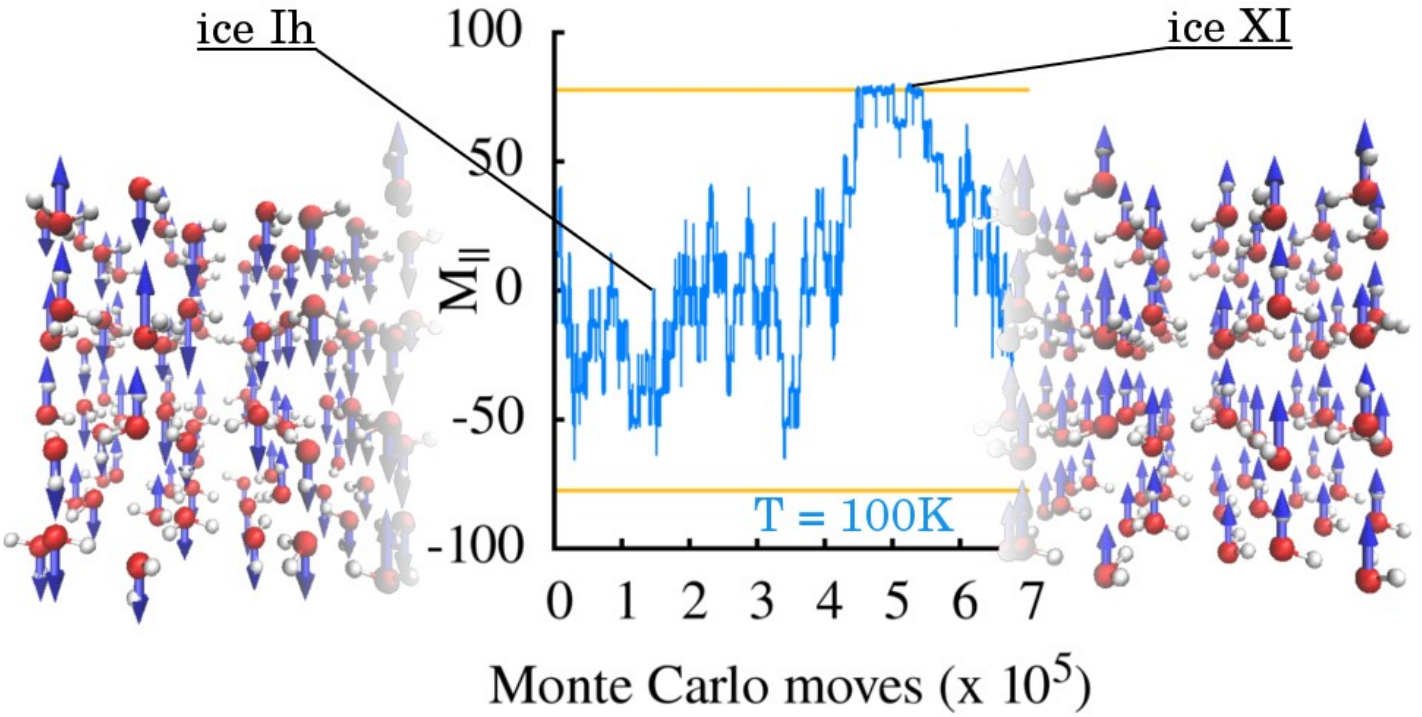
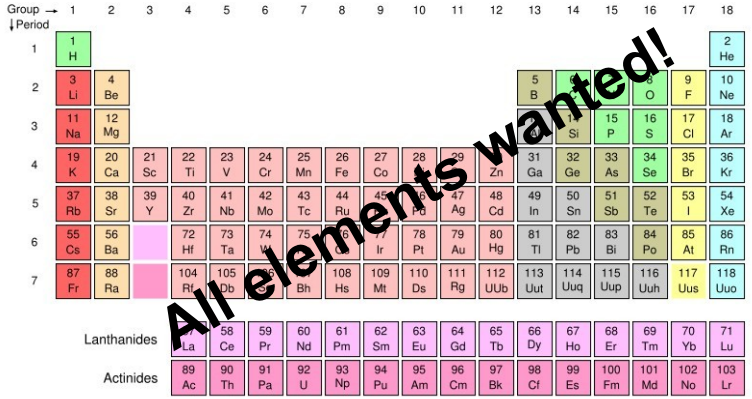
Summary of new & upcoming development in CP2K:

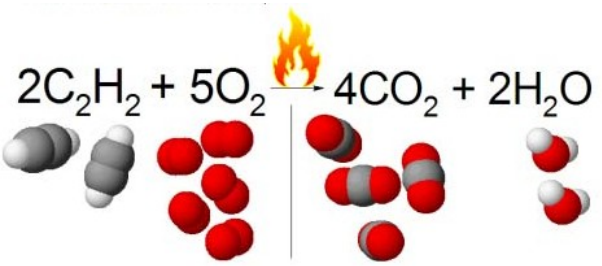
Improving the Predictive Nature of Atomistic Simulation



Joost VandeVondele
Nanoscale Simulations
Department of Materials, ETH Zurich

Modeling complex systems

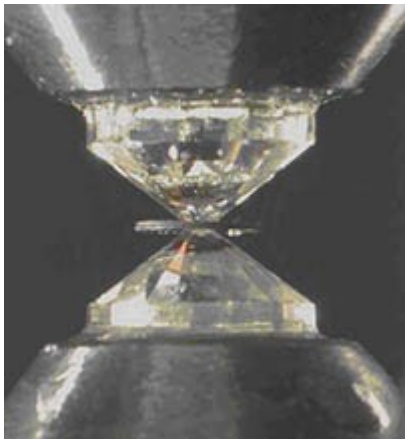




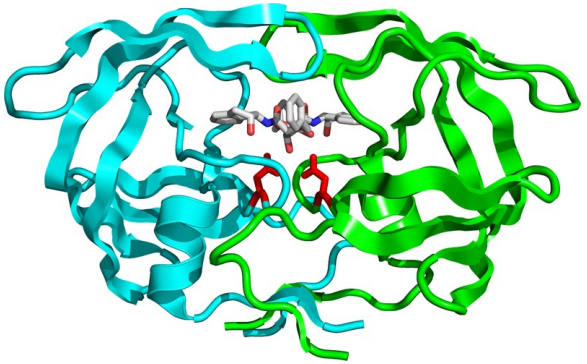
Reactivity

Needs a versatile approach...
including atoms and electrons

Electronic properties



Extreme conditions



Weak interactions

CP2K: the swiss army knife of atomistic simulation

- A wide variety of models Hamiltonians
  - Empirical (classical)
  - semi-empirical
  - local and non-local DFT
  - MP2 & RPA
  - Combinations (e.g. QM/MM)
- Various sampling/dynamics algorithms
  - Molecular dynamics & Monte Carlo
    - NVE, NVT, NPT
  - Free energy and PES tools
  - Ehrenfest MD
- Properties
  - Vibrational
  - NMR, EPR, XAS, TDDFT
- Open source & rapid development
  - 1.000.000 lines of code

Made available as open source software to the community at www.cp2k.org

CP2K: algorithms & implementation

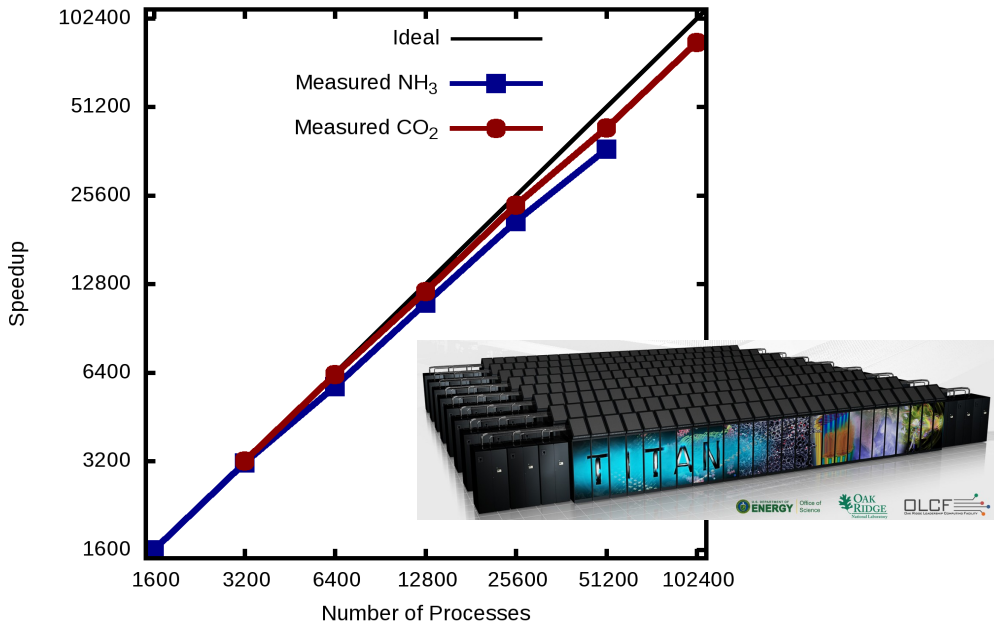
cscs

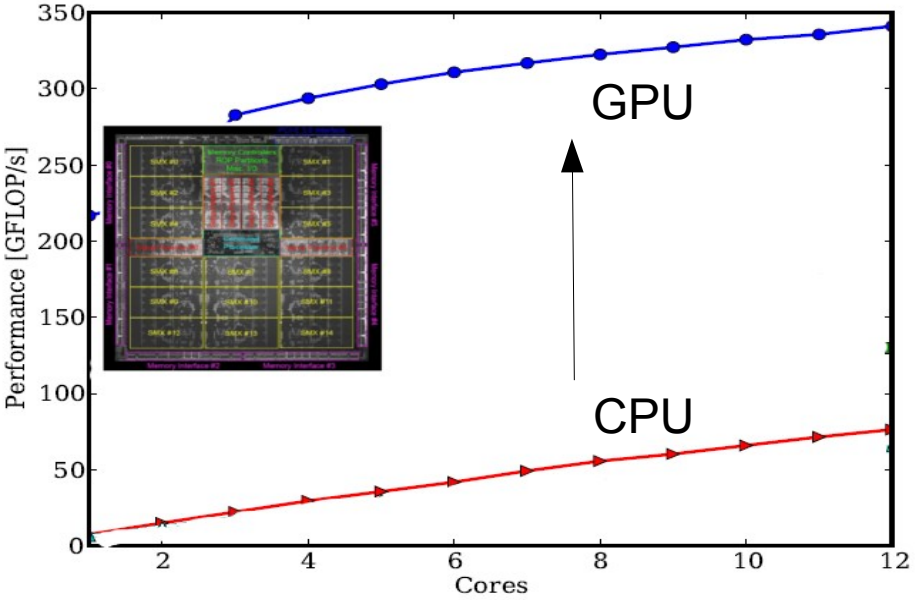
Research & co-design: Hardware vendors & scientists look together for the best solution (both soft- and hardware)

How can we program

for 10'000 – 1'000'000 cores ?

for 'emerging' architectures ?





Could save 300 MWh/yr for our group.

M. Del Ben, J. Hutter, J. VandeVondele, J. Chem. Theory Comput 8, 4177-4188 (2012)

Examples from 10 years ago

The two algorithms that enabled CP2K to do new science

- GPW in QS:
  - Combine the computational approaches (basis sets) from chemistry and physics, gas and condensed phases.
- OT
  - New approach to robustly and efficiently obtain electronic structure

J. VandeVondele, M. Krack, F. Mohamed, M. Parrinello, T. Chassaing and J. Hutter, Comp. Phys. Comm. 167, 103 (2005).
J. VandeVondele, J. Hutter, *J. Chem. Phys.,* 118 (10), 4365-4369 (2003)

http://www.cp2k.org/science/

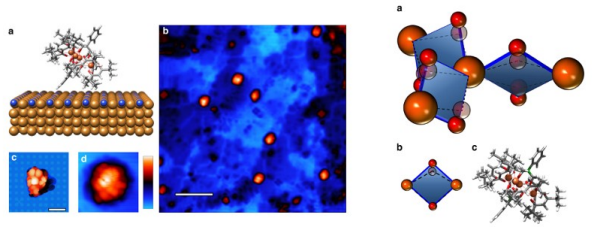
nature COMMUNICATIONS

ARTICLE

Received 21 Apr 2015 | Accepted 30 Jul 2015 | Published 11 Sep 2015 DOI: 10.1038/ncomms9216 OPEN

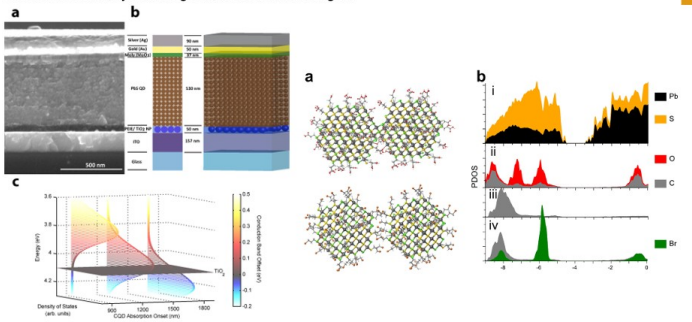
Magnetic fingerprint of individual Fe_4 molecular magnets under compression by a scanning tunnelling microscope

Jacob A.J. Burgess[1,2], Luigi Malavolti[1,2,3], Valeria Lanzilotto[3], Matteo Mannini[3], Shichao Yan[1,2], Silviya Ninova[3], Federico Totti[3], Steffen Rolf-Pissarczyk[1,2], Andrea Cornia[4], Roberta Sessoli[3] & Sebastian Loth[1,2]



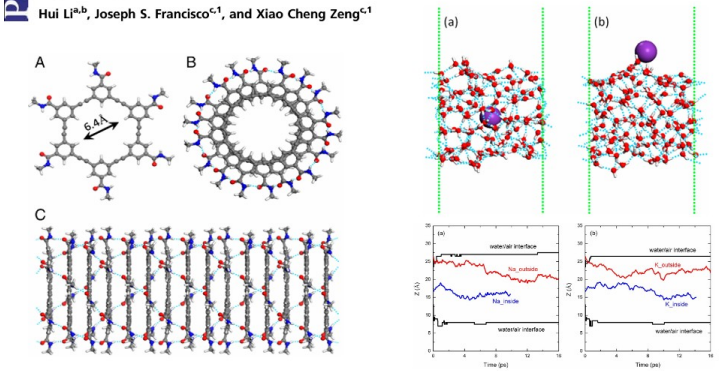
Infrared Colloidal Quantum Dot Photovoltaics *via* Coupling Enhancement and Agglomeration Suppression

Alexander H. Ip,‡ Amirreza Kiani,‡ Illan J. Kramer,‡ Oleksandr Voznyy, Hamidreza F. Movahed, Larissa Levina, Michael M. Adachi, Sjoerd Hoogland, and Edward H. Sargent*



Unraveling the mechanism of selective ion transport in hydrophobic subnanometer channels

Hui Li[a,b], Joseph S. Francisco[c,1], and Xiao Cheng Zeng[c,1]

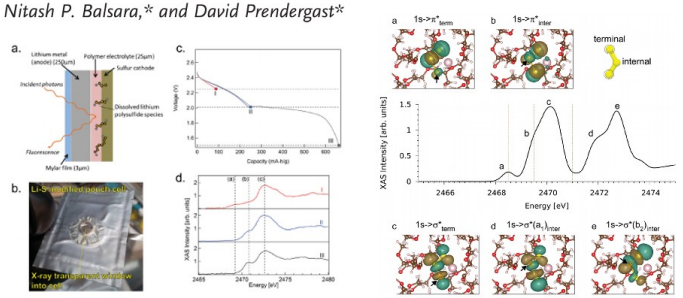


Materials Views www.MaterialsViews.com

ADVANCED ENERGY MATERIALS www.advenergymat.de

Characterization of Polysulfide Radicals Present in an Ether-Based Electrolyte of a Lithium–Sulfur Battery During Initial Discharge Using In Situ X-Ray Absorption Spectroscopy Experiments and First-Principles Calculations

Kevin H. Wujcik, Tod A. Pascal, C. D. Pemmaraju, Didier Devaux, Wayne C. Stolte, Nitash P. Balsara, and David Prendergast**



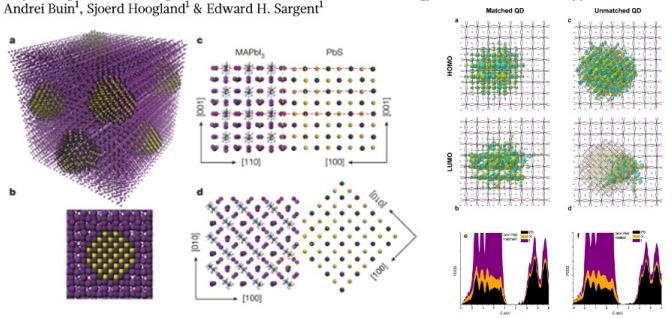
http://www.cp2k.org/science/

LETTER

doi:10.1038/nature14563

Quantum-dot-in-perovskite solids

Zhijun Ning[1]†*, Xiwen Gong[1]*, Riccardo Comin[1]*, Grant Walters[1], Fengjia Fan[1], Oleksandr Voznyy[1], Emre Yassitepe[1], Andrei Buin[1], Sjoerd Hoogland[1] & Edward H. Sargent[1]



ACS Catalysis

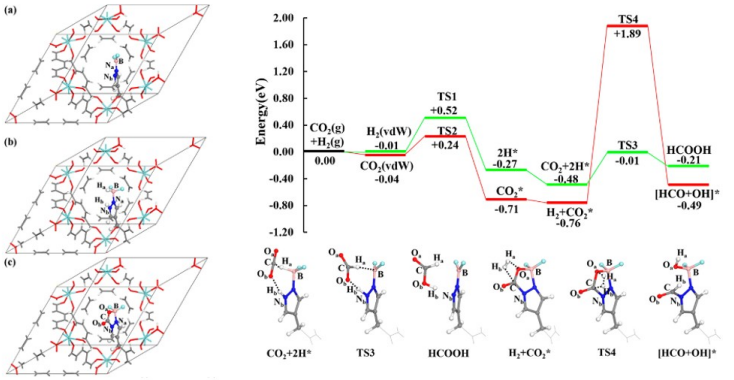
Research Article

pubs.acs.org/acscatalysis

Design of Lewis Pair-Functionalized Metal Organic Frameworks for CO_2 Hydrogenation

Jingyun Ye† and J. Karl Johnson*,†,‡

†Department of Chemical & Petroleum Engineering, University of Pittsburgh, Pittsburgh, Pennsylvania 15261, United States
‡National Energy Technology Laboratory, Pittsburgh, Pennsylvania 15236, United States



nature COMMUNICATIONS

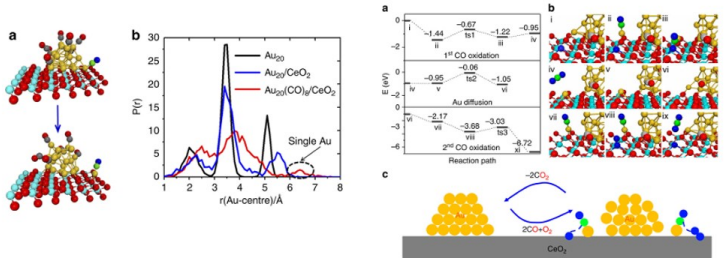
ARTICLE

Received 21 Oct 2014 | Accepted 4 Feb 2015 | Published 4 Mar 2015

DOI: 10.1038/ncomms7511 OPEN

Dynamic formation of single-atom catalytic active sites on ceria-supported gold nanoparticles

Yang-Gang Wang[1,2], Donghai Mei[1], Vassiliki-Alexandra Glezakou[1], Jun Li[2,3] & Roger Rousseau[1]



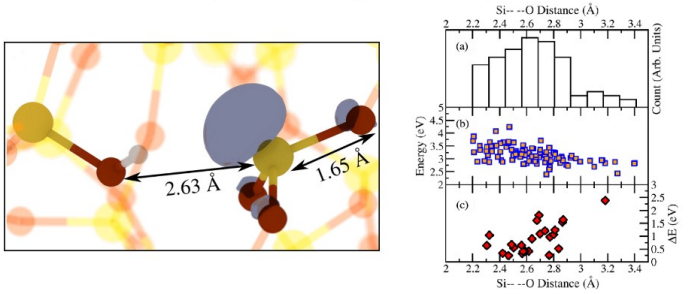
PRL 114, 115503 (2015) PHYSICAL REVIEW LETTERS week ending 20 MARCH 2015

Hydrogen-Induced Rupture of Strained Si–O Bonds in Amorphous Silicon Dioxide

Al-Moatasem El-Sayed,[1,*] Matthew B. Watkins,[1,†] Tibor Grasser,[2,‡] Valery V. Afanas'ev,[3,§] and Alexander L. Shluger[1,¶]

[1]Department of Physics and Astronomy and London Centre for Nanotechnology, University College London, Gower Street, London WC1E 6BT, United Kingdom
[2]Institute for Microelectronics, Technische Universität Wien, A-1040 Vienna, Austria
[3]Department of Physics, University of Leuven, Celestijnenlaan 200D, 3001 Leuven, Belgium

(Received 2 November 2014; published 18 March 2015)



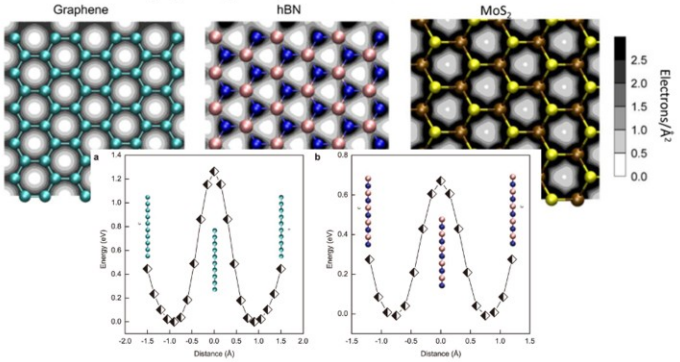
http://www.cp2k.org/science/

LETTER

doi:10.1038/nature14015

Proton transport through one-atom-thick crystals

S. Hu[1,2], M. Lozada-Hidalgo[1], F. C. Wang[3], A. Mishchenko[1], F. Schedin[2], R. R. Nair[1], E. W. Hill[2], D. W. Boukhvalov[4], M. I. Katsnelson[4], R. A. W. Dryfe[5], I. V. Grigorieva[1], H. A. Wu[3] & A. K. Geim[1,2]



NANO LETTERS

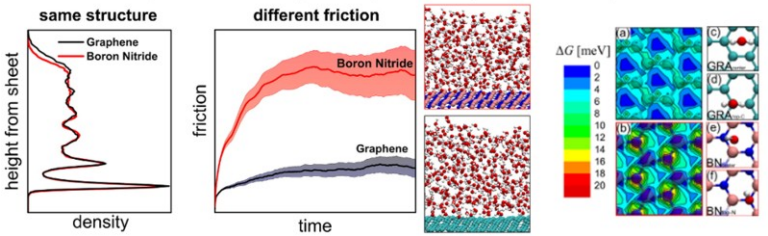
Letter

pubs.acs.org/NanoLett

Friction of Water on Graphene and Hexagonal Boron Nitride from *Ab Initio* Methods: Very Different Slippage Despite Very Similar Interface Structures

Gabriele Tocci,[†,‡,§] Laurent Joly,[∥] and Angelos Michaelides*[,†,‡,§]

[†]Thomas Young Centre, [‡]London Centre for Nanotechnology, University College London, London WC1E 6BT, United Kingdom
[§]Department of Chemistry, University College London, London WC1H 0AJ, United Kingdom
[∥]Institut Lumière Matière, UMR5306 Université Lyon 1-CNRS, Université de Lyon 69622 Villeurbanne, France

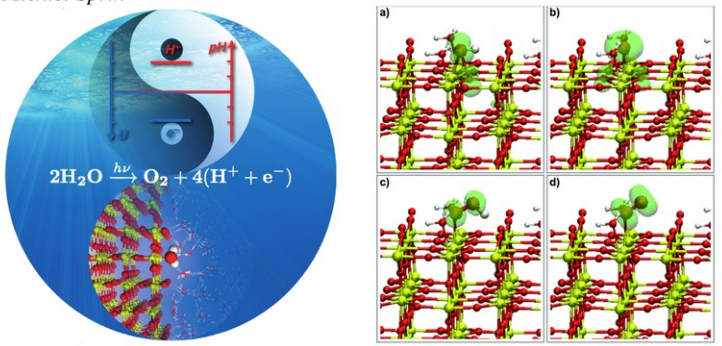


Thermodynamics

DOI: 10.1002/anie.201405648

Aligning Electronic and Protonic Energy Levels of Proton-Coupled Electron Transfer in Water Oxidation on Aqueous TiO_2**

Jun Cheng, Xiandong Liu, John A. Kattirtzi, Joost VandeVondele, and Michiel Sprik*

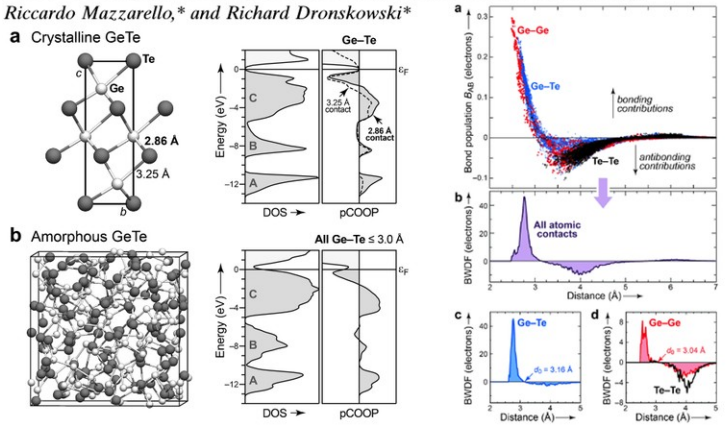


Amorphous Materials Very Important Paper

DOI: 10.1002/anie.201404223

Bonding Nature of Local Structural Motifs in Amorphous GeTe**

Volker L. Deringer, Wei Zhang, Marck Lumeij, Stefan Maintz, Matthias Wuttig, Riccardo Mazzarello, and Richard Dronskowski**



http://www.cp2k.org/science/

nature COMMUNICATIONS

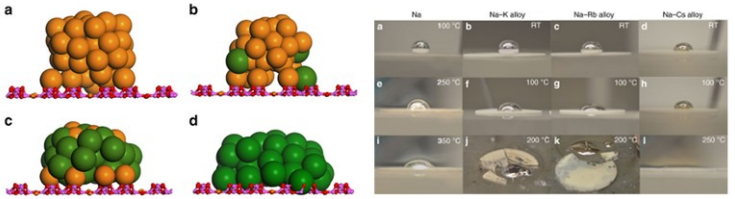
ARTICLE

Received 22 Jan 2014 | Accepted 2 Jul 2014 | Published 1 Aug 2014

DOI: 10.1038/ncomms5578

Liquid-metal electrode to enable ultra-low temperature sodium–beta alumina batteries for renewable energy storage

Xiaochuan Lu[1], Guosheng Li[1], Jin Y. Kim[1], Donghai Mei[2], John P. Lemmon[1], Vincent L. Sprenkle[1] & Jun Liu[1]



JACS

JOURNAL OF THE AMERICAN CHEMICAL SOCIETY

Article

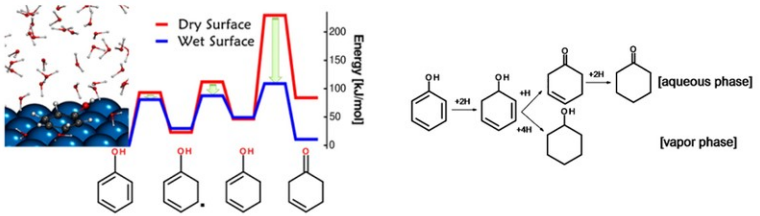
pubs.acs.org/JACS

First-Principles Study of Phenol Hydrogenation on Pt and Ni Catalysts in Aqueous Phase

Yeohoon Yoon,[†] Roger Rousseau,[*,†] Robert S. Weber,[†] Donghai Mei,[*,†] and Johannes A. Lercher[*,†,‡]

[†]Institute for Integrated Catalysis, Pacific Northwest National Laboratory, Richland, Washington 99352, United States

[‡]Department of Chemistry and Catalysis Research Institute, Technische Universität München, Garching 85747, Germany



ADVANCED MATERIALS
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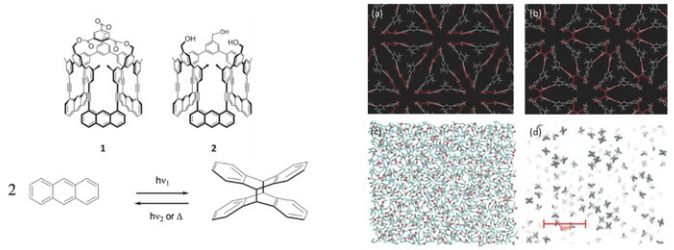
Materials Views
www.MaterialsViews.com

Synthesis of a Covalent Monolayer Sheet by Photochemical Anthracene Dimerization at the Air/Water Interface and its Mechanical Characterization by AFM Indentation

*Payam Payamyar, Khaled Kaja, Carlos Ruiz-Vargas, Andreas Stemmer, Daniel J. Murray, Carey J. Johnson, Benjamin T. King, Florian Schiffmann, Joost VandeVondele, Alois Renn, Stephan Götzinger, Paola Ceroni, Andri Schütz, Lay-Theng Lee, Zhikun Zheng, Junji Sakamoto, and A. Dieter Schlüter**



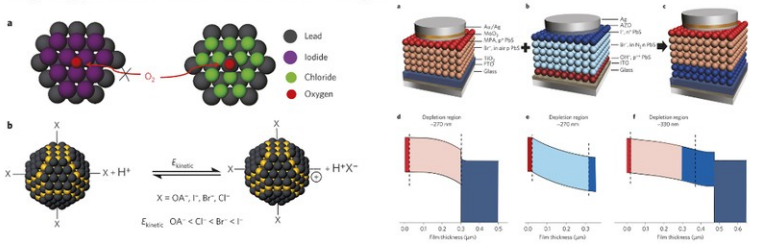
ARTICLES

PUBLISHED ONLINE: 8 JUNE 2014 | DOI: 10.1038/NMAT4007

nature materials

Air-stable n-type colloidal quantum dot solids

Zhijun Ning[1], Oleksandr Voznyy[1], Jun Pan[2], Sjoerd Hoogland[1], Valerio Adinolfi[1], Jixian Xu[1], Min Li[3], Ahmad R. Kirmani[2], Jon-Paul Sun[4], James Minor[1], Kyle W. Kemp[1], Haopeng Dong[1], Lisa Rollny[1], André Labelle[1], Graham Carey[1], Brandon Sutherland[1], Ian Hill[4], Aram Amassian[2], Huan Liu[3], Jiang Tang[5], Osman M. Bakr[2] and Edward H. Sargent[1]*



http://www.cp2k.org/science/

nature COMMUNICATIONS

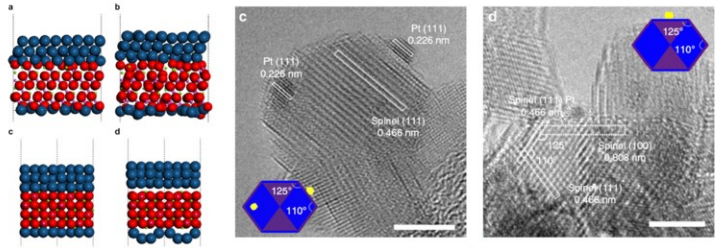
ARTICLE

Received 19 Feb 2013 | Accepted 21 Aug 2013 | Published 25 Sep 2013

DOI: 10.1038/ncomms3481

Stable platinum nanoparticles on specific $MgAl_2O_4$ spinel facets at high temperatures in oxidizing atmospheres

Wei-Zhen Li[1], Libor Kovarik[1], Donghai Mei[1], Jun Liu[1], Yong Wang[1,2] & Charles H.F. Peden[1]



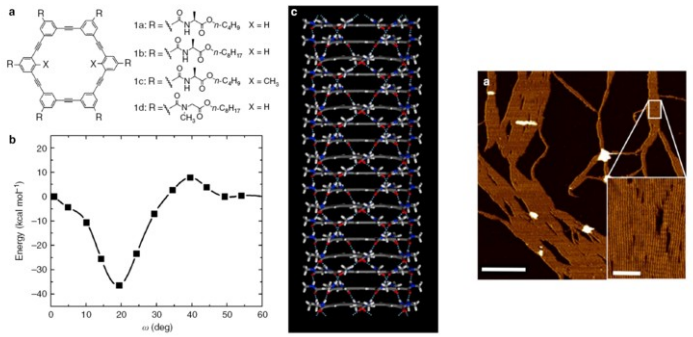
ARTICLE

Received 2 Apr 2012 | Accepted 11 Jun 2012 | Published 17 Jul 2012

DOI: 10.1038/ncomms1949

Self-assembling subnanometer pores with unusual mass-transport properties

Xibin Zhou[1,*], Guande Liu[2,*], Kazuhiro Yamato[3], Yi Shen[4], Ruixian Cheng[1], Xiaoxi Wei[3], Wanli Bai[1], Yi Gao[4,5], Hui Li[5], Yi Liu[1], Futao Liu[1], Daniel M. Czajkowsky[4], Jingfang Wang[2], Michael J. Dabney[3], Zhonghou Cai[6], Jun Hu[4], Frank V. Bright[3], Lan He[1], Xiao Cheng Zeng[5], Zhifeng Shao[2] & Bing Gong[1,3]



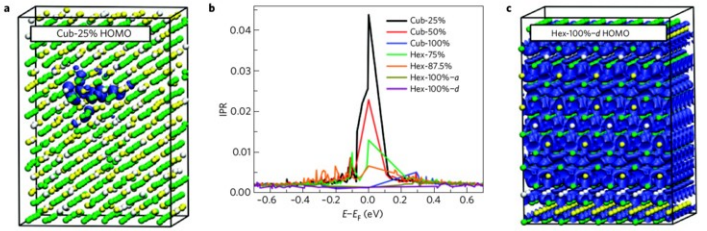
ARTICLES

PUBLISHED ONLINE: 14 OCTOBER 2012 | DOI: 10.1038/NMAT3456

nature materials

Role of vacancies in metal–insulator transitions of crystalline phase-change materials

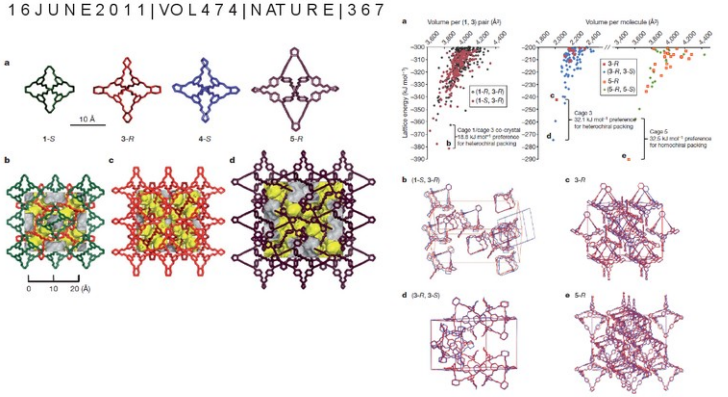
W. Zhang[1], A. Thiess[2,3], P. Zalden[4], R. Zeller[2], P. H. Dederichs[2], J-Y. Raty[5], M. Wuttig[4,6]*, S. Blügel[2,6] and R. Mazzarello[1,6]*



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[1] & Andrew I. Cooper[1]

16 JUNE 2011 | VOL 474 | NATURE | 367

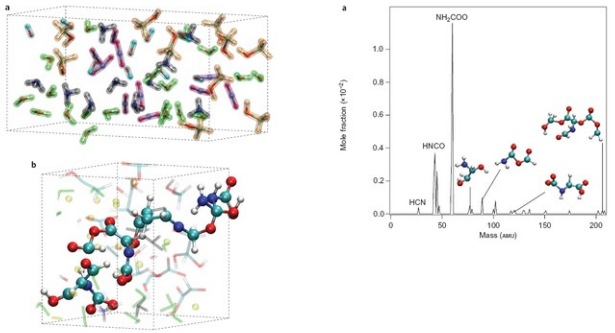


http://www.cp2k.org/science/

nature chemistry
ARTICLES
PUBLISHED ONLINE: 12 SEPTEMBER 2010 | DOI: 10.1038/NCHEM.827

Synthesis of glycine-containing complexes in impacts of comets on early Earth

Nir Goldman*, Evan J. Reed†, Laurence E. Fried, I.-F. William Kuo and Amitesh Maiti

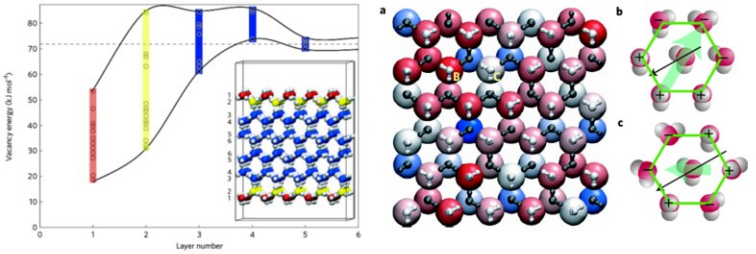


Large variation of vacancy formation energies in the surface of crystalline ice

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.

NATURE MATERIALS | VOL 10 | OCTOBER 2011

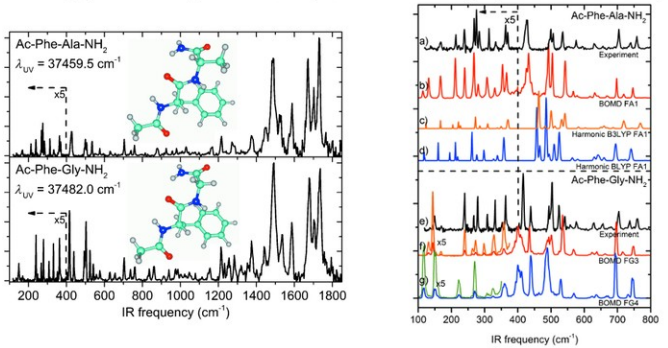


Far-IR Spectroscopy

DOI: 10.1002/anie.201311189

Gas-Phase Peptide Structures Unraveled by Far-IR Spectroscopy: Combining IR-UV Ion-Dip Experiments with Born–Oppenheimer Molecular Dynamics Simulations**

Sander Jaeqx, Jos Oomens, Alvaro Cimas, Marie-Pierre Gaigeot, and Anouk M. Rijs**



nature chemistry
ARTICLES
PUBLISHED ONLINE: 7 NOVEMBER 2010 | DOI: 10.1038/NCHEM.891

Surface-assisted cyclodehydrogenation provides a synthetic route towards easily processable and chemically tailored nanographenes

Matthias Treier[1†], Carlo Antonio Pignedoli[1], Teodoro Laino[2†], Ralph Rieger[3], Klaus Müllen[3], Daniele Passerone[1] and Roman Fasel[1,4]*

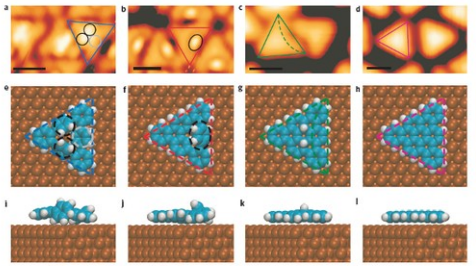
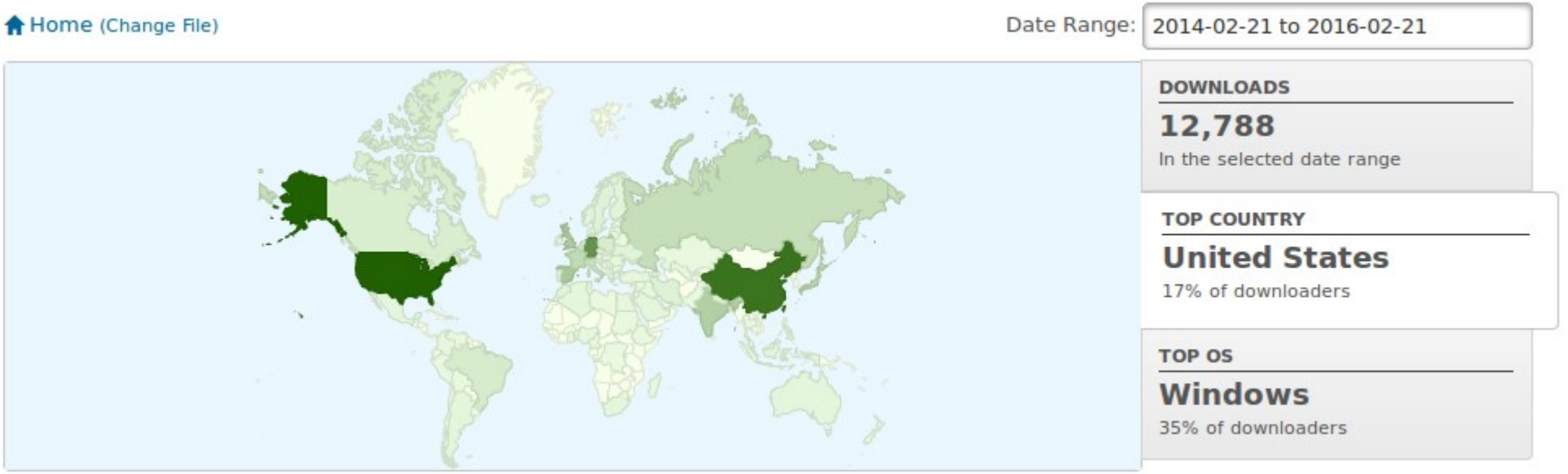


Figure 3 | High-resolution STM images of reactant, intermediates and final product on Cu(111). a-d, Triangles and circles are used to highlight

CP2K user base



Unique visitors of .cp2k.org: ~10.000 / month
Unique visitors of manual.cp2k.org: ~ 2.000 / month

(Jan 2016)

2015 (manual):

>100 US .edu including:

Berkeley, harvard, mit, purdue, princeton, rice, stanford, ucdavis, uchicago, ucla, ucsb, yale, …

>30 UK .ac.uk including:

Bham, bris, cam, ox, ucl, ic, kcl, qub, warwick

.ch including:

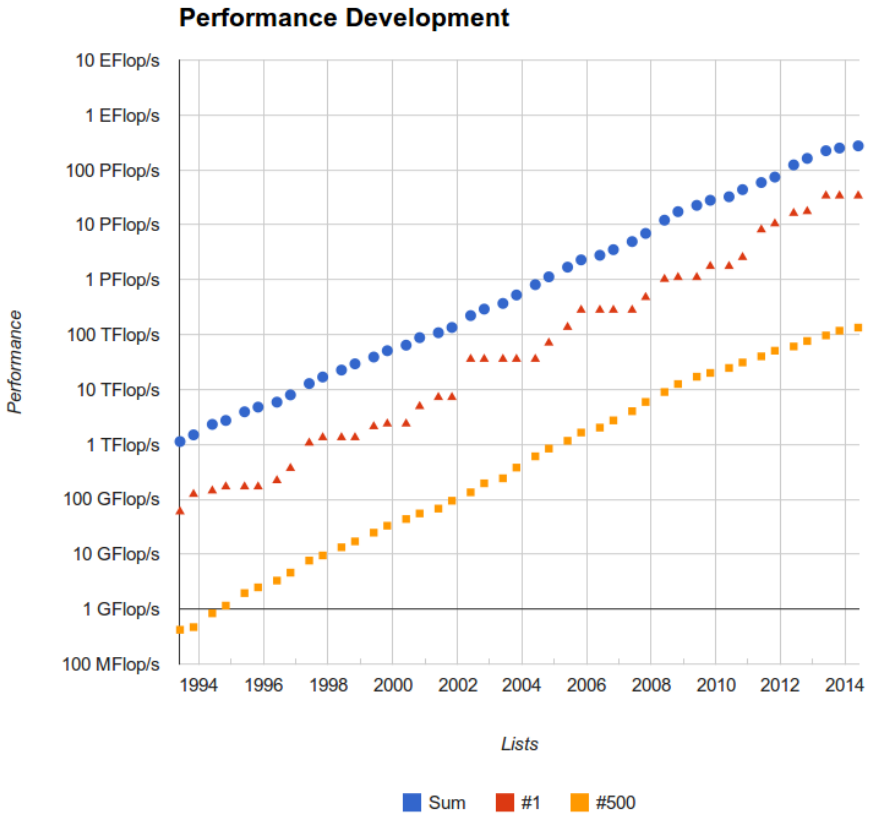
Ethz, epfl, psi, empa, unibas, unifr, unige, usi, uzh

Petascale supercomputing

1 petaflops = solve 100'000 coupled equations for 100'000 unknowns in 1 sec.
= 1'000'000'000'000'000 multiplications/additions per sec.

#1 = 34 petaflops (June 2015), Switzerland: 6 petaflops (rank 6, 1st in europe)

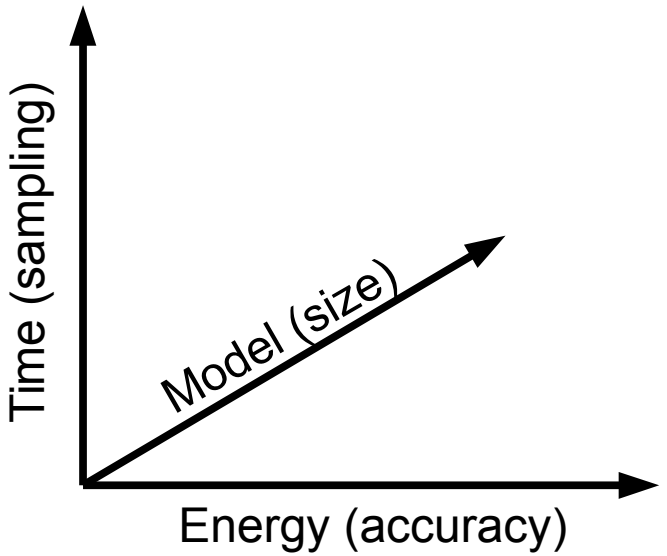
The 68 fastest computers in the world have peak petaflop performance



Parallel computers have followed a path of sustained *exponential growth* for 20 years

- Serial computers.... do not exist anymore
  Serial programs become irrelevant
- 1 month now = 1 day in 5 years
- Few experimental techniques show exponential increases in throughput, performance, or resolution

Improving the predictive nature of atomistic simulations

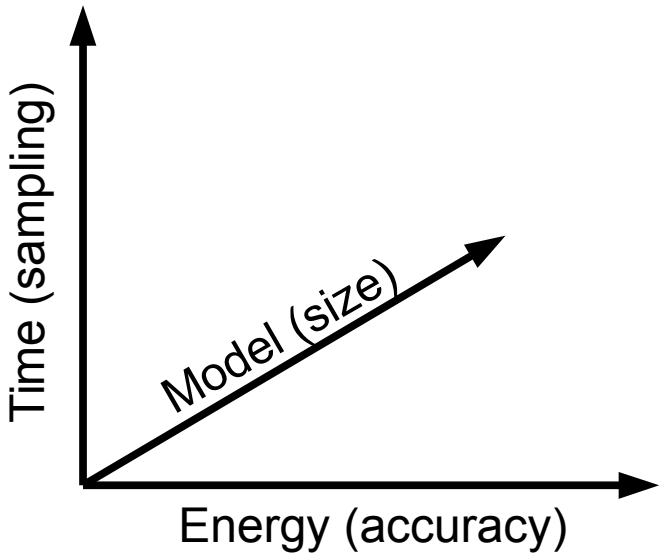


Time:
- Longer simulation
- Sampling (Entropy)
- Parameter scans
- Uncertainty quantification

Energy:
- 'eliminate' technicalities (basis)
- beyond GGA

Model:
- reduce size effects (small unit cells?)
- include explicit solvents
- nanoparticles vs. slabs

Improving the predictive nature of atomistic simulations



Time:

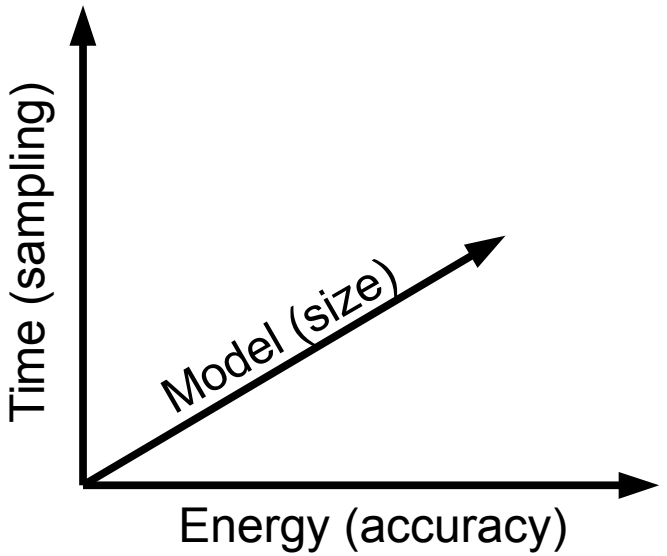
- Long time: TMC
- Short time: EMD
- Imaginary time: PIMD

Energy:

MP2 and RPA in the condensed phase

Model:

Linear scaling DFT



MODEL

Linear scaling DFT: concepts

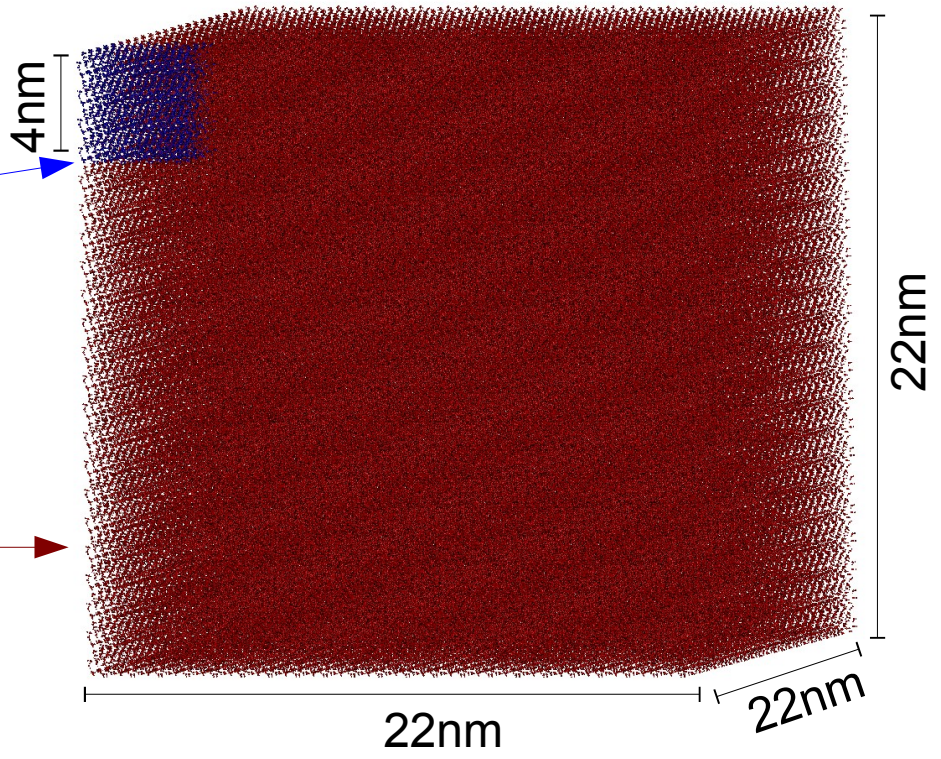
A different perspective on the equations of quantum mechanics, no more wavefunctions...

$$\hat{H}\psi_i = \varepsilon_i \psi_i \quad ; \quad E = \sum_i \varepsilon_i$$

$$\hat{P} = f(\hat{H}) \quad ; \quad E = \mathrm{trace}(\hat{P}\hat{H})$$

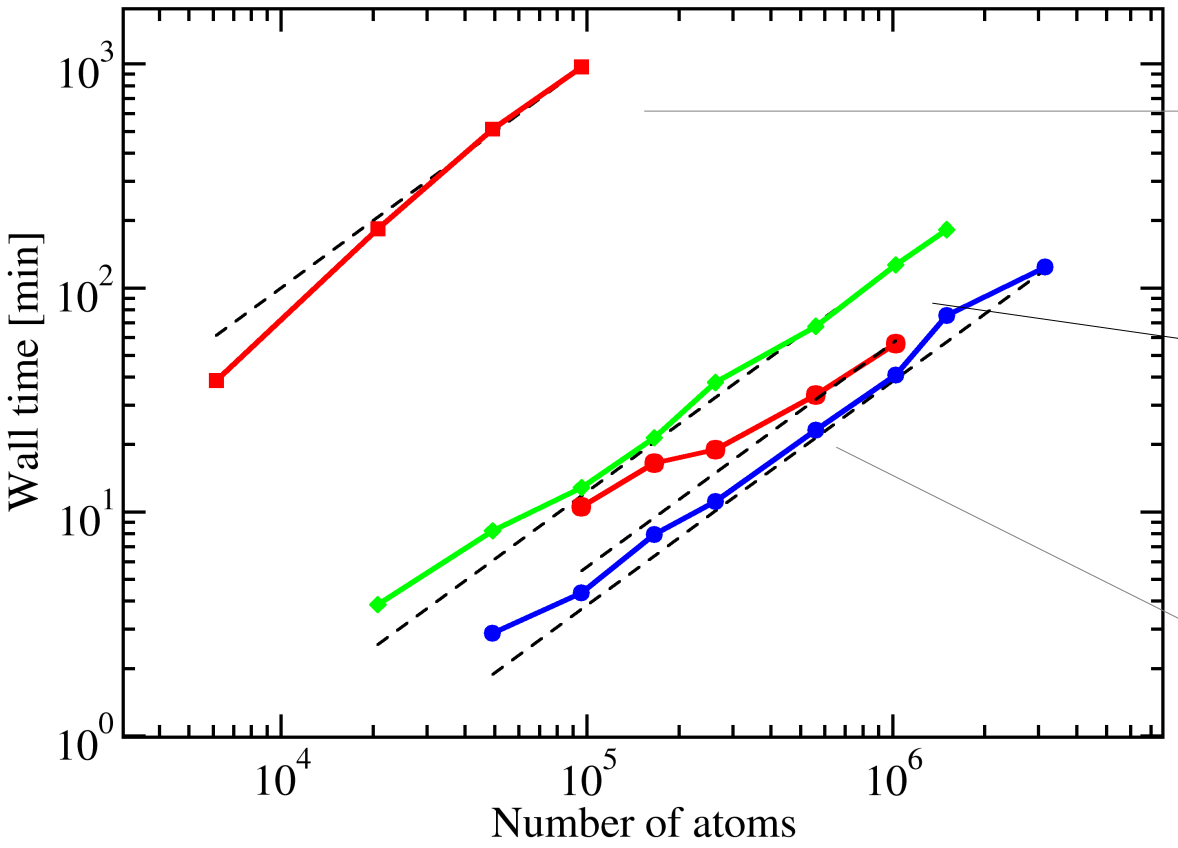
The density matrix is the natural quantity that allows for exploiting the nearsightedness of nature!

Largest O(N^3) calculation with CP2K (~6000 atoms)



Largest O(N) calculation with CP2K (~1'000'000 atoms)

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

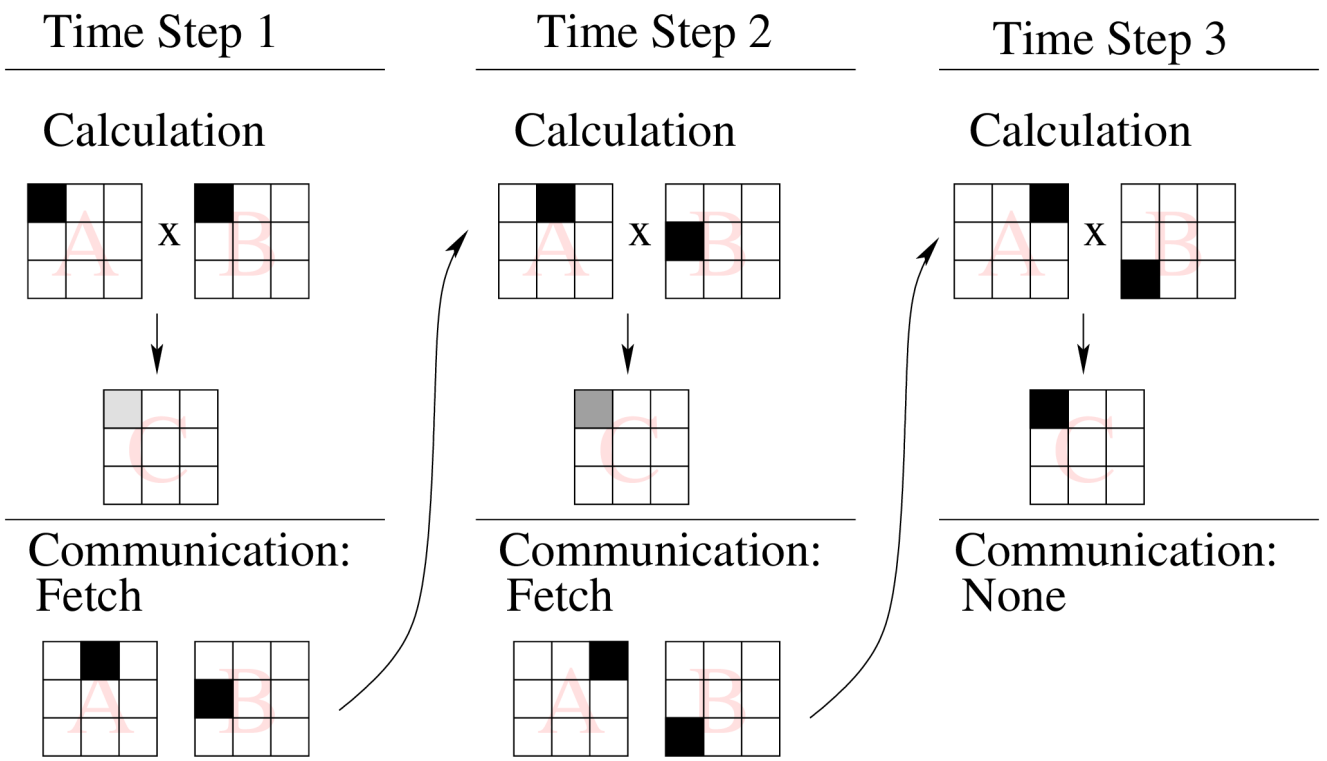
Bulk liquid water. Dashed lines represent ideal linear scaling.

VandeVondele, Borstnik, Hutter, JCTC, 8(12) 3565 (2012)

DBCSR: a sparse matrix library

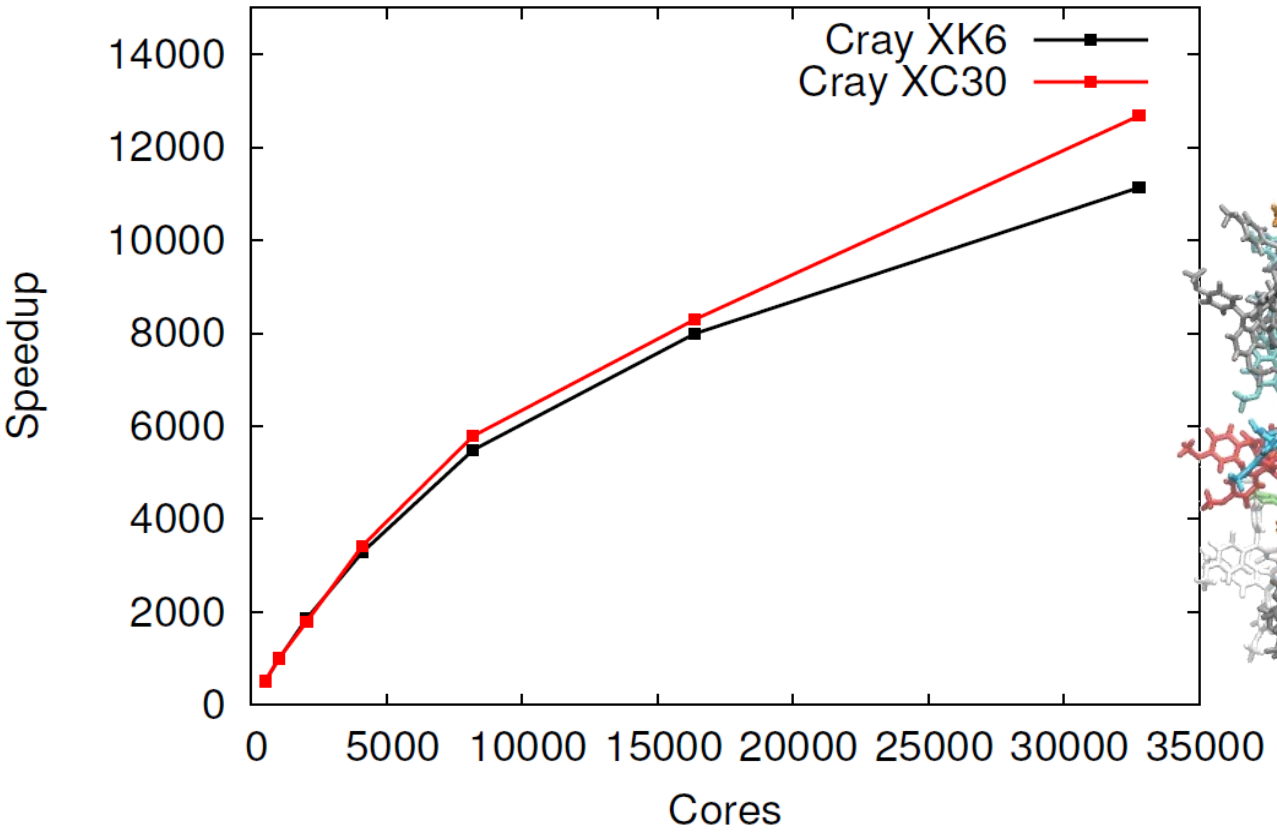
Distributed Blocked Compressed Sparse Row
Distributed Blocked Cannon Sparse Recursive

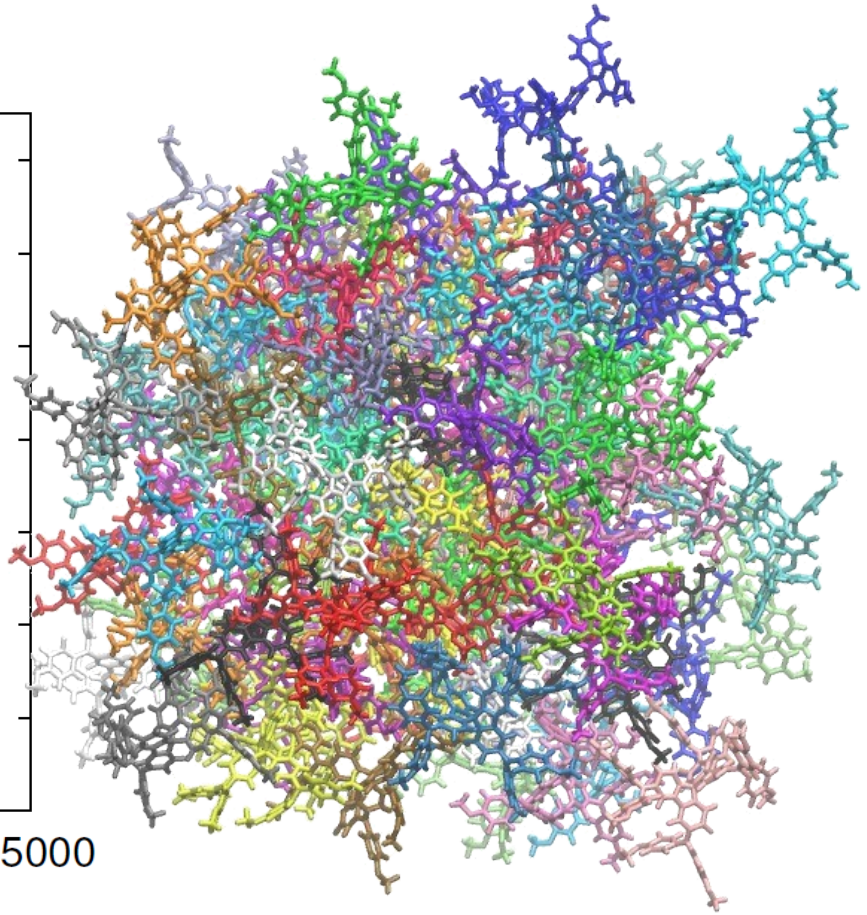
Optimized for the science case: 1000s of non-zeros per row.
Standalone library available: dbcsr.cp2k.org



Borstnik et al. : parallel computing (2014)

Performance: strong scaling



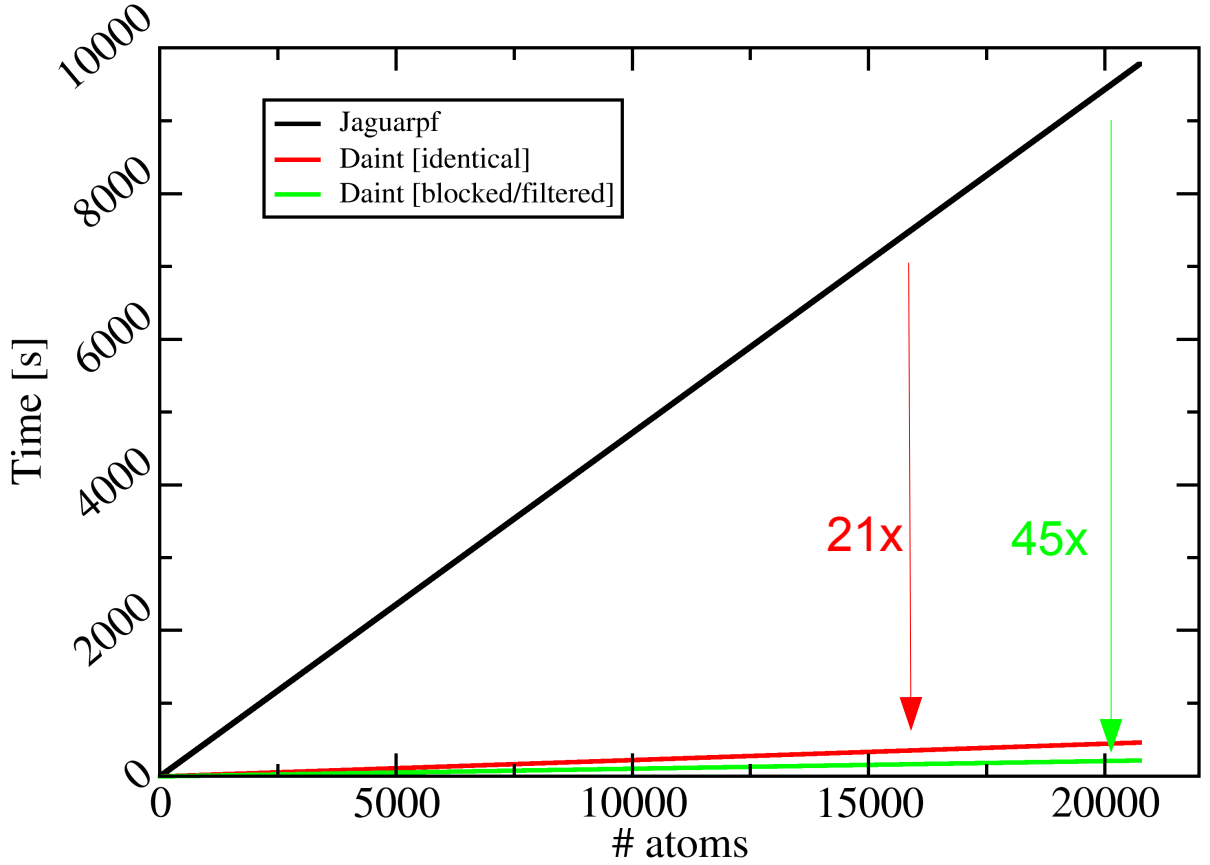


13846 atoms and 39560 electrons (cell 53.84 A), 133214 basis functions.

At full scale-out on the XC30 one multiplication takes less than 0.5s on average, one SCF step 24s.

'Historical' comparison

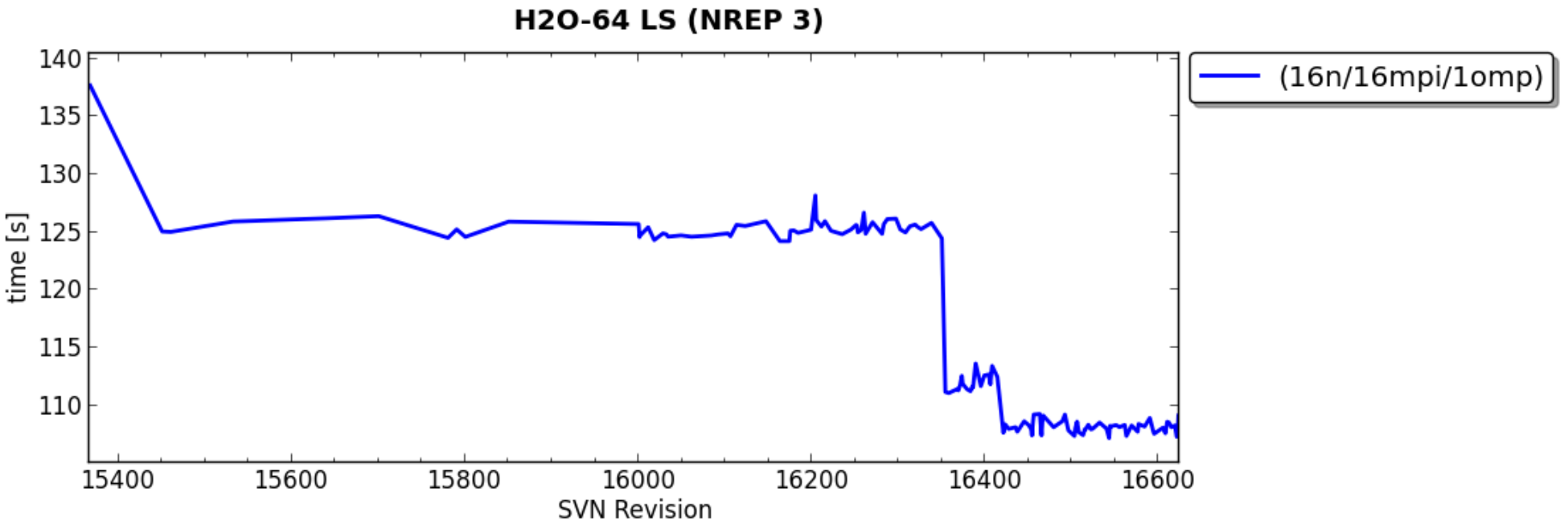
1) Run on Jaguarpf (XT5, 2011-01-01), 3888 nodes (12 cores)
2) Run on Daint (XC30, 2013-11-17), 3844 nodes (8 cores + 1 GPU)



Testcase 'H2O-dft-ls-orig' : 20'000 atoms

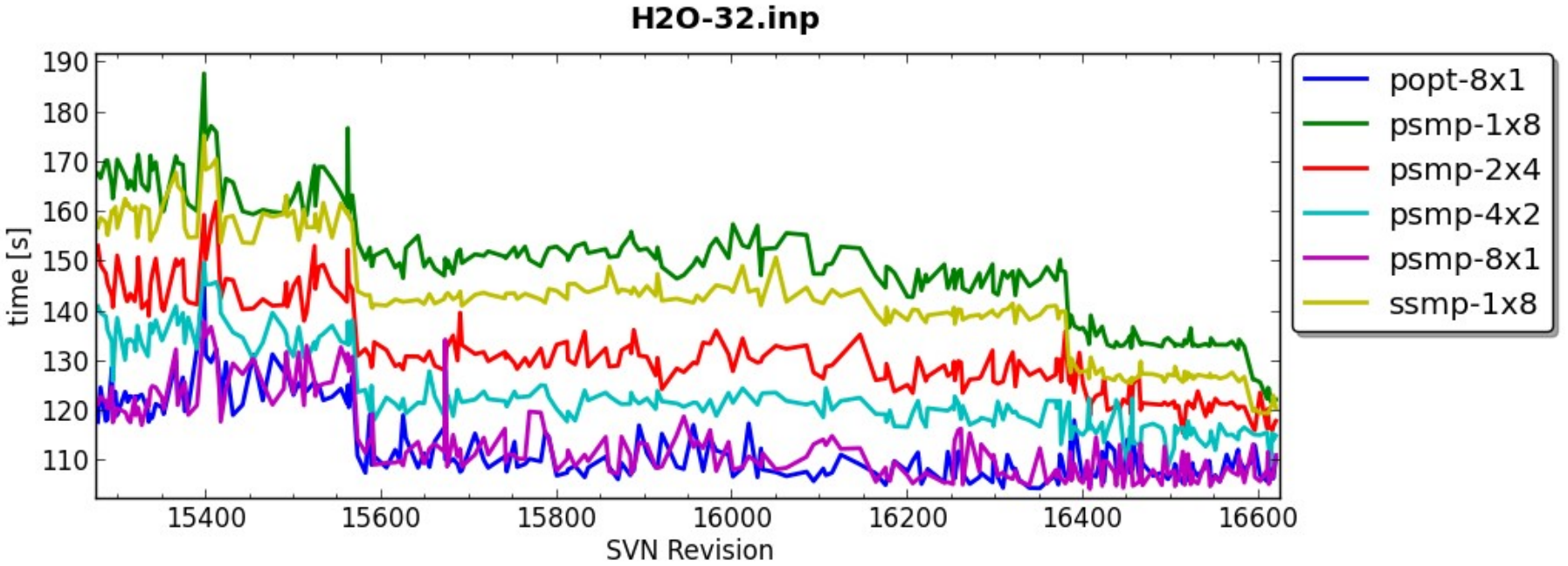
Original run published in : VandeVondele, Borstnik, Hutter, JCTC, 2012

Tracking progress: https://dashboard.cp2k.org/



Our regular testing now includes 'selected' performance data.
This will document the progress that comes in small steps.

Tracking progress: https://dashboard.cp2k.org/



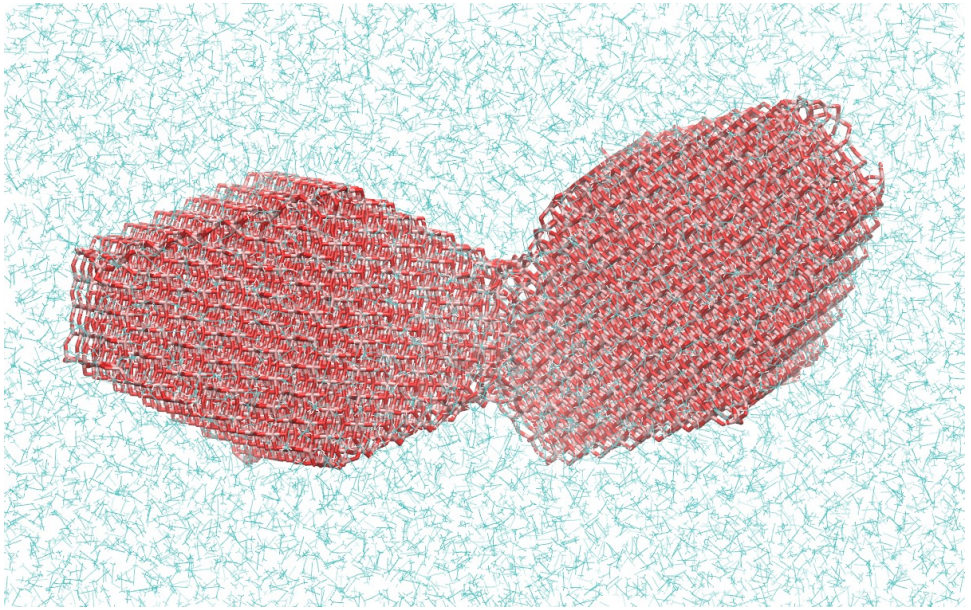
OMP improvements... 40% speedup or almost there ?

Piz Daint acceptance: science case

Piz Daint, Cray XC30, CSCS

Where are the trap states?

Matrix dims ~ 772868 x 772868
Threshold ~1E-6
% non-zero ~ 4%
SCF steps ~ 50
multiplies needed ~ 2000



80'000 atoms DFT, high accuracy settings
Aggregated nanoparticles in explicit solution
Relevant for 3rd generation solar cells

Dense flops needed =
184661334367982412800O

Actual flops needed =
84992840373629580 2

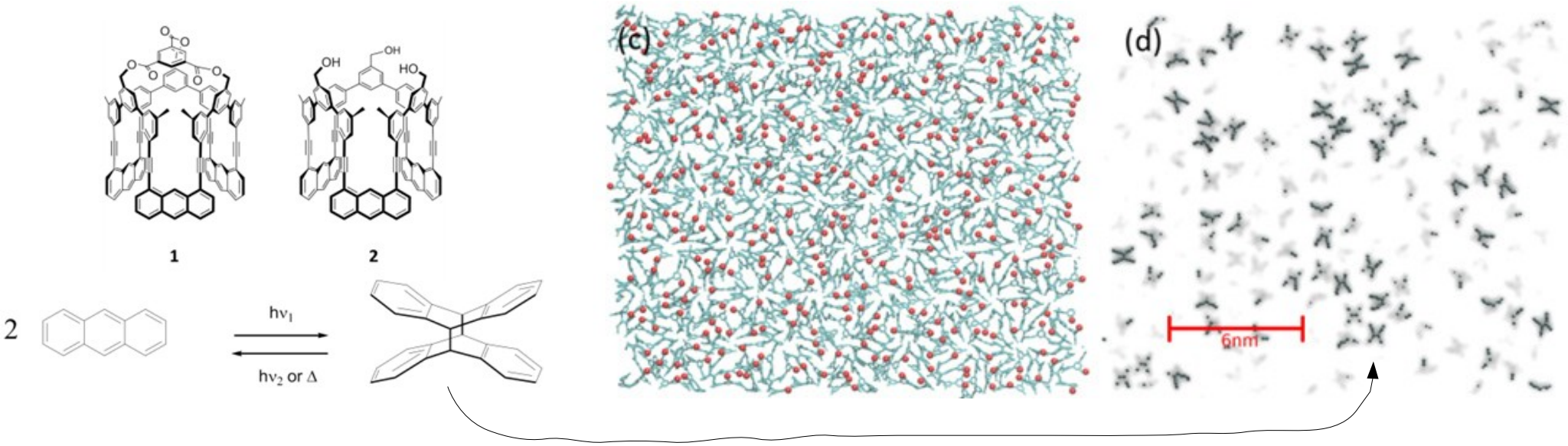
Sparsity boost = 2172x

GPU flop % = 99.4

Time on 5184 nodes = 6264s

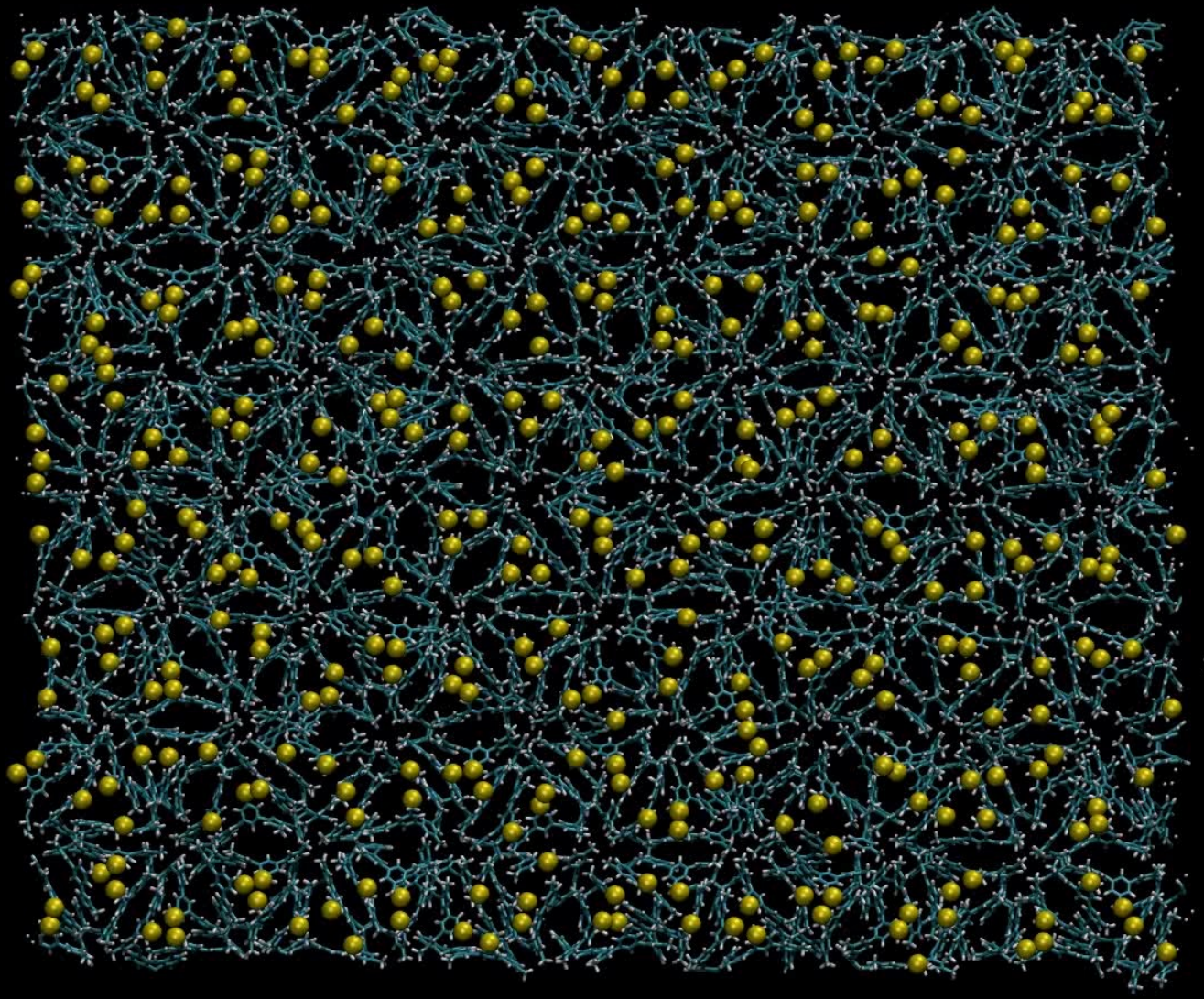
Bridging from linear scaling SCF to materials properties

2D polymers: synthetically tailored 2D materials beyond graphene



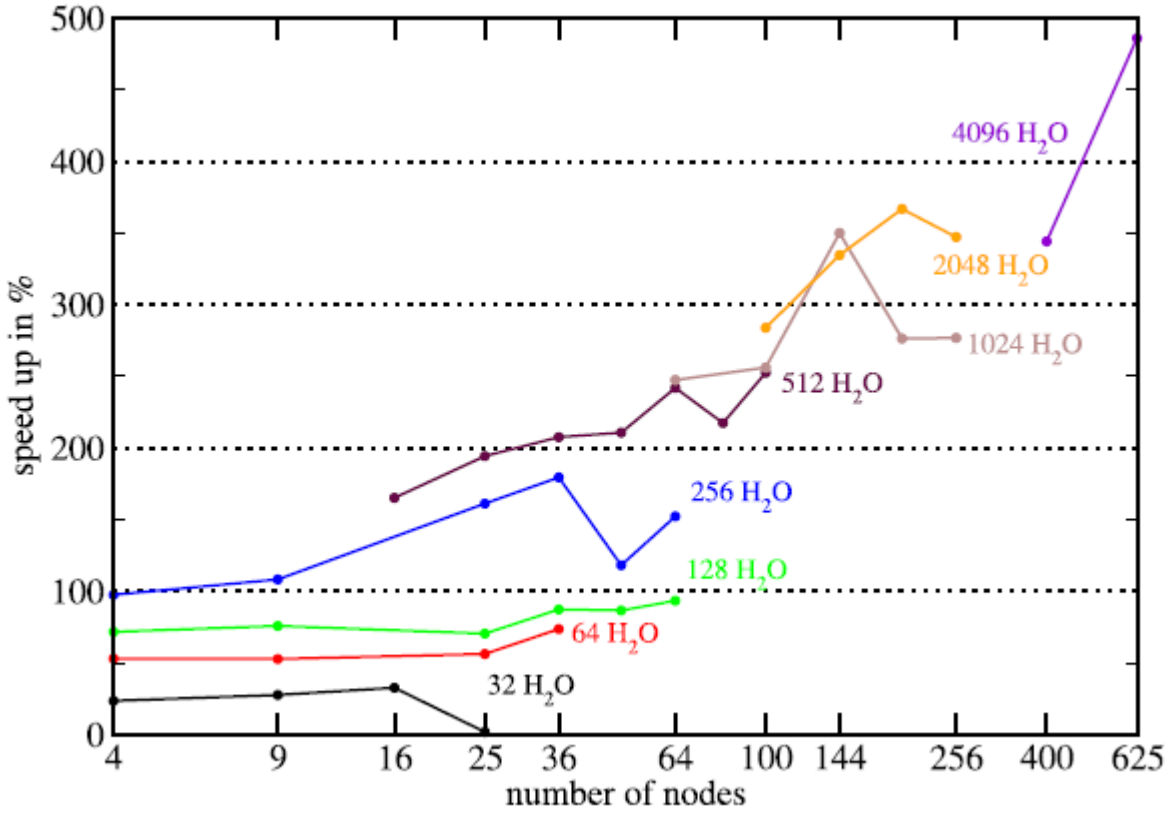
Based on <u>linear scaling MD simulations for 10'000s of atoms</u>, the morphology and properties of the proposed 2D polymer sheets has been investigated using DFTB

Payam Payamyar, Khaled Kaja, Carlos Ruiz Vargas, Andreas Stemmer, Daniel J. Murray, Carey Johnson, Benjamin T. King, Florian Schiffmann, Joost VandeVondele, Alois Renn, Paola Ceroni, Andri Schütz, Lay-Theng Lee, Zhikun Zheng, Junji Sakamoto, A. Dieter Schlüter, Accepted in ADVANCED MATERIALS (2014).



But OT is hard to beat !

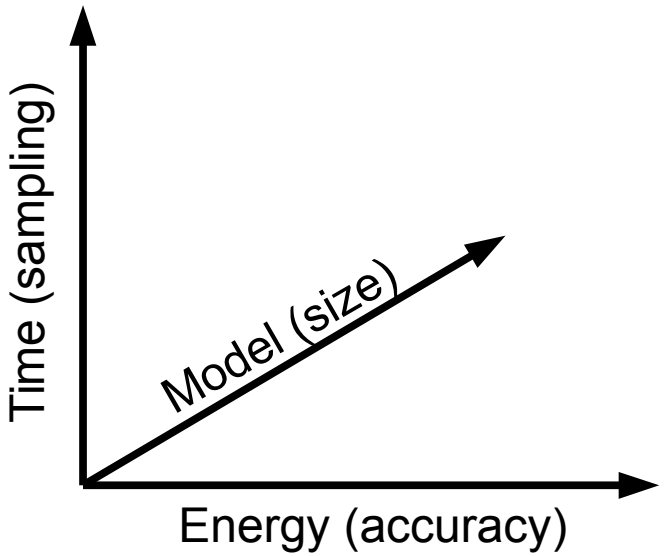
Refined preconditioner, most effective during MD of large systems with well conditioned basis sets



Improved Single Inverse Preconditioner

Preconditioner Solver based on an inverse update.

Schiffmann, VandeVondele, JCP 142 244117 (2015)



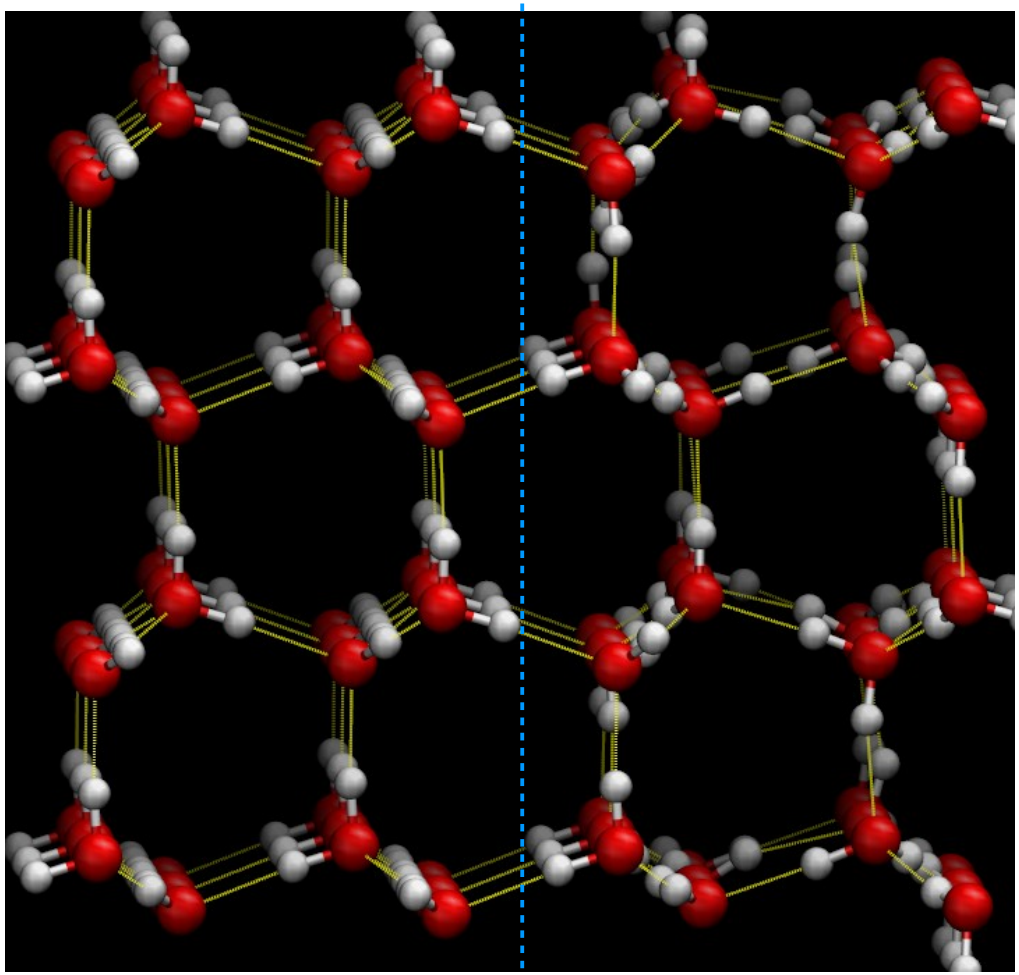
TIME

Reaching long time scales: Tree Monte Carlo

Ih ↔ XI phase transition

Order
XI

Disorder
Ih



Low temperature ~76K 'High' temperature

Ih : proton disordered hexagonal phase of ice
XI : proton ordered

The same oxygen lattice,
and both satisfying the ice rules

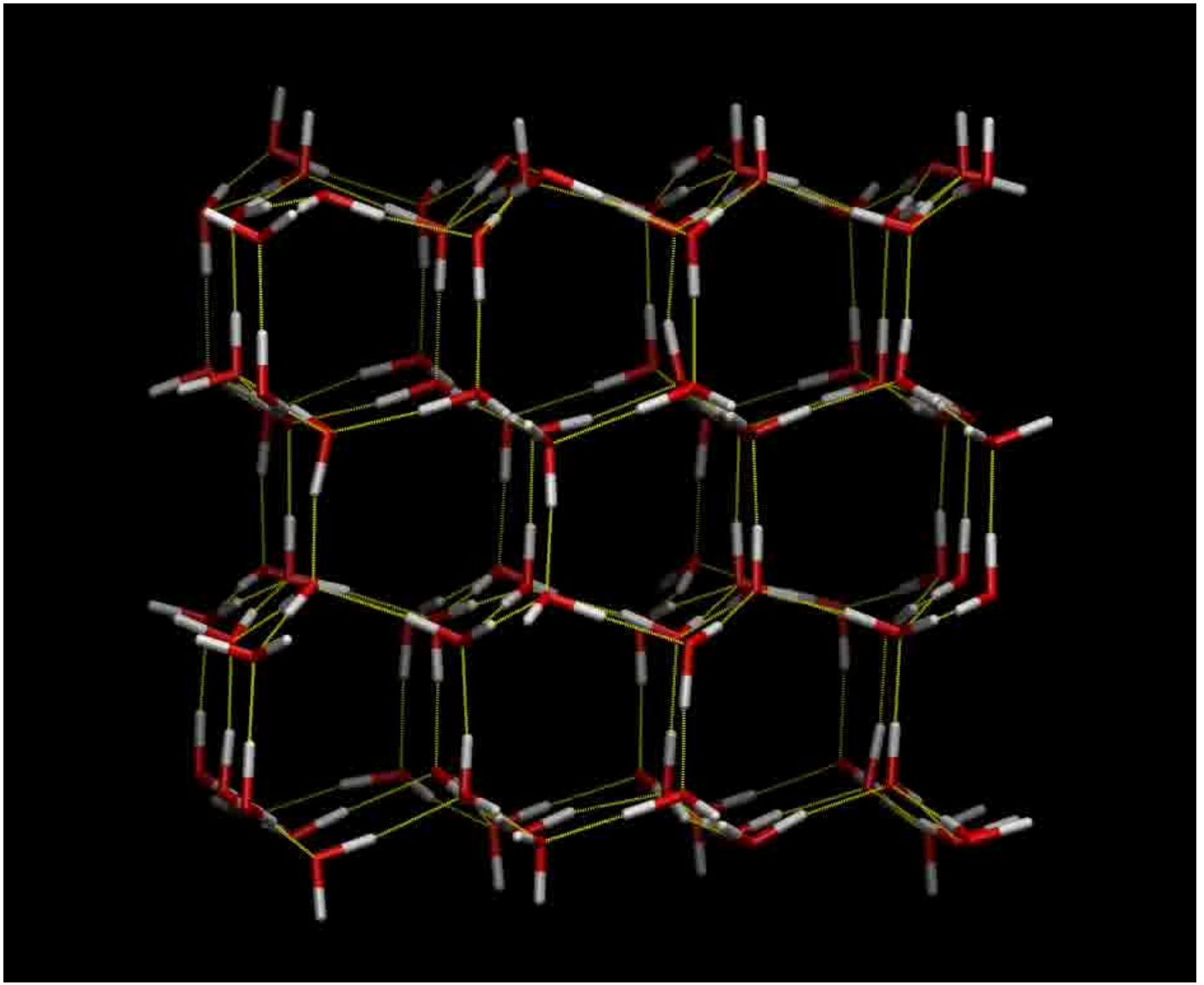
Experimentally obtaining XI is hard!
- Long time scales (>years, doping required)
- Has never been made pure

A balance between delicate energetics and entropy

Can we confirm the experimental XI phase ?
- The phase transition temperature ?
- The properties of the XI/Ih phases

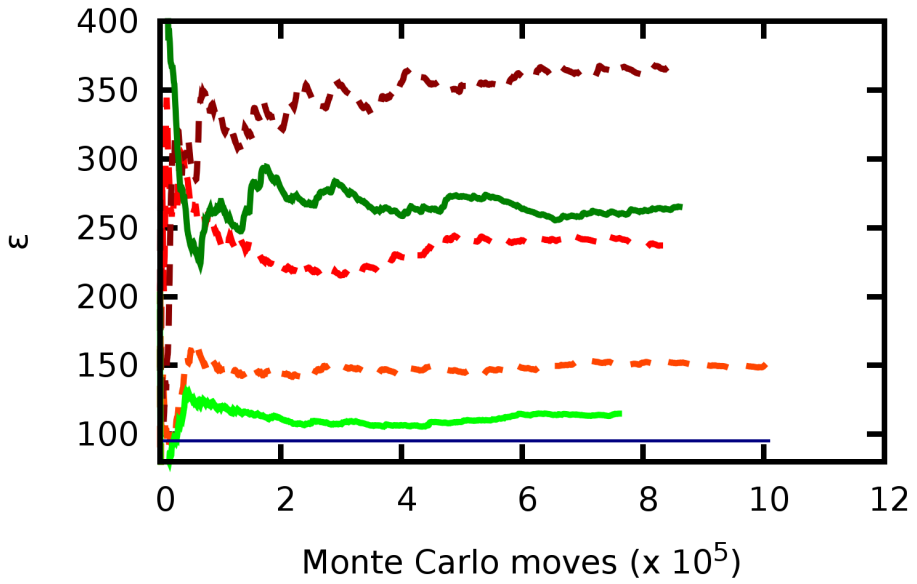
⇨ Assesment of DFT for water in the condensed phase

Ice Ih DFT based Monte Carlo

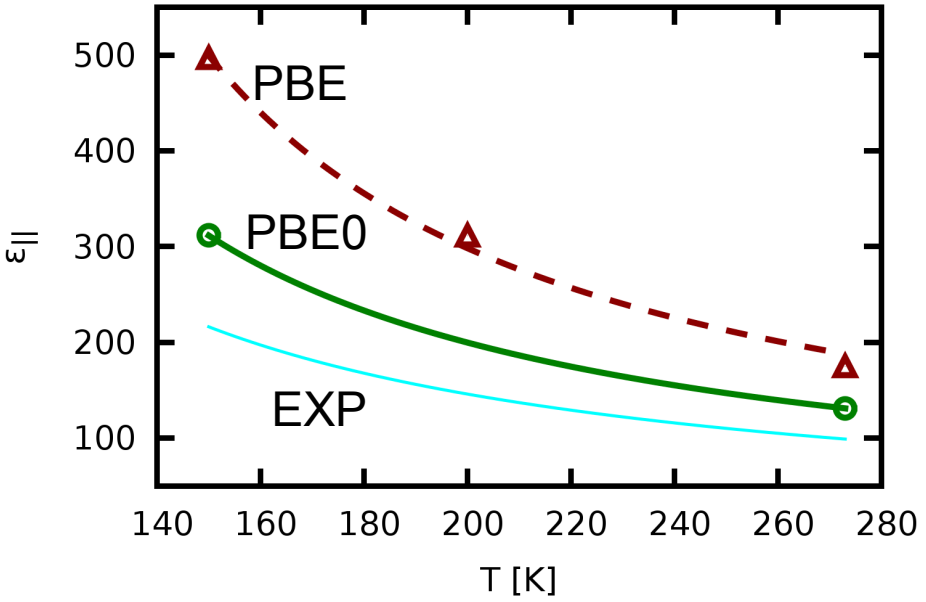


Converged dielectric constant

Convergence > 100000 moves



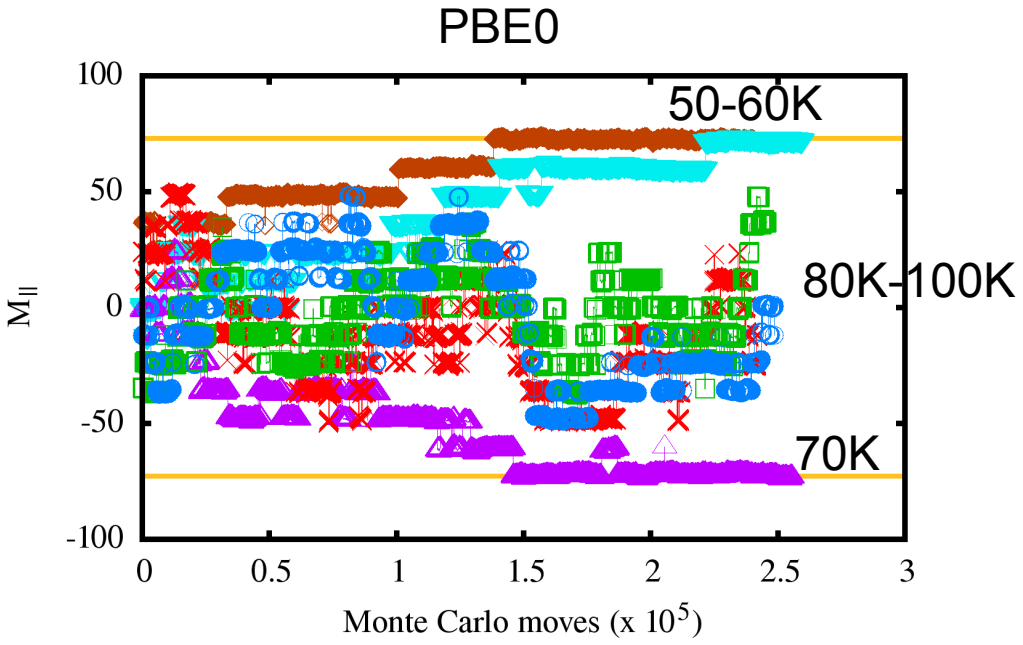
Temperature dependent ε

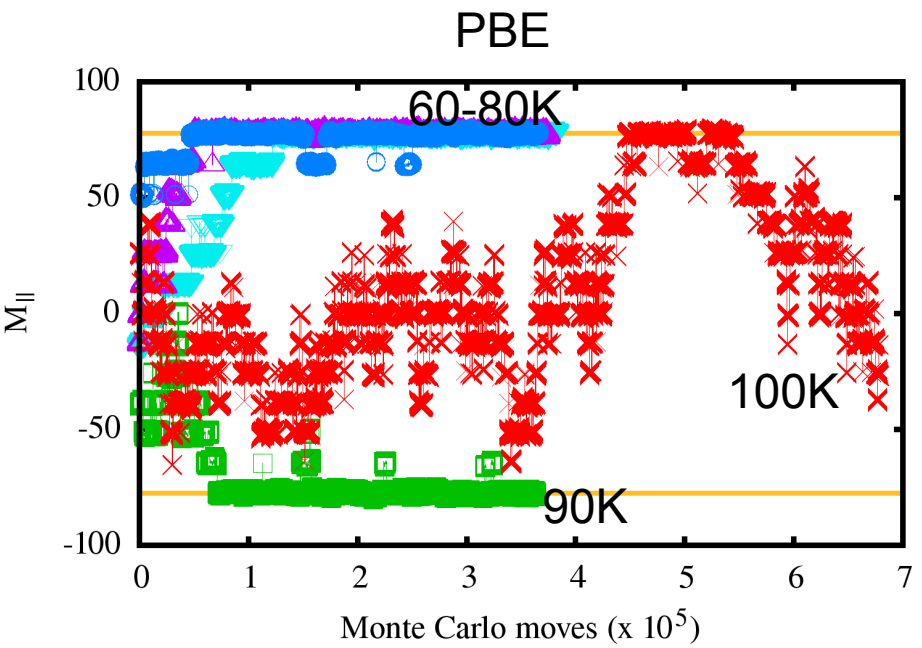


- PBE significantly overestimates (151 vs 95 @273K)
- PBE0 fair agreement with EXP (116 vs 95 @273K)
- Anisotropy suggests transition to a ferro-electric phase
- Curie-Weiss estimated transition temp. 60K (PBE0) / 79K (PBE) ~76K EXP

Schönherr M, Slater B, Hutter J, VandeVondele J (2014) J. Phys. Chem. B, 118(2), 590-596

Direct observation of the Ih → XI phase transition





In sufficiently long simulations, the expected ferro-electric XI phase is spontaneously formed at low temperatures. PBE0 [70,80]K, PBE [90,100]K, Exp 76K

Schönherr M, Slater B, Hutter J, VandeVondele J (2014) J. Phys. Chem. B, 118(2), 590-596

Reaching short time scales:
Ehrenfest Molecular Dynamics

EMD / NAMD : electronic dynamics

$$\psi^j(\boldsymbol{r},t) = \sum_\alpha a^j_\alpha(t)\phi_\alpha(\boldsymbol{r}-\boldsymbol{R}_{A_\alpha})$$

$$\dot{a}^j_\alpha = -\sum_{\beta\gamma} S^{-1}_{\alpha\beta}(iH_{\beta\gamma}+B_{\beta\gamma})a^j_\gamma,$$

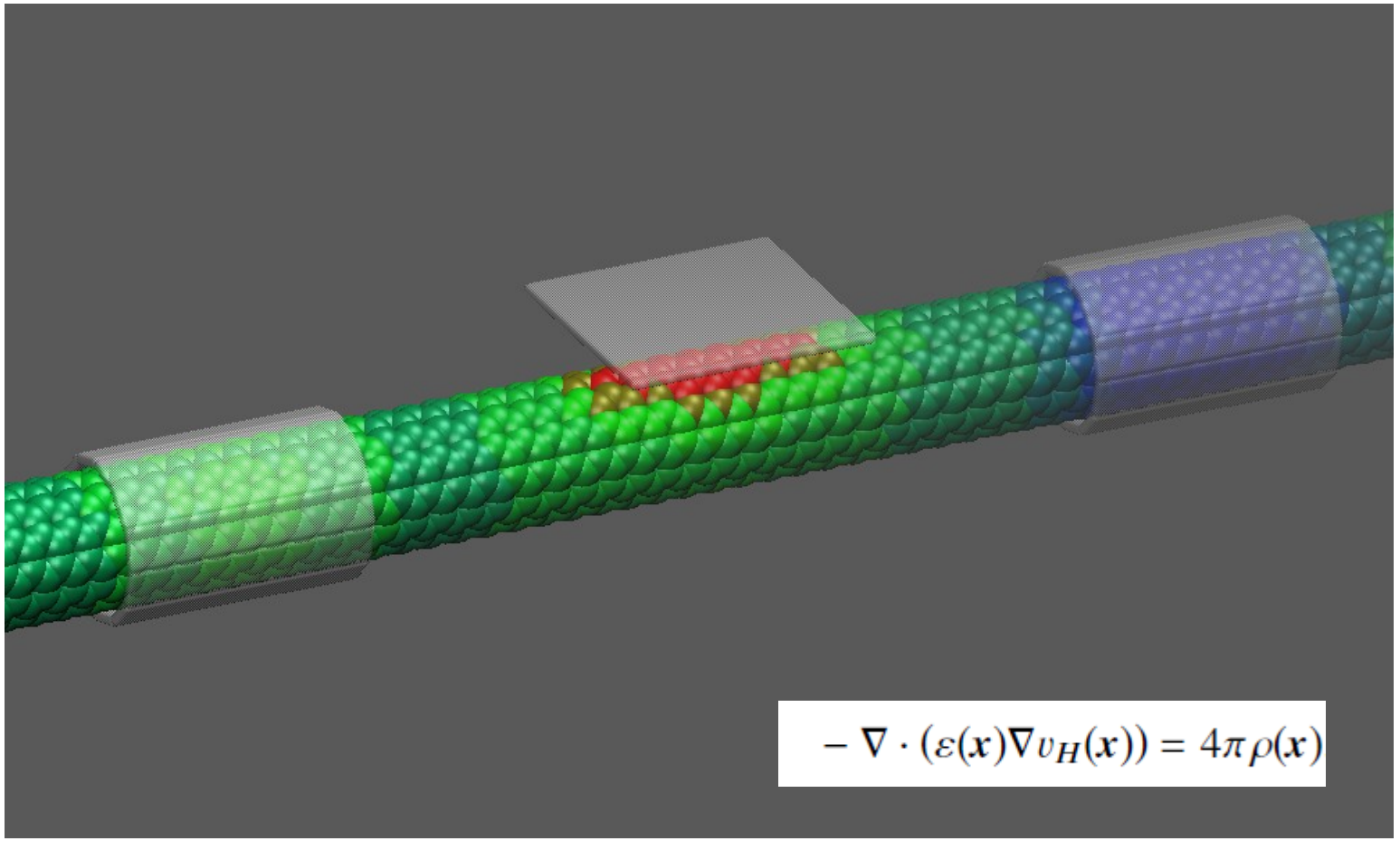
Explicitly follow the dynamics of ions and electrons.

With ~ O(1) as time step,
up to at most 1ps.

Can be used to extract e.g. the UV/VIS spectra of molecules.

$$M_A\ddot{R}_A = -\frac{\partial U(R,t)}{\partial R_A} + \sum_{j=1}^{N_e}\sum_{\alpha\beta} a^{j*}_\alpha(D^A_{\alpha\beta} - \frac{\partial H_{\alpha\beta}}{\partial R_A})a^j_\beta.$$

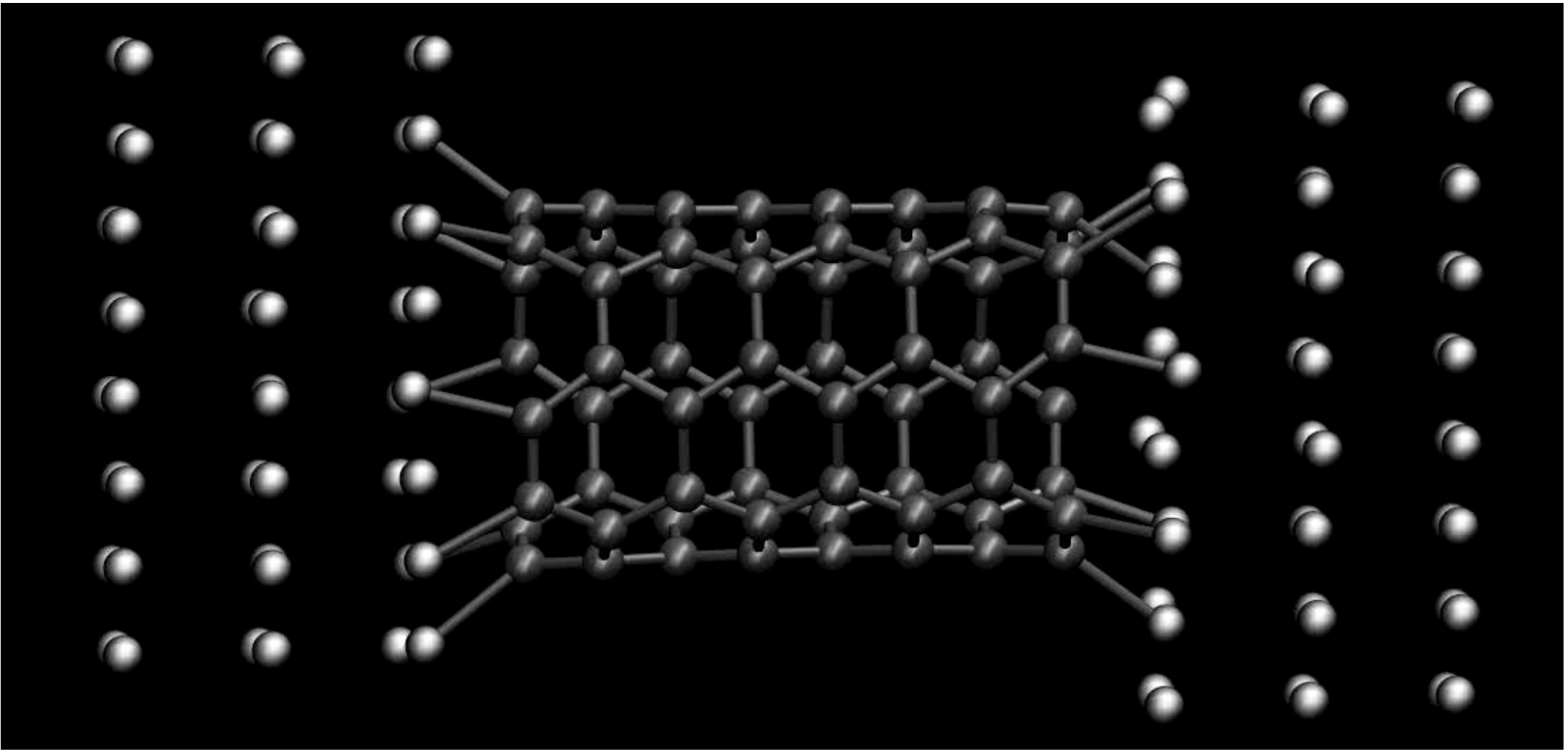
Generalized Poisson Solver



Solve the Poisson Equation subject to 'arbitrary' Dirichlet
and Neumann boundary conditions in the presence of (a density dependent) dielectric constant, includes consistent ionic forces.

Bani-Hashemian MH; Brück S; Luisier M; VandeVondele J; J. Chem. Phys. 144, 044113 (2016)

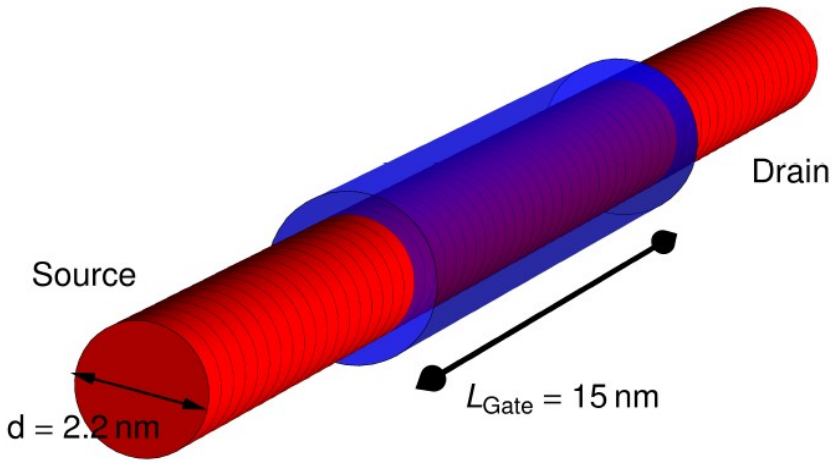
Simulation of miniature devices

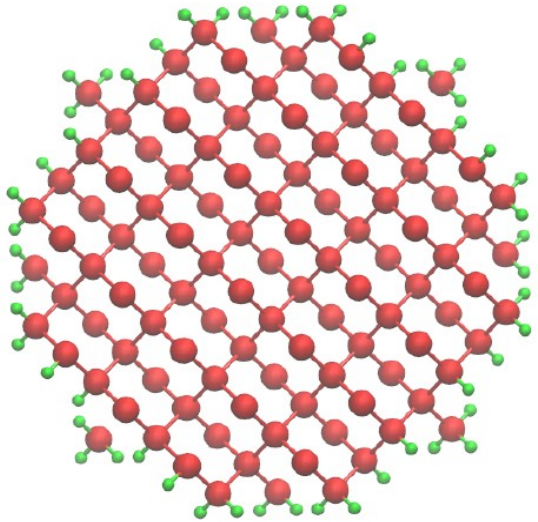


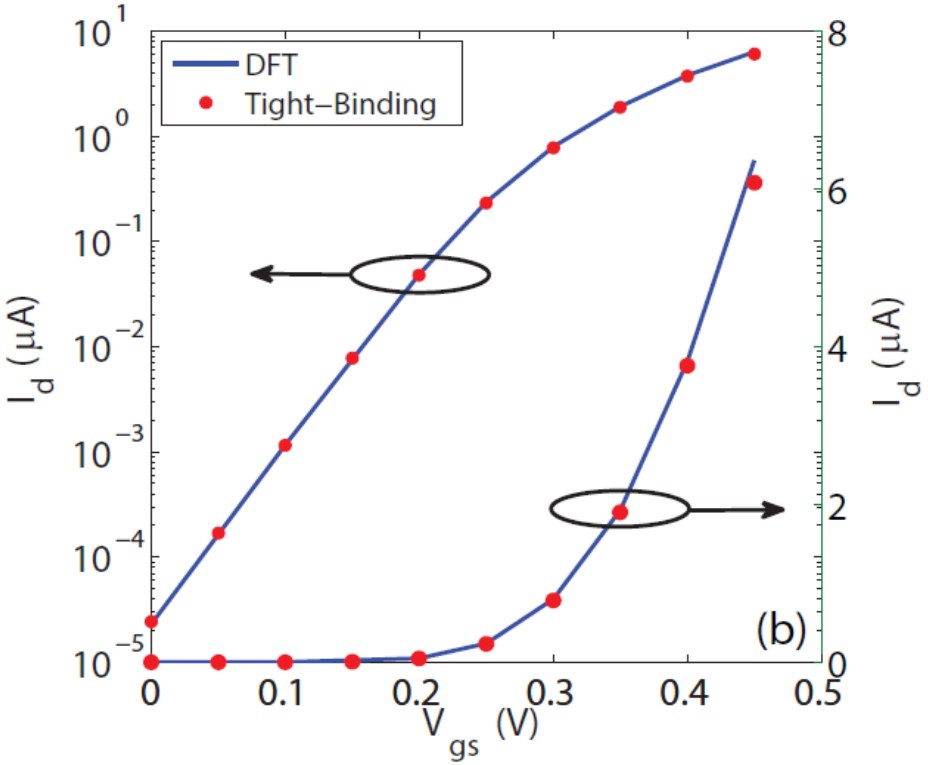
Quantum dynamics of switching the voltage (in 750 as)
across a Carbon nanotube, between Pd contacts

Samuel Andermatt et al : in preparation

Towards ab initio device simulations





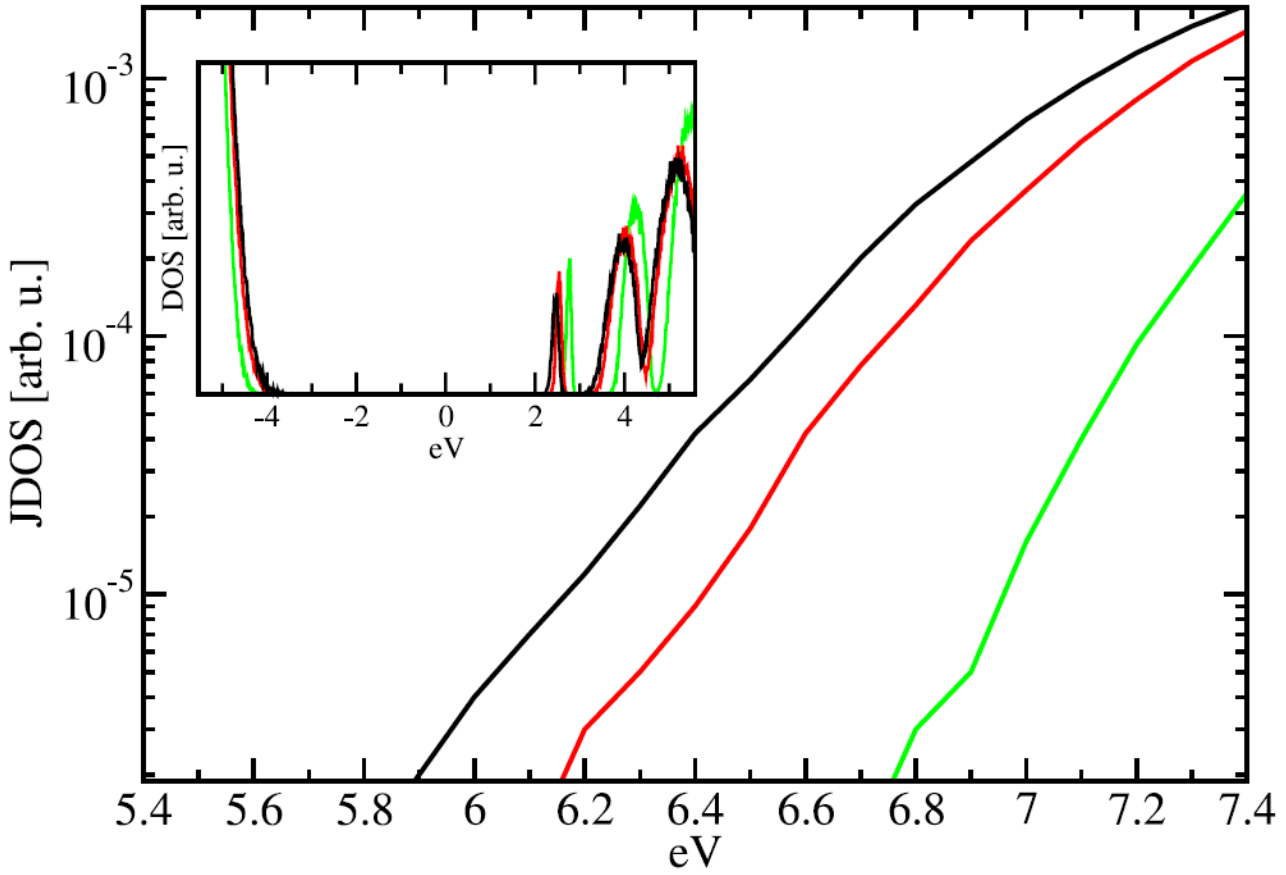


10000 atoms NEGF calculations on Si NWFET, a coupling between OMEN and CP2K

Brück S. Calderara M Bani-Hashemanian MH, VandeVondele J, Luisier M Proc. Int. W. Comput. Electronics (IWCE). (2014).

Reaching imaginary timescales: Improved Path-Integral Dynamics

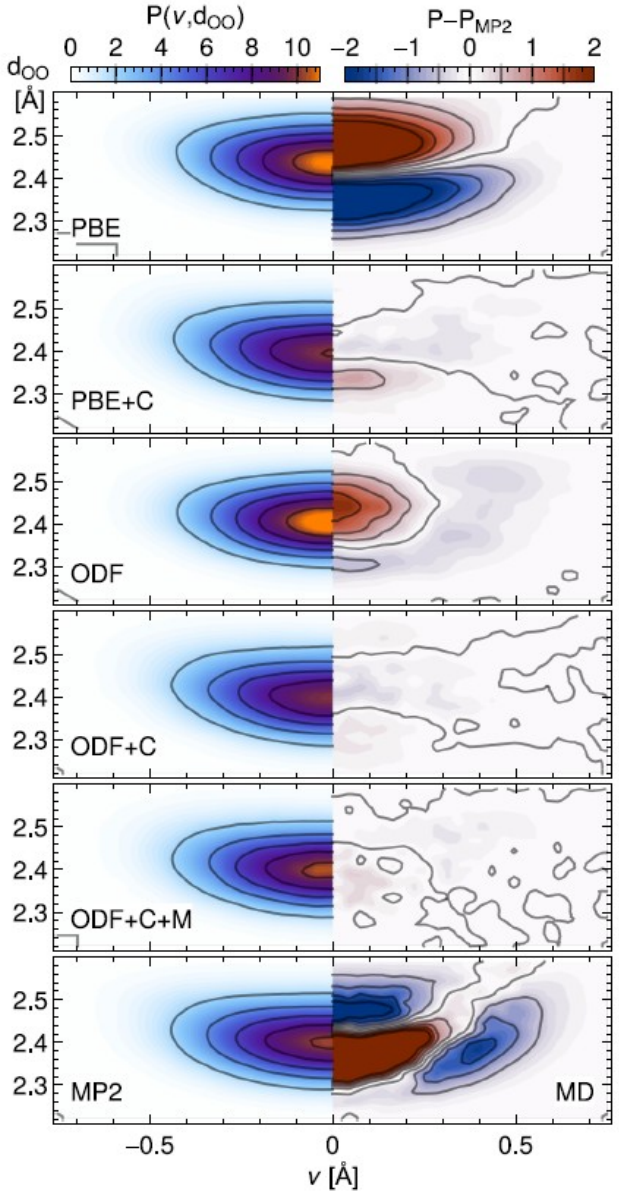
NQE on the band gap of liquid water



Surprisingly large effect of NQE on the band gap of liquid water, consistent with experiment (H->D), approximate NQE with GLE thermostat and ADMM-PBE0-D3

Del Ben M; Hutter J; VandeVondele J; 2015 JOURNAL OF CHEMICAL PHYSICS 143(5): 054506

Improved PI MD:
Multiple steps in real and imaginary time



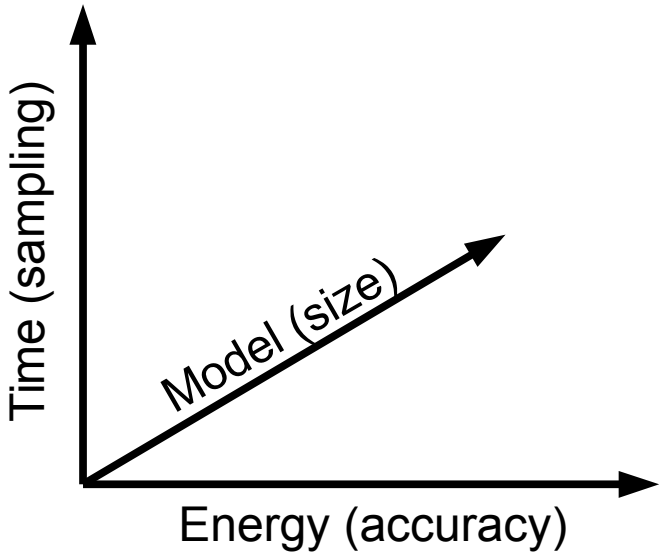
Split the Hamiltonian in a cheap and an expensive part (e.g. MP2 = GGA + (MP2 – GGA))

Perform Multiple Time Step (MTS) and Ring Polymer Contraction (RPC) using this split.

1 MP2 calculation (plus many GGA) yields (accurate) NQE and 'large' timestep MD.

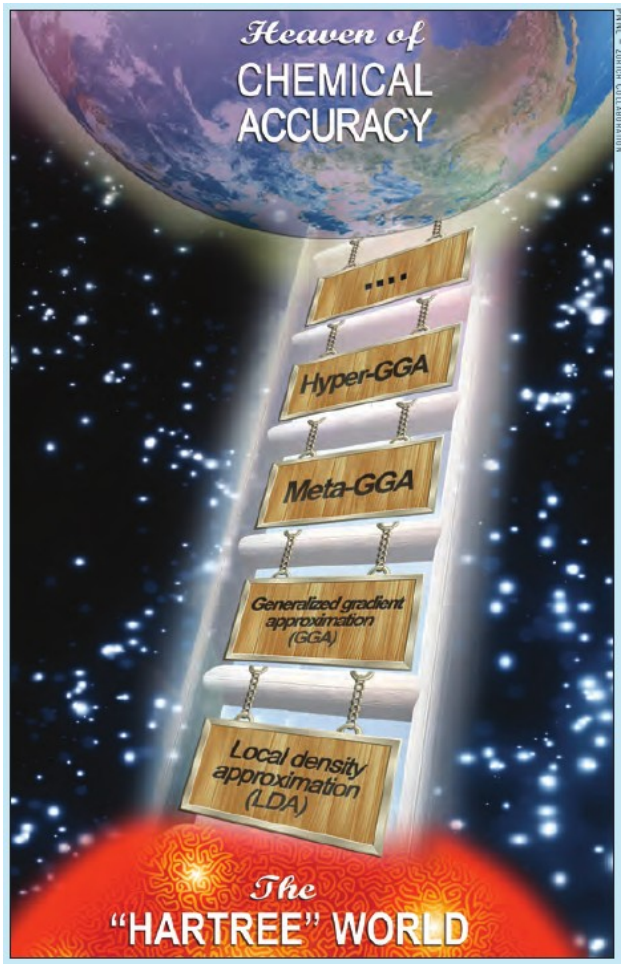
Available in CP2K via the iPI interface.

Kapil, VandeVondele, Ceriotti JCP 144, 054111 (2016)

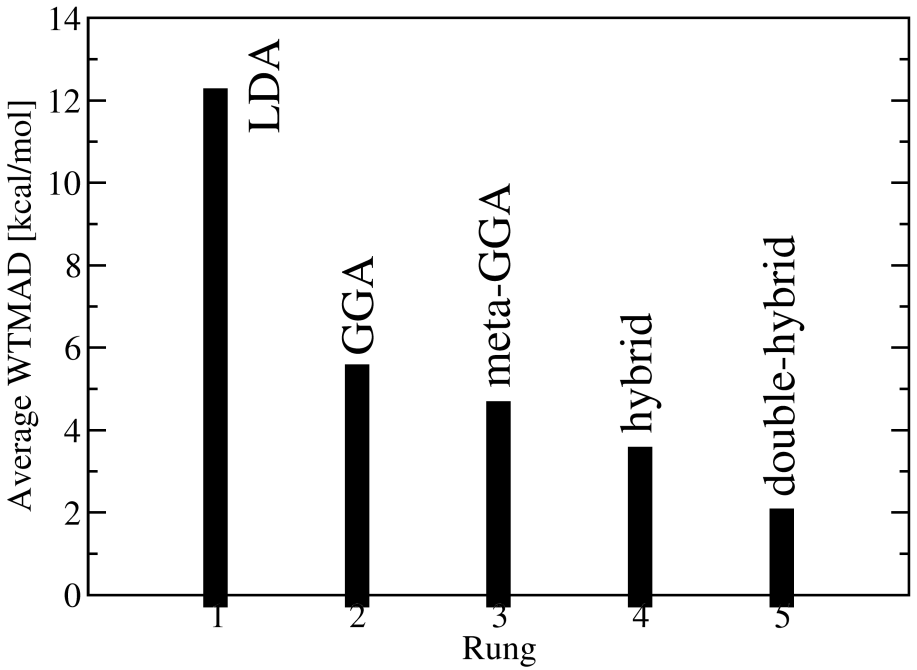


ENERGY

Beyond GGA
the 4th & 5th rung in DFT



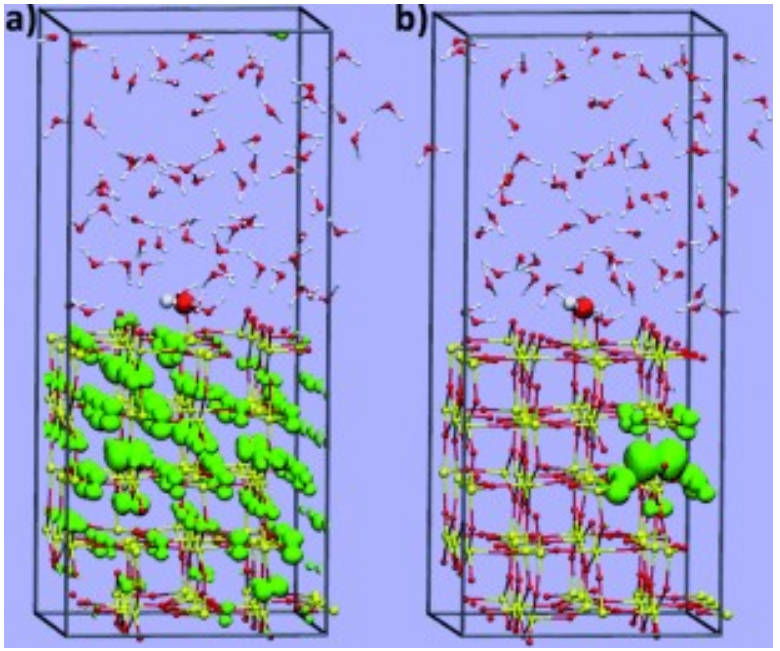
RPA and MP2-like correlation enable the next level of accuracy in DFT



data: S. Grimme

4^{th} rung (hybrids):
Band gaps, Importance for redox potentials

(photo-)electrochemistry beyond GGA DFT: why ?



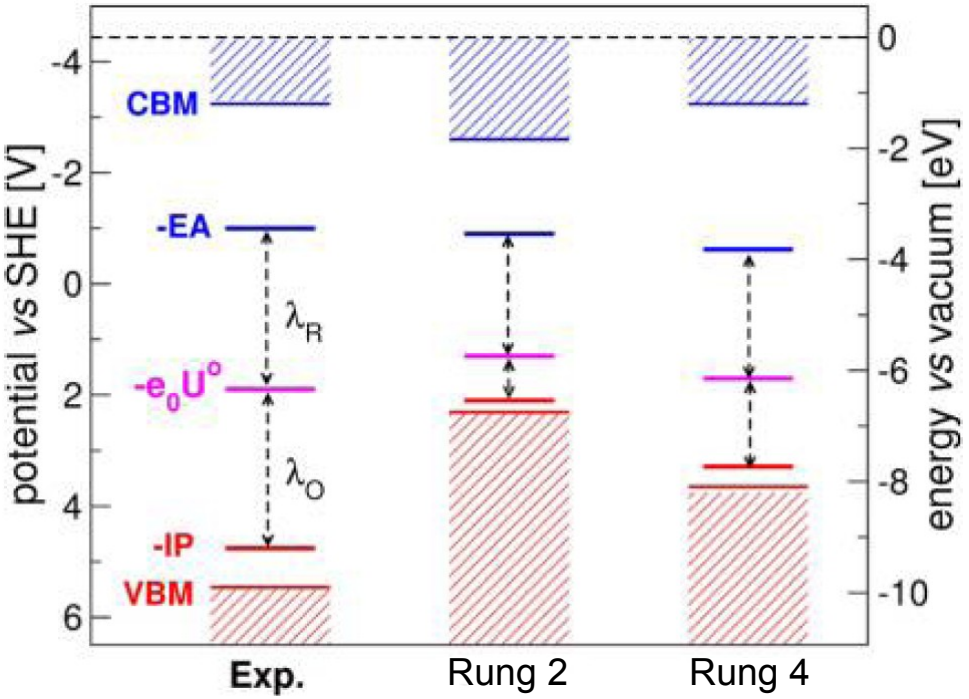
Hole localization at theTiO2 / water interface.

While GGA DFT fails to localize the electron hole created after photo-excitation (left), hybrids functionals are a first step towards a qualitatively correct picture of electrons at the water / oxide interface.

Cheng J; Marialore S; VandeVondele J; Sprik M; 2012, CHEMCATCHEM 4(5): 636-640

Electronic band structure : Aqueous electro-chemistry with hybrids

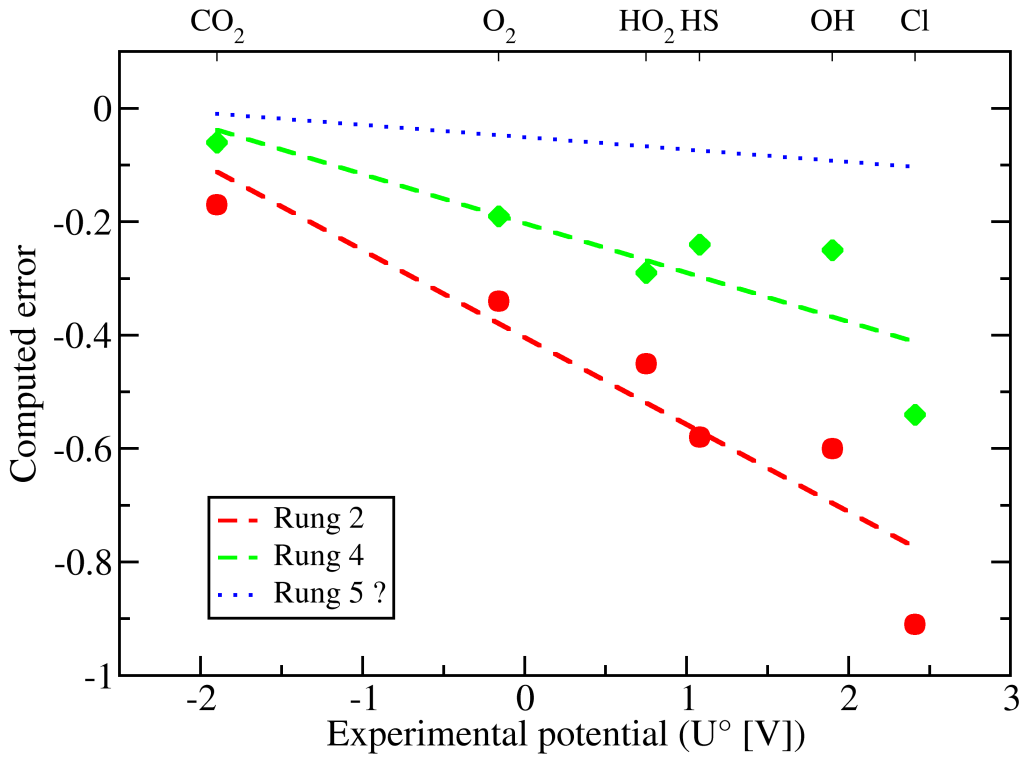
OH*/OH- aqueous redox chemistry
(defect physics in dihydrogen oxide)



'Qualitative correctness' of the band structure of liquid water is essential for aqueous electro-chemistry. This is provided at rung 4 (hybrids).

Adriaanse C; Cheng J; Sulpizi M; Chau V; VandeVondele J; Sprik M; 2012, JOURNAL OF PHYSICAL CHEMISTRY LETTERS 3(23): 3411–3415

Redox potentials: a quantitative and relevant testcase for theory



Redox levels/potentials are key (batteries, solar cells, etc.) for various applications.
Known aqueous potentials provide an excellent benchmark.
Hybrids improve, but systematic error remains : a strong case for beyond-hybrid functionals

Cheng J; Liu X; VandeVondele J; Sulpizi M; Sprik M (2014) Acc. Chem. Research. 47: 3522

5^{th} rung:
Dispersion, and advanced correlation

5th rung: (RI)-GPW-MP2/RPA

A Gaussian and plane waves approach to MP2/RPA, directly obtains half-transformed integrals

$$E^{(2)} = -\sum_{ij,ab}^{occ,vir} \frac{(ia|jb)[2(ia|jb)-(ib|ja)]}{\varepsilon_a+\varepsilon_b-\varepsilon_i-\varepsilon_j} \qquad (ia|jb) = \sum_{\mu\nu\lambda\sigma} (\mu\nu|\lambda\sigma) C_{\mu i} C_{\nu a} C_{\lambda j} C_{\sigma b}$$

$$(ia|jb) \approx (ia|jb)_{RI} = \sum_{lm} (ia|l)(l|m)^{-1}(m|jb)$$

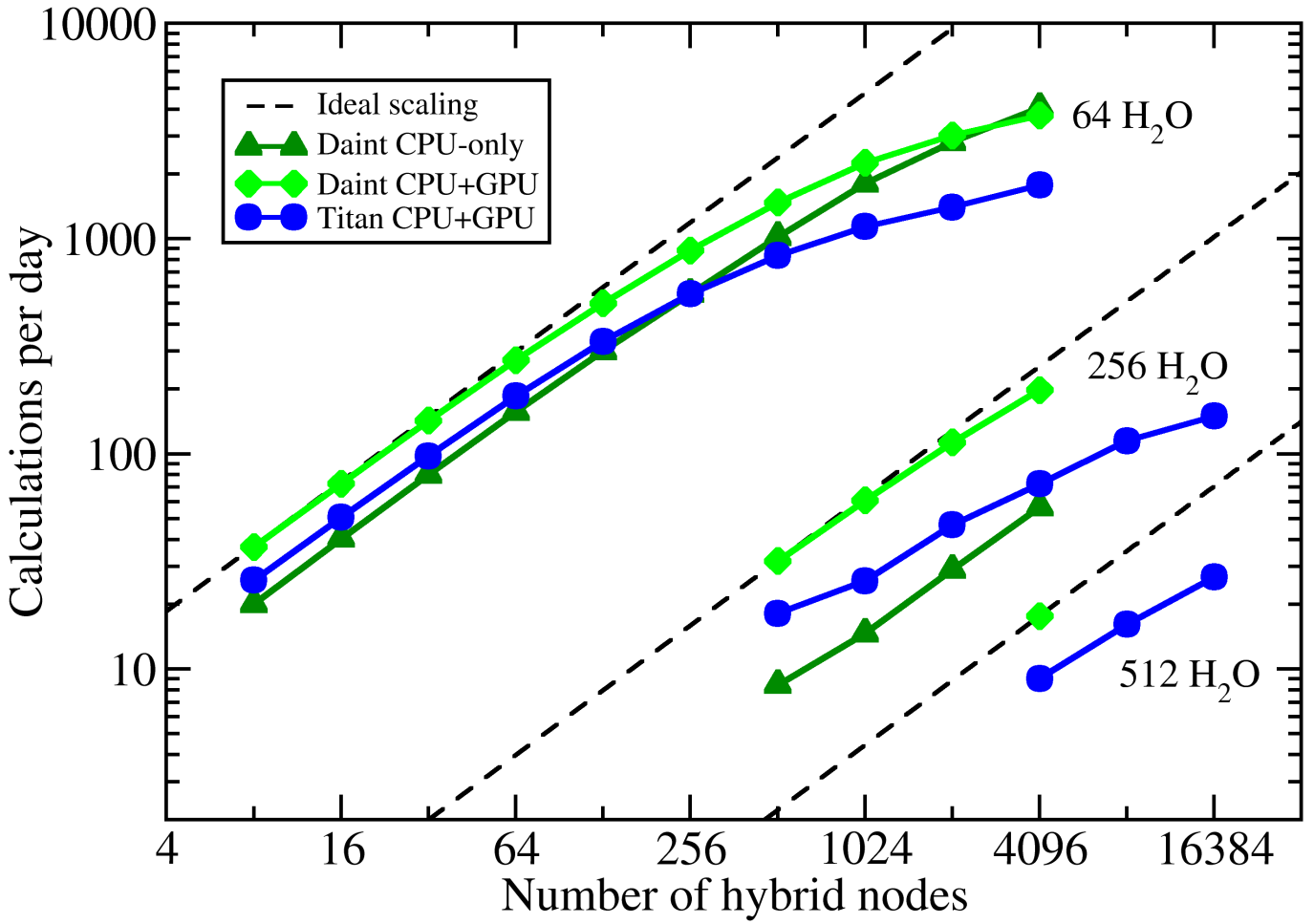
$$\begin{aligned}
(ia|\lambda\sigma) &= \int\int \psi_i(\vec{r}_1)\psi_a(\vec{r}_1)\frac{1}{\vec{r}_{12}}\phi_\lambda(\vec{r}_2)\phi_\sigma(\vec{r}_2)d\vec{r}_1 d\vec{r}_2 \\
&= \int\left[\int \frac{\psi_i(\vec{r}_1)\psi_a(\vec{r}_1)}{\vec{r}_{12}}d\vec{r}_1\right]\phi_\lambda(\vec{r}_2)\phi_\sigma(\vec{r}_2)d\vec{r}_2 \\
&= \int\left[\int \frac{\rho^{ia}(\vec{r}_1)}{\vec{r}_{12}}d\vec{r}_1\right]\phi_\lambda(\vec{r}_2)\phi_\sigma(\vec{r}_2)d\vec{r}_2 \\
&= \int v^{ia}(\vec{r}_2)\phi_\lambda(\vec{r}_2)\phi_\sigma(\vec{r}_2)d\vec{r}_2
\end{aligned}$$

$$E_{OS}^{(2)} = -\int_0^\infty dt \sum_{ia}\sum_{jb} (ia|jb)^2 e^{-t\Delta_{ij}^{ab}}.$$

$$E_c^{\text{RI-dRPA}} = \frac{1}{2}\int_{-\infty}^{+\infty}\frac{d\omega}{2\pi}\text{Tr}(\ln(\mathbf{1}+\mathbf{Q}(\omega))-\mathbf{Q}(\omega)).$$

Del Ben M, Hutter J, VandeVondele J, 2013, JCTC 9(6): 2654-2671
Del Ben M, Hutter J, VandeVondele J, 2012, JCTC 8(11): 4177–4188

RPA at the petascale

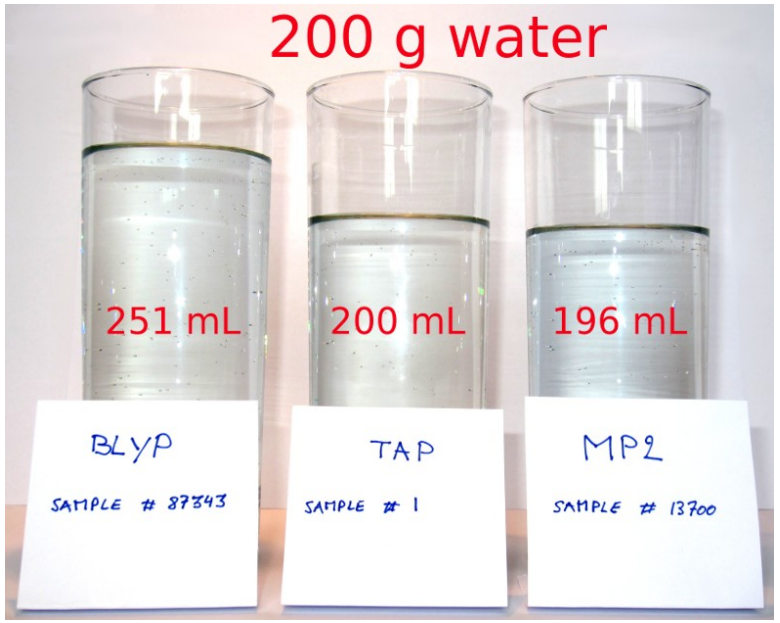


RPA calculations involving > 1000 atoms (~cc-pVTZ) have become possible,
Take a few hours on a petascale resource.

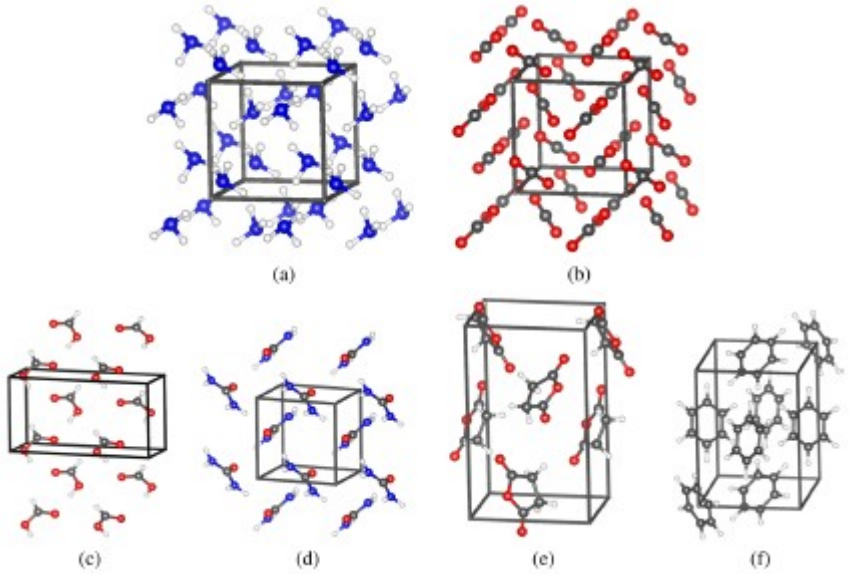
Del Ben M et al. Comp. Phys. Comm. (2015).

RPA and MP2: weak interactions 5th rung of DFT

Sampling liquid water



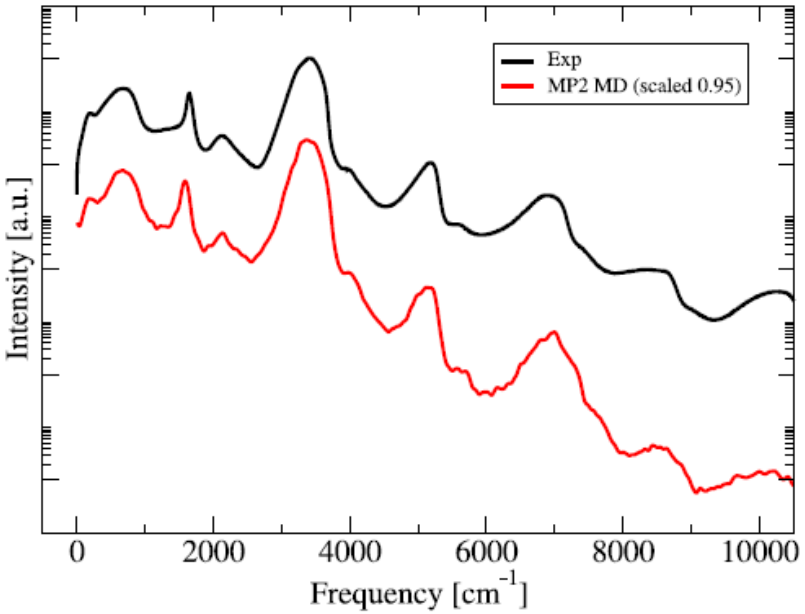
Polymorphs of Molecular Crystals



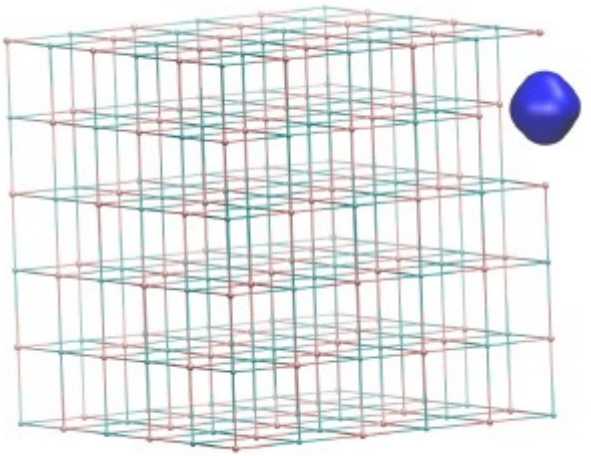
Del Ben M; Schönherr M; Hutter J, VandeVondele J; 2013, JPC L, 4, 3753-3759
Del Ben M; Hutter J; VandeVondele J; 2012, JCTC, 8, 4177-4188

MP2 gradients: restricted and unrestricted

Vibrational spectrum of liquid water @ MP2



Color center in LiF : spin density @ UMP2 in a relaxed geometry



Del Ben M; Hutter J; VandeVondele J; JCP, 143(10): 102803 (2015)
Del Ben M; Hutter J; VandeVondele J; JCP 143(5): 054506 (2015)
Rybkin V; VandeVondele J: Submitted

First non-empirical prediction that ice floats on water

Ice:

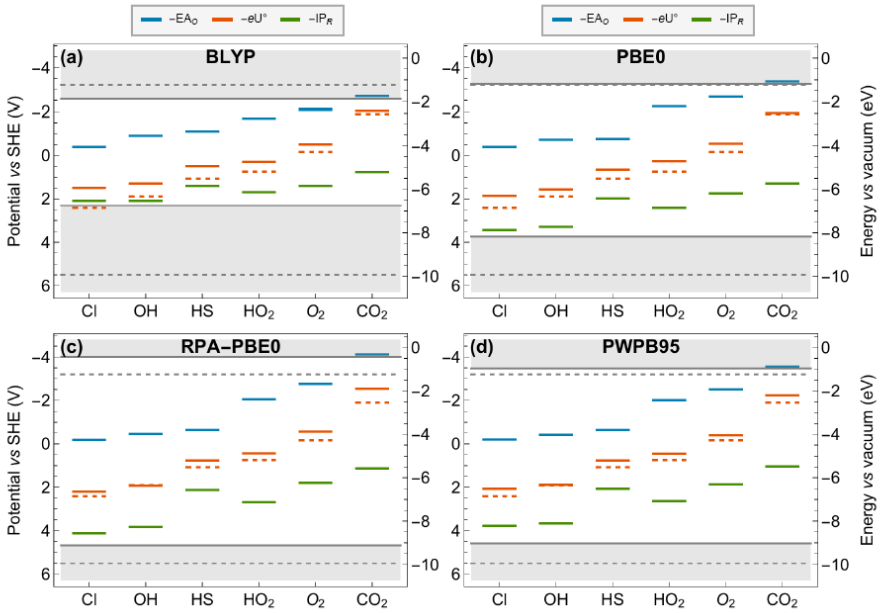
	E_{coh} [kJ/mol]	V_{mol} [Å^3]	ρ [g/mL]
MP2	-58.7	31.34	0.955
PWPB95-D3	-58.5	32.15	0.930
RPA	-52.5	32.37	0.924
exp.	-58.9	32.05	0.933

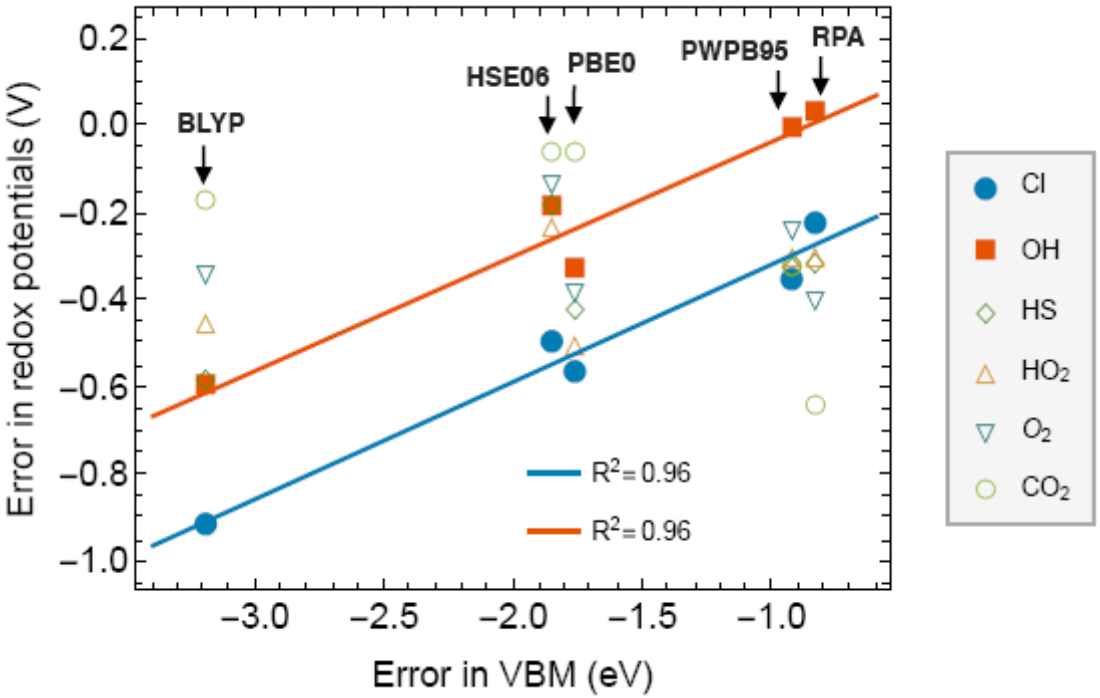
Water:

	Density	1^{st} Max		1^{st} Min		2^{nd} Max	
	ρ [g/mL]	r [Å]	$g_{OO}(r)$	r [Å]	$g_{OO}(r)$	r [Å]	$g_{OO}(r)$
MP2	1.020	2.76	3.05	3.32	0.72	4.41	1.21
PWPB95-D3 (LD)	1.002	2.80	2.80	3.60	0.86	4.59	1.12
RPA	0.994	2.78	2.93	3.41	0.78	4.49	1.19
exp.	1.00	2.80	2.57	3.45	0.84	4.5	1.12

Del Ben M; Hutter J; VandeVondele J; JCP 143, 054506 (2015)

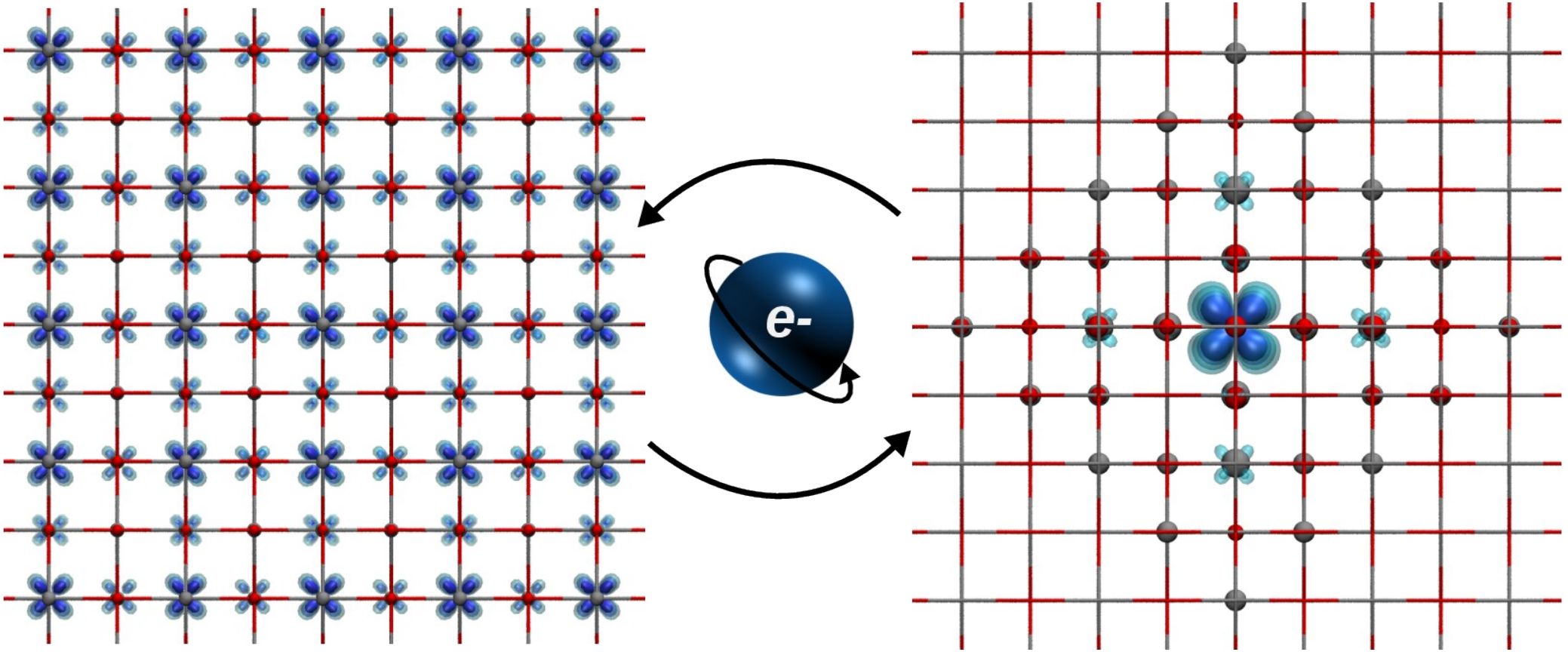
Redox potentials @ RPA / DH





VandeVondele, Cheng to appear in PRL (2016)

Polarons in TiO_2: to be or not to be

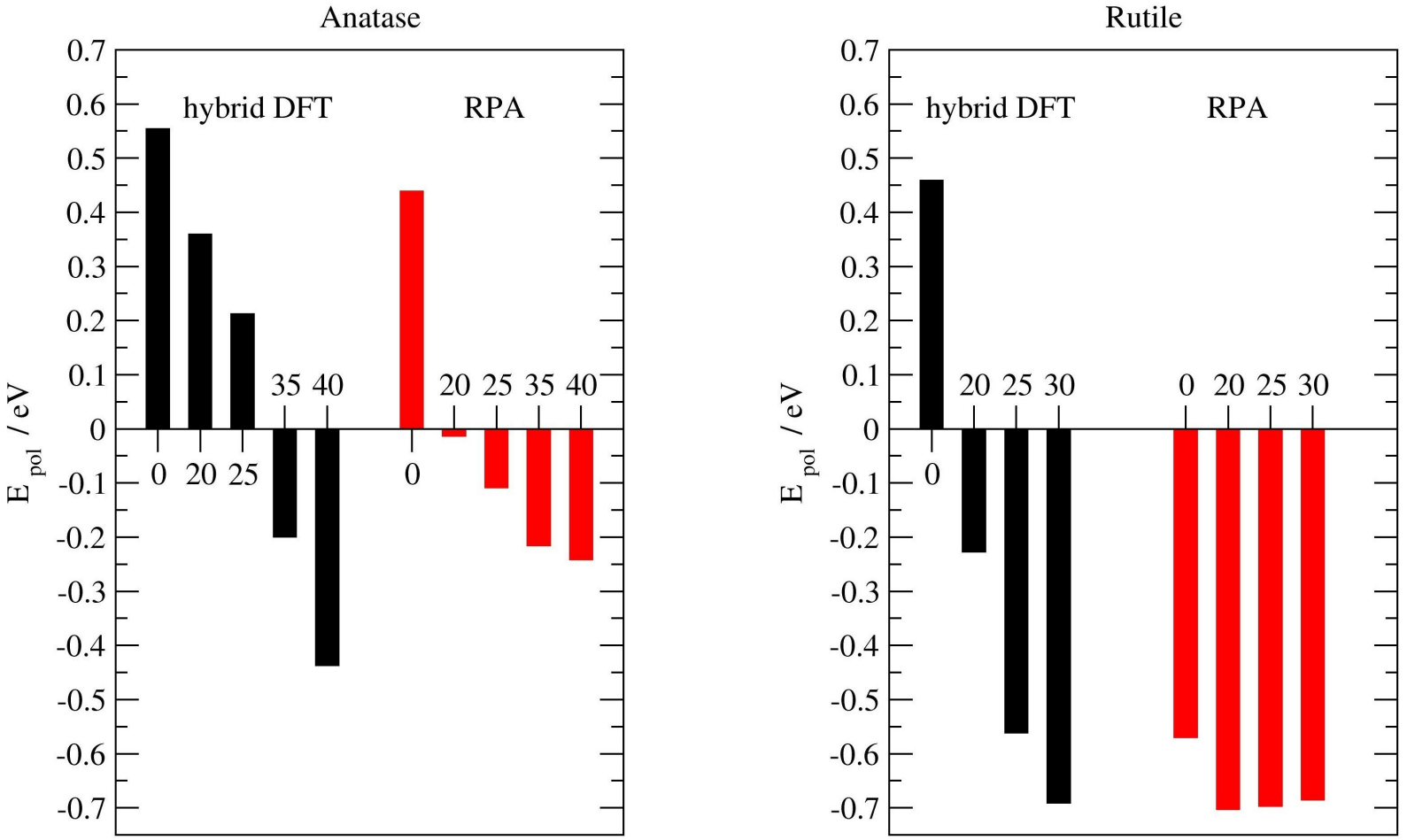


Conduction Band

Polaron

Spreafica C and VandeVondele J accepted in PCCP (2014)

Beyond the 4th rung : RPA



RPA depends on the starting orbitals used, i.e. GGA or hybrid
RPA reduces the strong dependence on the %HFX

Ongoing developments

K-points : the number 1 feature ?

- Basic functionality works for GGA functionals (energy, forces)
- Only with diagonalization based approaches
- Not all properties
- Not using symmetry pruned k-point grids
- Known (but unsolved) abort in parallel
- Not for HFX and higher rungs.
- needs your help... testing, fixing bugs, extending functionality

Ongoing developments

G0W0 :

- Works well for molecules
- Slow convergence with system size for PBC... work in progress

RPA / MP2 :

- Advanced functionals
- O(N^x) (x=1..3)
- Faster 3 center integrals
- forces ?

Spectroscopy (not ongoing ?)

- CC2 ?
- BSE ?

Ongoing developments

DBCSR / LS :

- Communication reduction based on filtering
- Communication reduction based on 2.5D algorithms.

PAO / LS :

- Small basis sets optimized on-the-fly

Transport / NEGF :

- Coupling to external codes (OMEN)
- Implementation of internal methods

Ongoing developments

UK is doing great in CP2K usage **and** development

We welcome contributions of small and big developments, synergy is important
(the pri{c|z|d}e of open source)

Prepare to take the CP2K project to a next level.

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PRACE

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ORNL

You for your attention!