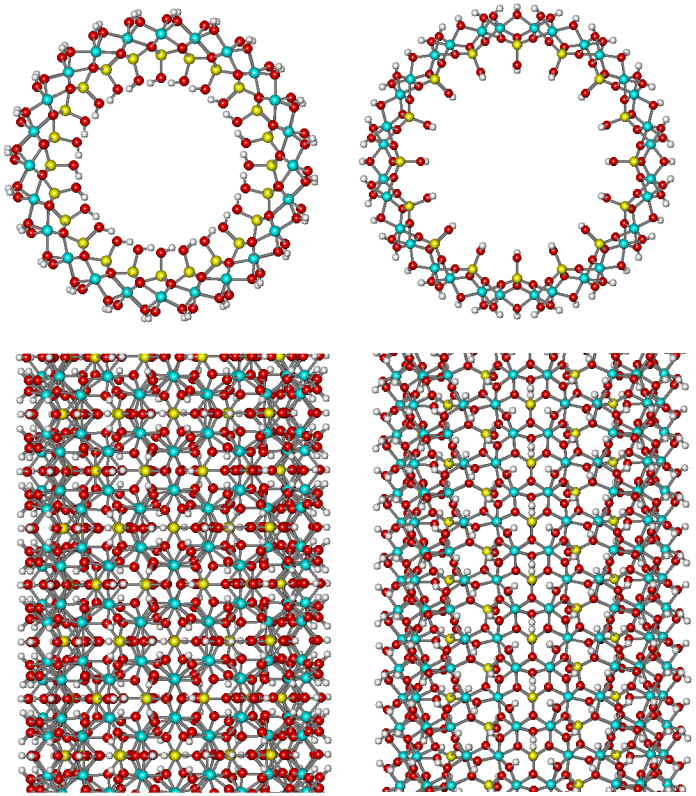
Closing 2D band gaps in MoWSeS monolayers (2D DFT + E Field)



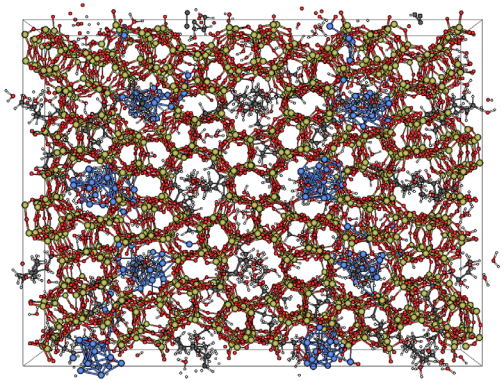
Electron transport in MoWSeS monolayers in the presence of an external electric field, Phys. Chem. Chem. Phys. (2014)

Approximate Quantum-based methods

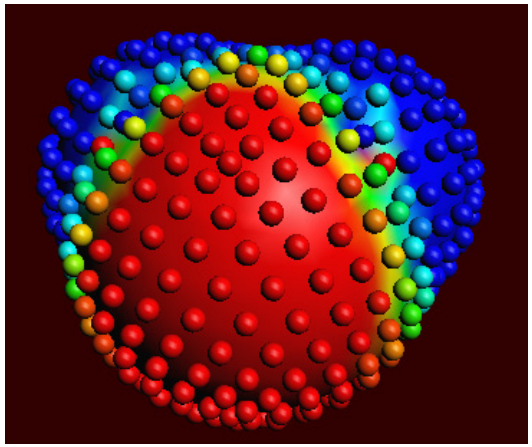
DFTB



ReaxFF

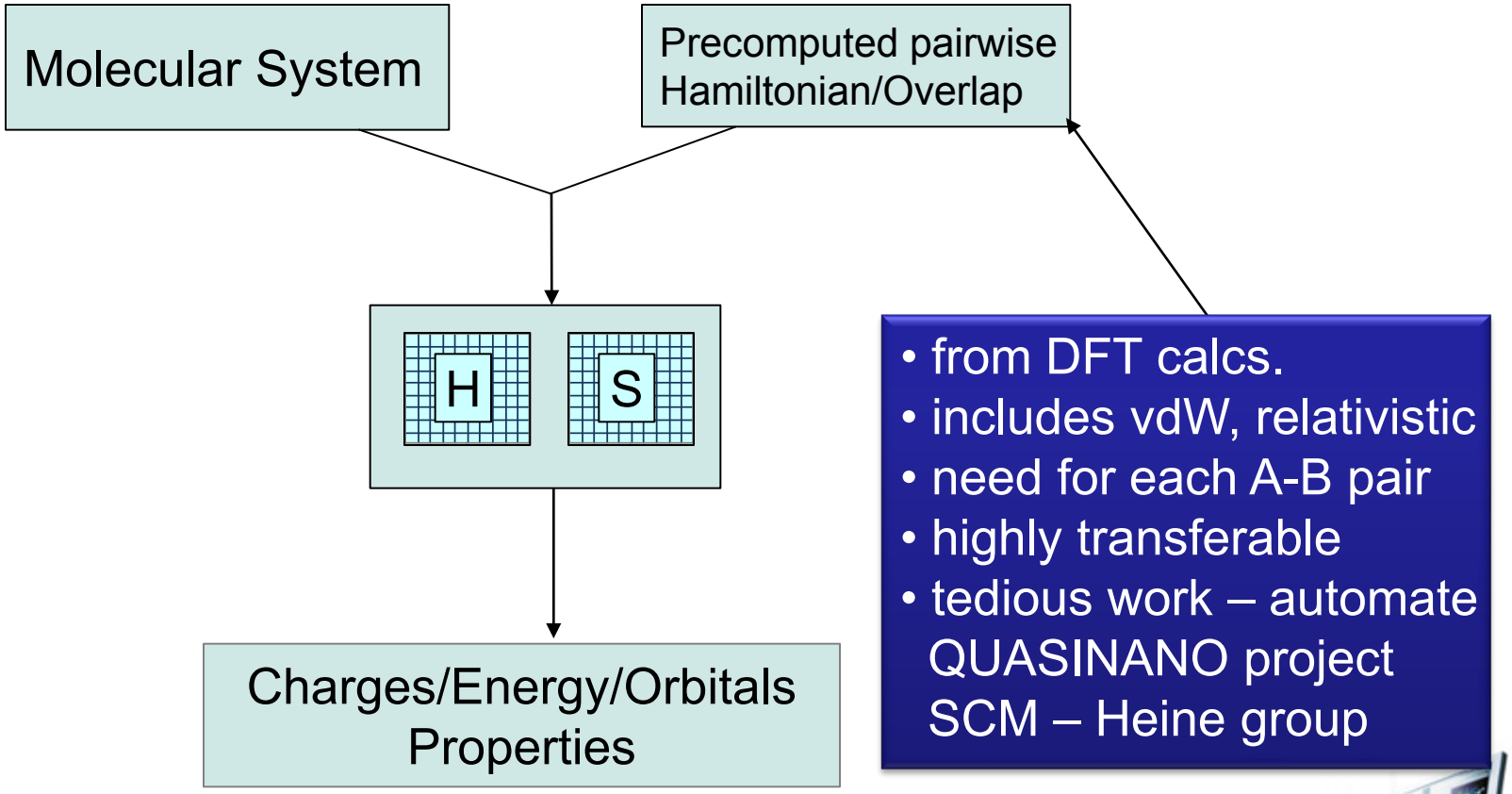


COSMO-RS



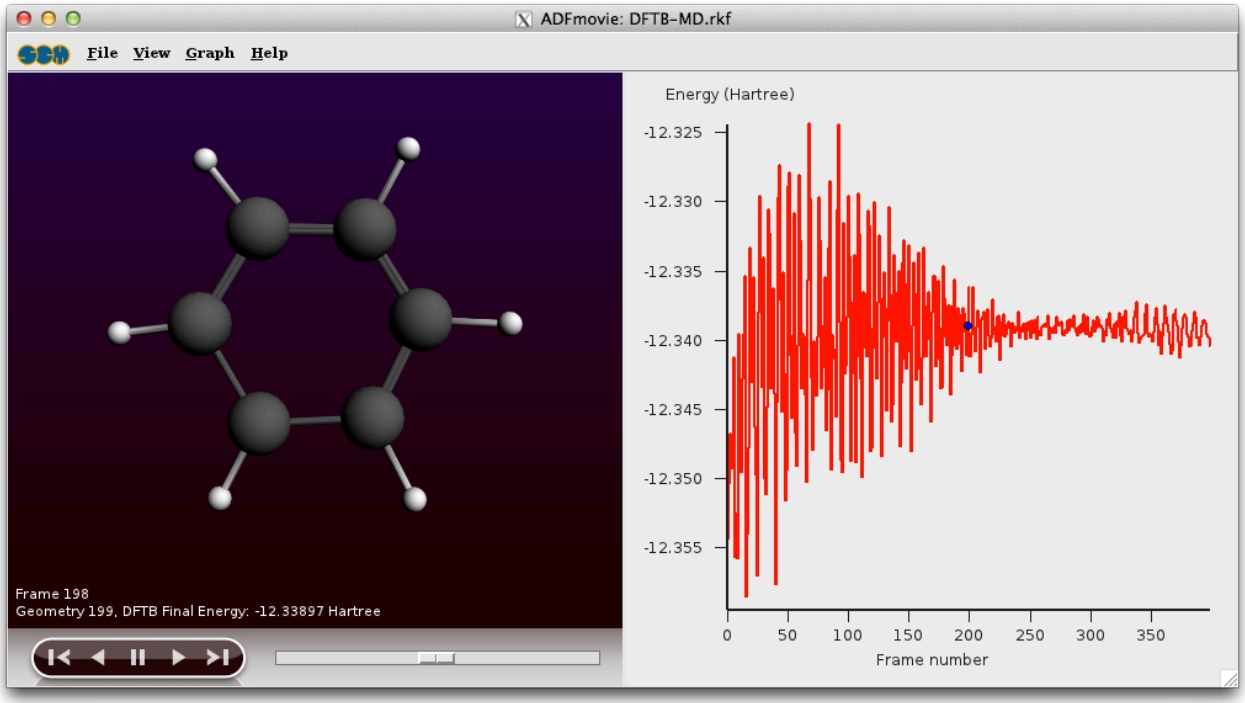
Density-functional Based Tight-Binding (DFTB)

Fast and efficient approximated DFT: ideally suited for large systems

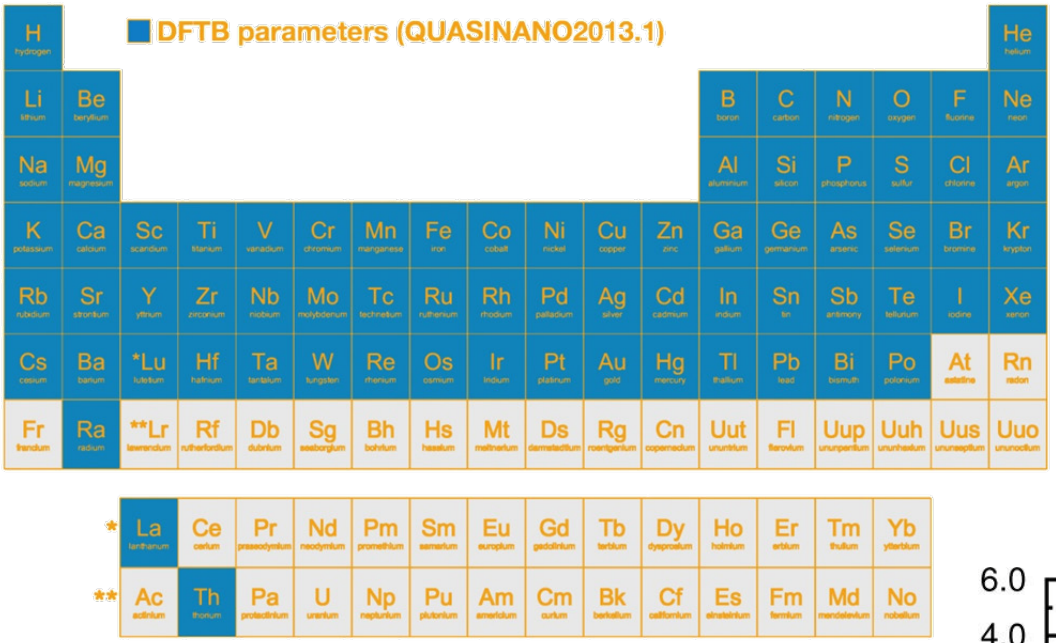


DFTB: current capabilities

- Second-order or third-order self-consistent charges (SCC, DFTB3)
- Molecules, polymers, surfaces, bulk
- Geometry and transition state optimization
- Frequencies, phonons, (P)DOS, band structure, Mulliken analysis, UV/VIS
- Molecular Dynamics: velocity Verlet, Scaling or Berendsen thermostat
- Fully integrated in GUI (pre-optimization/Hessian re-use ADF/BAND)



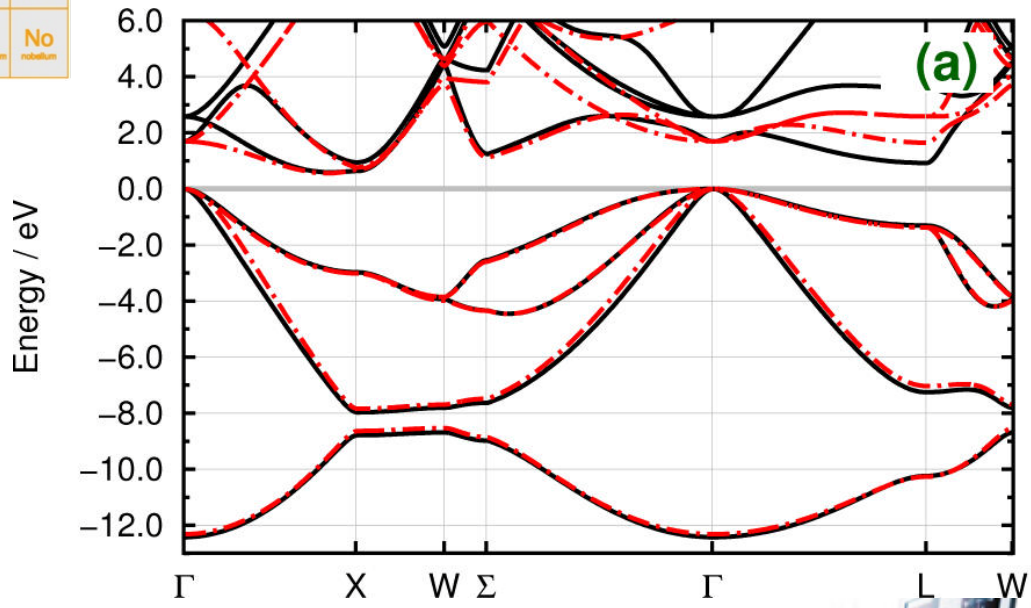
Semi-automated electronic DFTB parameters



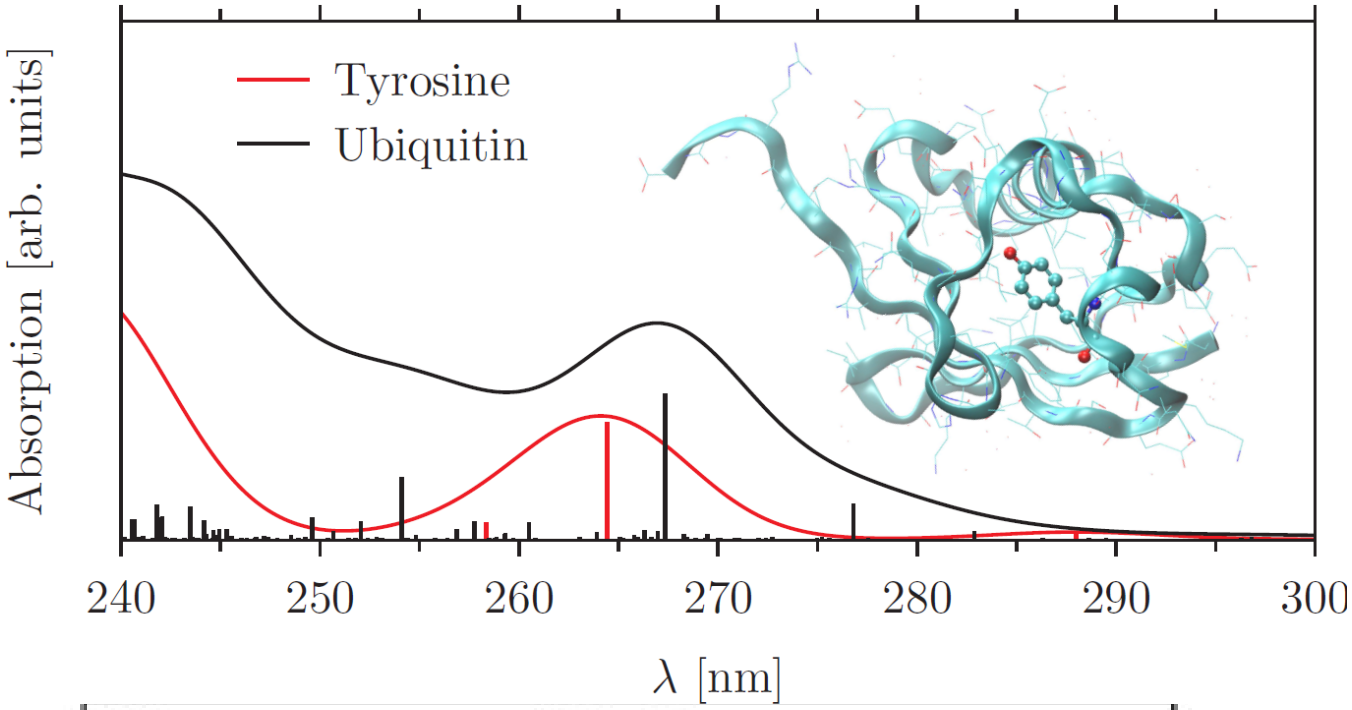
GeSi (zinc blende)
- DFT (PBE/TZP)
- DFTB

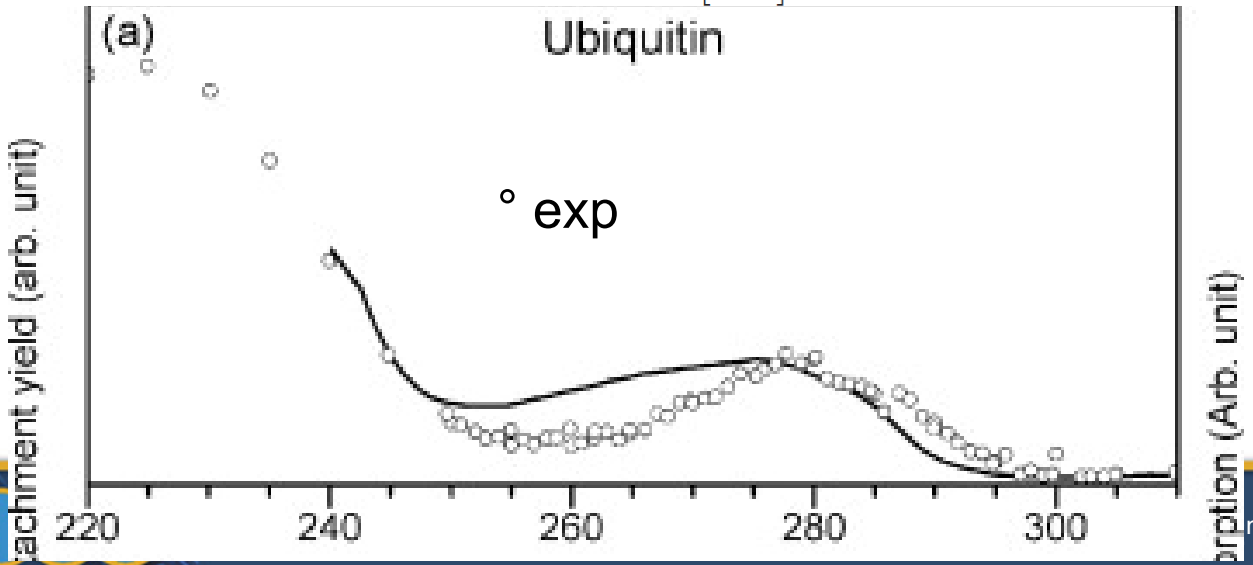
SCM & Jacobs U, *J. Chem. Theory Comput.* **9**, 4006−4017 (2013)

Automated repulsive parameters not yet in a useful state…



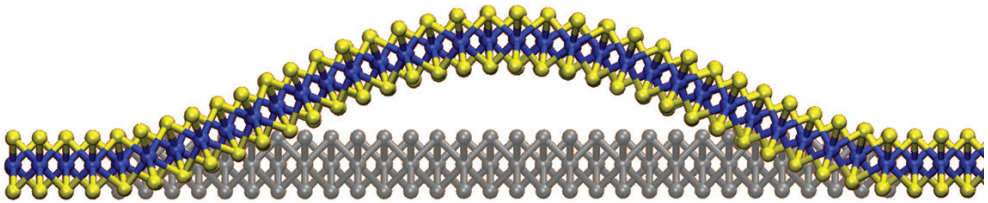
Time-dependent DFTB: excitation of a protein

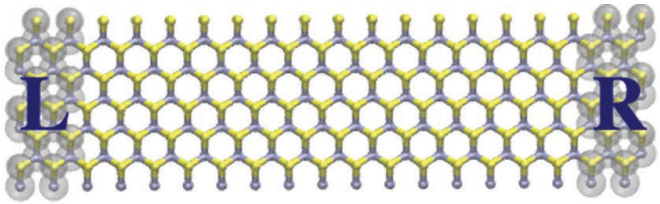


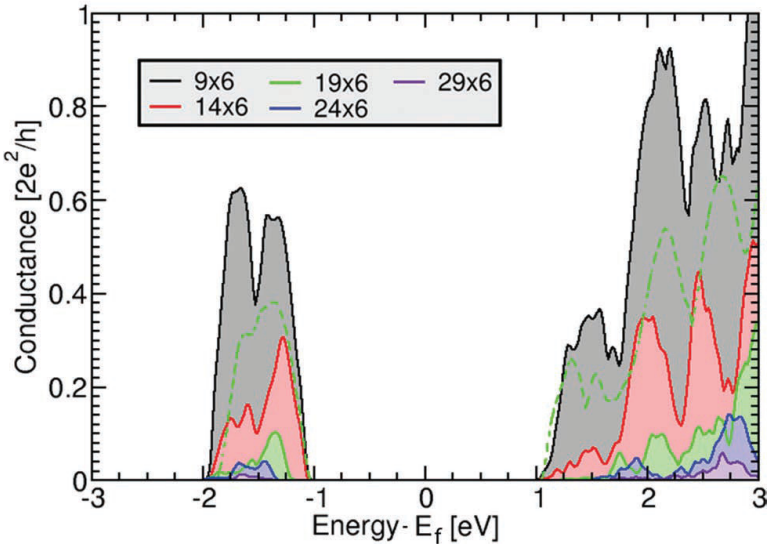


NEGF in DFTB: charge transport

Rippling in MoS_2 strongly reduces conductance





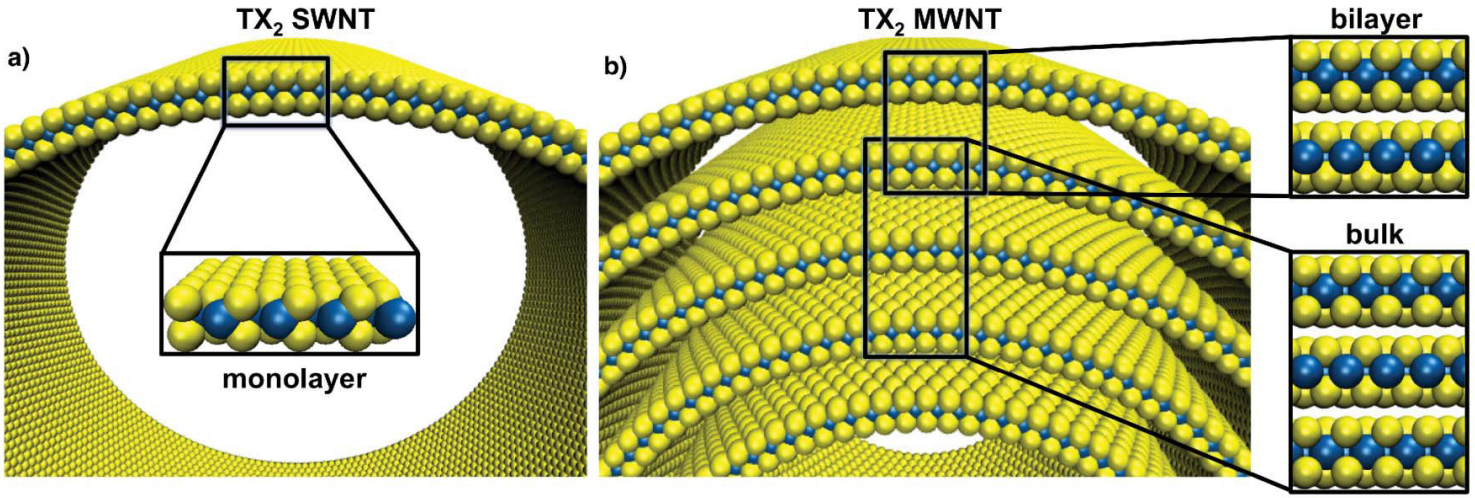


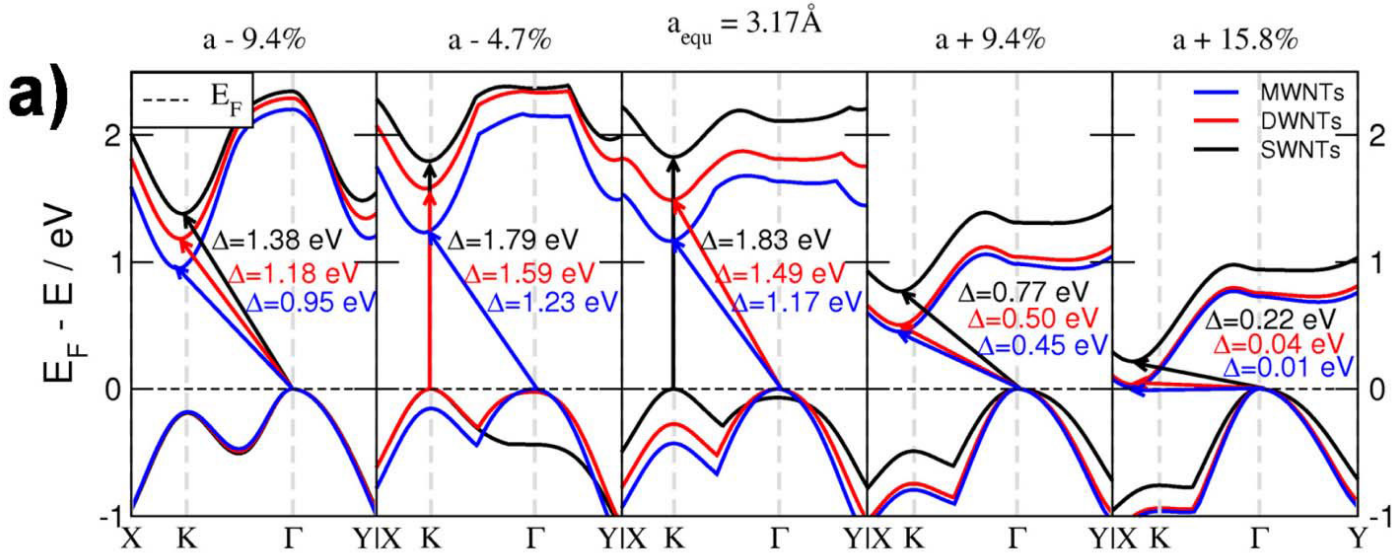
Performance of these materials may strongly depend on production methods.

Heine group (Jacobs U Bremen) *Adv. Mater.* 2013, **25**, 5473–5475

NEGF in DFTB

Conductance in SWNT vs MWNT





Heine group (Jacobs U Bremen) SCIENTIFIC REPORTS | 3 : 2961 (2013)

Planned / desired DFTB developments

- DFTB-MD: BOMD, Ehrenfest, TSH

- Spin-orbit coupling (icw with TSH: intersystem crossing)

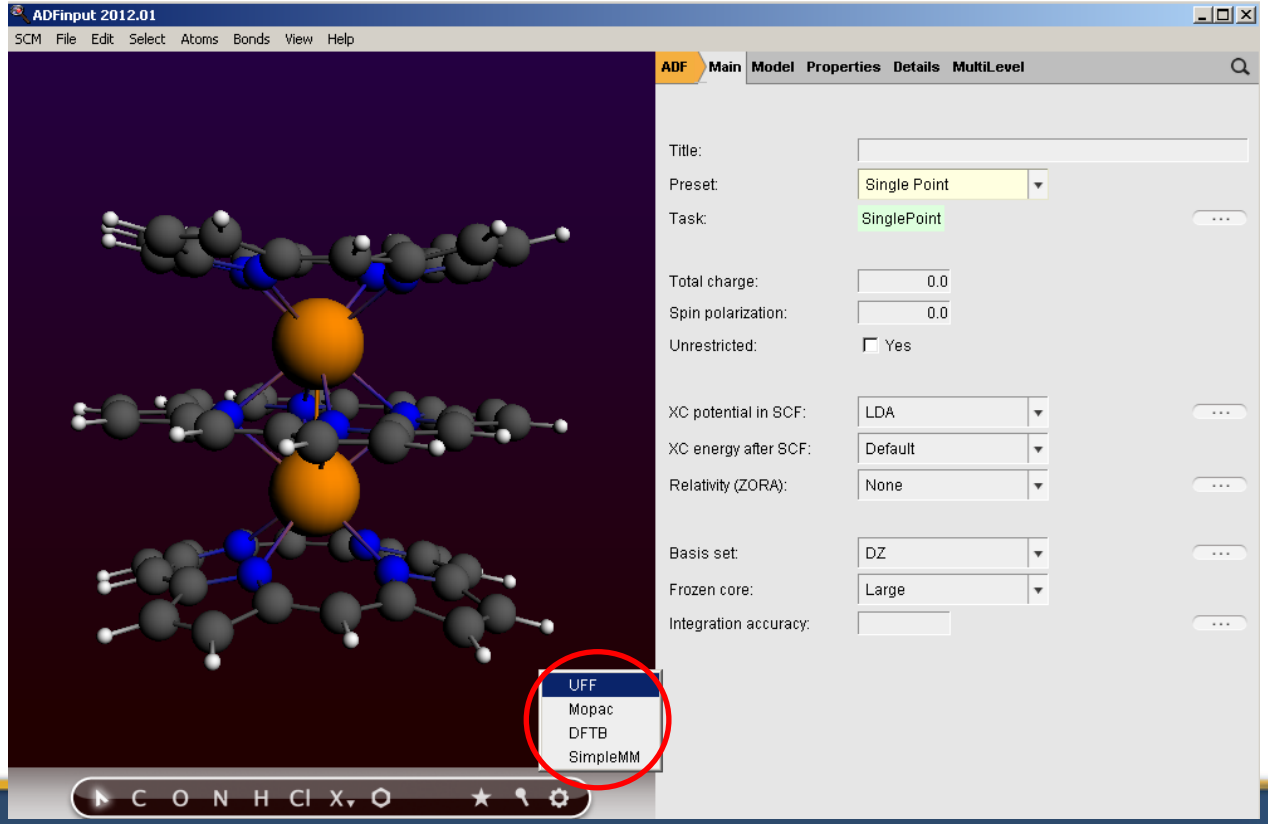
- Excited state MD (Liouville - von Neumann)

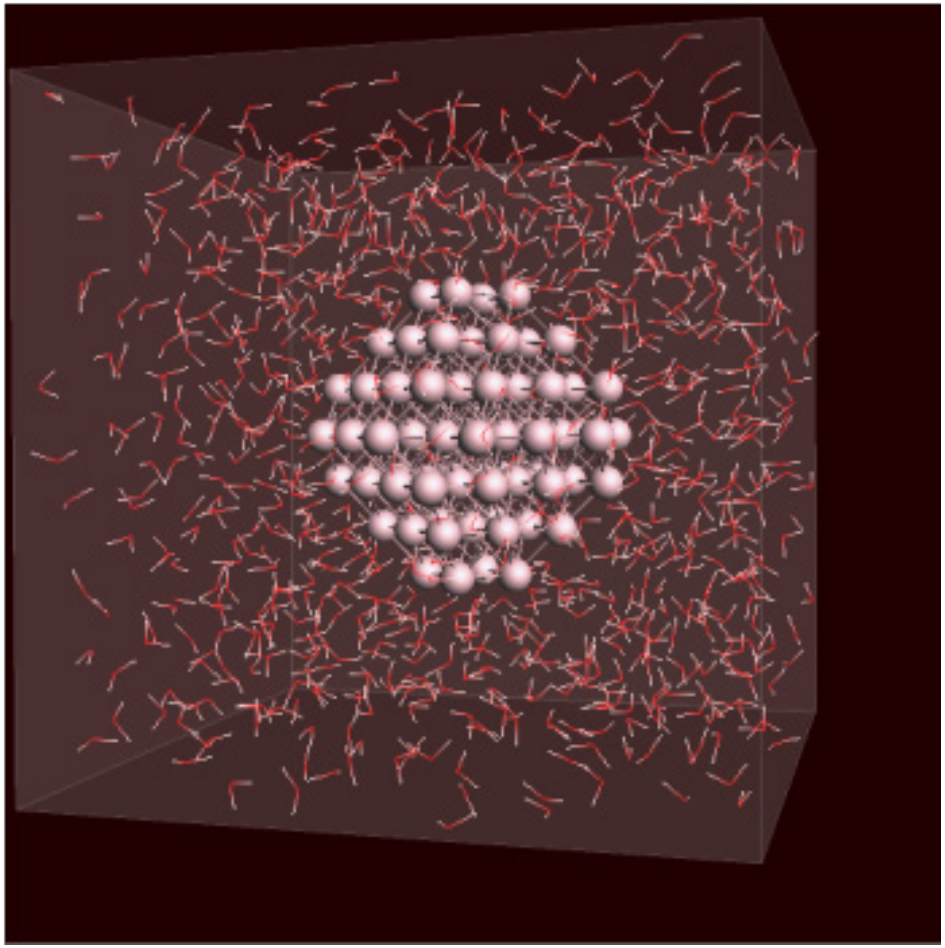
- DFTB embedding in DFT

- automated repulsive parameters, on-the-fly fitting

Other fast approximate methods with our GUI

- MOPAC: Stewart's semi-empirical AM1, PM3, PM6, PM6-DH, …
  - molecules, periodic systems (gamma point only)
  - 70 atoms parametrized (up to Bi, lanthanides with 'Sparkles')
  - **MOPAC2012: PM7** (more accurate, esp. for solids), sped up ~100x in 2014
- UFF: Universal Force Field: all elements; molecules & periodic; **UFF4MOF**





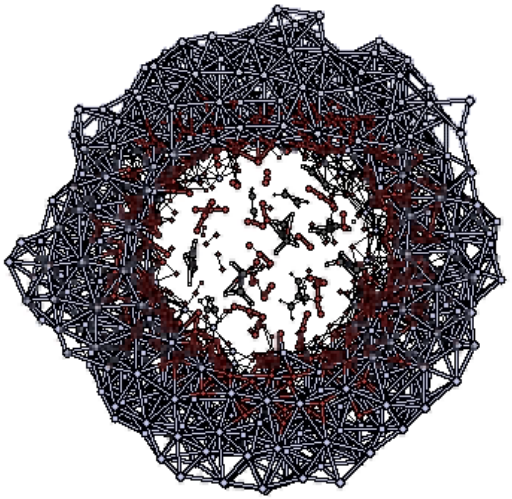
ReaxFF

Engineering challenges….

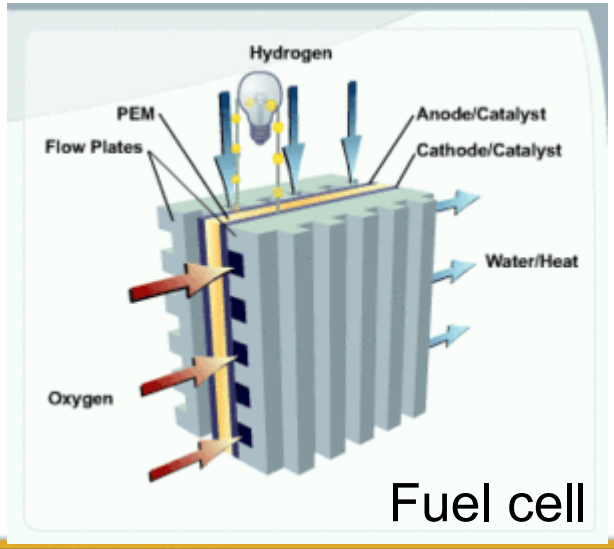
…require atomistic-scale solutions

Coal power plant

- Higher efficiency
- Lower exhaust
- Higher combustion temperature
- Need new materials that can sustain higher temperatures and oxidation chemistry

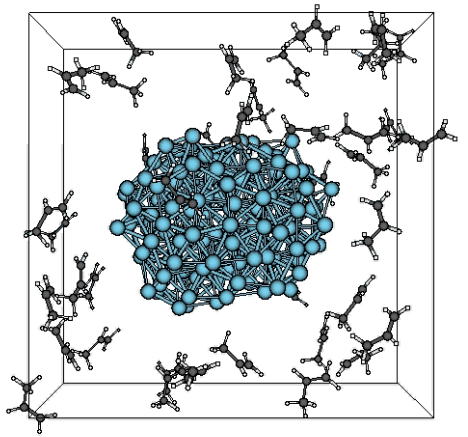


Pre-oxidized Al-tube with ethylene/O_2/ozone mixture



Fuel cell

- Higher efficiency
- Longer lifetime
- Cheaper
- Need new, cheap catalyst materials that are resistant to poisoning

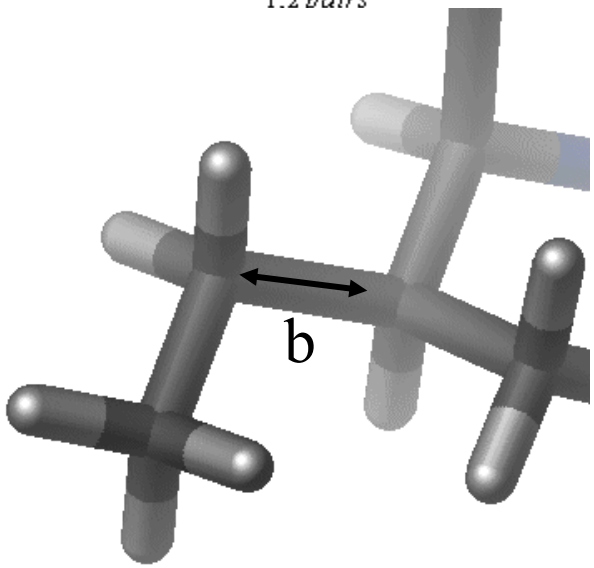


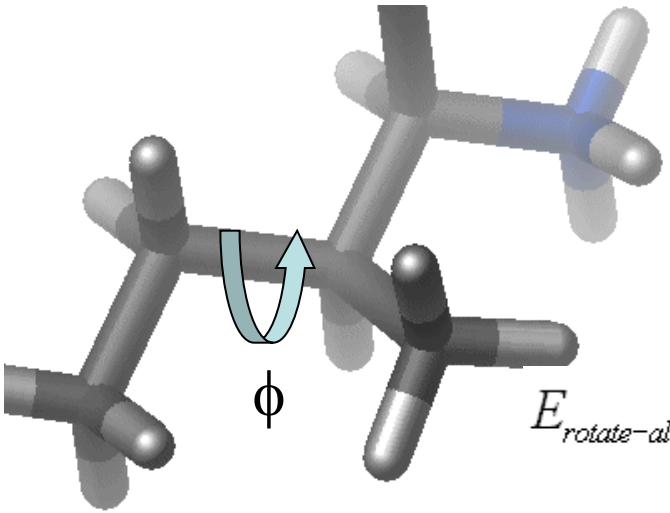
Ni-particle reacting with propene at T=1500K

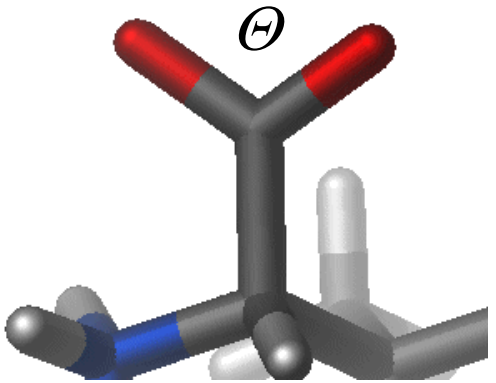
Force field methods

$$E_{bond-stretch} = \sum_{1,2\,pairs} K_b (b - b_0)^2$$

$$E_{bond-bend} = \sum_{angles} K_\theta (\theta - \theta_0)^2$$







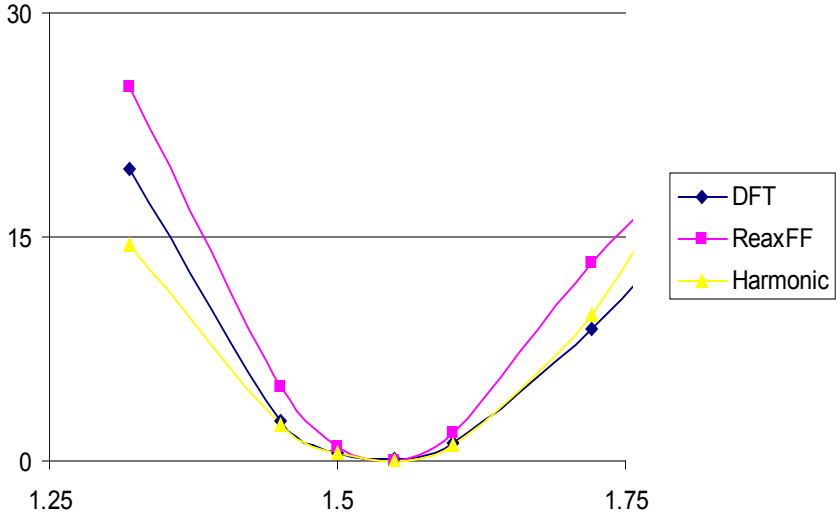
$$E_{rotate-along-bond} = \sum_{1,4\,pairs} K_\phi (1 - \cos(n\phi))$$

- Empirical, we need to derive values for the force field parameters (intuition, compare to experiment, compare to QM)
- MUCH faster than QM; can be applied to bigger systems

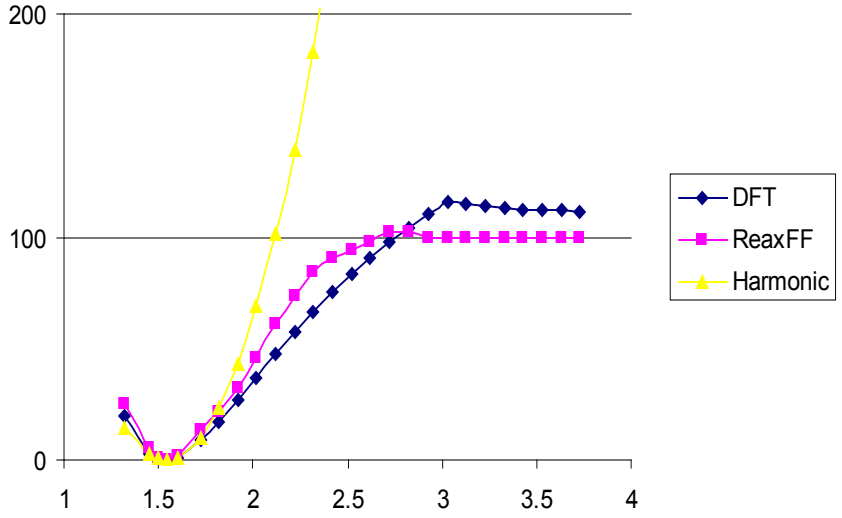
Failure of the harmonic model

C-C bond stretching in Ethane

Around the equilibrium bond length

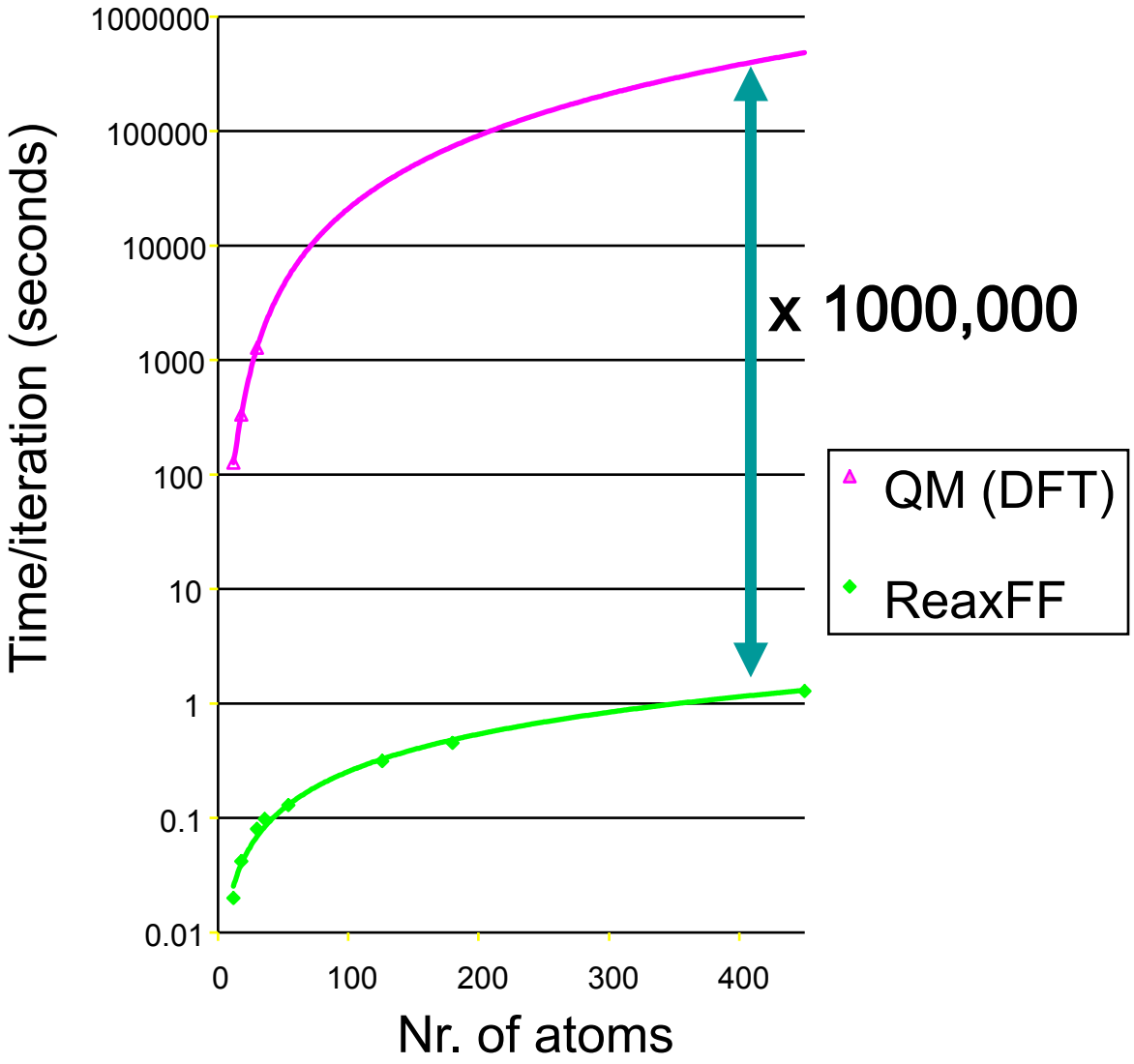


Full dissociation curve



-ReaxFF employs a bond length/bond order relationship
-All connectivty-dependent-parameters bond-length dependent

ReaxFF Computational expense



-ReaxFF allows for reactive MD-simulations on systems containing more than 1000 atoms

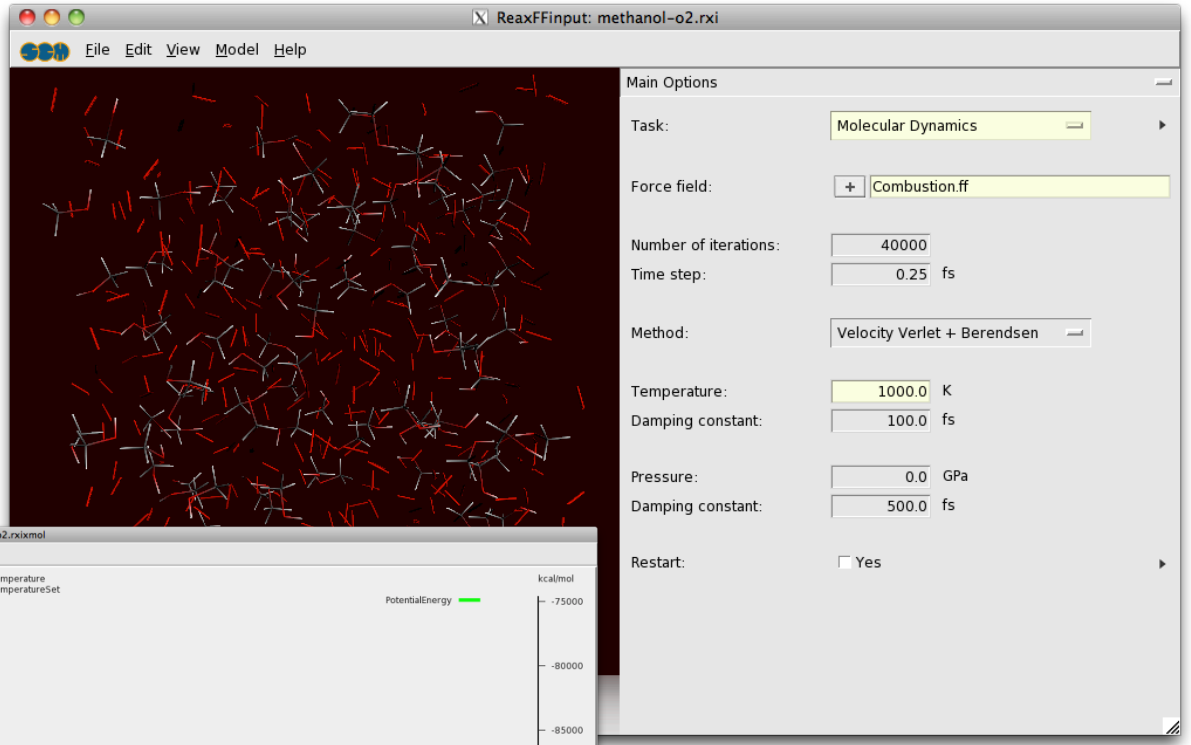
- ReaxFF is 10-50 times slower than non-reactive force fields

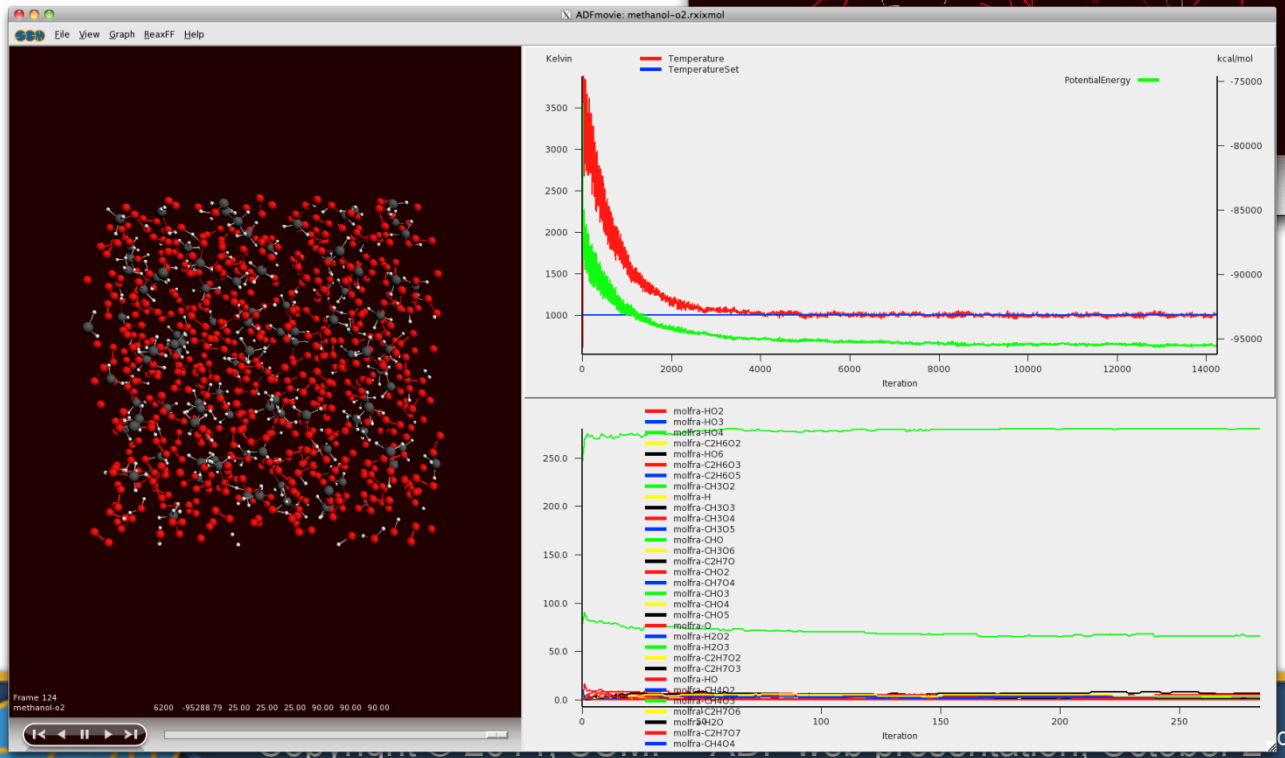
- Better scaling than most QM-methods (NlogN for ReaxFF, N^3 or worse for many QM)

ReaxFF integration into ADF with GUI

Collaboration
van Duin group – SCM

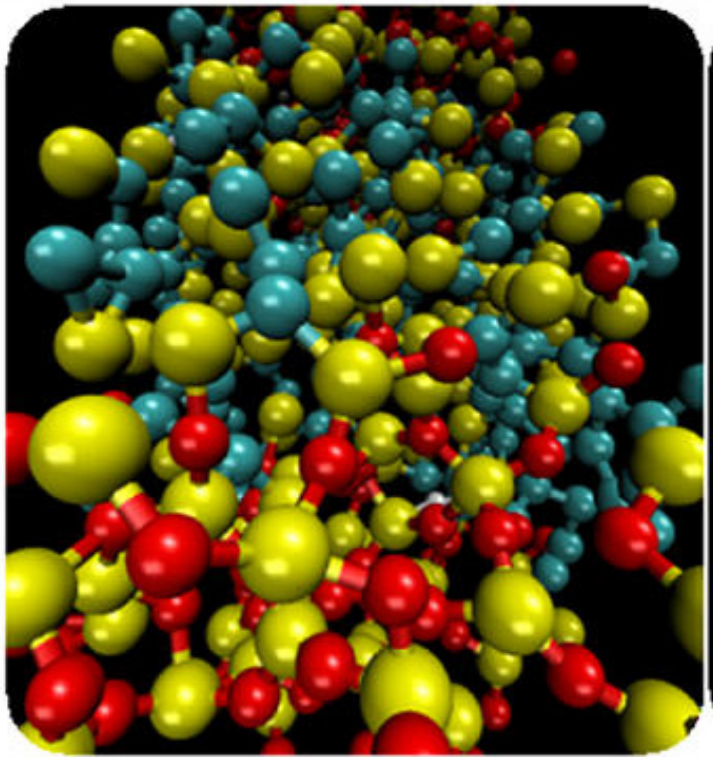
- Serial speed-ups
- Parallelization
- Remove bottle-necks

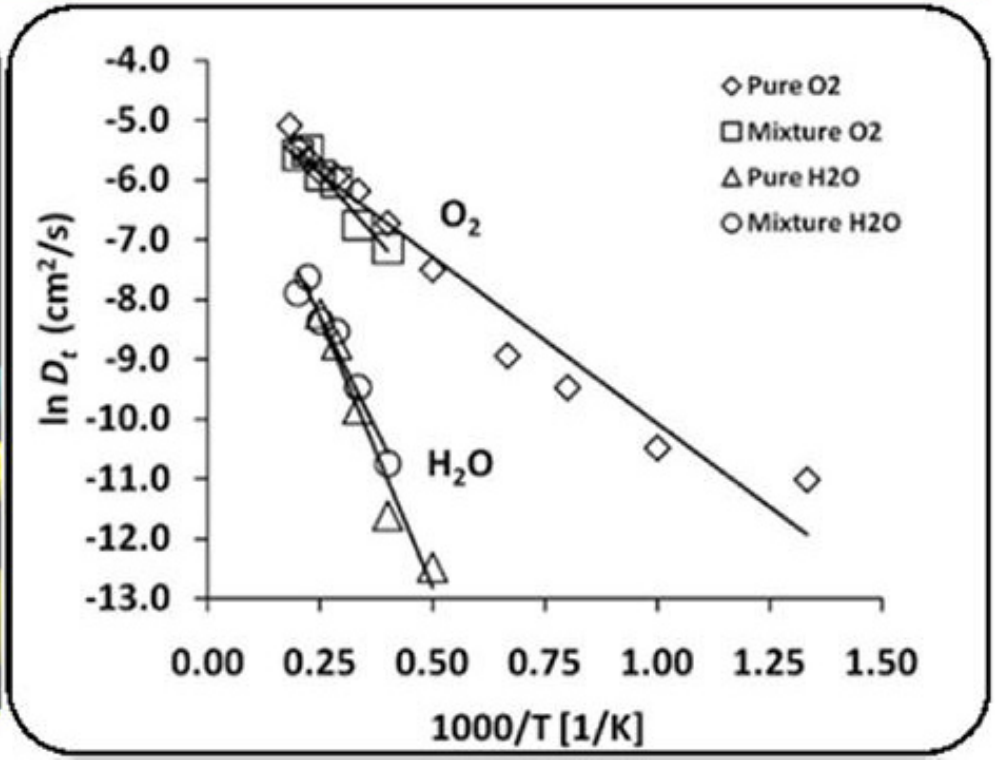




Integration team:
Olivier Visser, Alexei Yakovlev (SCM)
- Mike Russo, Kaushik Joshi (Penn State)

ReaxFF rate constants for SiC degradation





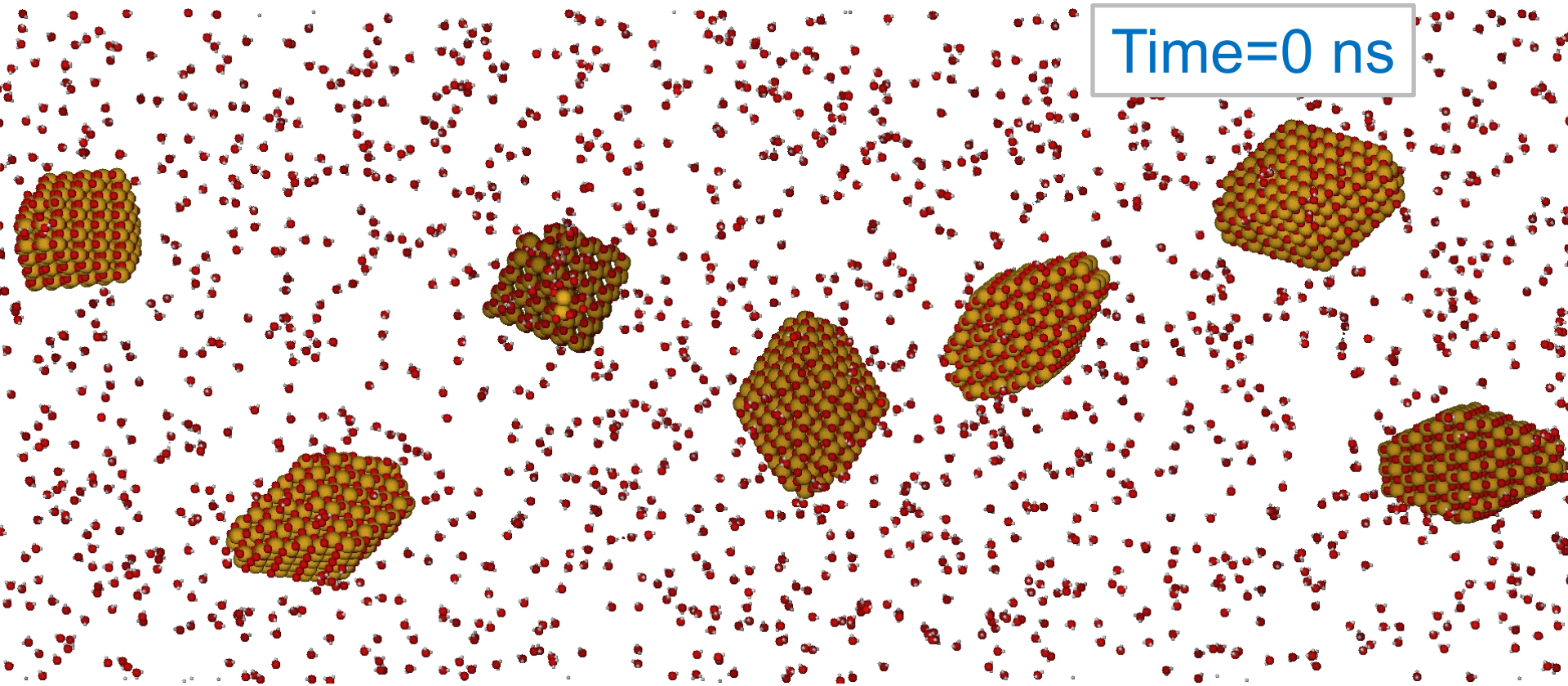
Transport barrier for oxidation:

O_2 40−70 kJ/mol

H_2O 125−150 kJ/mol

D. A. Newsome, D. Sengupta, A. C. T. van Duin, *J. Phys. Chem. C* **117**, 5014 (2013)

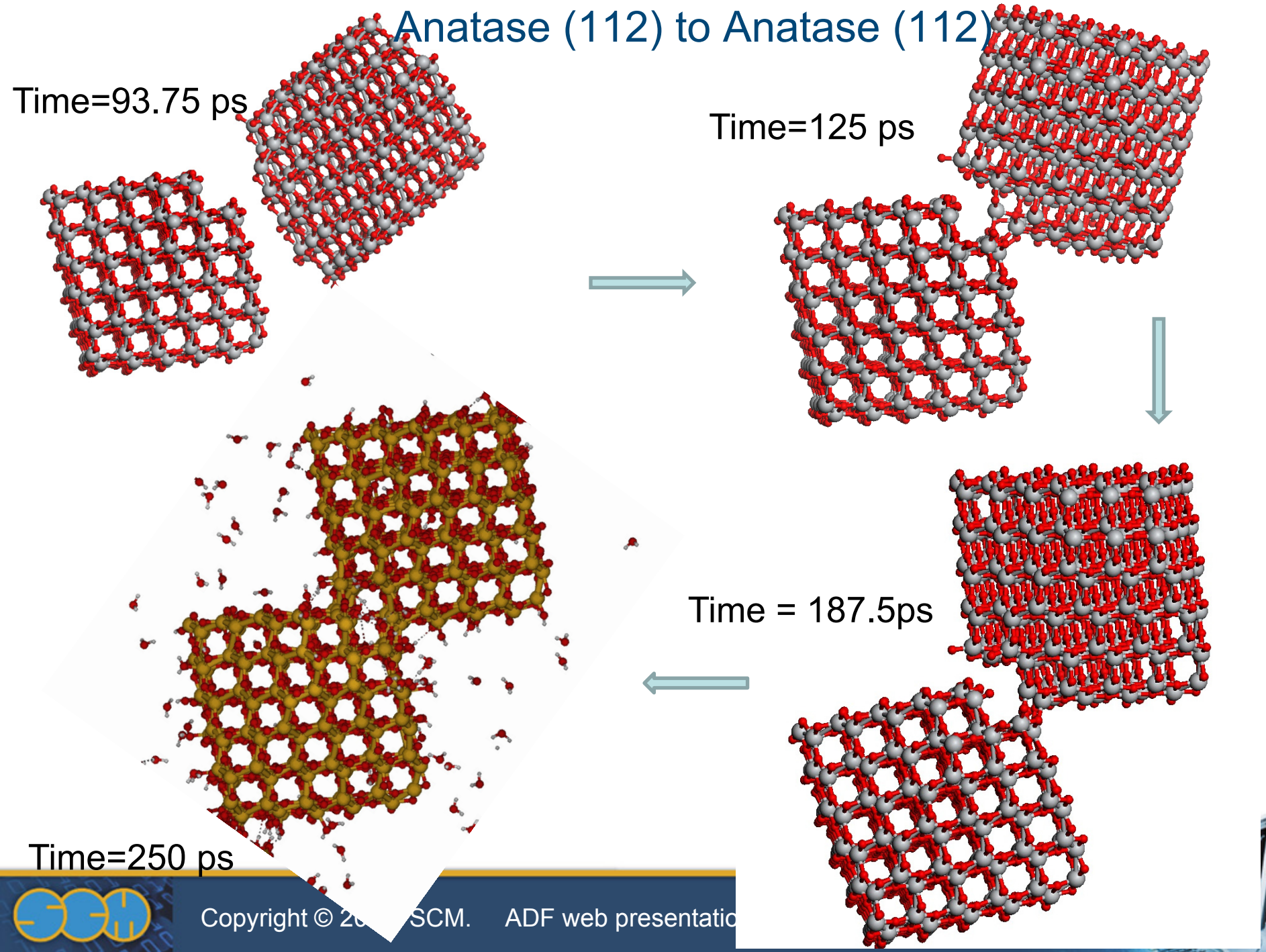
TiO_2 nanoparticle aggregation



Temperature- 1100K
Box size- 125 Å x 325 Å x 125 Å
Number of atoms- 10904
Number of Water molecules- 1800
ADF/ReaxFF; 4 processors

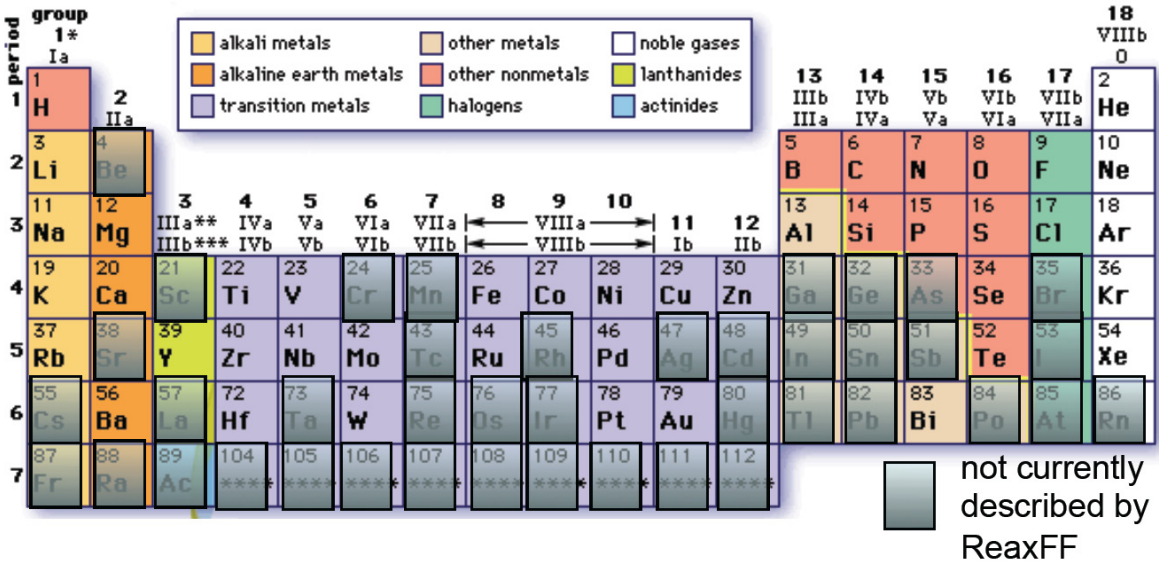
NVT simulation at 1100K
Nanoparticles and water molecules are placed randomly
no bias or restraints in the system

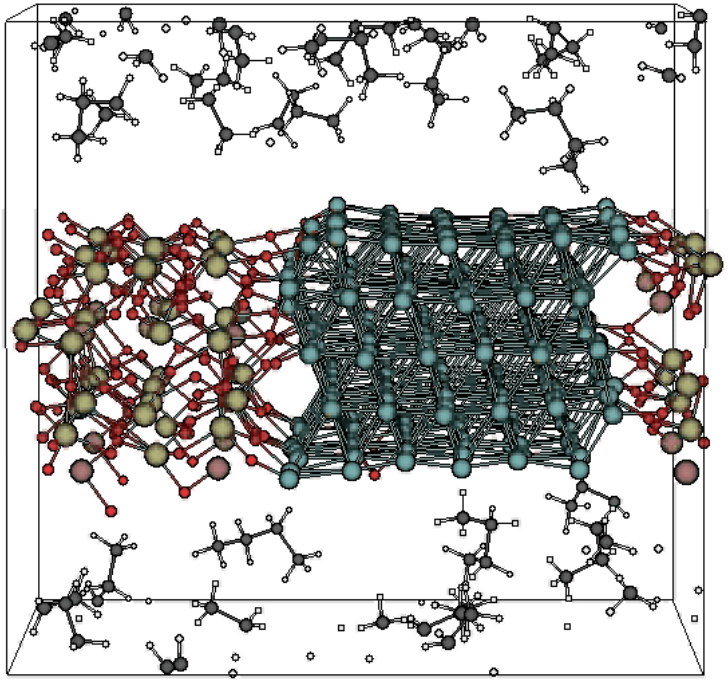
Anatase (112) to Anatase (112)



ReaxFF: Reactions in large, dynamical systems

ReaxFF transferability





YSZ/Ni/butane interface simulation at T=750K

Large part of periodic table covered, including metals
Enables dynamics studies of reactions in material science

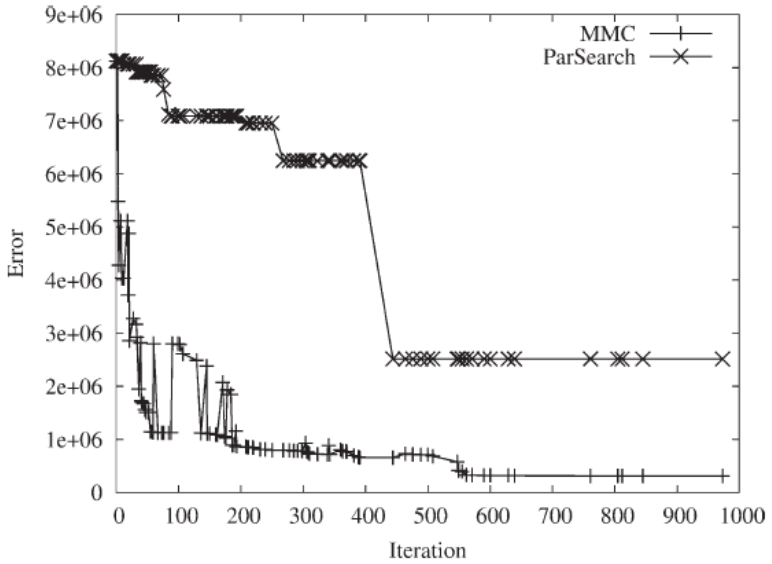
2013: 17 forcefields, 19 atom types (Al Au B C Ca Cl Cu F Fe H N Na Ni O Pt S Si V Zn)
2014: 38 forcefields, 29 atom types (Al Au B Ba C Ca Cl Co Cu F Fe H Li Mg Mo N Na Ni O P Pd Pt S Si Ti V Y Zn Zr)
Adri van Duin, Goddard, and coworkers (expanding network)
Semi-automated optimization (genetic algorithms, MMC)

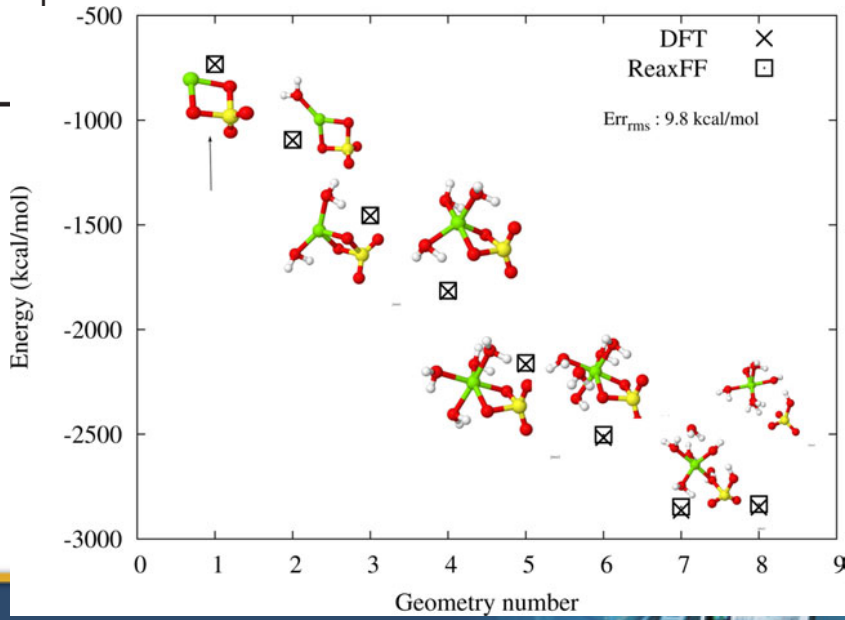
Semi-automatic parametrization: MMC-SA

Caveat: training set is important!

Table 4. Comparison of the RMS errors (kcal/mol) for the ReaxFF optimized data.

Data set	Figure	Parabolic-search	Metropolis	Metropolis (low-weightage)
$MgSO_4.xH_2O$	5	30	9.8	
Proton transfer	7	27	8.4	9.4
EOS- *$MgSO_4$*	8	70	4.8	4.5
$MgSO_4.7H_2O$ EOS-	9	80	3.4	7.0
EOS- $MgSO_4.4H_2O$	10	90	13.5	7.8
Binding energy	11	22	18.0	10.7
EOS- $MgSO_4.5H_2O$	12	51.5	41.3	



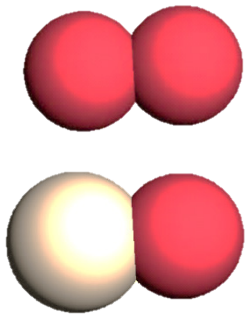


E. Iype, M. Hutter, A. P. J. Jansen, S. V. Nedea, C. C. M. Rindt,
J. Comp. Chem. **34**, 1143–1154 (2013)

New features / coming up / wish list

- Grand-Canonical Monte Carlo (Senftle, Janik, van Duin)
- Parallel Replica Dynamics + event detection
- Force biased Monte Carlo (Neyts)
- Other **accelerator** tools (QuanTis, hyperdynamics)
- FF development (Adri, Wasatch Molecular, academics)
- More advanced MD drivers; MD trajectory analysis tools

Grand Canonical-Monte Carlo + ReaxFF to Assess Activity as a Function of *T, P*



Reactants

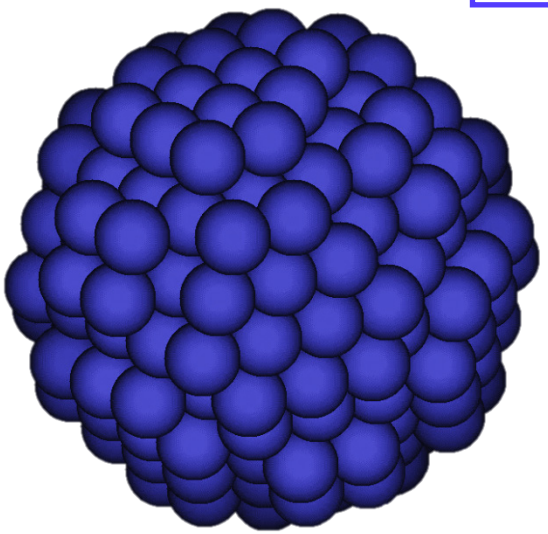
$\mu_{O_2}(T,P)$

$\mu_{CO}(T,P)$

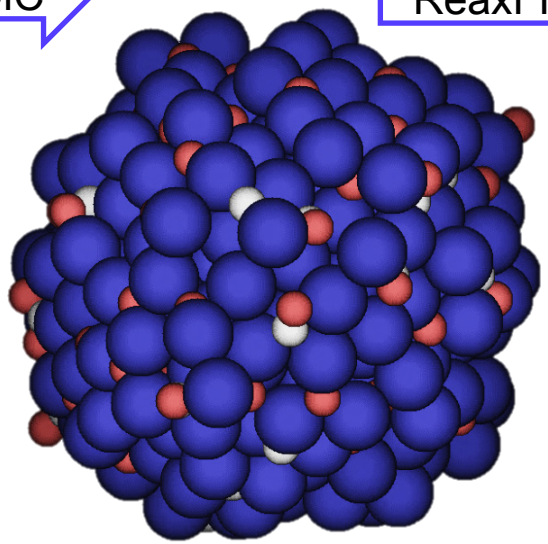
GC-MC: What is Stable?
RMD: What is Active?

GC-MC

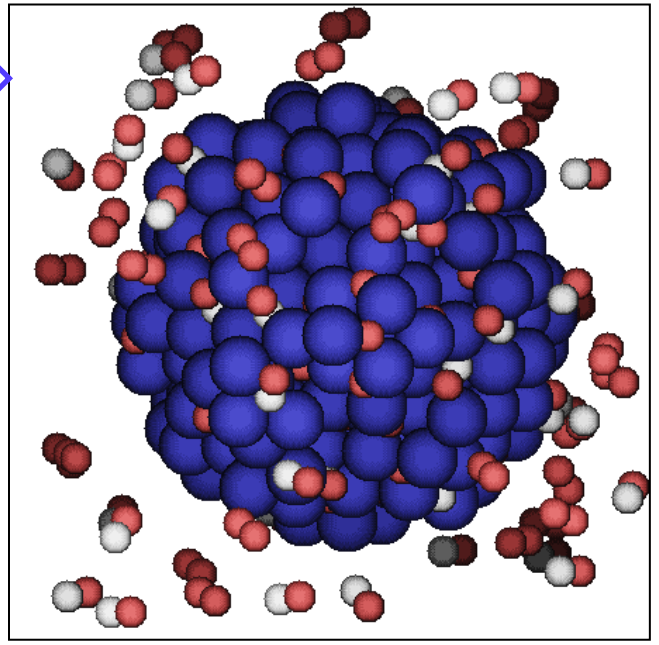
ReaxFF



Model Catalyst



Stable "In Situ" Structure



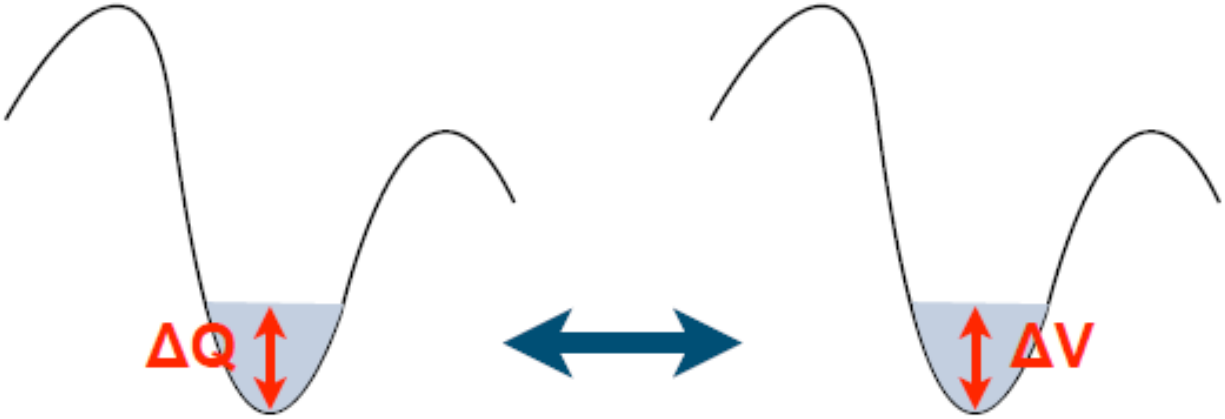
Kinetics

T.P. Senftle, R.J. Meyer, M.J. Janik, A.C.T. van Duin, *J. Chem. Phys.*, 139 (2013) 044109

Collaboration with Erik Neyts (U. Antwerpen)

Uniform Acceptance Force Biased Monte Carlo

Timonova, Groenewegen, Thijsse, Phys. Rev. B *81* **(2010)** 144107



fbMC

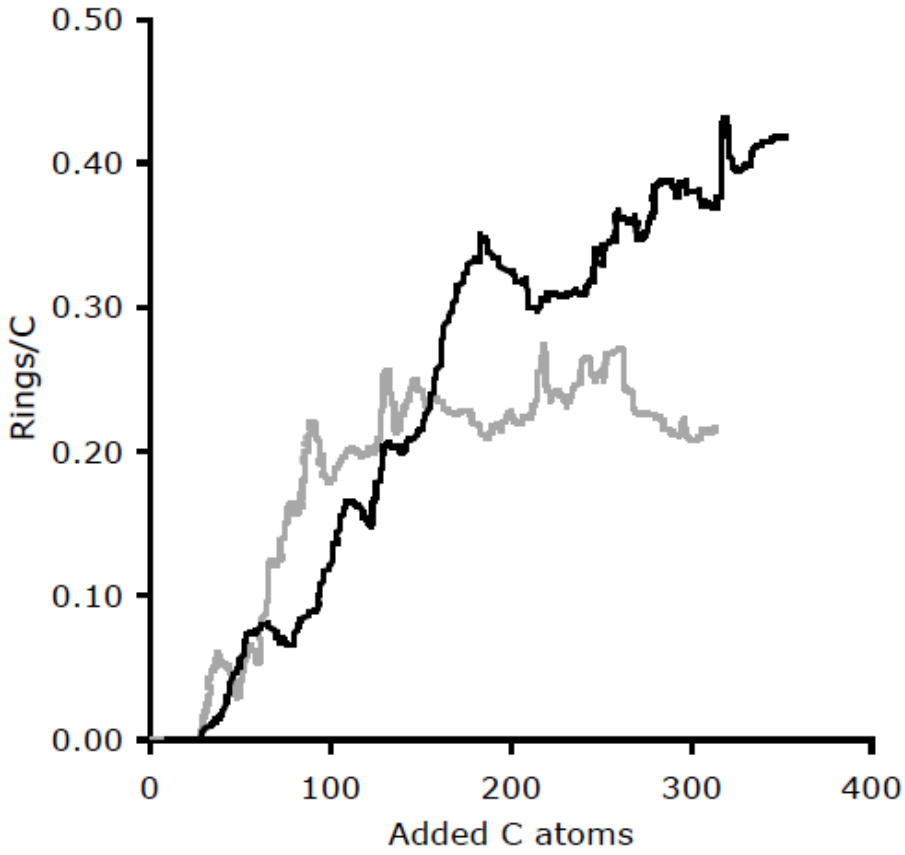
- increase of basin is consequence of atom displacements
- control over shape?
- control over height?
- time scale?

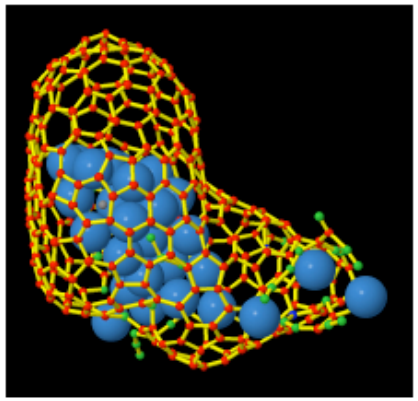
Hyperdynamics

- increase of basin is user defined
- control over shape and height
- associated time scale

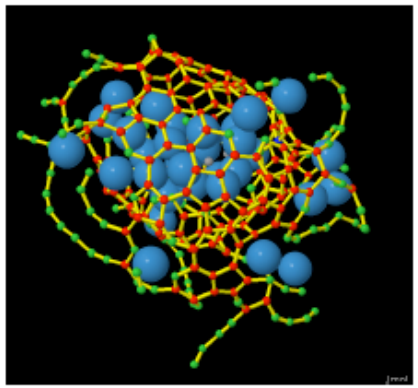
Collaboration with Erik Neyts (U. Antwerpen)

CNT growth: hybrid ReaxFF MD + fbMC



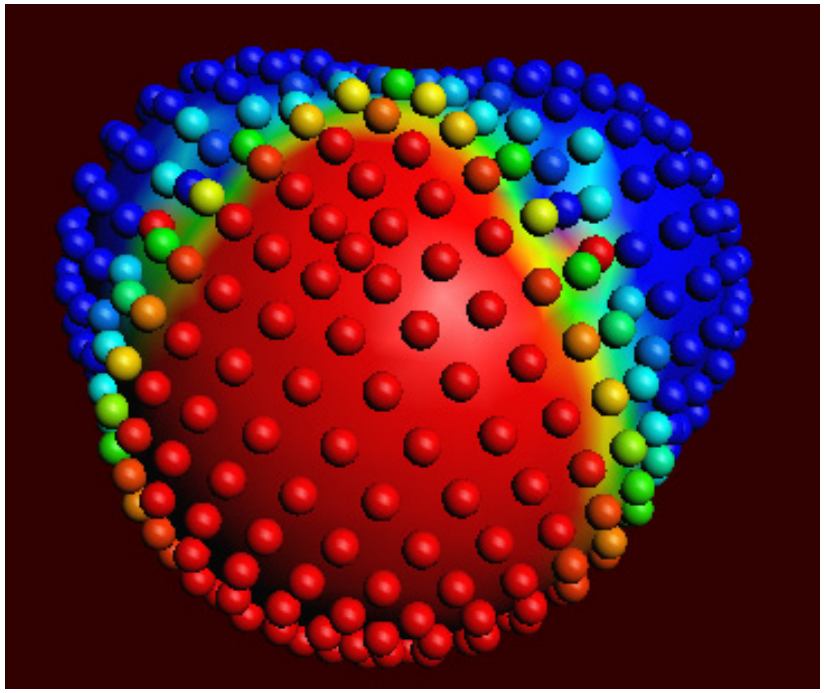


MD + fbMC



MD

E. C. Neyts, A. C. T. van Duin, A. Bogaerts, J.Am. Chem. Soc. **134**, 1256–1260 (2012)

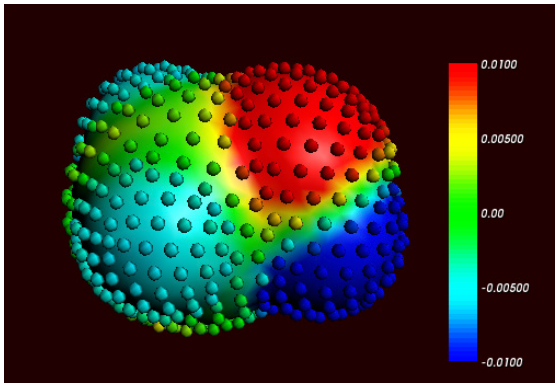


COSMO-RS

COSMO-RS (COnductor-like Screening Model for Realistic Solvents)

- *Quantum-based* (post-SCF) thermodynamic properties liquids
- Original: Dr. Klamt (J. Phys. Chem. A 102 (1998) 5074; book)
- ADF: reparametrized by Pye, Ziegler, van Lenthe, Louwen
  - 216 molecules against 642 exp. data:
  - vapor p: ~0.2 log, partition coeff.: ~0.35 log, hydration ~0.37 kcal/mol
- Instantaneous prediction of thermodynamic properties of mixed liquids:
  - activity coefficients, solvent free energies
  - excess energies for mixing G^E, H^E, TS^E
  - solubilities, partition coefficients (log P), VLE, LLE, boiling points
  - pKa
- Database of 1892 precalculated molecules, including many solvents
- Easy to calculate more compounds with ADF
- Database and COSMO-RS GUI included in license
- Also implemented COSMO-SAC and COSMO-X (to be published)

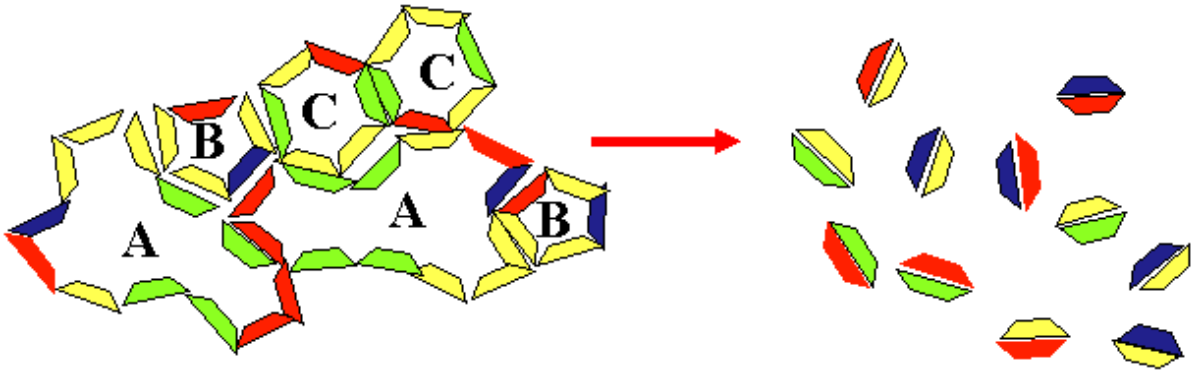
COSMO-RS



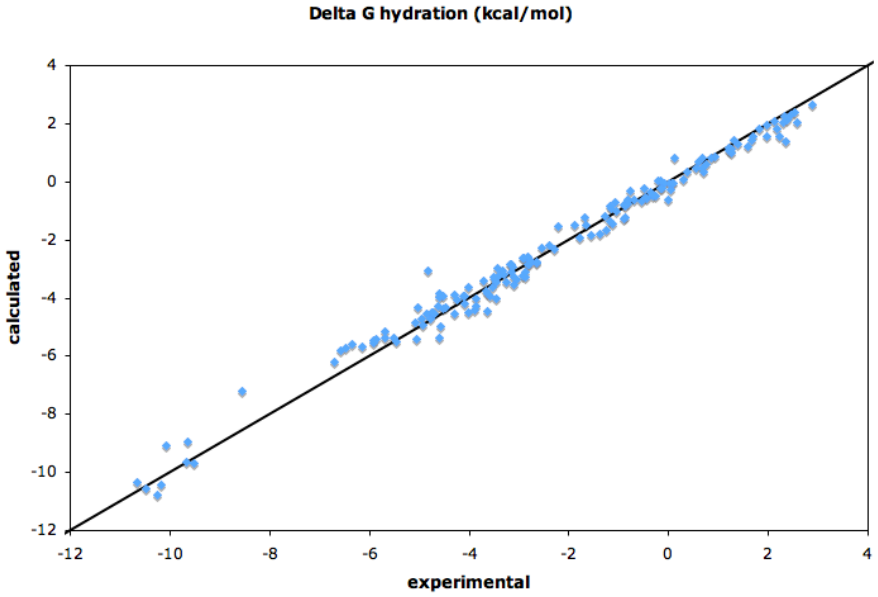
Conductor-like Screening Model for Real Solvents

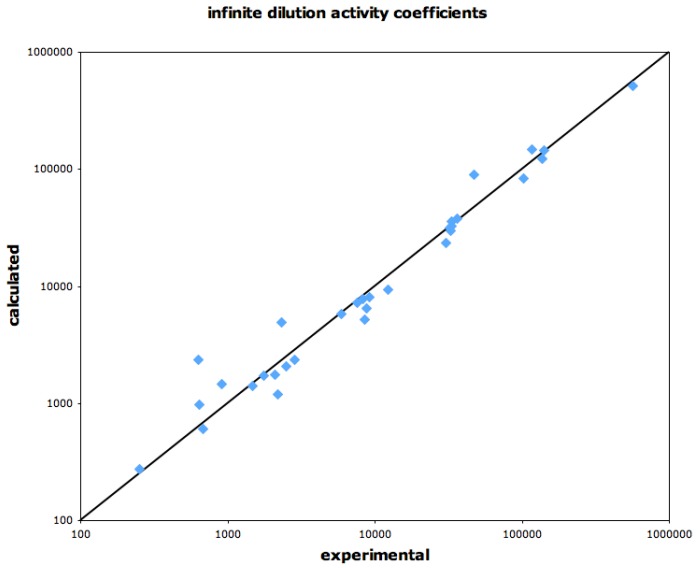
Calculation of the chemical potential

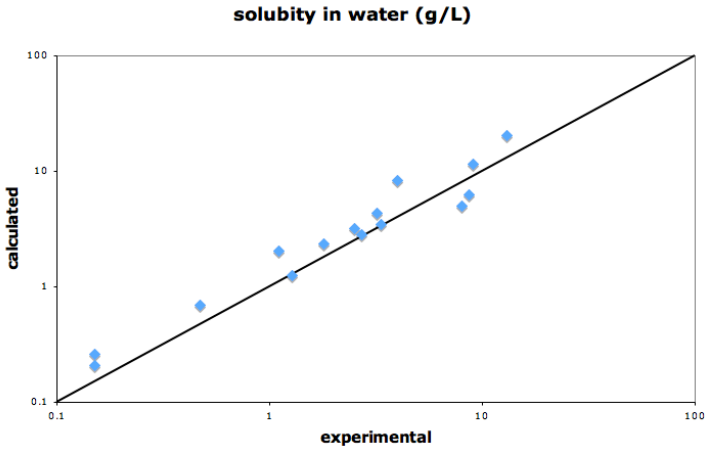
- σ-profile: charge density on COSMO (ε = ∞) surface
- pair-wise interaction between molecules
- statistical thermodynamics



Solvation energies, activity coefficients, solubility







Water is the solvent

Experimental values taken from:

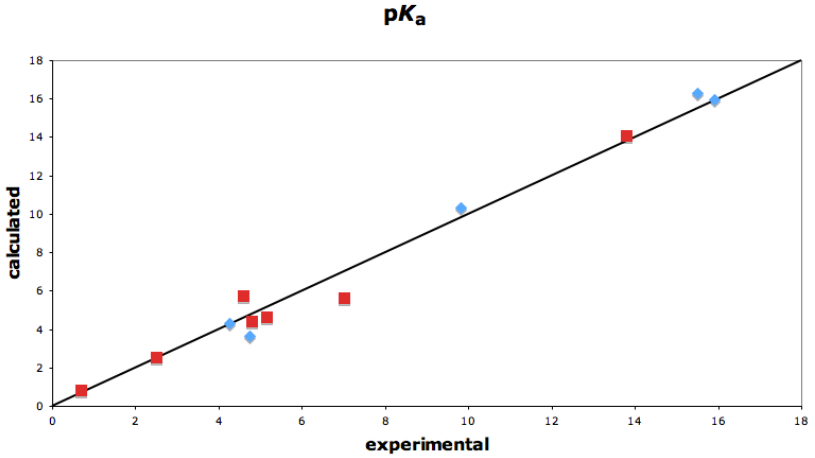
- A. Klamt et al., J. Phys. Chem. A 102 (1998) 5074
- J. Li et al., Analytical Chemistry 65 (1993), 3212
- Wikipedia

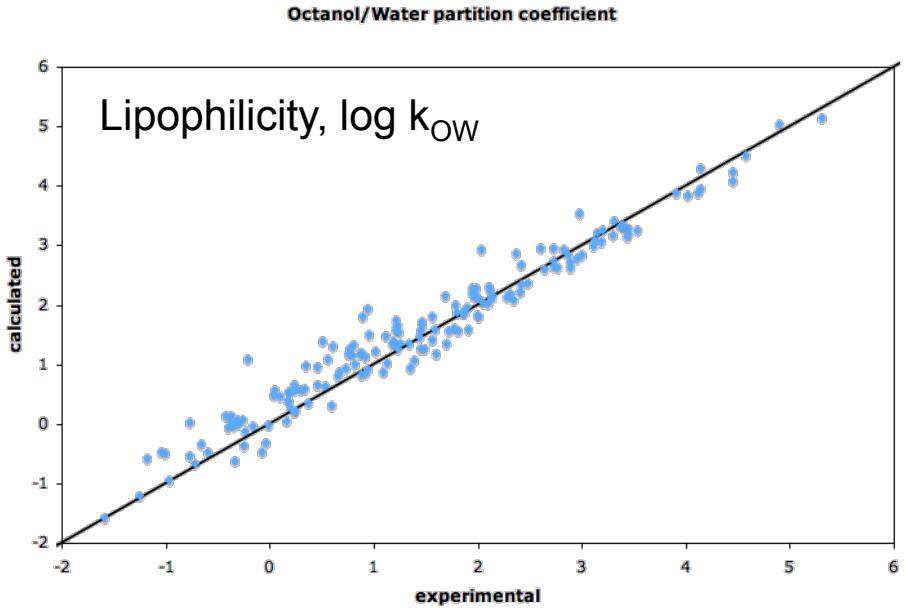
pK_a values, log p, vapour-liquid equilibrium

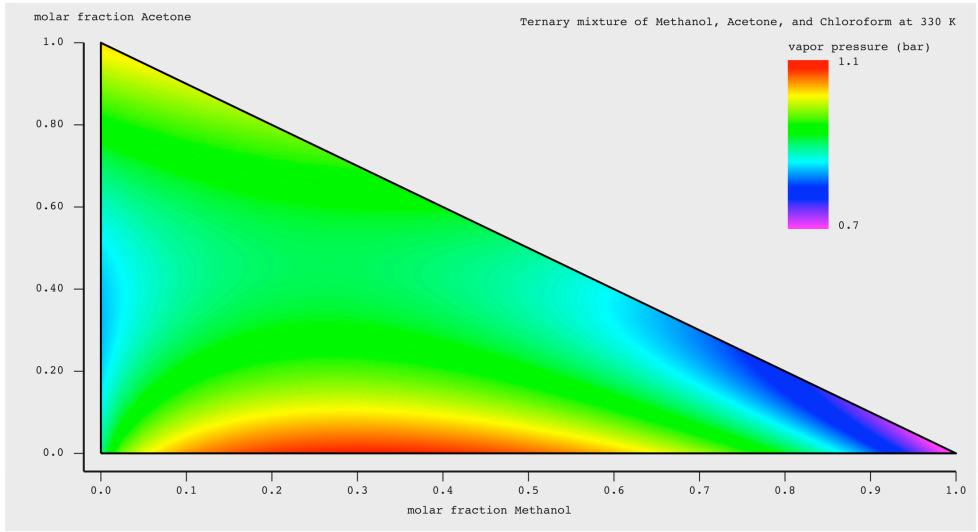
(acid) AH (aq) + H_2O (l) → H_3O^+ (aq) + A^- (aq)
(base) BH^+ (aq) + H_2O (l) → H_3O^+ (aq) + B (aq)

Empirical fitting as in Klamt Mol. Phys. 2010
different parameters used for ADF COSMO-RS

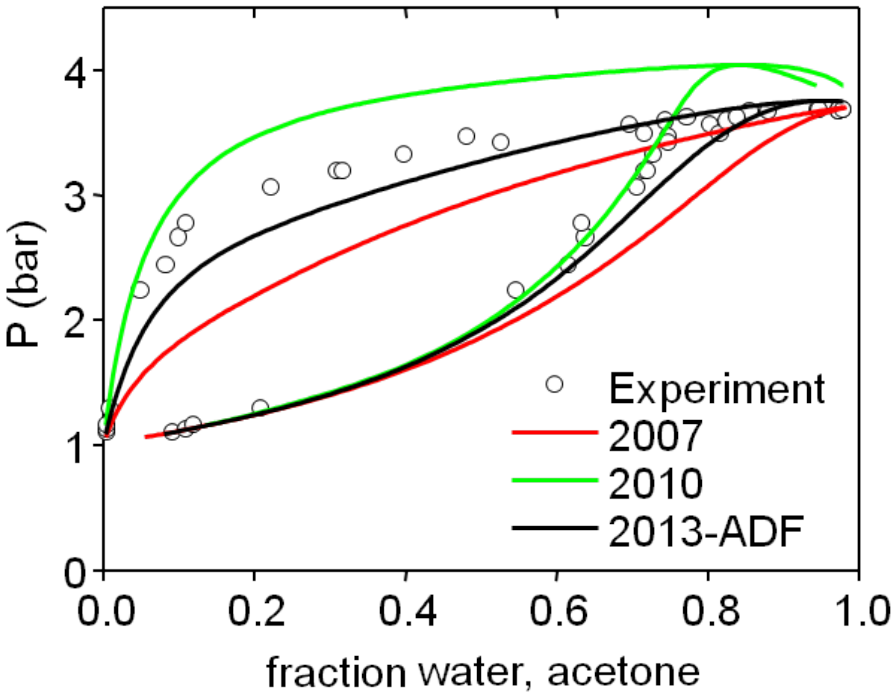
Fitting calculated Δg_{diss} against experimental pK_a
(acid) $pK_a = 0.62\ \Delta G_{diss}/(RT\ \ln(10)) + 2.10$
(base) $pK_a = 0.67\ \Delta G_{diss}/(RT\ \ln(10)) - 2.00$



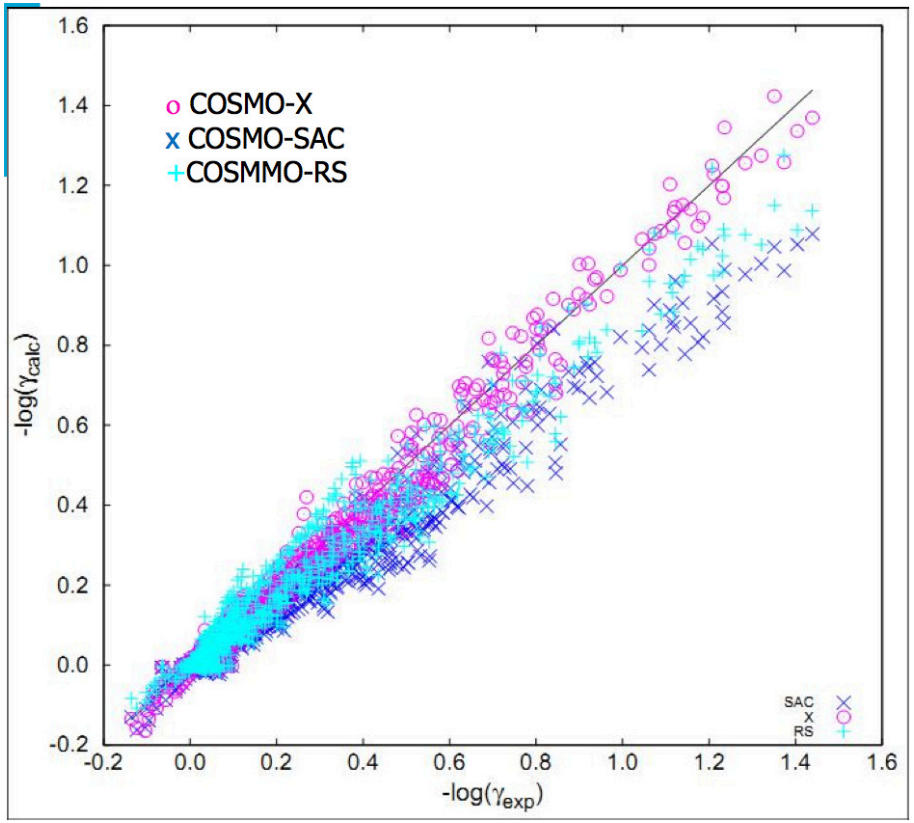




New: COSMO-SAC-2013, planned: COSMO-SAC-3D



R. Xiong, S.I. Sandler, and R.I. Burnett, *An Improvement to COSMO-SAC for Predicting Thermodynamic Properties*, Ind. Eng. Chem. Res., 53, 8265–8278 (2014).

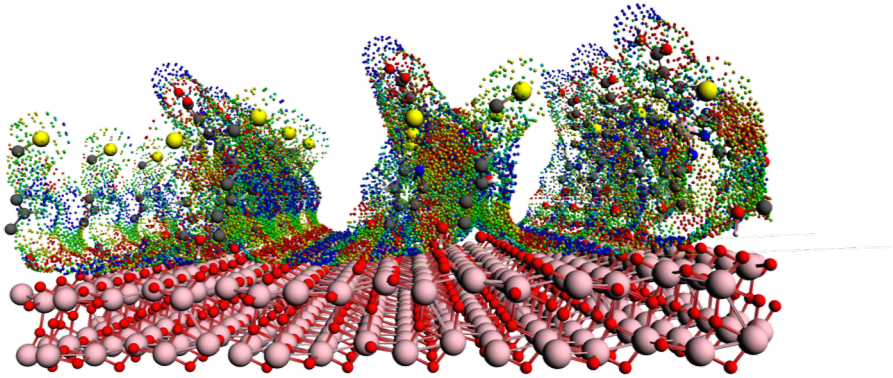


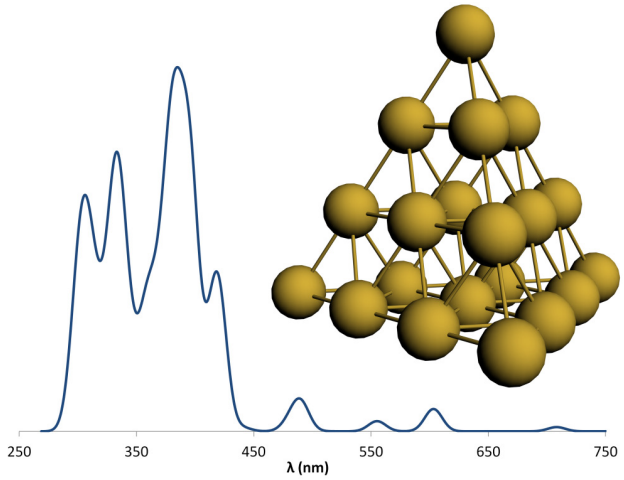
VLE data outperforms UNIFAC with less parameters, only CHO, no H-bond, includes 3D contact info

Needs writing up. Post-doc TU Delft left, now with DSM

Summary

- DFT:
  - accurate, static calcs of <1000 atoms/periodic systems
  - larger systems: QM/MM, FDE (entire proteins)
- ADF/BAND strong points: spectroscopy + relativity + analysis
- BAND unique: STO/NAO, ZORA, COSMO, E-field,





- Approximate Quantum-based
- DFTB: larger systems, ReaxFF: reactive molecular dynamics limited by parameters - work in progress to automate
- COSMO-RS: thermodynamic properties fluids and solutions

NEXAFS (SO-TDDFT): V_2O_5 catalyst

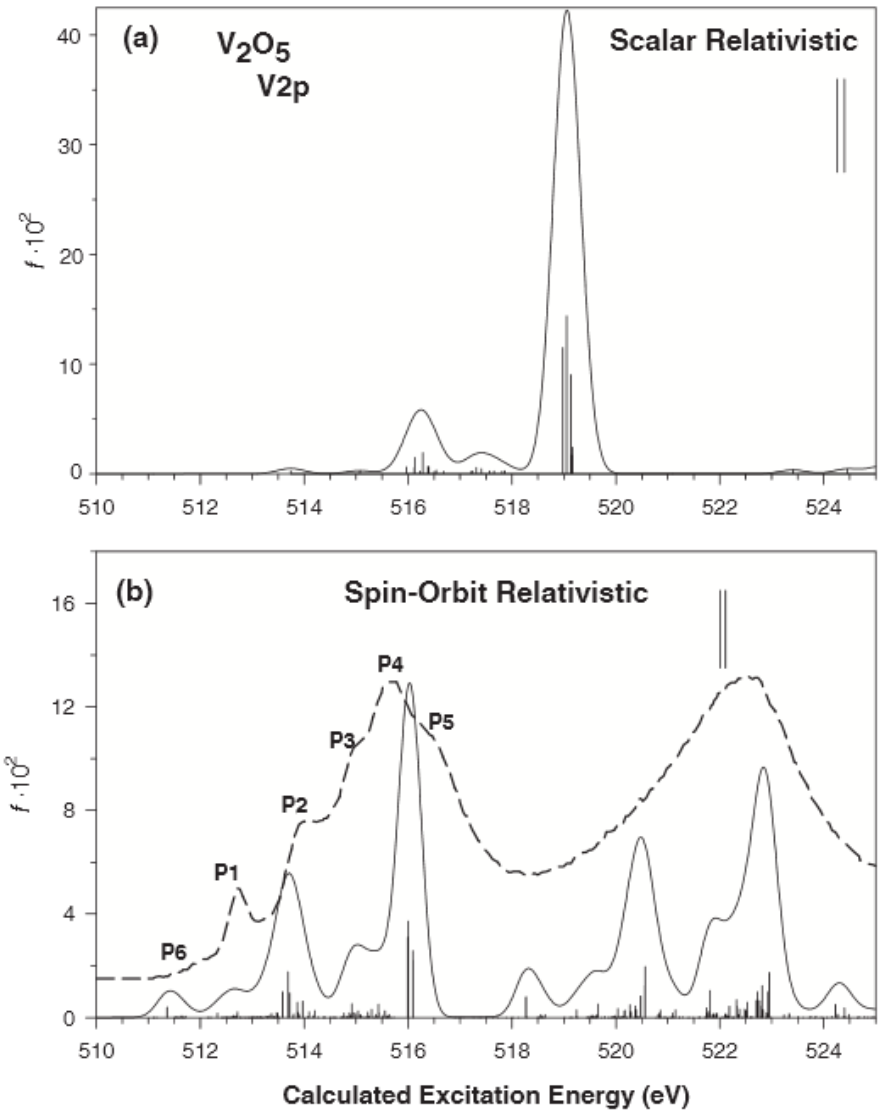
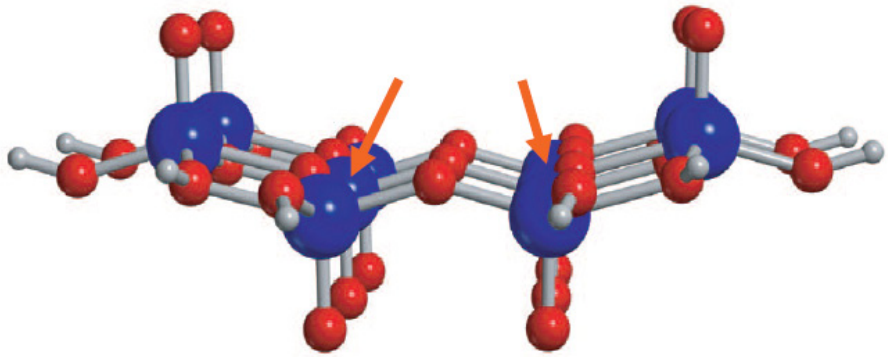


FIG. 3. TDDFT V $L_{2,3}$-edge excitation spectra of V_2O_5 obtained with $V_{10}O_{31}H_{12}$ cluster from scalar-ZORA TDDFT (upper panel) and two-component ZORA TDDFT (lower panel) calculations. Convoluted profiles are obtained with a fixed Gaussian broadening (FWHM = 0.5 eV). The vertical lines show the calculated L_3 ionization limits. (Lower panel) Dashed line shows the experimental spectrum from Ref. 3.

$V_{10}O_{31}$



G. Fronzoni, R. de Francesco, M. Stener
J. Chem. Phys. **137,** 224308 (2012)