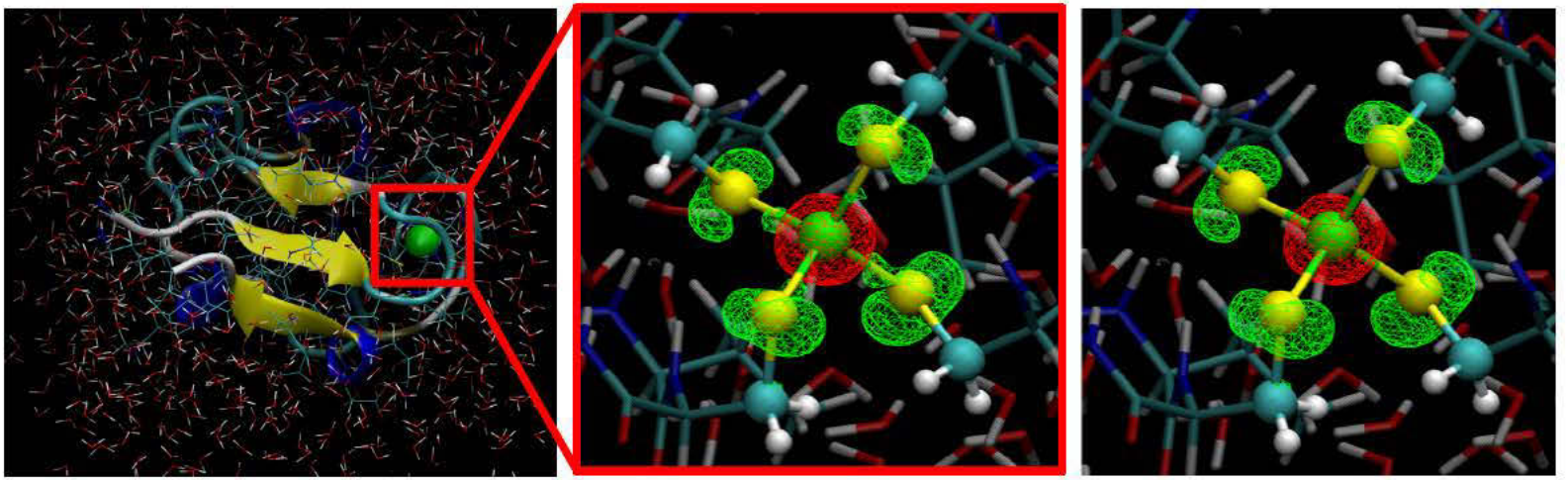
Large scale DFT based Molecular Dynamics in the condensed phase



Standard hybrid

ADMM based hybrid

The DFT model: a solvated protein

- 48'000 cores
- 1. SCF step: 45 min

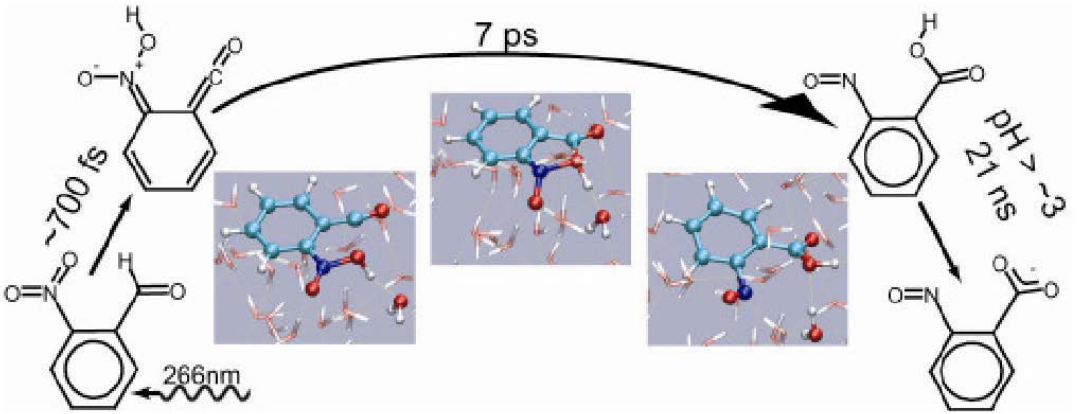
- 1'152 cores
- 1. SCF step: 75 s

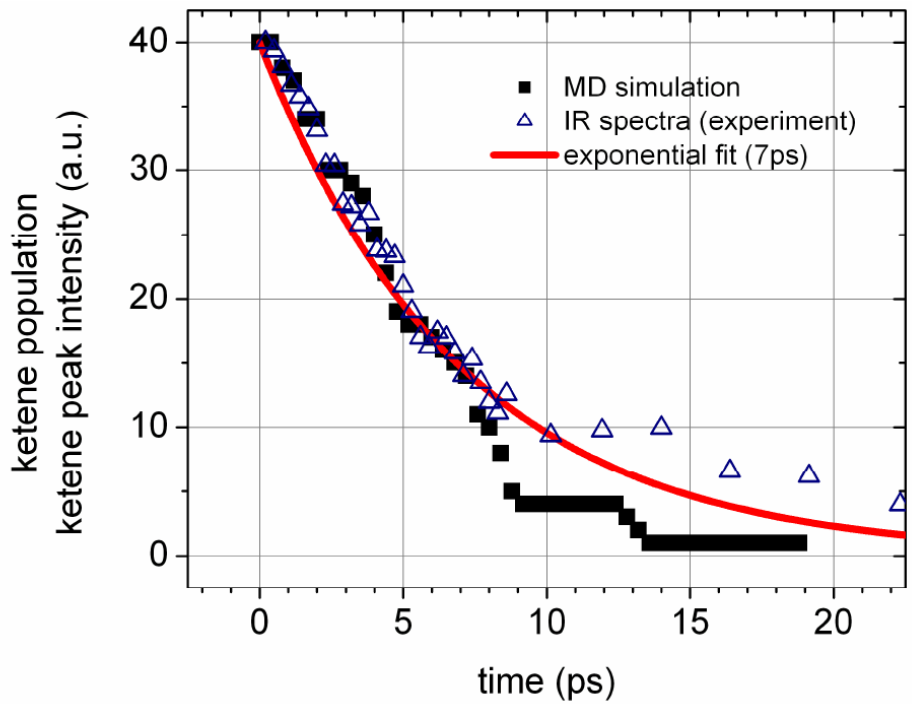
Joost VandeVondele
Nanoscale Simulations, ETH Zurich

Ab Initio Molecular Dynamics

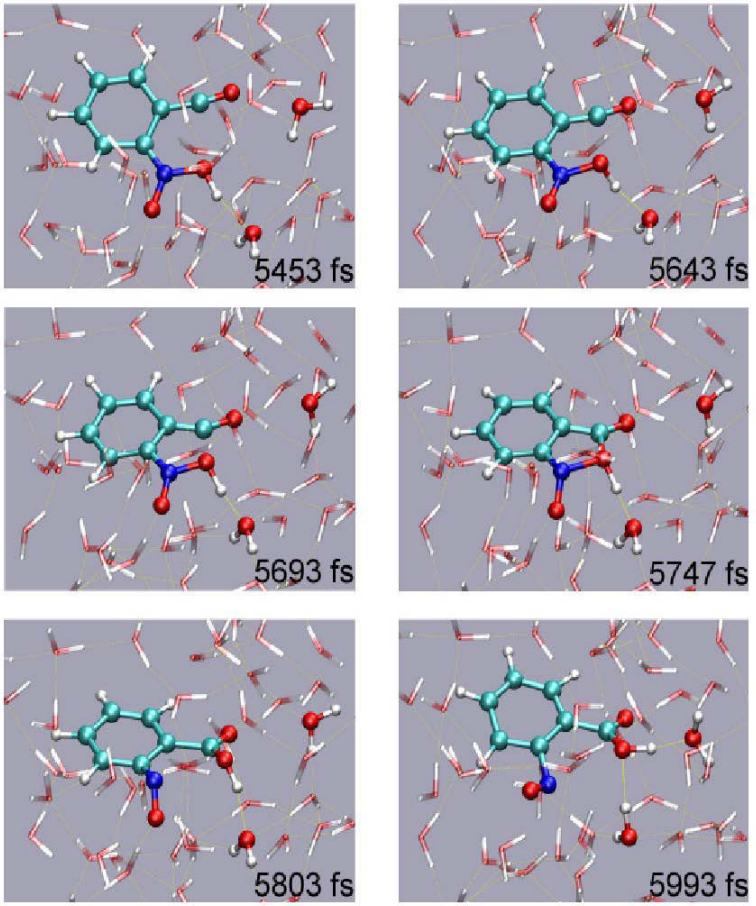
- Molecular Dynamics
  - Classical equations of motion for the ions: F=ma
  - NVE and other ensembles (NVT, NPT)
  - Crucial for systems including liquids
- 'Ab Initio' or 'First Principles'
  - Forces on atoms derive from a non-empirical description of the electronic structure
  - 99% DFT

An chemist's example: oNBA



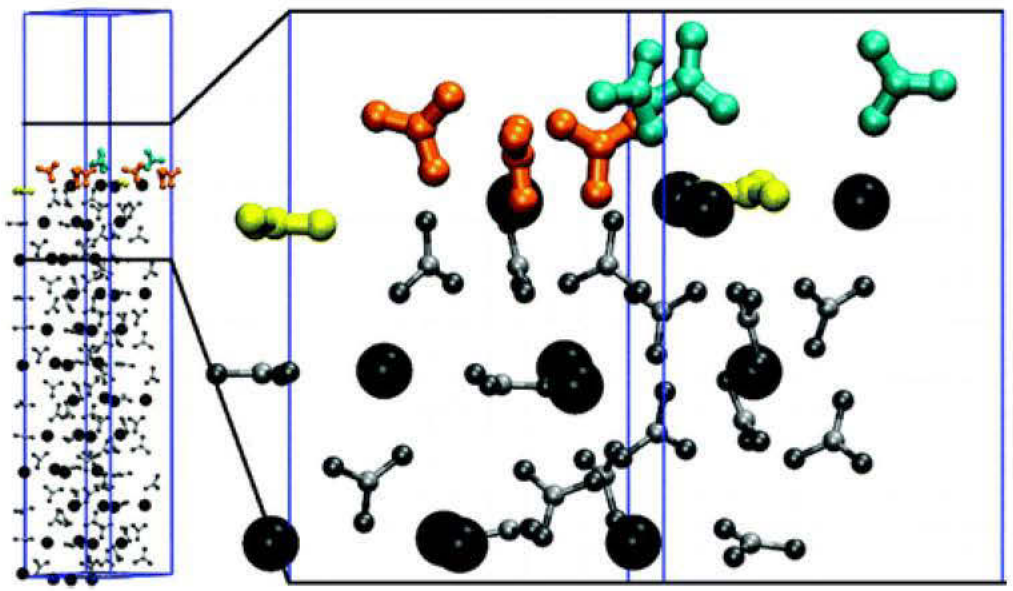


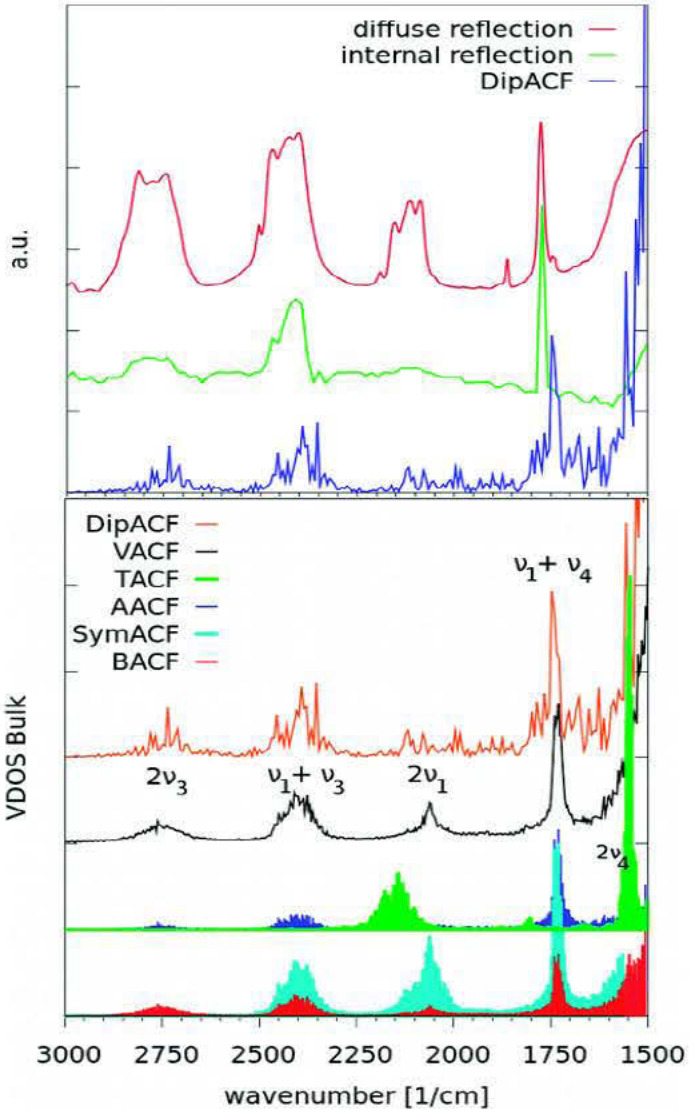
ortho-
Nitrobenzaldehyde



Donten M; Hamm P; VandeVondele J; JPC B 115(5): 1075-1083 (2011)

Solids: spectroscopy at interfaces



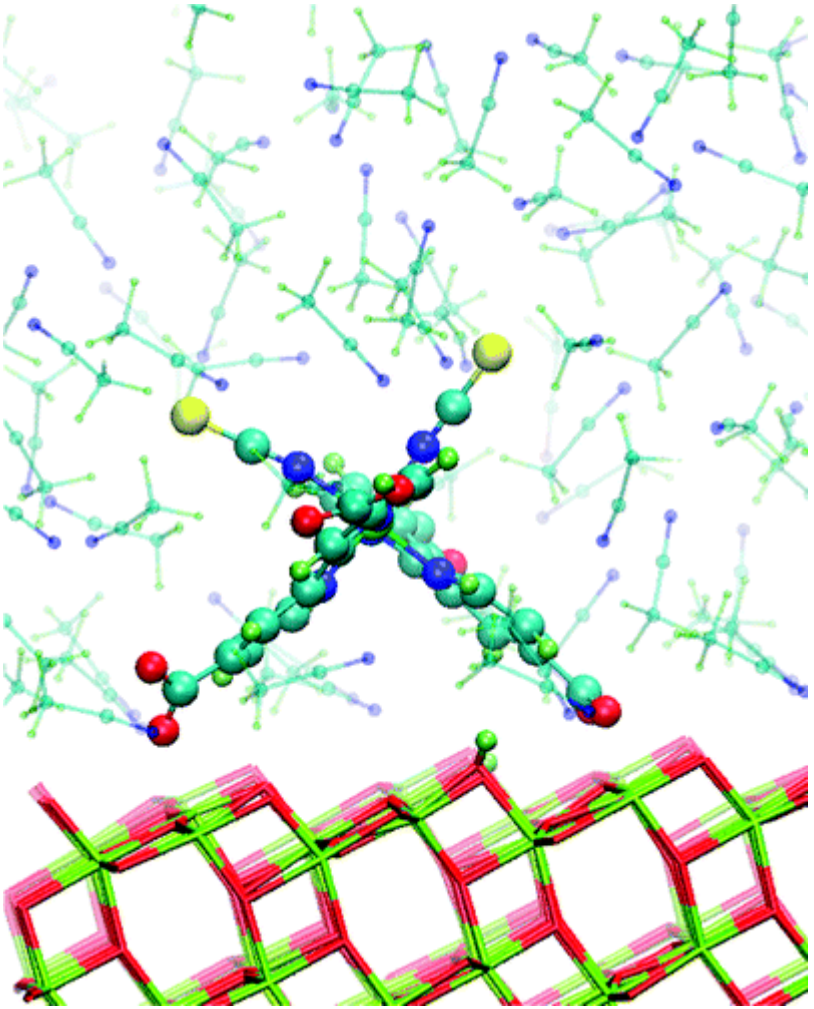


BariumNitrate (Ba(No3)2) :
a catalyst for automotive applications (NO_x)

Ab initio MD can be used to capture non-harmonic effects
Such as overtones and combination bands.

Hesske, Urakawa, VandeVondele, Baiker, J. Phys. Chem. C, 2010, 114 (35), pp 15042–15048

Interfaces at ambient conditions



We want to build and study models that realistically include solids, liquids, molecules

An example interface, as found in Dye sensitized solar cells.

Schiffmann, VandeVondele, Hutter, Wirz, Urakawa, Hutter, baiker, J. Phys. Chem. C, 2010, 114 (18), pp 8398–8404

AIMD is GGA dominated

In order for AIMD to be practical,
the SCF + forces (BOMD) need to be computed
in O(60sec) for typical systems O(100 atoms)

20000 MD steps of 0.5 fs * 60sec / step = 2 weeks for 10 ps

- Highly efficient schemes for GGAs are needed
- Highly robust methods are essential

AIMD is for short timescales

10ps – 100ps is the typical lengthscale of AIMD

- Only very fast processes can be observed spontaneously
- Activated events (reactions) or slow dynamics (diffusion) need more advanced techniques
  - Free energy methods (constraints, enhanced sampling, etc... needed).

Efficient GGA DFT

CP2K

Gaussian and plane waves: GPW in CP2K

- Primary basis: Gaussians → Chemistry
  - compact
  - sparse H^{ks} (and P)
  - Many terms analytic
- Auxiliary basis: Plane waves → Physics
  - regular grid for e^- density
  - FFT for Poisson equation
  - No four center integrals needed

The GPW algorithm : compute the GGA Kohn-Sham matrix in O(N) time, PBC are natural.

J. VandeVondele, M. Krack, F. Mohamed, M. Parrinello, T. Chassaing and J. Hutter, Comp. Phys. Comm. 167, 103 (2005).
Lippert, G; Hutter, J; Parrinello, M. Mol. Phys., 92 (3), 477-487 (1997).

Basic Computational local DFT

$$n(r)=\sum_{\mu\nu} P^{\mu\nu}\varphi_\mu(r)\varphi_\nu(r)$$

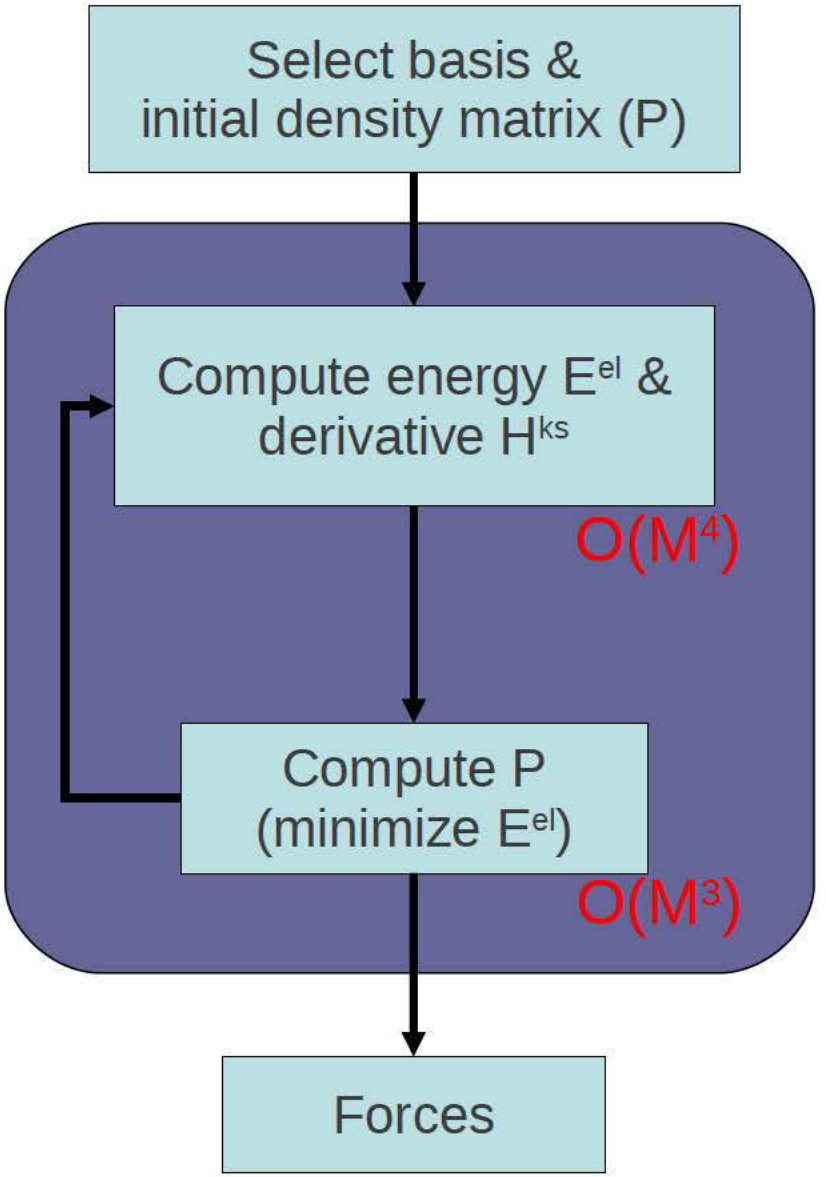
$$E^{el}[P^{\mu\nu}]=\sum_{\mu\nu} P^{\mu\nu}\int \varphi_\mu(r)(-\frac{\Delta}{2})\varphi_\nu(r)$$

$$+\sum_{\mu\nu} P^{\mu\nu}\int\int \varphi_\mu(r)V^{PP}_{sep}(r,r')\varphi_\nu(r')$$

$$+\frac{1}{2}\int\int \frac{n(r)n(r')}{|r-r'|}$$

$$+\int n(r)\varepsilon_{xc}[n](r)$$

Formally O(M⁴) → O(M) with GPW



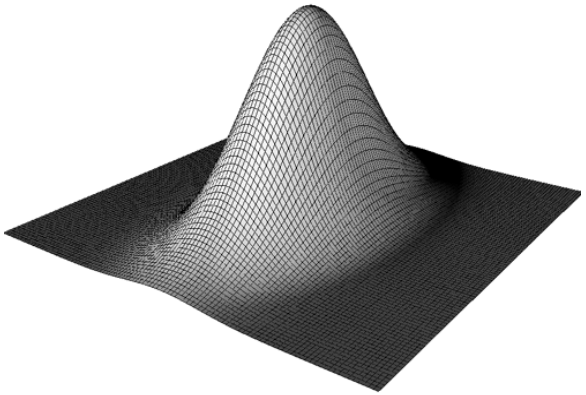
A closer look at GPW

Real space (rs) density mapping and integration
Fourier space (FFT) for the coulomb problem

Only a linear number of terms have a non-zero contribution to the sum.
Each term affects only a constant volume in space

O(N)

$$\sum_{\mu\nu} P^{\mu\nu}\varphi_\mu(r)\varphi_\nu(r) \underbrace{\Rightarrow}_{RS} n(r) \underbrace{\Rightarrow}_{FFT} n(G)$$



$$\Rightarrow V_H(G)=\frac{4\pi n(G)}{G^2}, \quad E_H=\Omega\sum_G n^{cc}(G)V_H(G) \underbrace{\Rightarrow}_{FFT} V_H(r)$$

$$\underbrace{\Rightarrow}_{RS} V_{\mu\nu}=\int V_H(r)\varphi_\mu(r)\varphi_\nu(r)$$

A Gaussian basis allows for a very efficient procedure to compute the density on the grid

Orbital transformations (OT)

A cubic, very robust algorithm avoiding the of traditional diagonalization

- New variables

$$C(X) = C_0 \cos\left(\sqrt{X^T S X}\right) + X \frac{\sin\left(\sqrt{X^T S X}\right)}{\sqrt{X^T S X}}$$

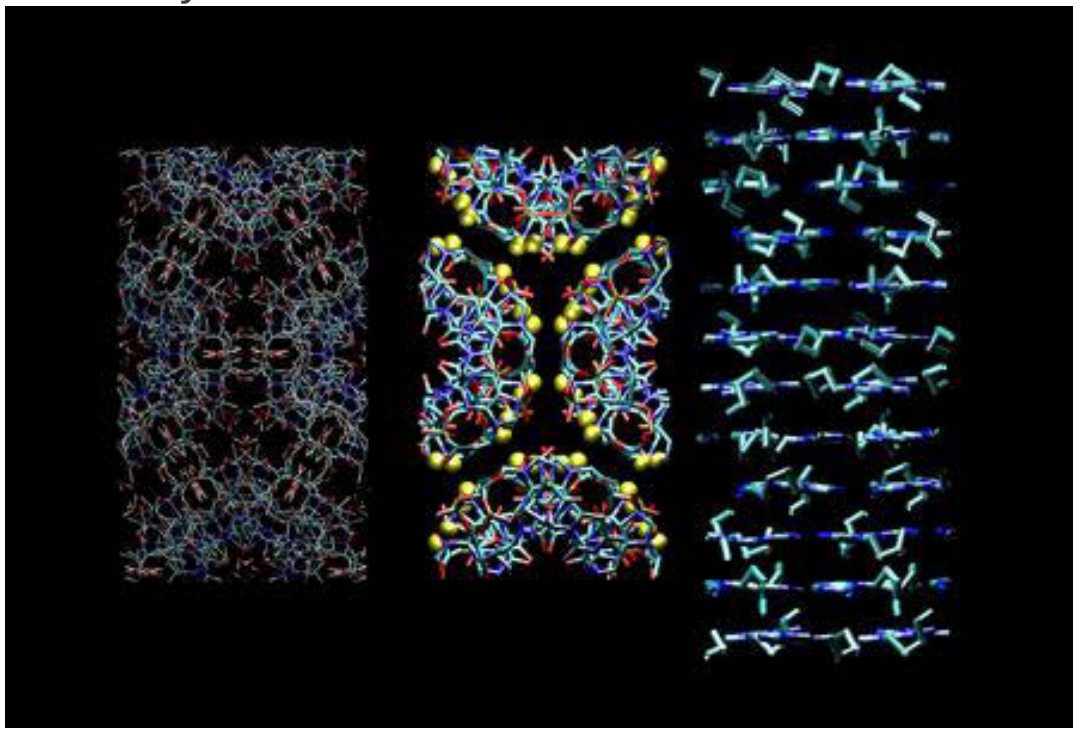
$$X^T S C_0 = 0 \qquad C(X)^T S C(X) = 1 \;\; \forall \; X$$

- Direct minimization of $E_{ks}[\{X\}]$
- Linear constraint -> guaranteed convergence!

J. VandeVondele, J. Hutter, *J. Chem. Phys., 2003,* Vol. 118 No. 10, 4365-4369

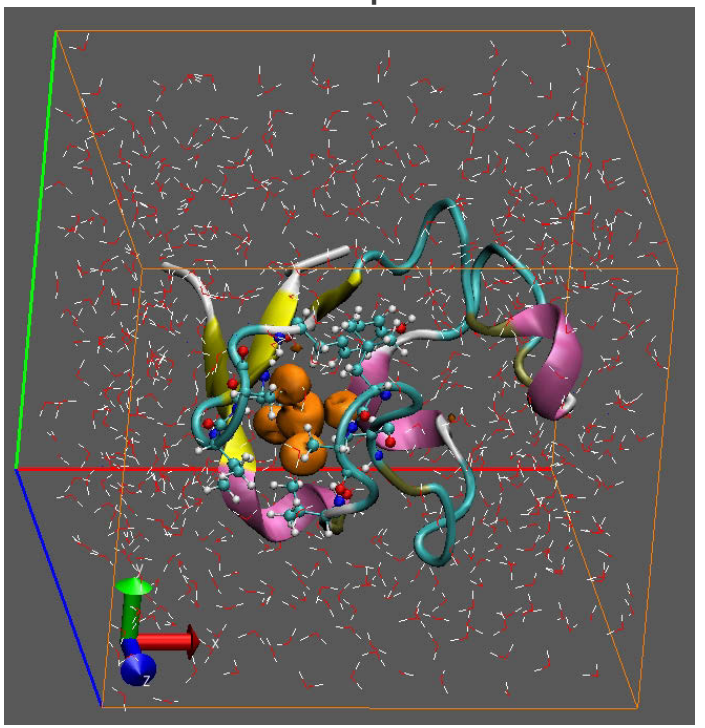
DFT for large systems

DNA crystal



2388 atoms

Solvated metallo-protein



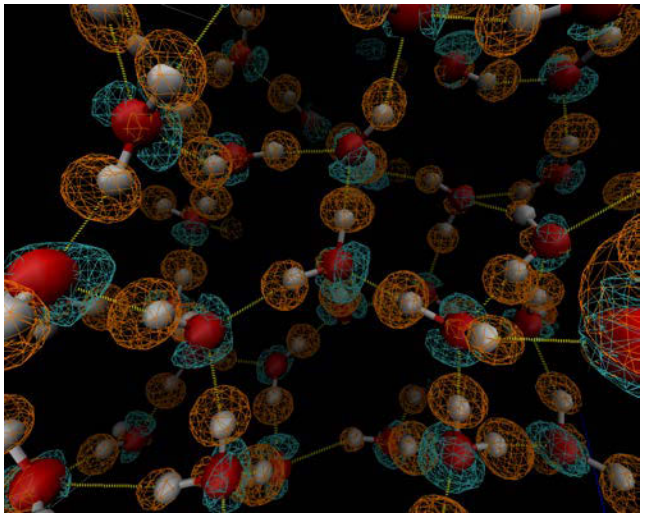
2825 atoms

Linear scaling construction of the Kohn-Sham matrix,
robust and efficient O(N^3) electronic minimization
Parameter free & out-of-the-box for H-Rn

J. VandeVondele, J. Hutter, JCP 118, 4365-4369 (2003).
Sulpizi, M.; Raugei, S.; VandeVondele, J.; Carloni, P.; Sprik, M. JPCB 111, 3969 (2007).

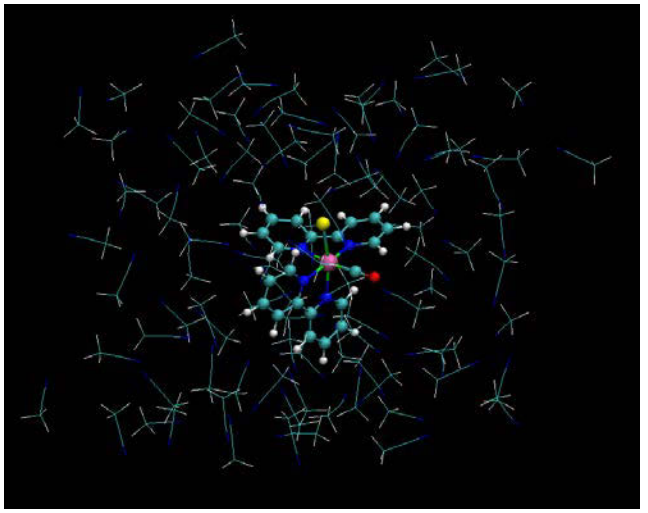
Robust Ab initio MD

'Simple' liquids



Hydrogen bonding in H_2O

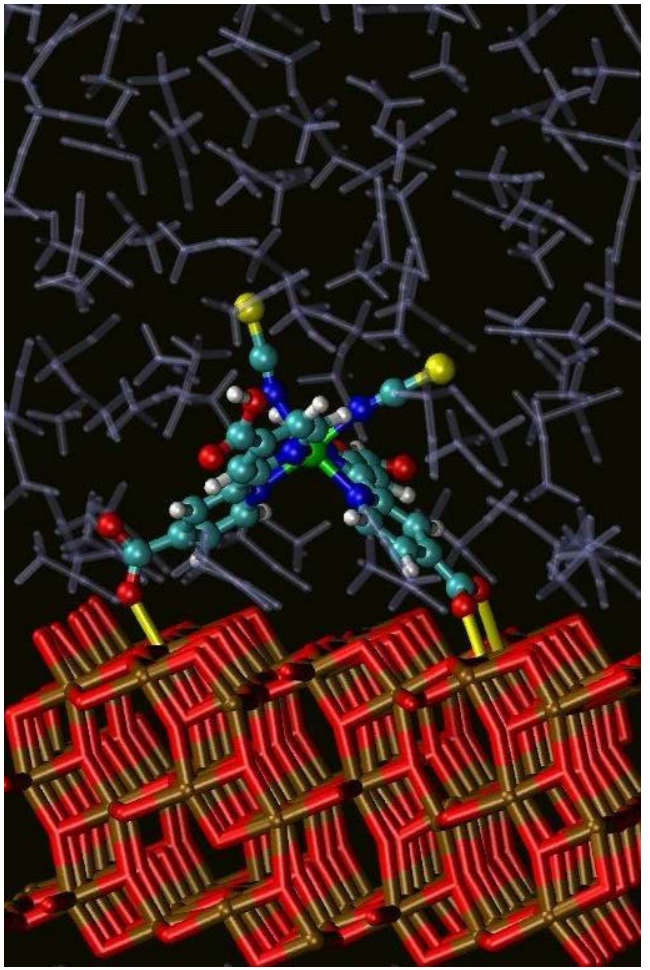
Solutes in explicit solvent



$Ru(bpy)_2COCl$ in acetonitrile, $[21.43Å]^3$ or 620 Atoms

e.g. Redox properties

Complex Interfaces

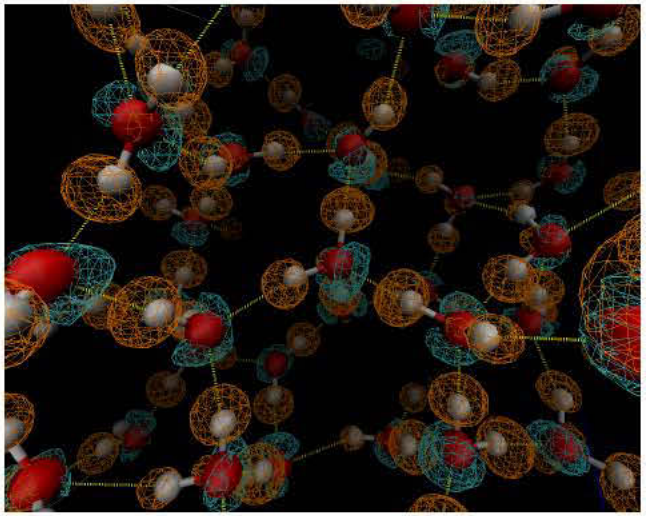


In situ IR spectroscopy (1300 atoms)

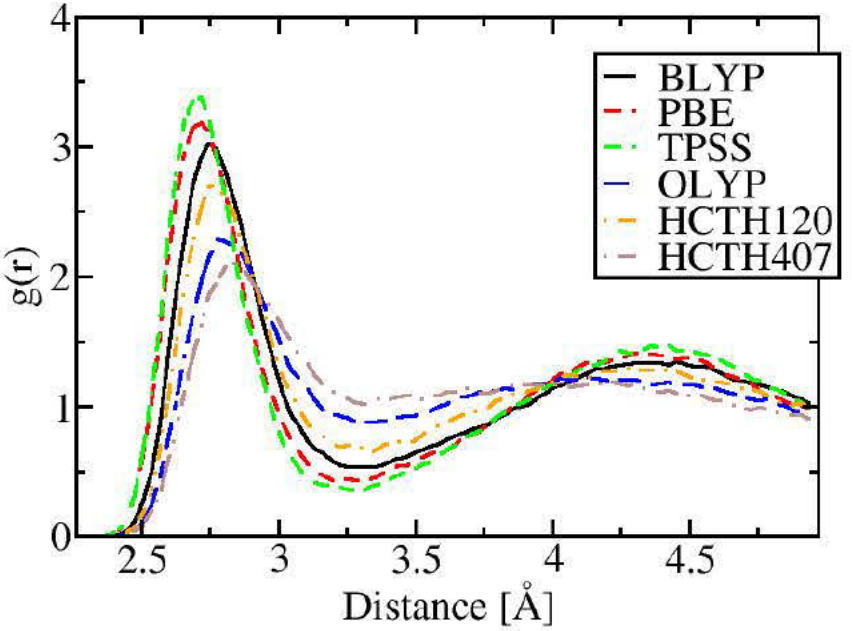
Water: the most important liquid

In depth investigation of the performance of DFT for liquid water

Hybrid functionals



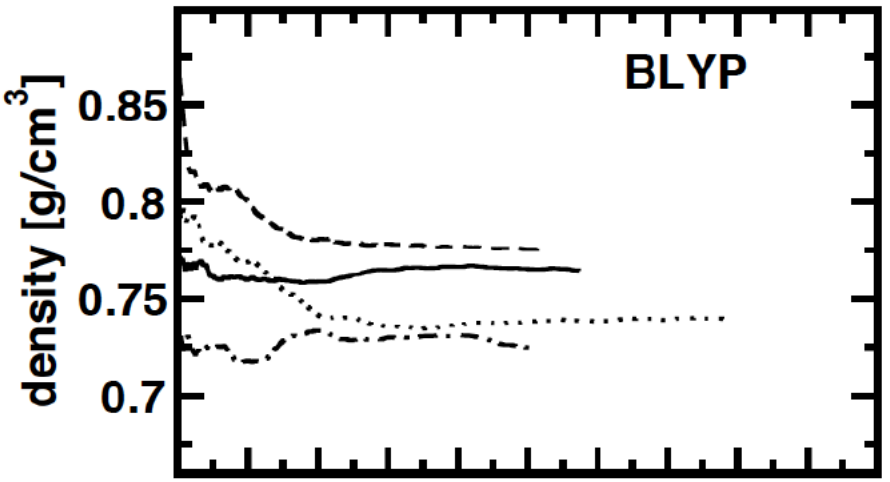
local functionals



J. VandeVondele, F. Mohamed, M. Krack, J. Hutter, M. Sprik, M. Parrinello, J. Chem. Phys. 122, 014515 (2005).
M. Guidon, F. Schiffmann, J. Hutter, J. VandeVondele J. Chem. Phys. 128, 214104 (2008)

Water: the most important liquid

Simulation in the NPT ensemble



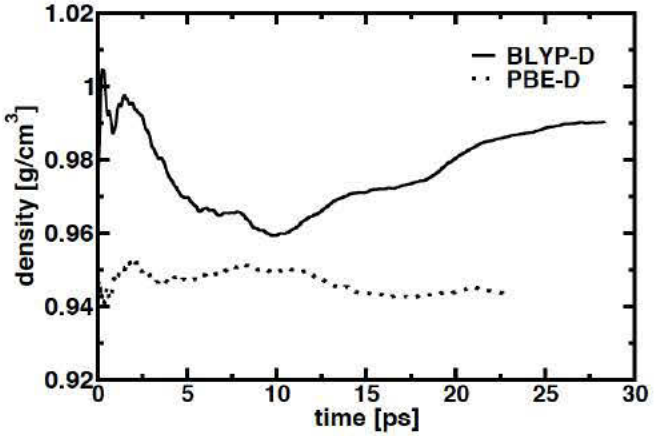
25ps

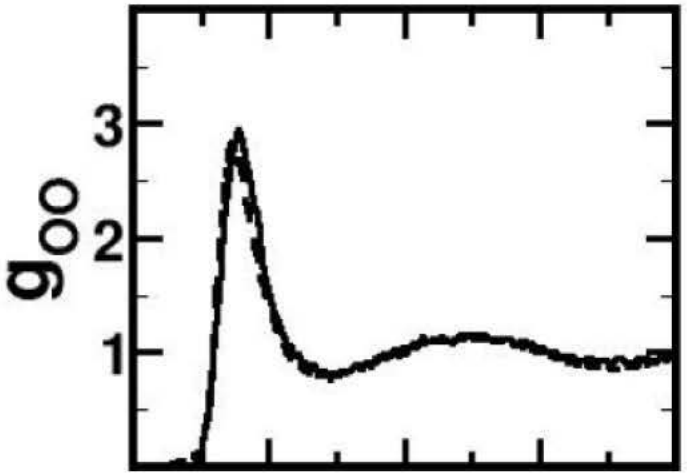
Standard functional gets density very wrong

J. Schmidt, J. VandeVondele, IFW Kuo, D. Sebastiani, JI Siepmann, J. Hutter, CJ Mundy JPC B 113(35):11959–11964 (2009)

Water: the most important liquid

Simulation in the NPT ensemble





Dispersion corrected BLYP (BLYP-D) yields:
- correct density
- excellent pair correlation function

Generally: D correction improves energetics for biologically relevant interactions, such as pi-stacking and hydrogen bonding. Is empirical, but computationally free.

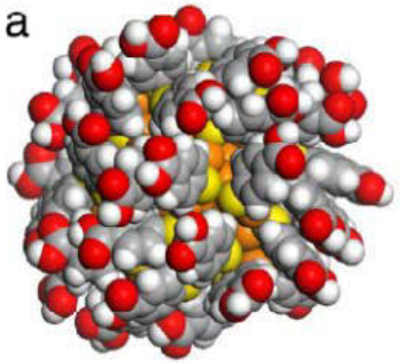
J. Schmidt, J. VandeVondele, IFW Kuo, D. Sebastiani, JI Siepmann, J. Hutter, CJ Mundy JPC B 113(35):11959–11964 (2009)
Grimme, S. JOURNAL OF COMPUTATIONAL CHEMISTRY, 27 (15), 1787-1799 (2006).

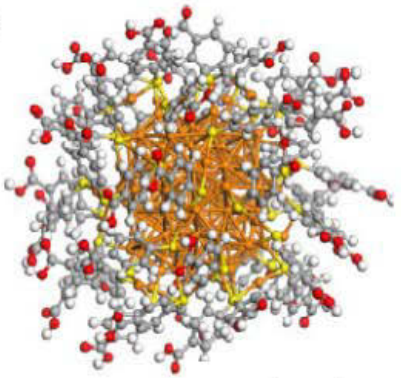
CP2K: science (I)

A unified view of ligand-protected gold clusters as superatom complexes

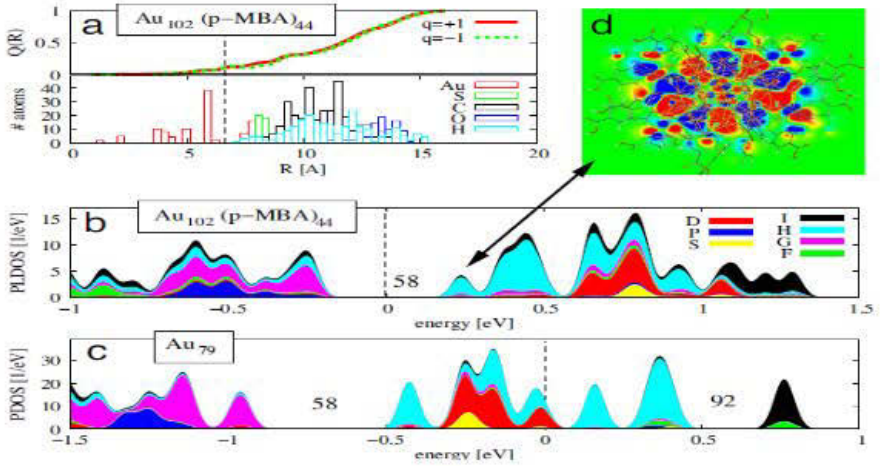
Michael Walter[†], Jaakko Akola[†‡], Olga Lopez-Acevedo[†], Pablo D. Jadzinsky[§¶], Guillermo Calero[§], Christopher J. Ackerson[§‖], Robert L. Whetten[††], Henrik Grönbeck[‡‡], and Hannu Häkkinen[†§§¶¶]

PNAS July 8, 2008 vol. 105 no. 27 9157–9162





System size: 762 Atoms
~3400 electrons



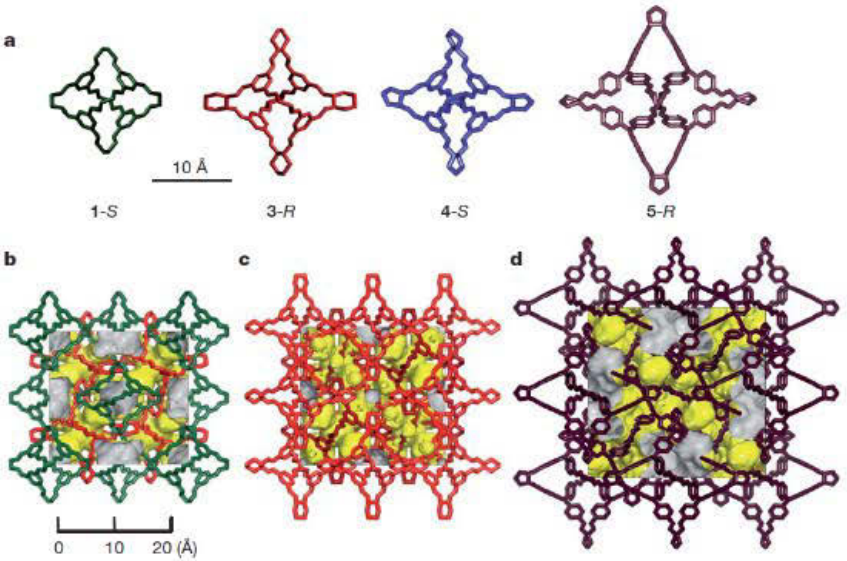
Electronic structure of nanoparticles

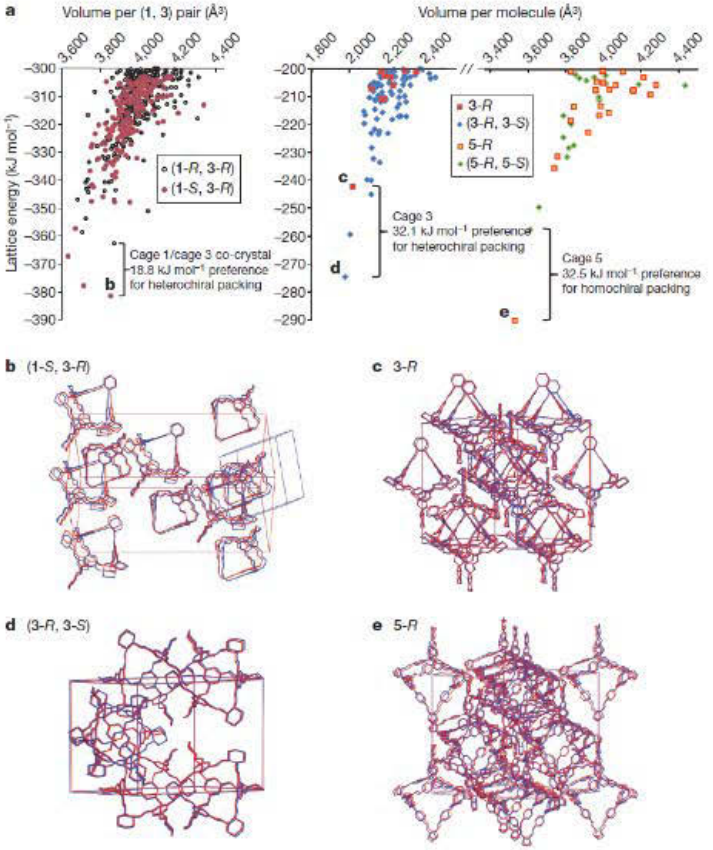
CP2K: science (II)

Modular and predictable assembly of porous organic molecular crystals

James T. A. Jones[1], Tom Hasell[1], Xiaofeng Wu[1], John Bacsa[1], Kim E. Jelfs[1], Marc Schmidtmann[1], Samantha Y. Chong[1], Dave J. Adams[1], Abbie Trewin[1], Florian Schiffman[2], Furio Cora[2], Ben Slater[2], Alexander Steiner[1], Graeme M. Day[3] & Andrew I. Cooper[1]

16 JUNE 2011 | VOL 474 | NATURE | 367





Structure prediction of metal organic frameworks

CP2K: science (III)

Large variation of vacancy formation energies in the surface of crystalline ice

M. Watkins[1,2,3], D. Pan[4], E. G. Wang[5], A. Michaelides[1,2,3], J. VandeVondele[6] and B. Slater[1,3]*

[1]Department of Chemistry, Christopher Ingold Building, 20 Gordon Street, University College London, London WC1H 0AJ, UK, [2]London Centre for Nanotechnology, University College London, London WC1H 0AJ, UK, [3]TYC@UCL, University College London, London WC1H 0AJ, UK, [4]Institute of Physics, Chinese Academy of Sciences, PO Box 603, Beijing 100190, China, [5]School of Physics, Peking University, Beijing 100871, China, [6]Institute of Physical Chemistry, University of Zurich, Winterthurerstrasse 190, CH-8057 Zurich, Switzerland. *e-mail: b.slater@ucl.ac.uk.

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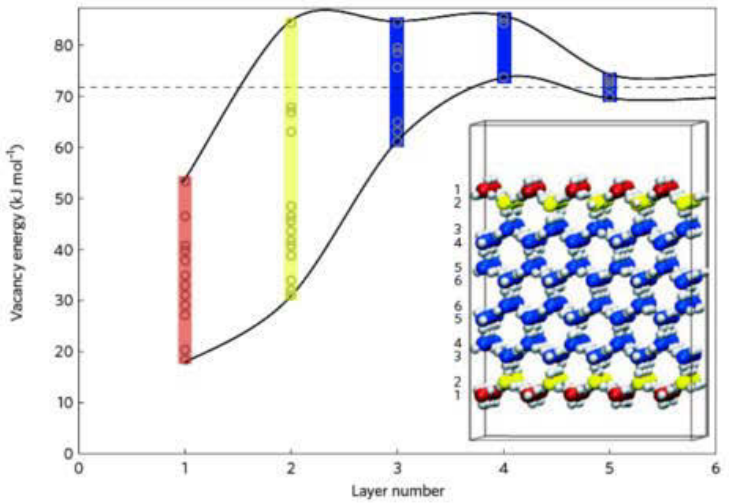
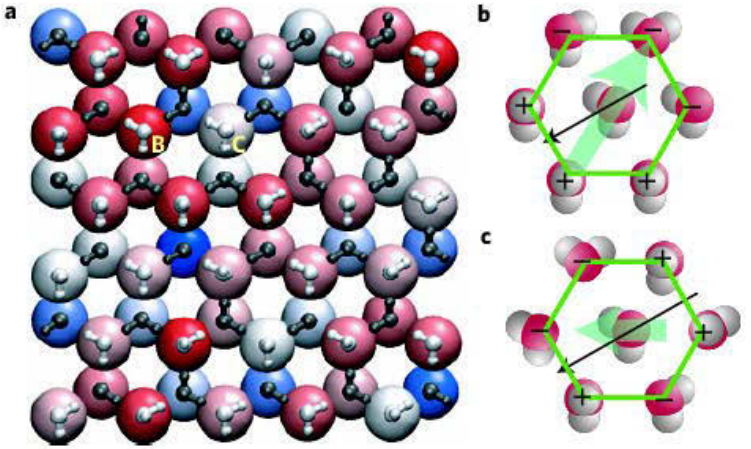




Disordered and frustrated materials

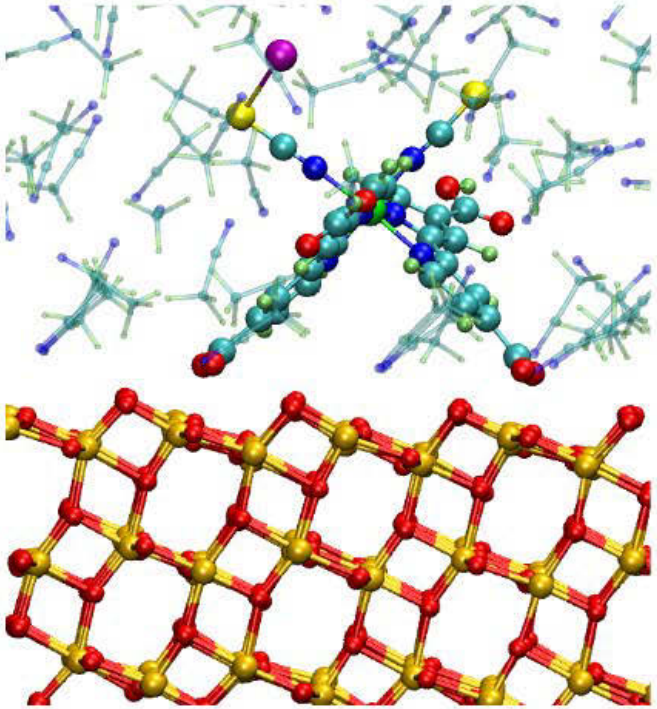
CP2K: science (IV)

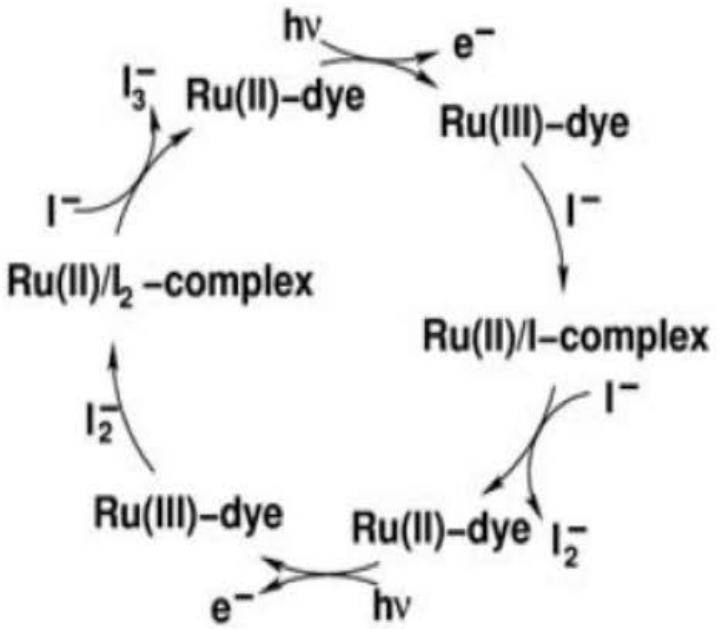
An atomistic picture of the regeneration process in dye sensitized solar cells

Florian Schiffmann[a], Joost VandeVondele[a,1], Jürg Hutter[a], Atsushi Urakawa[b], Ronny Wirz[b], and Alfons Baiker[b]

[a]Institute of Physical Chemistry, University of Zurich, Winterthurerstrasse 190, 8057 Zurich, Switzerland; and [b]Department of Chemistry and Applied Biosciences, Institute for Chemical and Bioengineering, ETH Zurich, Hönggerberg, HCI, 8093 Zurich, Switzerland

4830–4833 | PNAS | March 16, 2010 | vol. 107 | no. 11

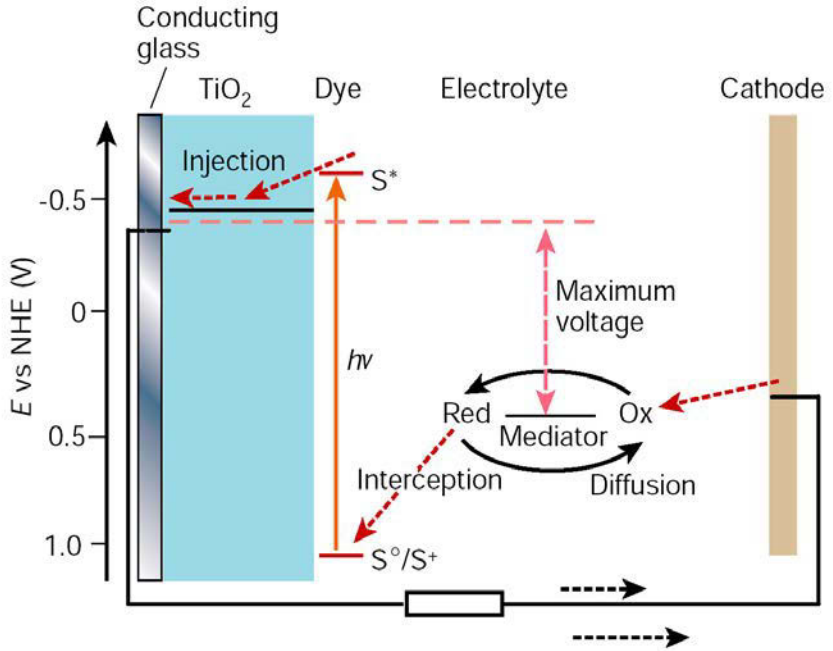


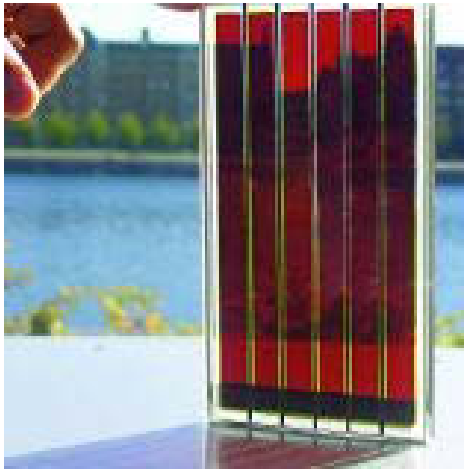


Functionalized solid/liquid interfaces

Dye sensitized solar cells (DSSC)

Sustainable energy production converting sunlight into electricity





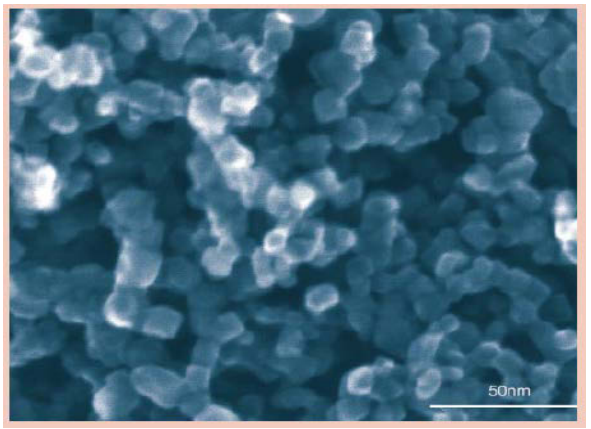
Grätzel, Nature (1991,2001)

~10% efficiency,short energy-payback, tolerant to impurities, inexpensive technologies, cheap materials, wide temperature range, diffuse light OK, various colors (semi-transparent), flexible

DSSC: atomistic engineering

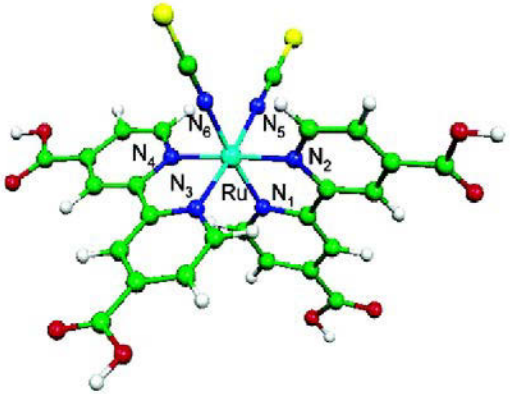
Prototypical high performance cells:

Mesoporous TiO_2 (Anatase)



Grätzel, Nature (1991,2001)

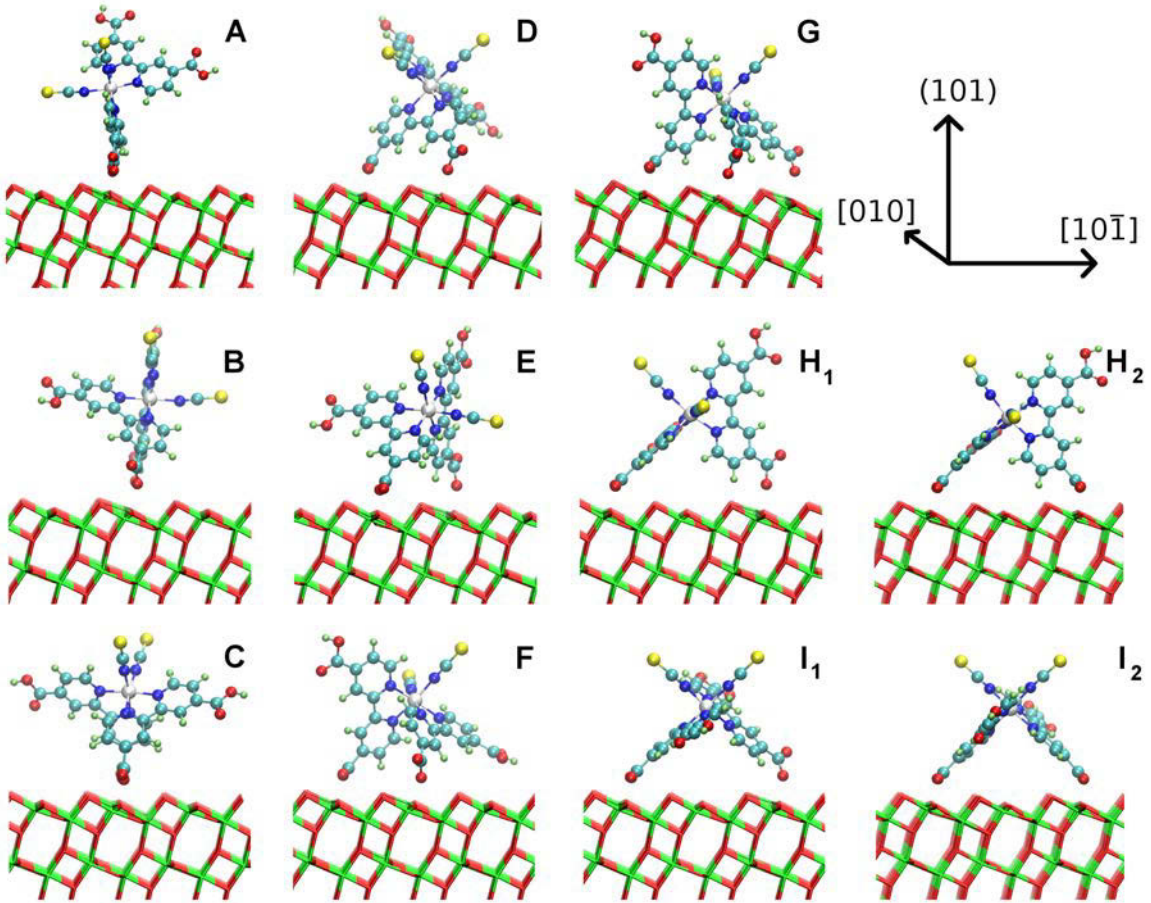
Ruthenium Dye (N3)

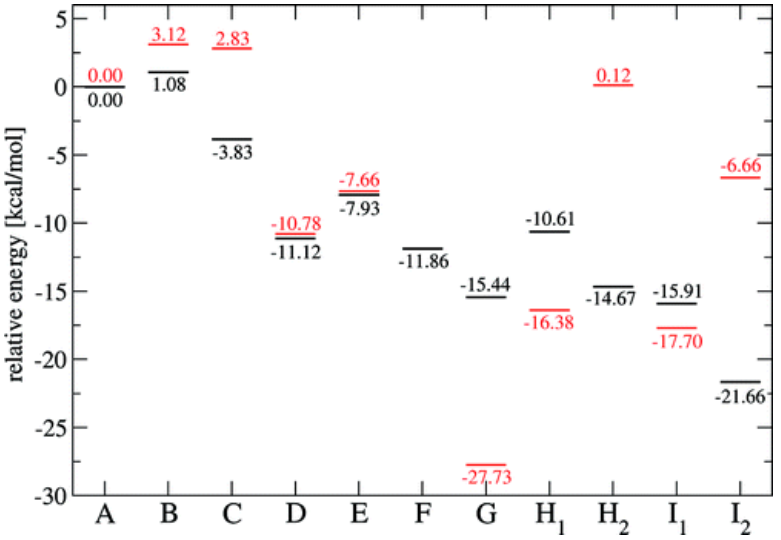


I^-/I_3^- in Acetonitrile

Taylor the interface to improve efficiency, stability and cost

N3 binding on anatase(101)



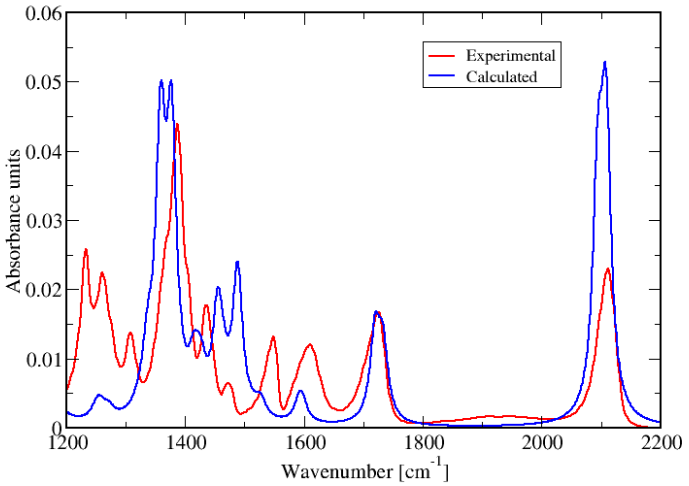


Relative binding energies are indicative:

- 2-3 carboxylate groups interact
- 2 bpy ligands involved
- Monodendate and bridged binding possible
- Protonation strongly influences relative stability

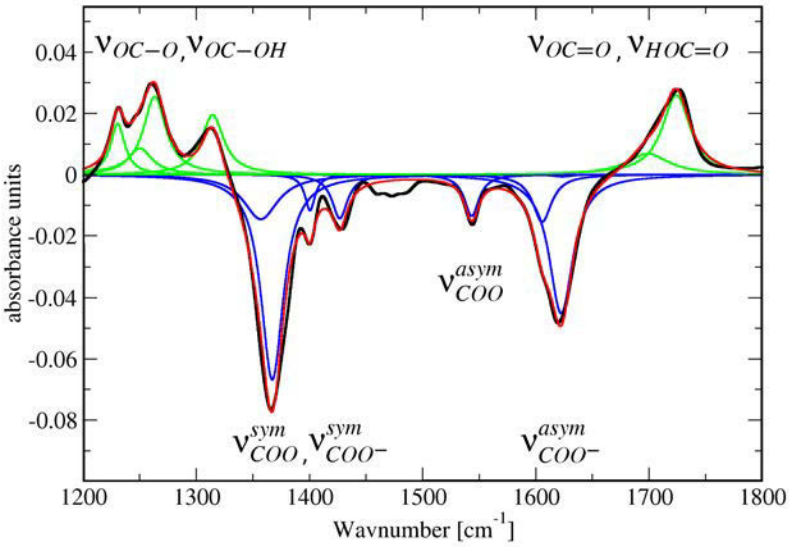
IR spectra: Theory & Experiment

Theory & Experiment



Promising agreement (± 30 cm^{-1}),
a unique binding geometry is not identified.

Exp. difference spectrum N3/N712

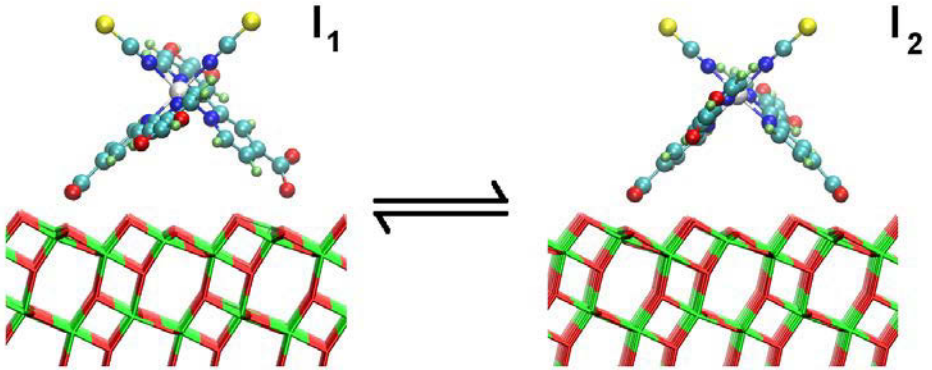


Theory provides assignments

Conclusions:

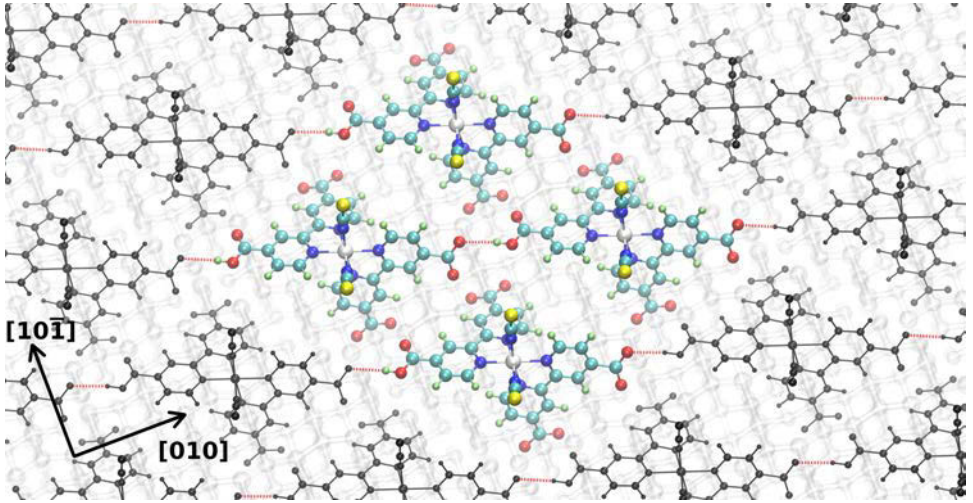
- base-induced desorption of dye adsorbed in the presence of protons
- change in binding mode depending on protonation

Suggested binding mode



Proposed monomer binding geometries

Equilibrium between two Configurations (pH dependent)



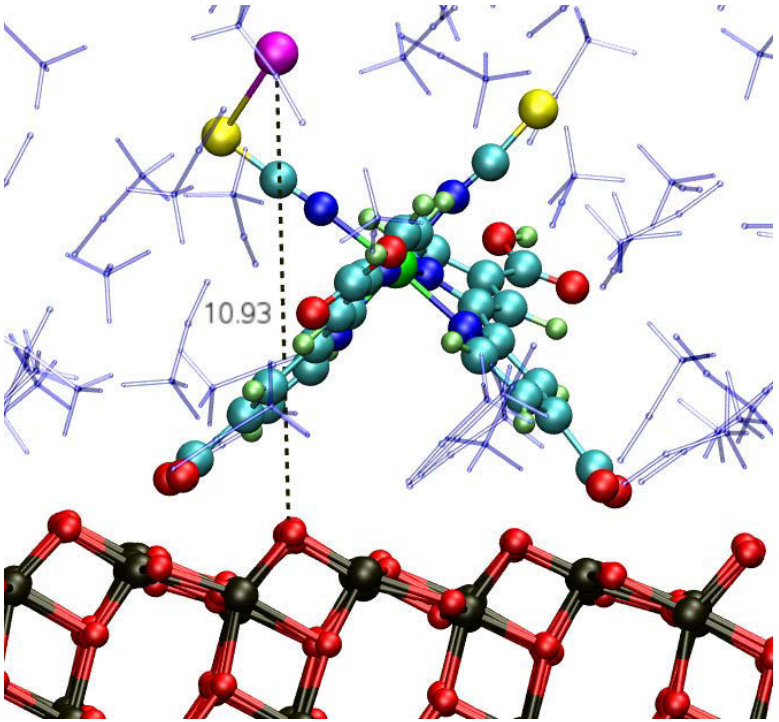
Computed self-assembly of I_2 on anatase(101)

Experimental data consistent with self-assembly:

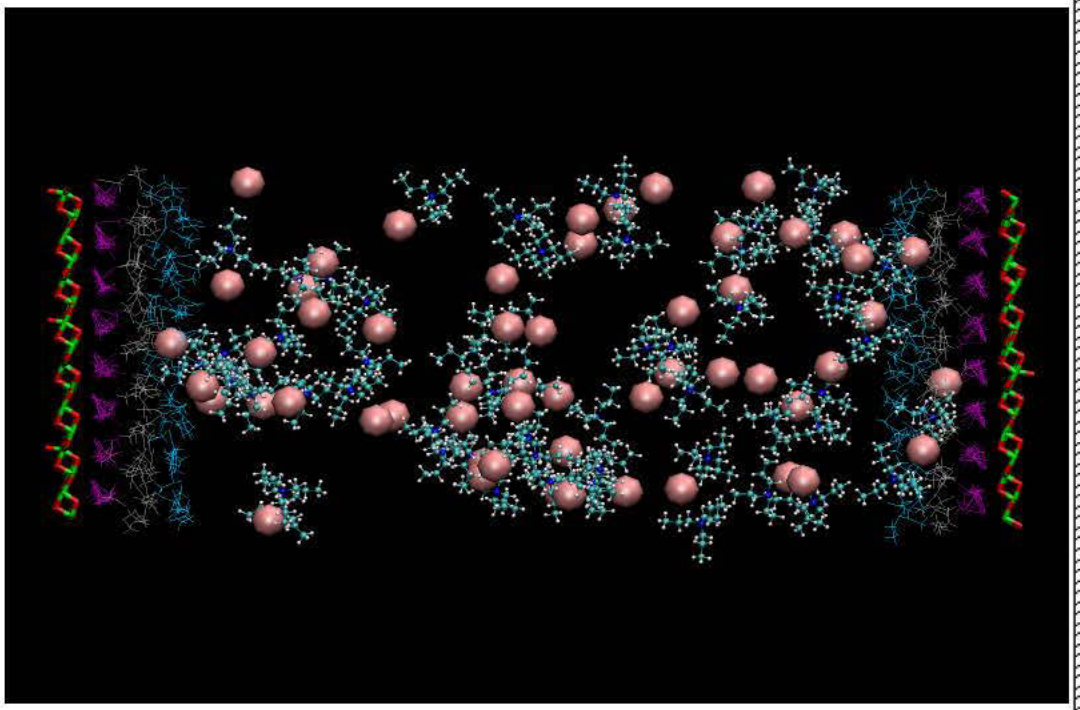
- Dense packing
- Dimers in STM (rutile)
- Desorption with base

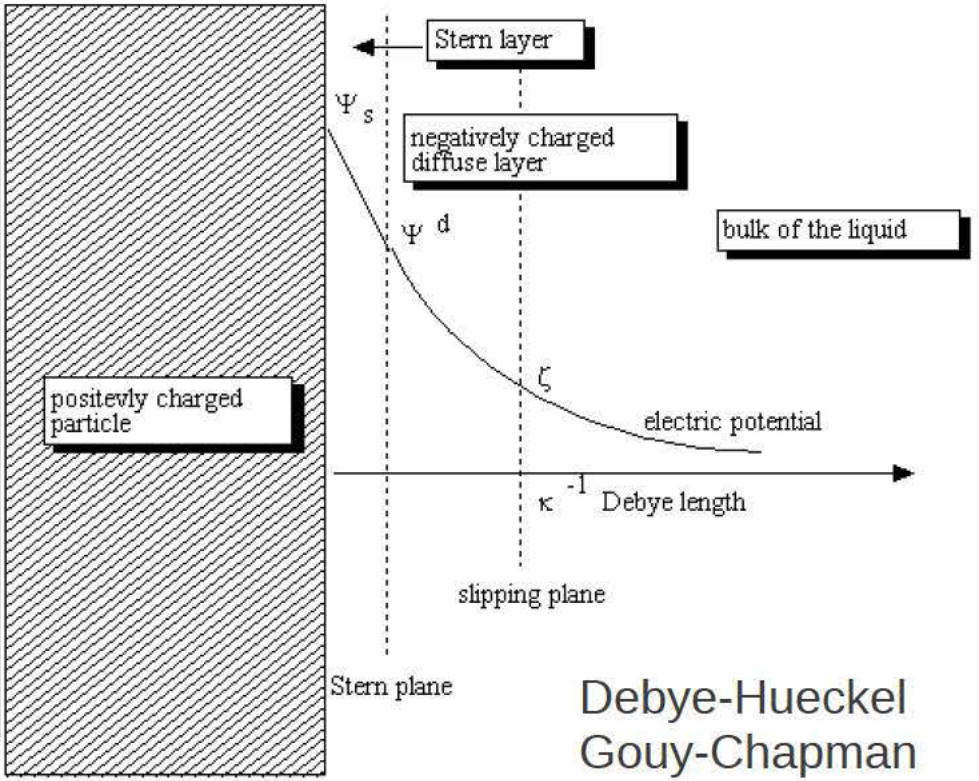
F. Schiffmann, J. VandeVondele, J. Hutter, R. Wirz, A. Urakawa, A. Baiker, J. Phys. Chem. C

Including the electrolyte



Electrolyte near the interface



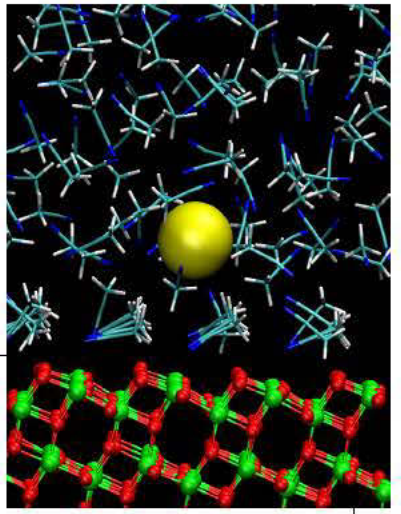


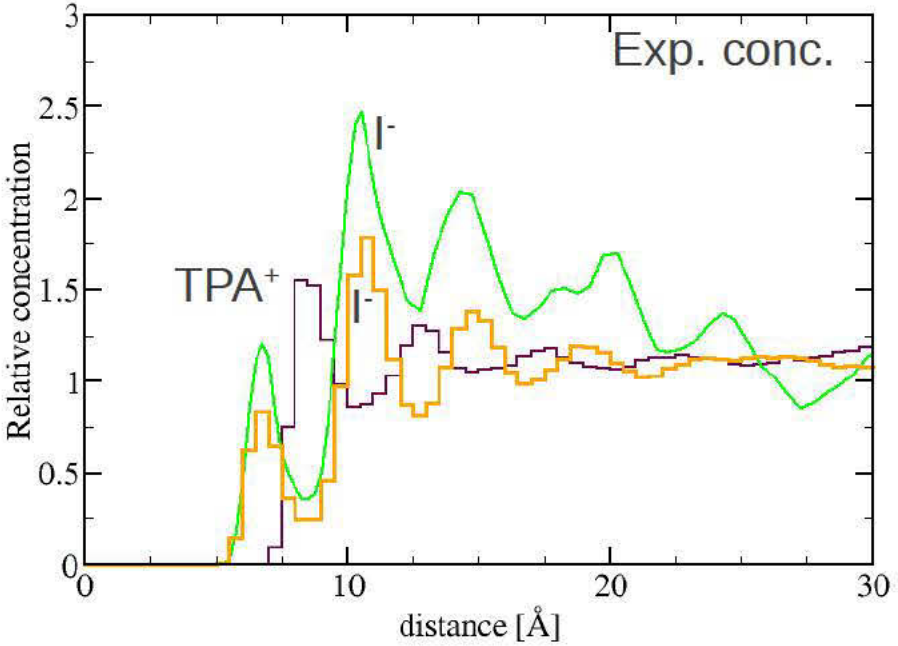
Debye-Hueckel
Gouy-Chapman

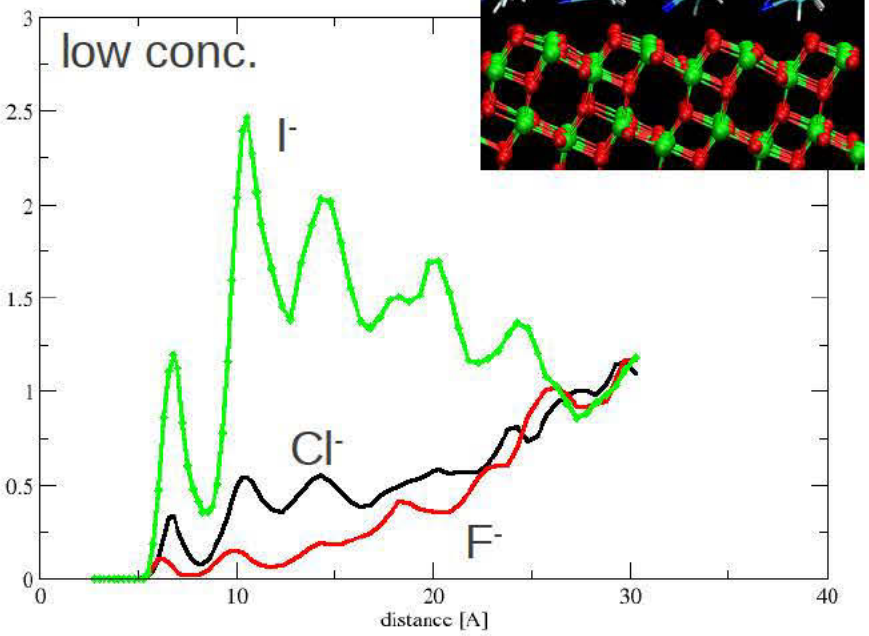
Atomistic vs. Continuum

I^- concentration profiles

- I^- specific enhancement near the interface
- The first solvent layer is passivating the interface





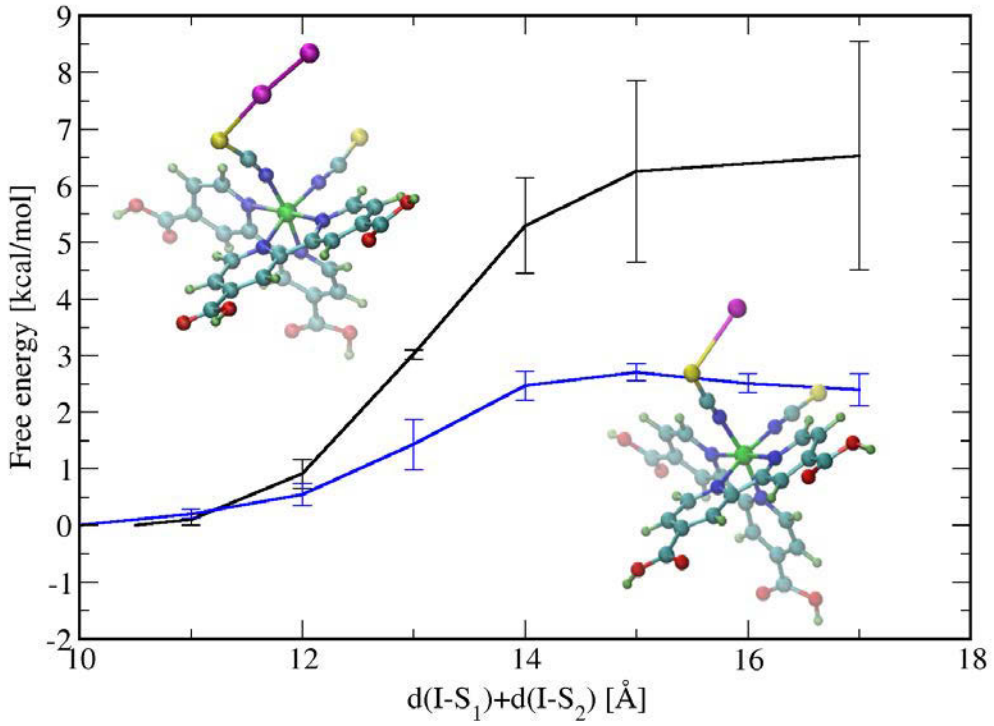


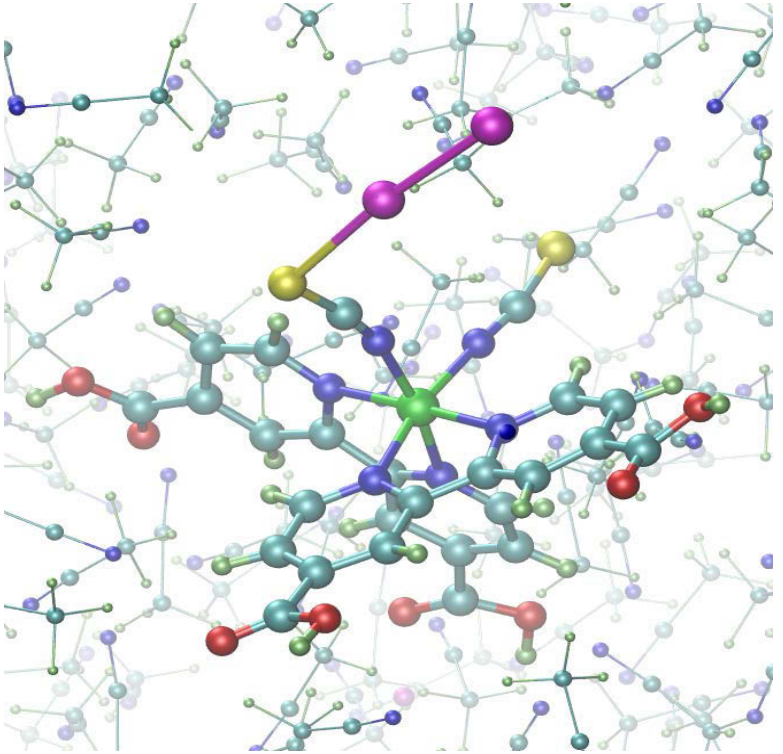
~microsecond simulation time (classical MD)

The molecular structure of the liquid near the interface is required to obtain a qualitatively correct ion distribution

Dye - Iodide interaction

DFT calculations of complex formation.
Free energies of binding in explicit solution.





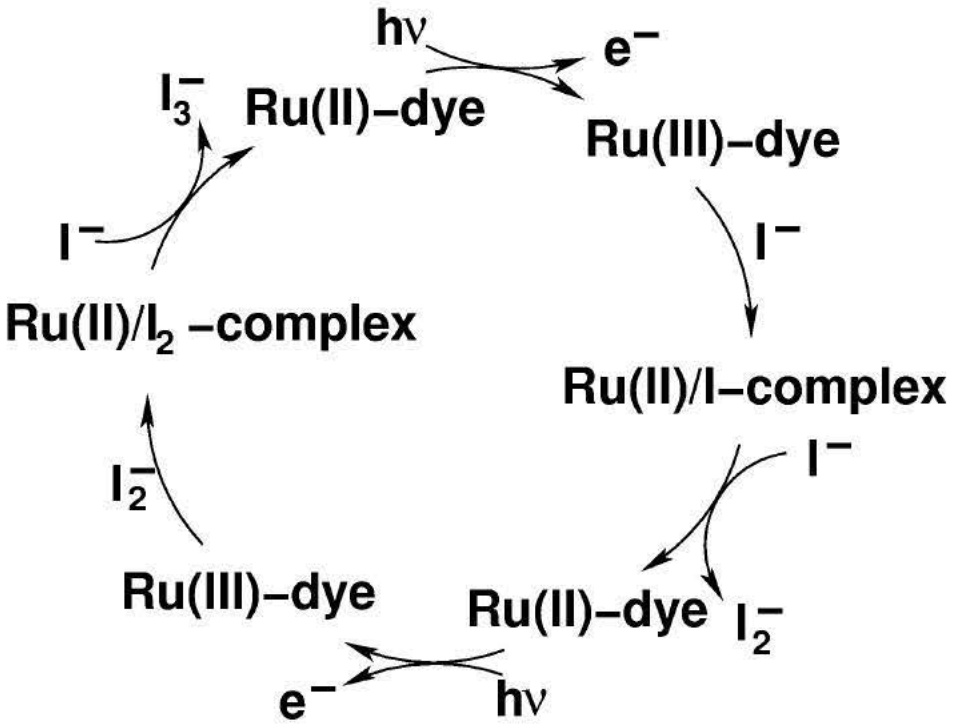
I^-, I_2^- form stable complexes in solution

SCN^- group essential in complex formation

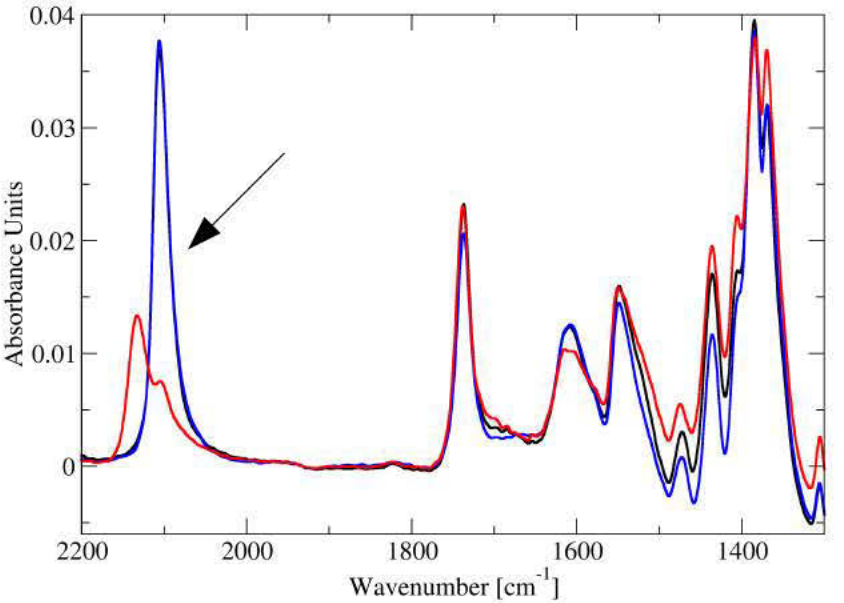
Dye regeneration

non-trivial:

$2\ Ru(III) + 3\ I^- \rightarrow 2\ Ru(II) + I_3^-$



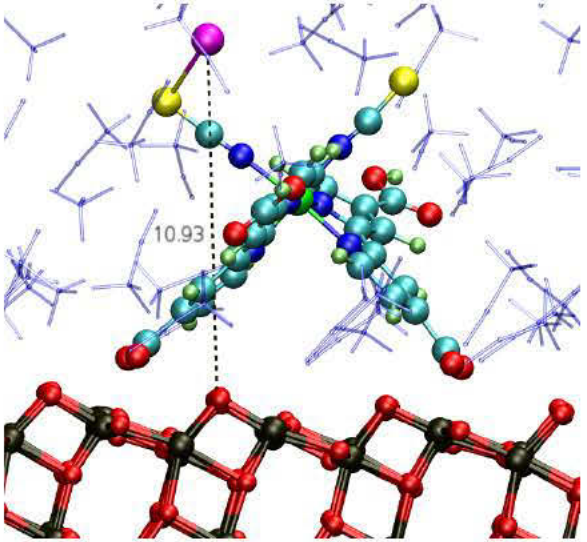
Exp. Confirmation of [Dye:I_2] complex

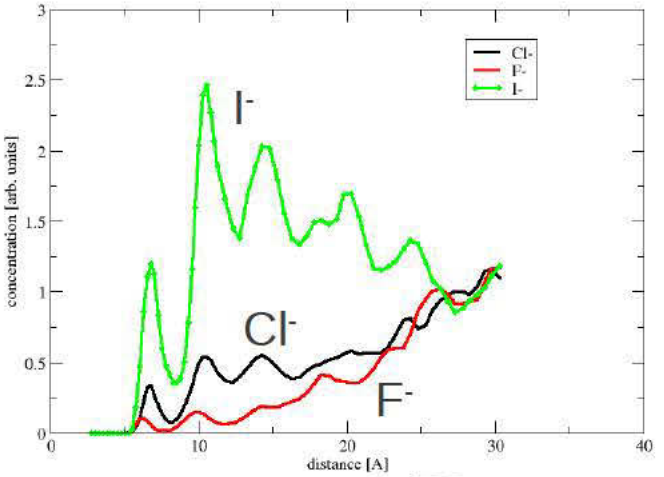


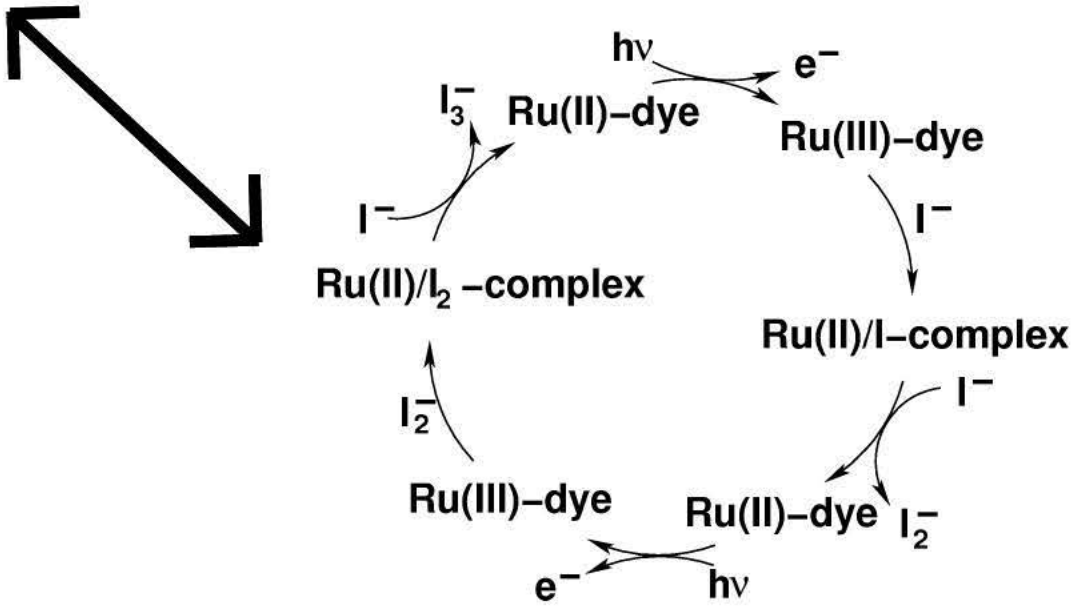
A highly efficient (barrierless) cycle.
[Dye:I_2] and [Dye:I] complexes formed.

F. Schiffmann, J. VandeVondele, J. Hutter, A. Urakawa, R. Wirz, A. Baiker, Proc. Natl. Acad. Sci. (2010)

Explanation of the superior performance







Recent developments

Full linear scaling GGA DFT

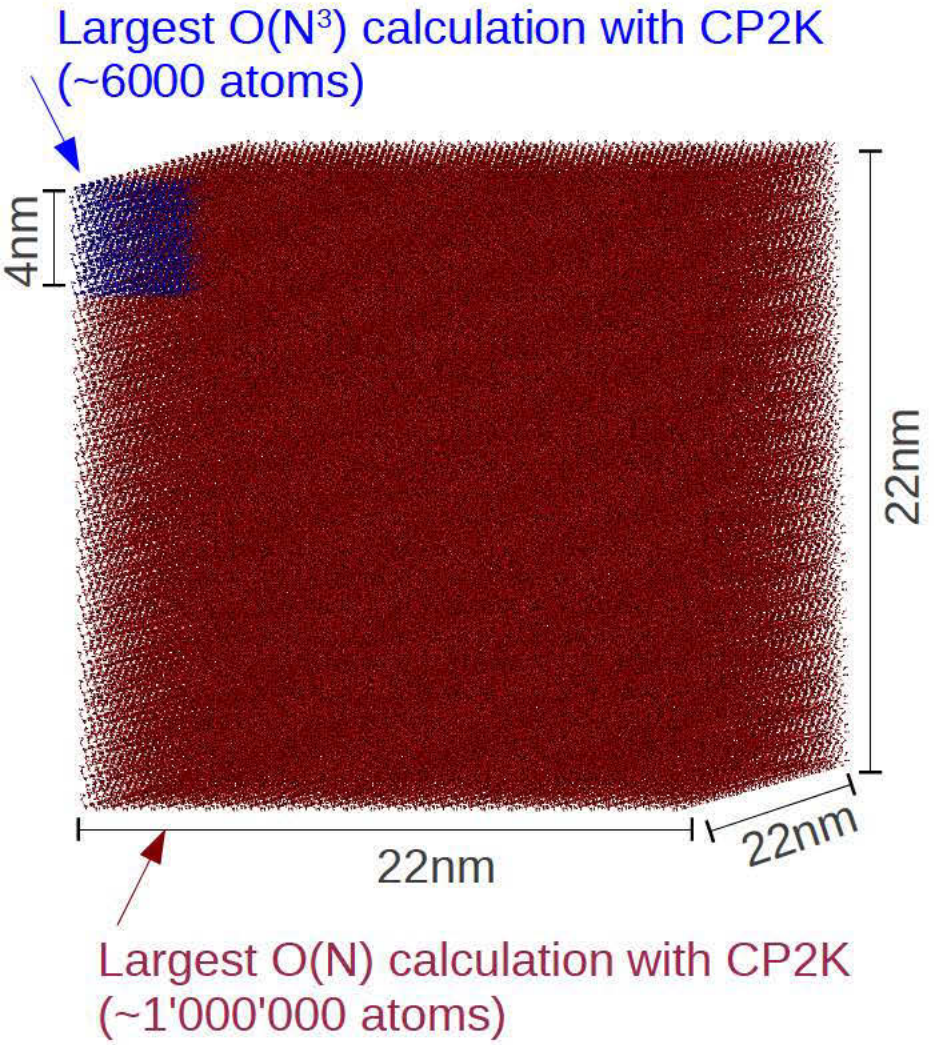
Efficiently using hybrid functionals

Linear scaling GGA DFT

Linear Scaling SCF

Traditional approaches to solve the self-consistent field (SCF) equations are $O(N^3)$ limiting system size significantly.

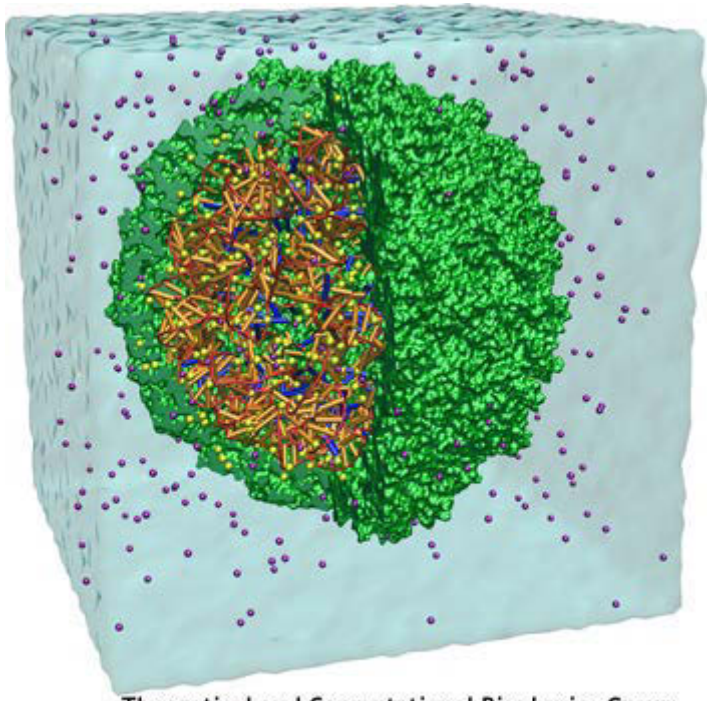
A newly implemented algorithm is O(N), allowing for far larger systems to be studied.



Linear Scaling SCF

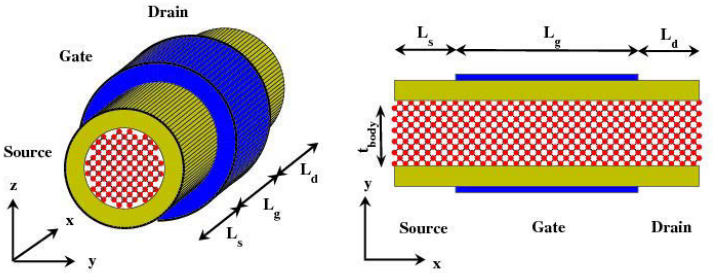
New regime: small devices, heterostructures, interfaces, nano-particles, a small virus.

Solvated STMV: 1M

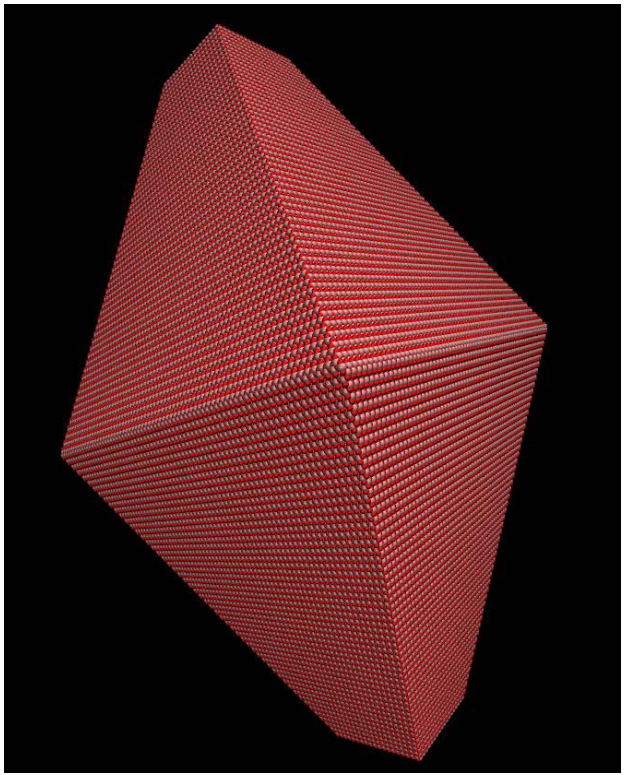


Theoretical and Computational Biophysics Group
Beckman Institute
University of Illinois at Urbana-Champaign

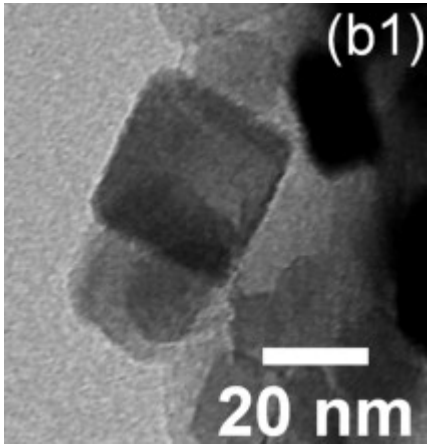
Gate-all-around FET



With Mathieu Luisier



1.5M atoms
Anatase nanocrystal



Caplovicova et al.
App. Cat. B, 224, 117

Sign matrix iterations

The density matrix (P) is function of H

$$P = \frac{1}{2}(I - \mathrm{sign}(S^{-1}H - \mu I))S^{-1}.$$

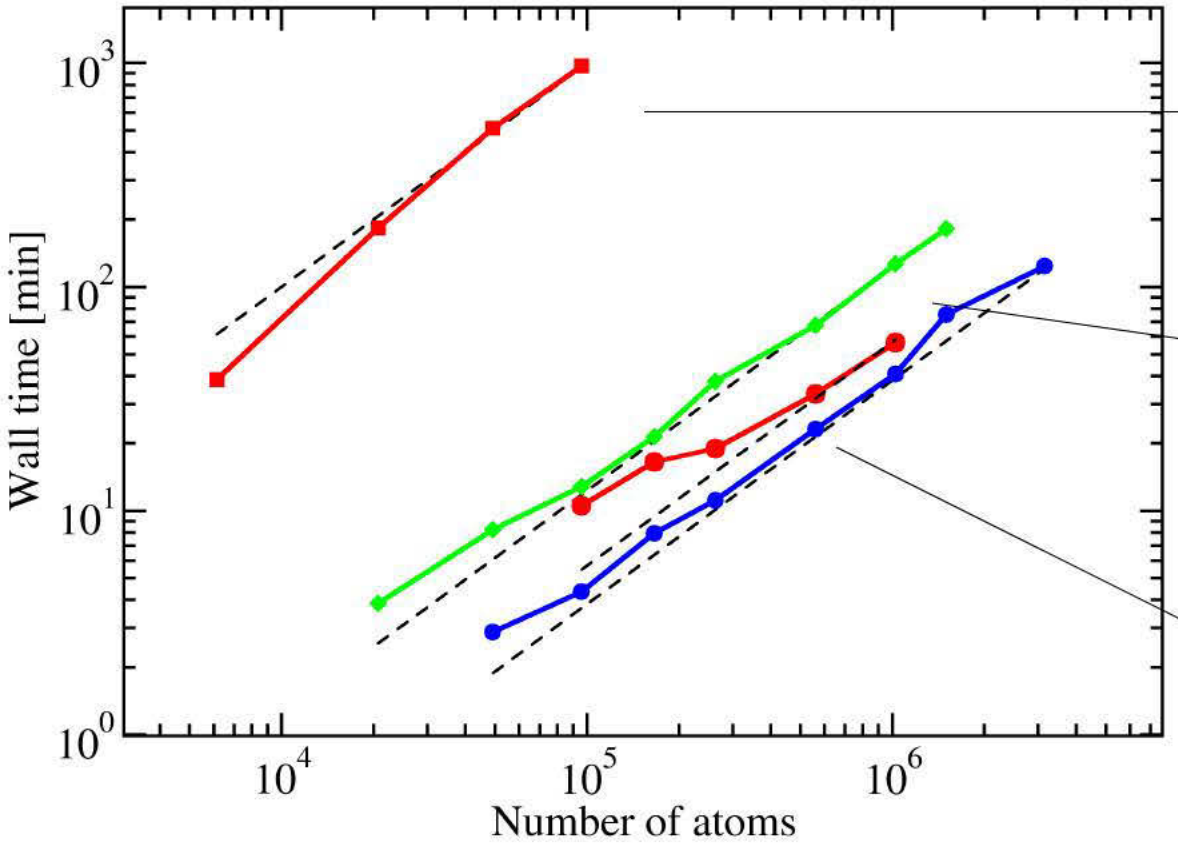
A simple iterative scheme (Newton-Schultz) gives sign(A):

$$X_{n+1} = \frac{1}{2}X_n(3I - X_n^2).$$

Using only sparse matrix matrix multiplies (not SPMV!)
linear scaling can be obtained

A dedicated sparse matrix multiply library is extremely important
This library is being ported to GPUs

Millions of atoms in the condensed phase



Accurate basis sets, DFT
46656 cores

The electronic structure
$O(10^6)$ atoms in < 2 hours

Minimal basis sets:
DFT, NDDO, DFTB
9216 cores

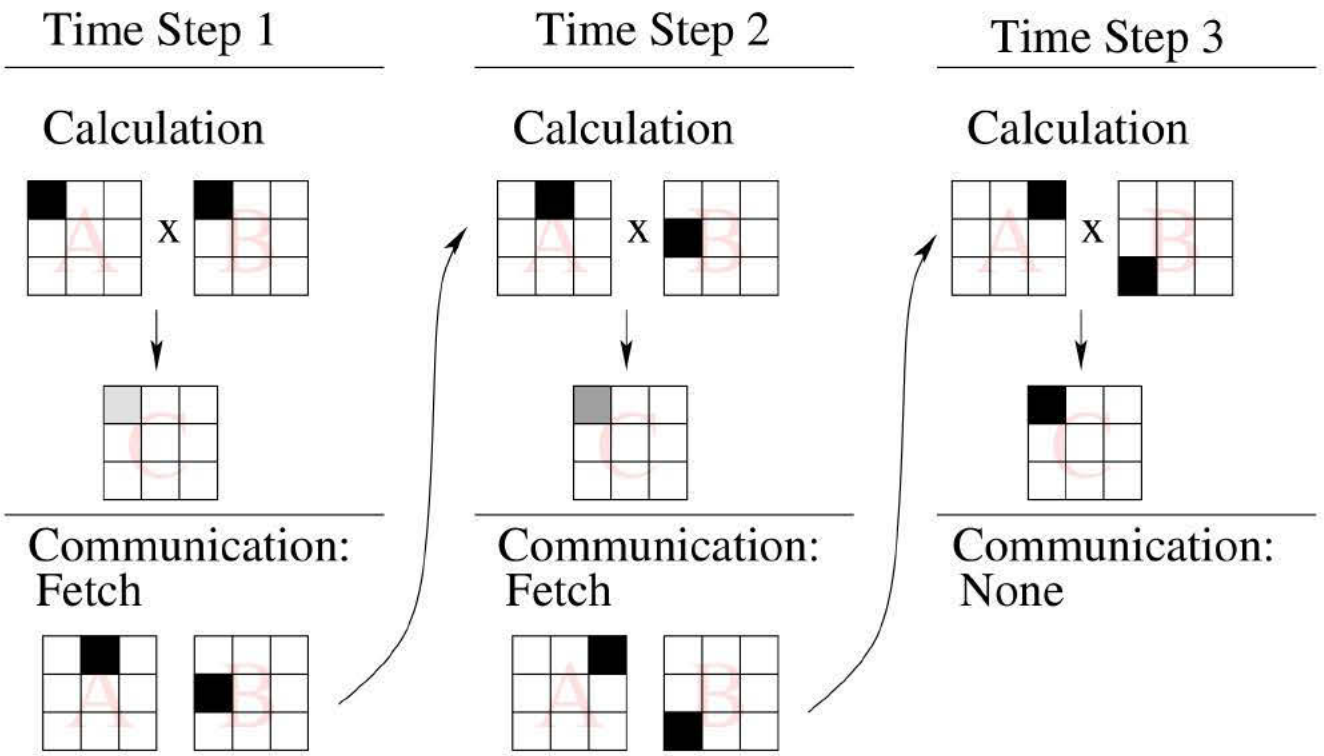
Bulk liquid water. Dashed lines represent ideal linear scaling.

VandeVondele, Borstnik, Hutter, JCTC, DOI: 10.1021/ct200897x

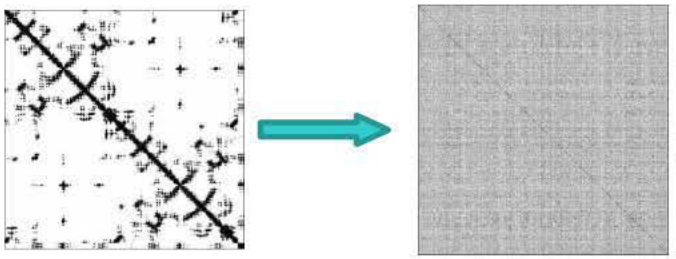
DBCSR: a sparse matrix library

Distributed Blocked Compressed Sparse Row
Distributed Blocked Cannon Sparse Recursive

Target the application: atoms → Blocks (e.g. 5x5, 13x13, 23x23)
Linear scaling → Sparse
Fully dense → Cannon
Large scale → Distributed
High Performance → Recursive

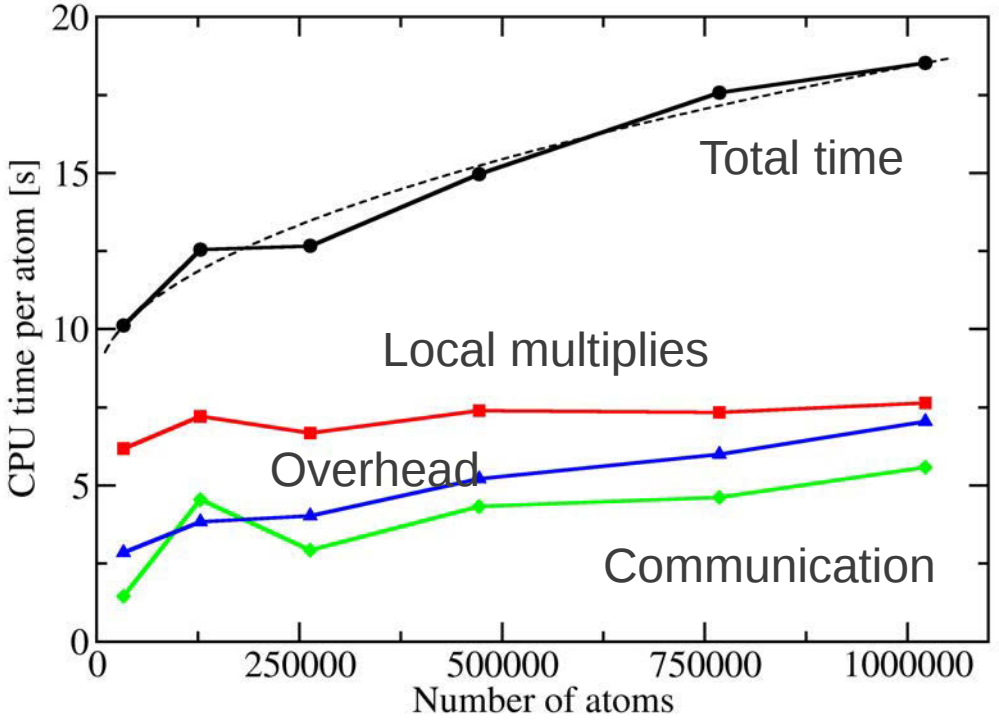


Cannon style communication on a homogenized matrix for strong scaling



Borstnik et al. : in preparation

Towards O(1) :
constant walltime with proportional resources



Stringent test:
- Small blocks, large overhead
- Very sparse matrices
- Running with 200 atoms / MPI task

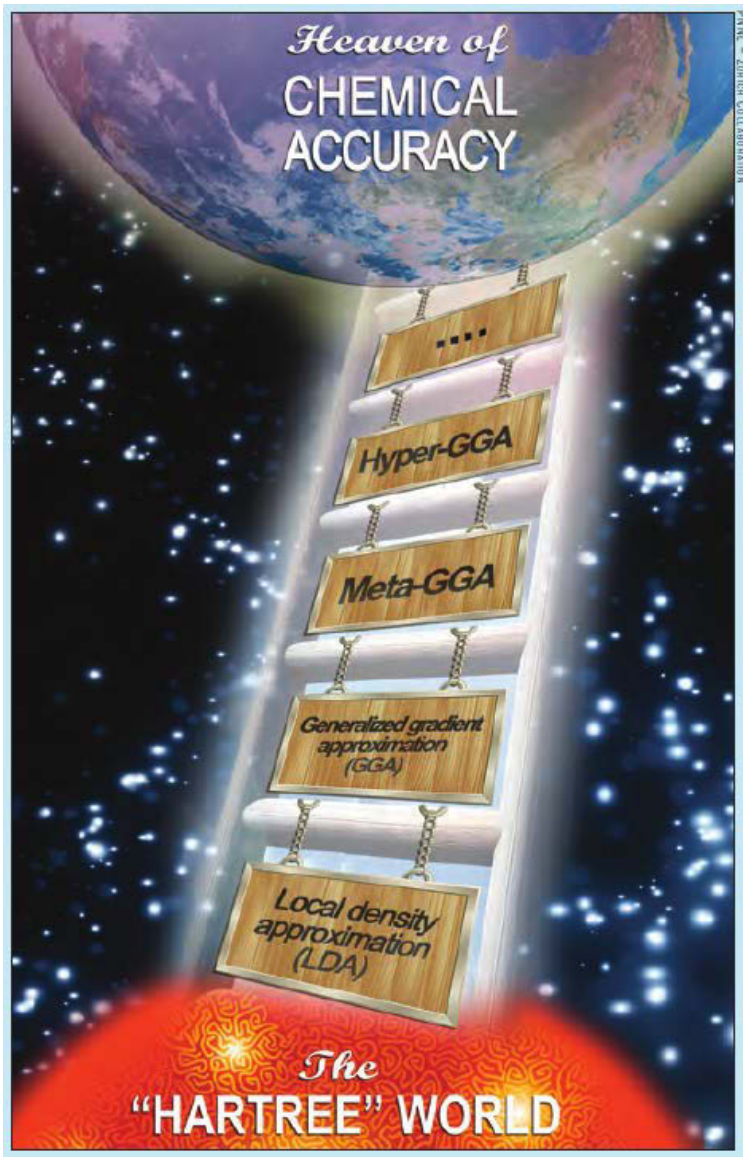
Local multiplies constant (OK!).

Overhead & Communication
- Grows with sqrt(N)
- Needs a replacement for Cannon

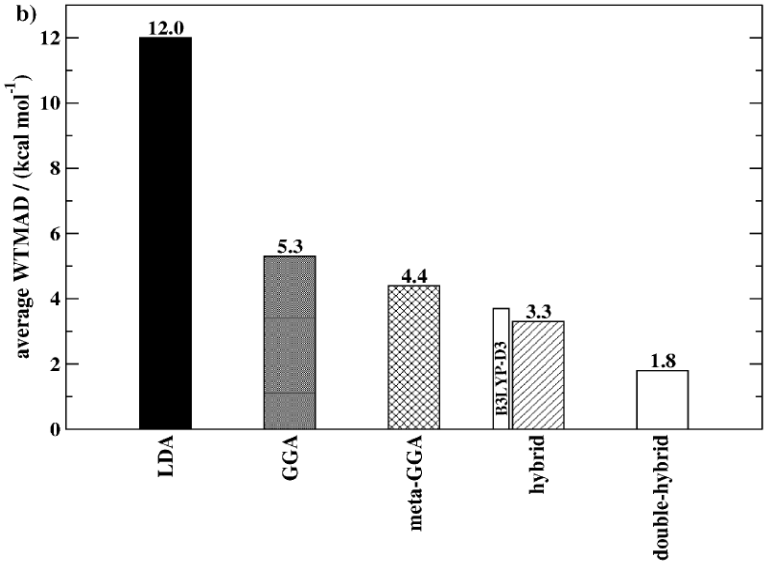
Work is underway to replace the Cannon algorithm with something new!
Retain the sqrt(N) max comm, yield constant comm in the limit.

Hybrid functionals

Advances in DFT



Exchange and correlation functionals of improving can be constructed by adding new ingredients:



Dispersion / van der Waals corrected functionals
(Screened) Hybrid functionals

Goerigk, L. and Grimme, S.
Phys. Chem. Chem. Phys. (2011) 13, 6670-6688.
Mundy, Kathmann, Rousseau, Schenter,
VandeVondele, Hutter, SCIDAC reviews (spring 2010).

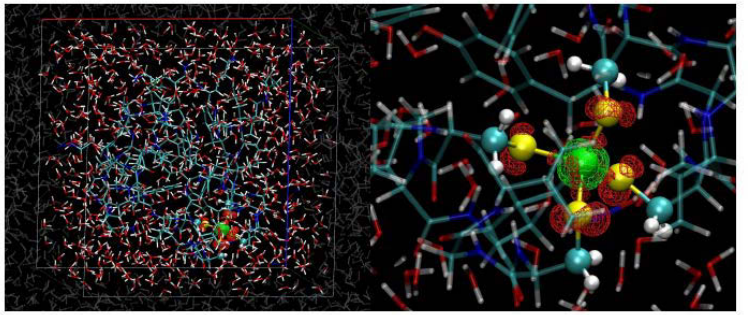
Hartree-Fock exchange

$$E_x^{\mathbf{HF}} = -\frac{1}{2}\sum_{\alpha\beta\gamma\delta} P_{\alpha\beta}P_{\gamma\delta}(\phi_\alpha\phi_\gamma|\phi_\beta\phi_\delta)$$

$$(\phi_\alpha\phi_\gamma|\phi_\beta\phi_\delta) = \int d\mathbf{r}d\mathbf{r}' \frac{\phi_\alpha(\mathbf{r})\phi_\gamma(\mathbf{r})\phi_\beta(\mathbf{r}')\phi_\delta(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}$$

An easy term in Gaussian basis sets, but brute force scaling as $O(N^4)$

2'825 atoms
→ 31'247 basis functions
→ 976'375'009 elements in P
→ 953'308'158'199'750'081 integrals
Exa-Pet-Ter-Gig-Meg-Kil



$O(N^4) \rightarrow O(N)$

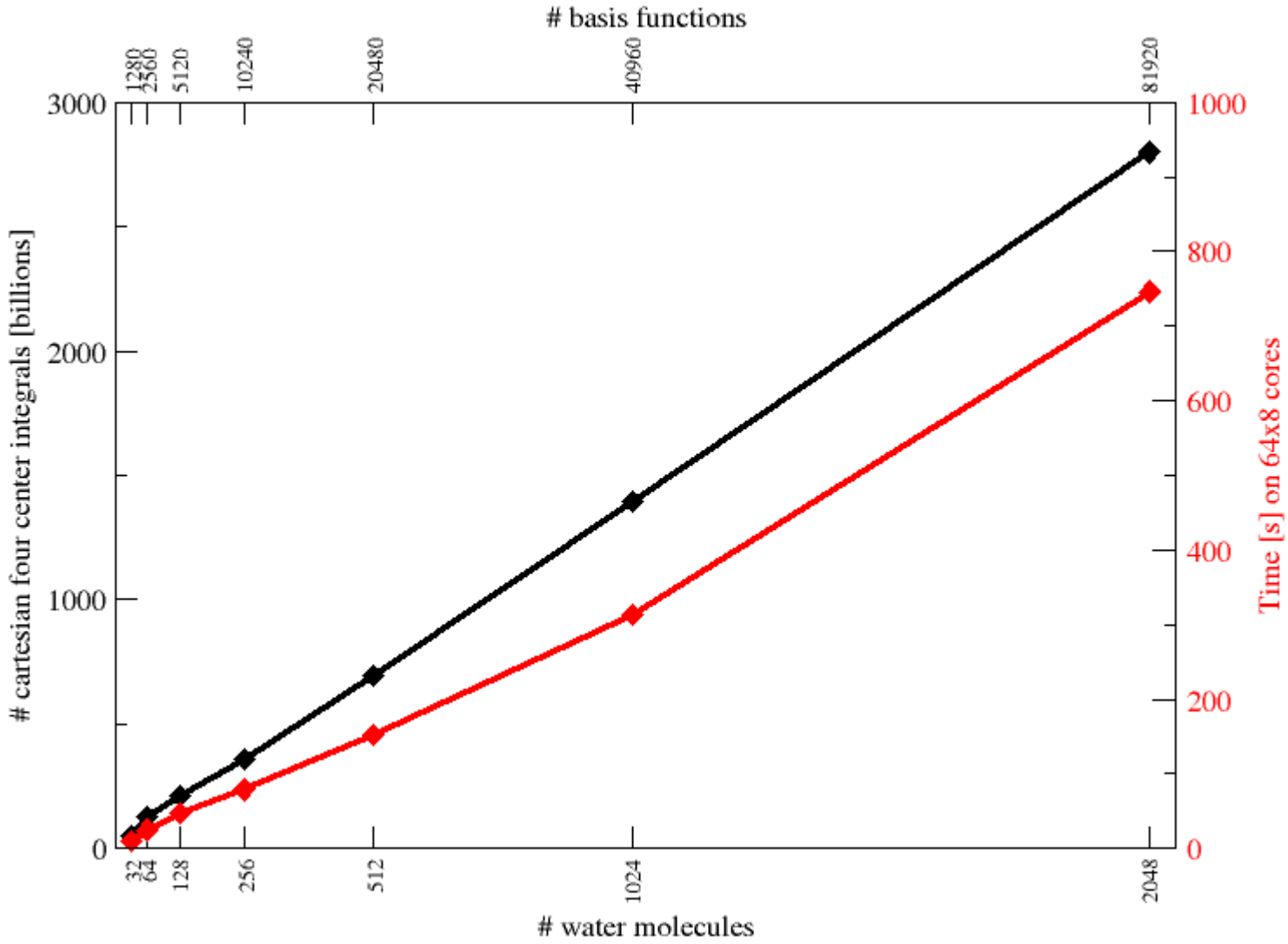
$$E_x^{\mathbf{HF}} = -\frac{1}{2}\sum_{\alpha\beta\gamma\delta} P_{\alpha\beta}P_{\gamma\delta}(\phi_\alpha\phi_\gamma|\phi_\beta\phi_\delta)$$

$$(\phi_\alpha\phi_\gamma|\phi_\beta\phi_\delta) = \int d\mathbf{r}d\mathbf{r}' \frac{\phi_\alpha(\mathbf{r})\phi_\gamma(\mathbf{r})\phi_\beta(\mathbf{r}')\phi_\delta(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}$$

Based on the fact that for large systems either the integrals
Or the density matrix become zero (to within a threshold eps)

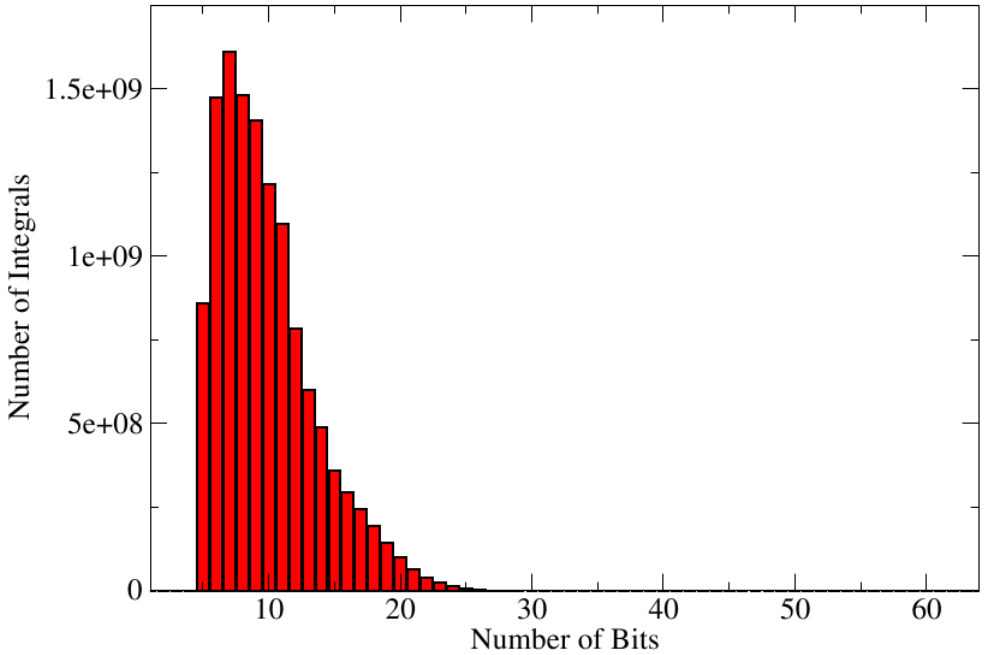
Cauchy-Schwarz screening	$\lvert(ab\lvert cd)\rvert \leq \sqrt{(ab\lvert ab)\lvert(cd\rvert cd)}$	$O(N^2)$
Density matrix screening	$P_{\alpha\beta}$ decays exponentially	O(N)
Operator screening	Operators other than 1/r	O(N)

O(N) HFX: measurements



Linear scaling is key .... thousands of molecules possible
On 'standard' cluster hardware in minutes.

In-core integral compression

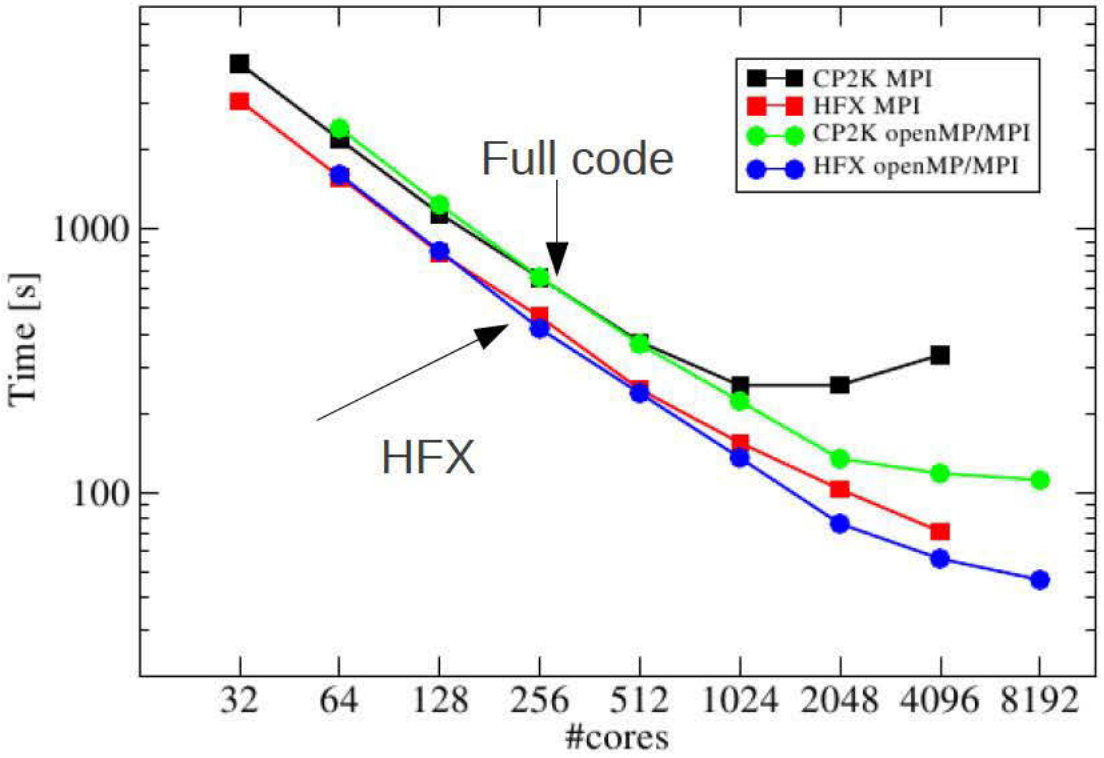


Almost all simulations are performed using an in-core algorithm
→ 10x speedup is observed.
Highly efficient scheme: index free and lossy compression

Guidon, M; Schiffmann, F; Hutter, J; VandeVondele, J. 2008 ; JCP 128(21): 214104

Parallel efficiency

HFX remains computationally much more demanding than GGA DFT (10x?)
A good parallel implementation is mandatory



10 steps of MD, 64 H_2O, 2560 BF,
OpenMP: 8 threads/node

HFX code out-scales the
Remaining (GGA) part of CP2K

Provided enough compute power,
Hybrid simulations run essentially
as fast as GGA
(9s / BOMD step @ 4096 cores)

Robust Hartree-Fock exchange in the condensed phase

$$E_x^{\mathrm{PBC}} = -\frac{1}{2N_k}\sum_{i,j}\sum_{\mathbf{k},\mathbf{k}'}\int\int \psi_i^{\mathbf{k}}(r_1)\psi_j^{\mathbf{k}'}(r_1)g(|r_1-r_2|)\psi_i^{\mathbf{k}}(r_2)\psi_j^{\mathbf{k}'}(r_2)\,d^3r_1 d^3r_2$$

How to treat this expression, k=k' is only conditionally convergent for g(r)=1/r ?

This 'difficult' point is integrable, but what for a Gamma-point code (k=k'=0) ?

$$g_{TC}(r_{12}) = \begin{cases} \frac{1}{r_{12}}, & r_{12} \leq R_c \\ 0, & r_{12} > R_c \end{cases}$$

Avoids spurious self-exchange interactions with images in other cells.
This can be implemented robustly in a simple way.

Truncated Coulomb: Needs, Alavi

LiH: demonstrating robustness & accuracy

A real benchmark system... a challenge inspired by the success of Quantum Chemistry

what is the final answer (i.e. many digits) for the HFX cohesive energy of LiH ?

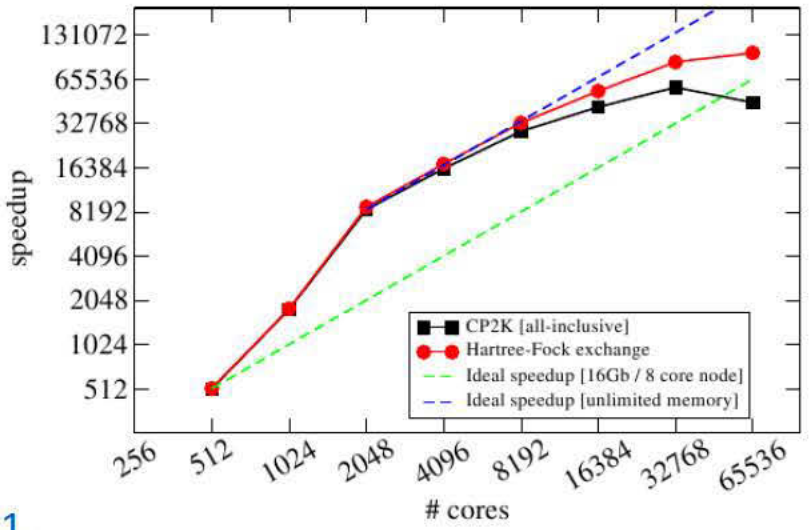
High quality basis (39000 functions for 5x5x5=1000 atoms)

	R_c[Å]	E(HF)[a.u.]	H[a.u.](a)	Li[a.u.](b)	ε_{HF}^{coh}[a.u.]
2x2x2	4.0	-32.244609	-0.499957	-7.428493	-0.132702
3x3x3	6.0	-32.256844	-0.499974	-7.432137	-0.132100
4x4x4	8.0	-32.258022	-0.499974	-7.432582	-0.131949
5x5x5	10.0	-32.258179	N/A	N/A	N/A

→ vs. -0.13195 by Gillan, Manby, et al

↓ vs. -32.258171 by Scuseria et al

Highly accurate calculations at the basis set limit, at gamma are possible... also for systems containing 1000 atoms

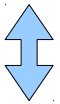


Paier J; Diaconu CV; Scuseria GE; Guidon M; VandeVondele J; Hutter J. 2009: PRB 80(17): 174114

Guidon M; Hutter J; VandeVondele J. 2009: JCTC 5(11): 3010-3021

The curse of HFX: The Basis

Good quality calculations need good quality basis sets



Increasing the quality of the basis steeply [O(N^4)] increases the cost of HFX

1st HFX step for 20 water molecules on 128 cores

basis	$\kappa(S)$	threshold	cost [ERIs]	cost [s]
3-21G*	4.9E+01	1.0E-04	2.3E+07	0.06
6-31G**	2.1E+02	1.0E-05	5.2E+08	0.35
6-311G++G**	1.2E+05	1.0E-07	1.1E+10	11.71
pc-0	5.2E+01	1.0E-04	1.7E+07	0.07
pc-1	4.5E+03	1.0E-05	4.4E+08	0.50
pc-2	5.7E+05	1.0E-07	2.0E+10	11.21
aug-pc-1	1.4E+06	1.0E-08	5.0E+10	53.23
aug-pc-2	3.9E+08	1.0E-09	1.5E+12	766.92
def2-QZVP	7.1E+04	1.0E-08	3.2E+11	127.16
aug-def2-QZVP	8.5E+05	1.0E-08	6.2E+11	331.61

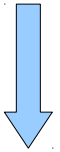
Most commonly used basis

'good' results

'Converged' results

Auxiliary Density Matrix Methods (ADMM)

For certain density matrices HFX can be computed very efficiently
(e.g. small basis sets or increased sparsity)



Transform an expensive matrix into a cheap one,
use a GGA for estimating the difference

$$
\begin{aligned}
E_x^{\mathrm{HFX}}[P] &= E_x^{\mathrm{HFX}}[\hat{P}] + \left(E_x^{\mathrm{HFX}}[P] - E_x^{\mathrm{HFX}}[\hat{P}]\right) \\
&\approx E_x^{\mathrm{HFX}}[\hat{P}] + \left(E_x^{\mathrm{DFT}}[P] - E_x^{\mathrm{DFT}}[\hat{P}]\right)
\end{aligned}
$$

One example: wavefunction fitting, using an auxiliary basis

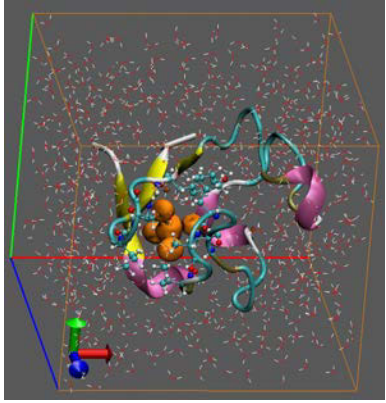
$$
\min_{\tilde{C}} \left[\sum_j \int \left(\psi_j(\mathbf{r}) - \tilde{\psi}_j(\mathbf{r})\right)^2 d\mathbf{r} + \sum_{k,l} \Lambda_{kl} \left(\int \tilde{\psi}_k(\mathbf{r}) \tilde{\psi}_l(\mathbf{r}) d\mathbf{r} - \delta_{kl} \right) \right]
$$

Guidon M; Hutter J; VandeVondele J; JCTC 6(8): 2348-2364

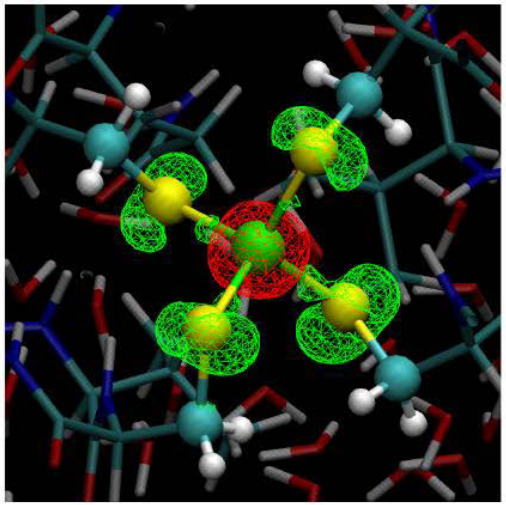
ADMM: accuracy

- GTMKN24 (>1000 datapoints)
  - using FIT3 and pFIT3 auxiliary basis sets
    - Error wrt to Exp. : identical (5.0 kcal/mol)
    - Error wrt to Ref. : < 1 kcal/mol
- BSSE tests
  - BSSE reduced by 5x compared to no ADMM
  - H_2O dimer: 0.5 kcal/mol FIT3, 0.2 kcal/mol aug-FIT3

ADMM: performance

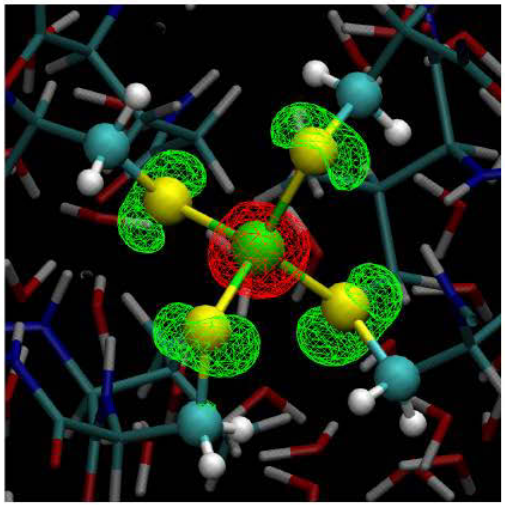


STD DZVP-MOLOPT-SR-GTH



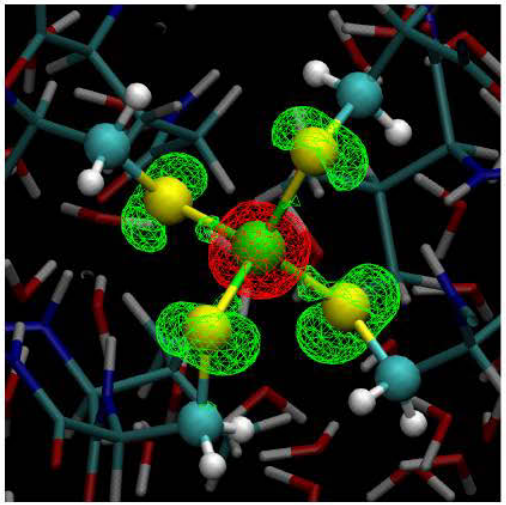
- 48'000 cores
- 1. SCF step: 45 min
- subsequent steps: 25 s
- 6.8 TB RAM

ADMM: MOLOPT/FIT3



- 1'152 cores
- 1. SCF step: 75 s
- subsequent steps: 25 s
- 5.2 GB RAM

ADMM: MOLOPT/EMBED



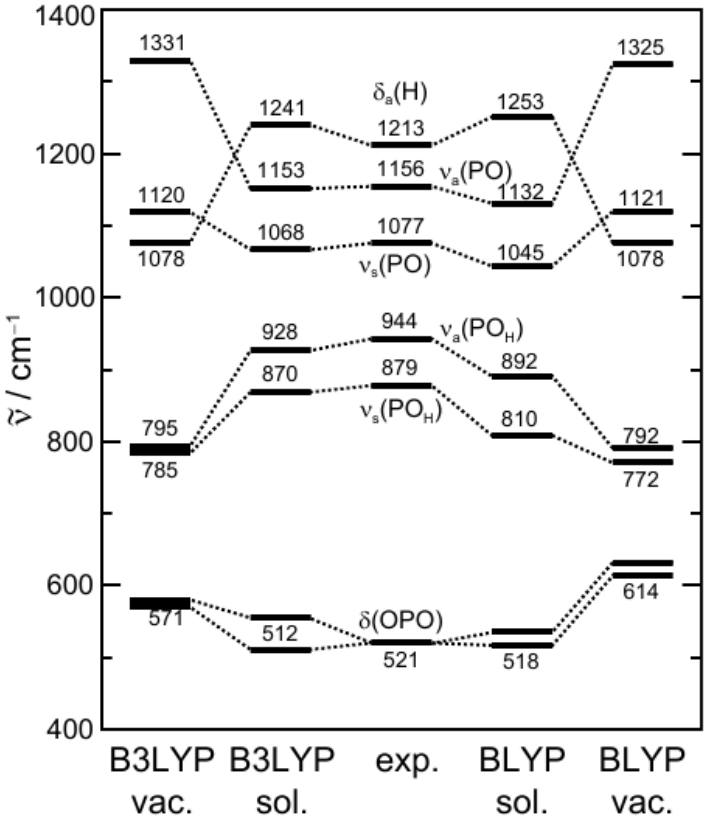
- 1'152 cores
- 1. SCF step: 80 s
- subsequent steps: 25 s
- 5.2 GB RAM

A fully solvated protein computed within minutes using hybrid functionals

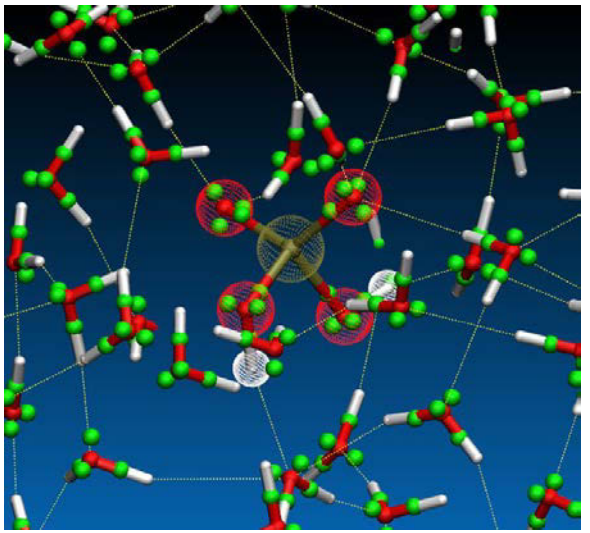
Guidon M; Hutter J; VandeVondele J; JCTC 6(8): 2348-2364

IR spectroscopy from AIMD with hybrid functionals

H_2PO4^-



$H_2PO_4^-$ in explicit water

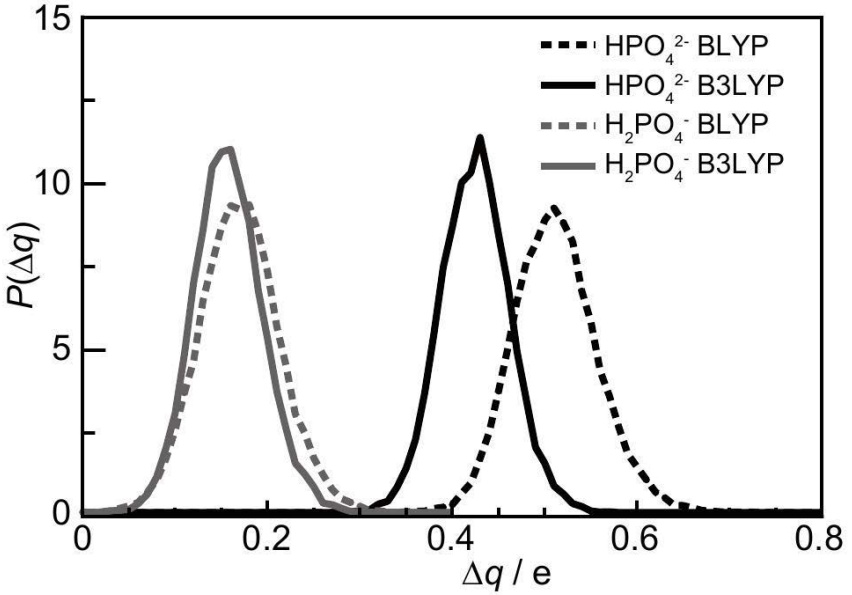


~ 100 ps AIMD / 64 waters

Both Hybrids and GGA capture the main effect of solvation.
Hybrid give 2x more accurate spectra

VandeVondele et al. JPCA

Phosphate in solution



Analyzing the amount of charge transfer in $H_2PO_4^-$ and HPO_4^{2-}:
Reduced charge transfer is observed with hybrid functionals, but only for the double anion.

The effect is partially electronic, partially geometric

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You for your attention!