Supercomputation and realistic models of photocatalysts nanoparticles

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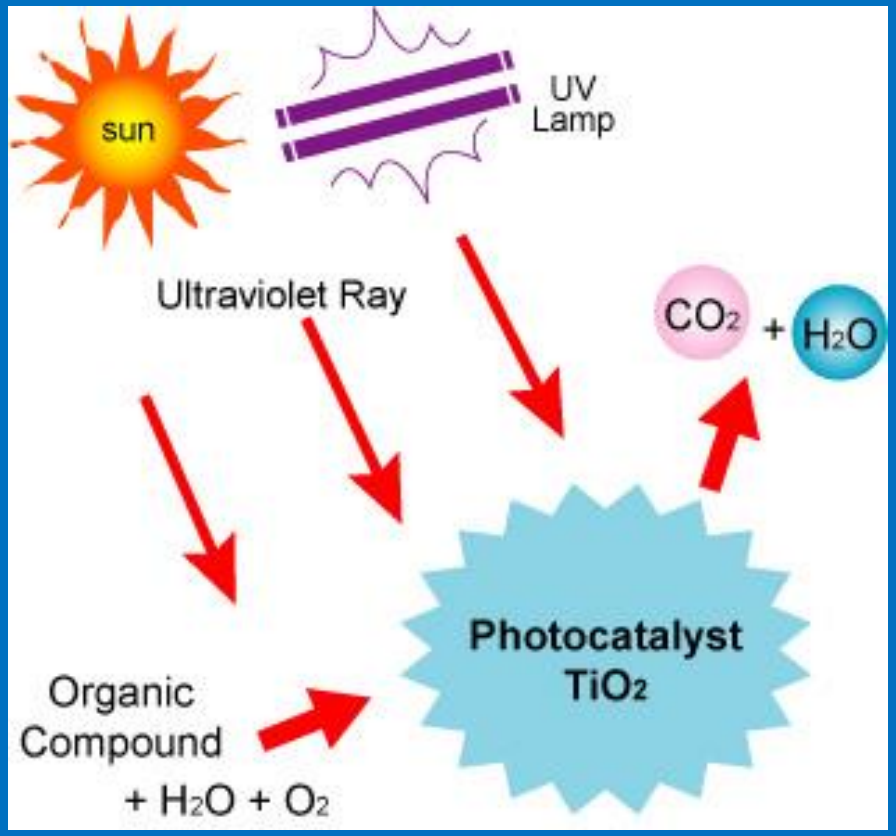
Outline

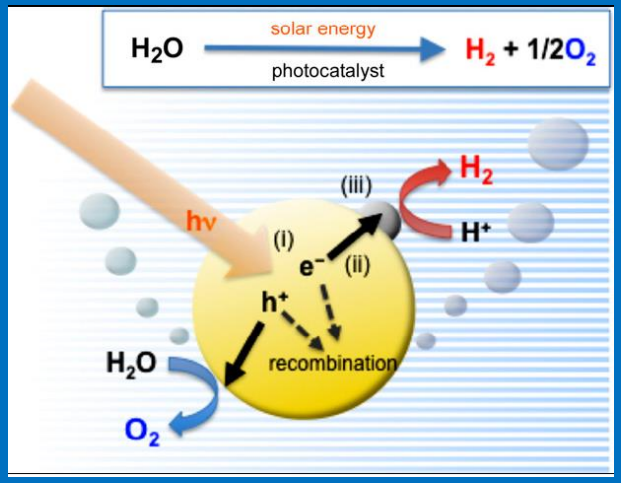
1. Photocatalysis, TiO_2 and H_2 production
2. TiO_2 bulk and surfaces versus nanoparticles
3. The computational challenge
4. Selected results on realistic models
5. Conclusions

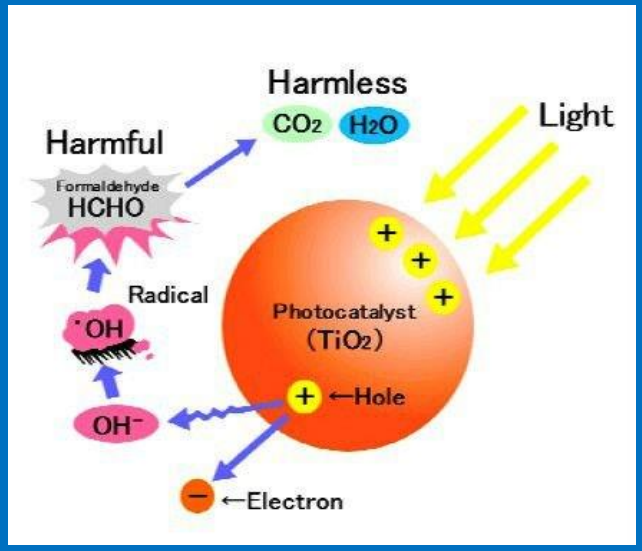
A cartoon description of photocatalysis



TiO_2 is the star system

Technological interest is huge an applications go from environment to sustainable energy



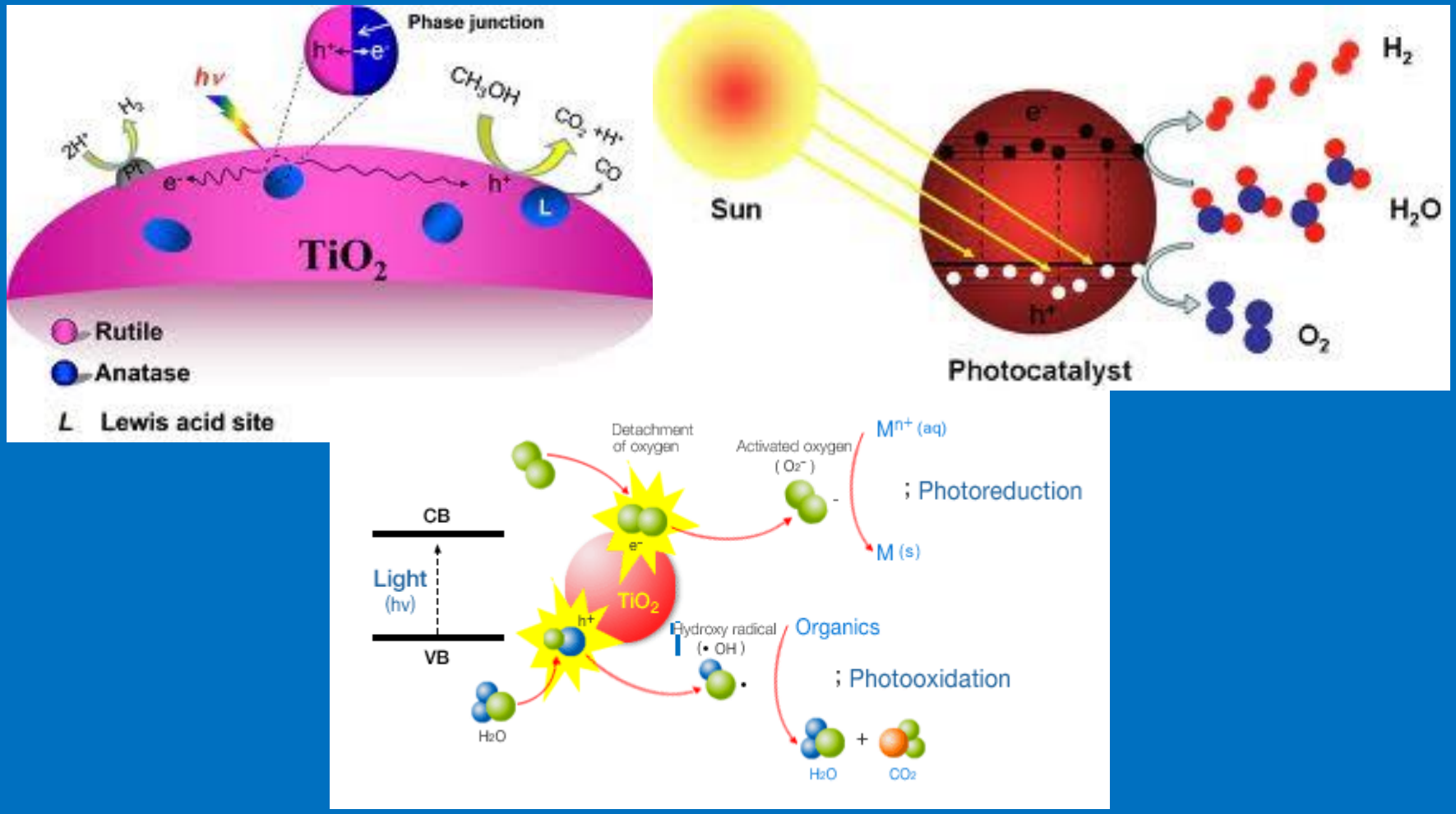


H_2 production from H_2O means unlimited energy supply

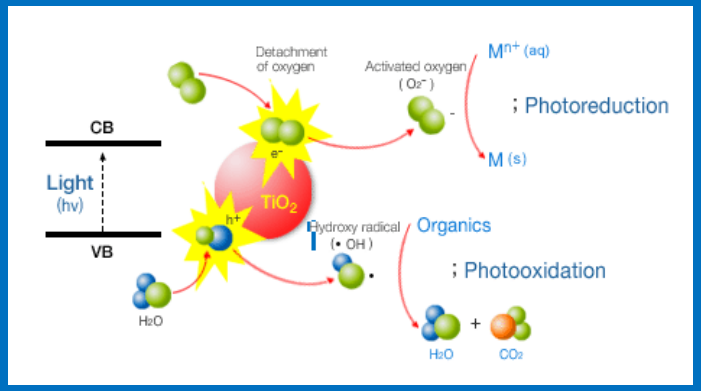
Air cleaning technology

Photocatalytic concrete already exist!

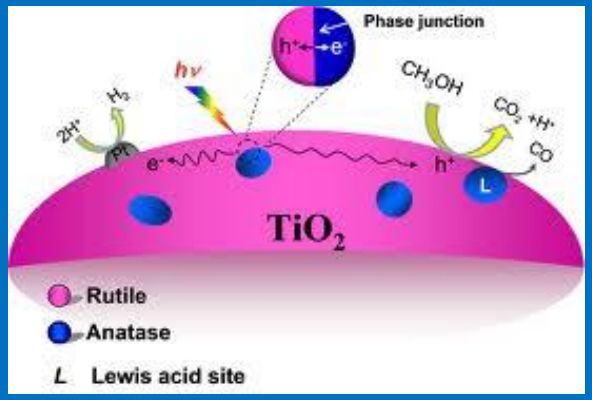
http://www.mandalaconcrete.com/



At first sight mechanisms of photocatalysis seem fairly simple

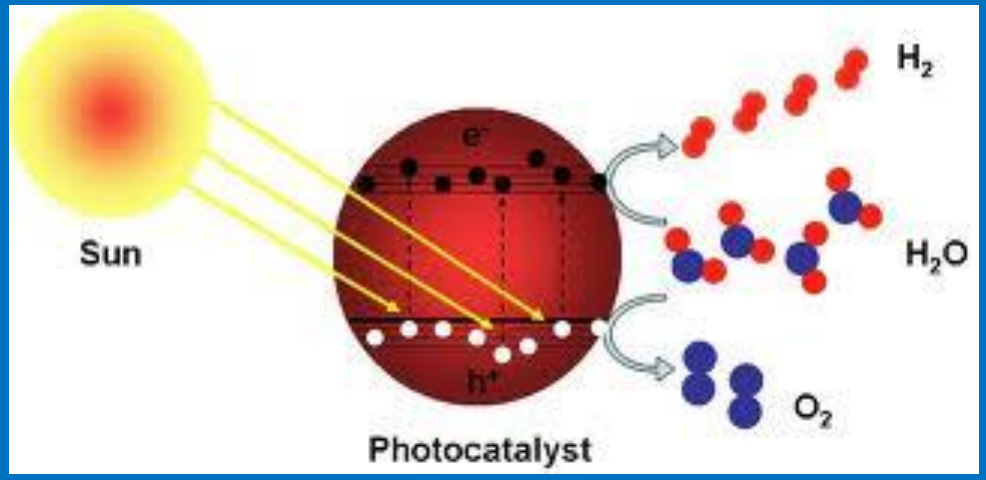


But…. how, where and when?



Underlying processes are vey complex and, to a large extent, details mostly unknown since excited states of nanoparticles of semiconducting transition metal oxides are involved

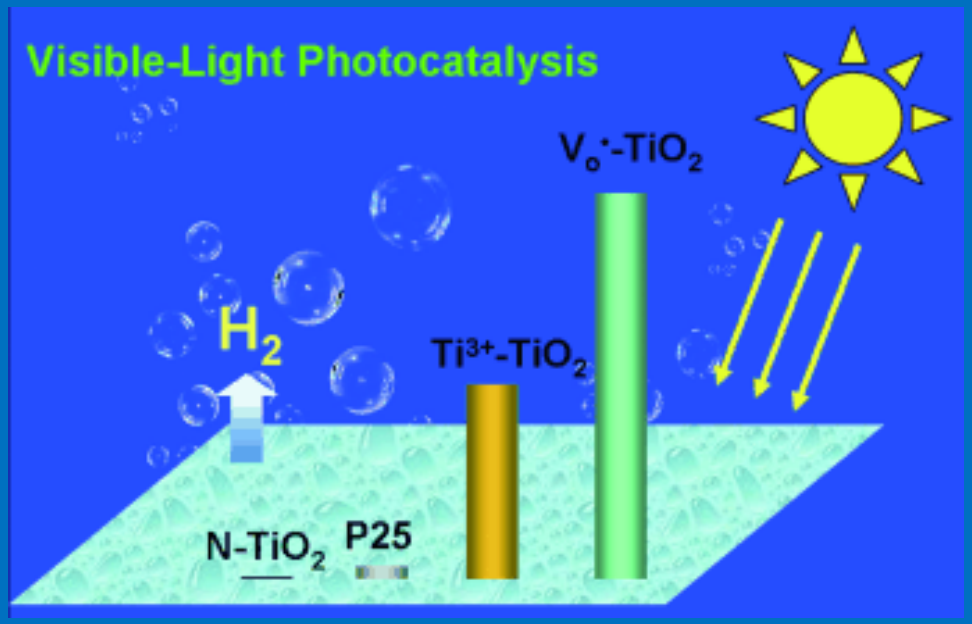
Where is the problem?



TiO_2 and related materials adsorb in the UV

Only a part of solar light harvested

MIND THE GAP!



Zou et al. Chem. Eur. J. 2013, 19, 2866

Engineer the GAP!

Need to predict new photocatalytic materials

Modifying, doping and/or co-doping existing ones

Need to understand the electronic structure

Most published work focuses on band gap of bulk TiO_2 Not a simple problem, hybrid functionals needed

	Rutile			Anatase		
	PBE	PBEx	Expt.	PBE	PBEx	Expt.
a,b (Å)	4.650 (1.3 %)	4.609 (0.4 %)	4.592	3.799 (0.4 %)	3.792 (0.2 %)	3.785
c (Å)	2.975 (0.6 %)	2.957 (0.0 %)	2.957	9.702 (2.0 %)	9.578 (0.7 %)	9.514
Eg (eV)	2.07 (31.7 %)	2.97 (2.0 %)	3.03	2.14 (33.1%)	3.22 (0.6 %)	3.20
ΔH_f (eV)	-9.22 (5.3 %)	-9.50 (2.5 %)	-9.74	-9.31 (3.9 %)	-9.60 (0.9 %)	-9.69

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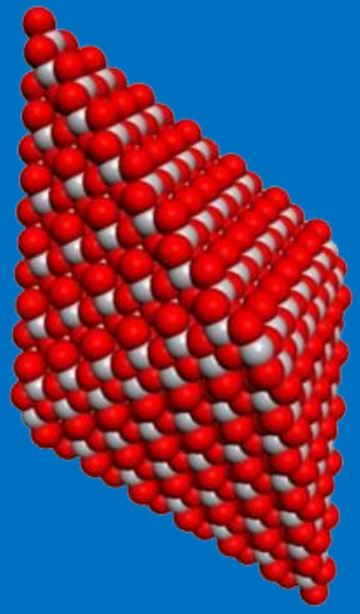
TiO_2 extended surfaces may provide better models

BUT

Reals systems are made of nanoparticles

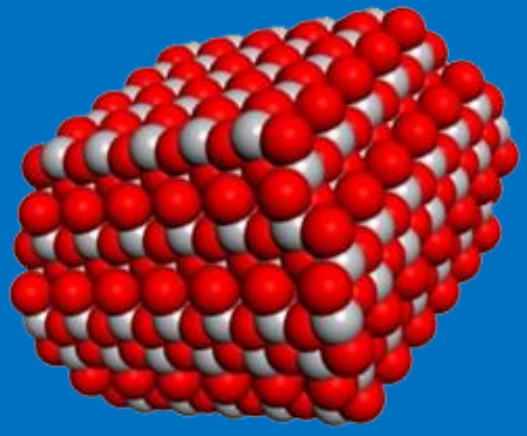


Composition?

Size?

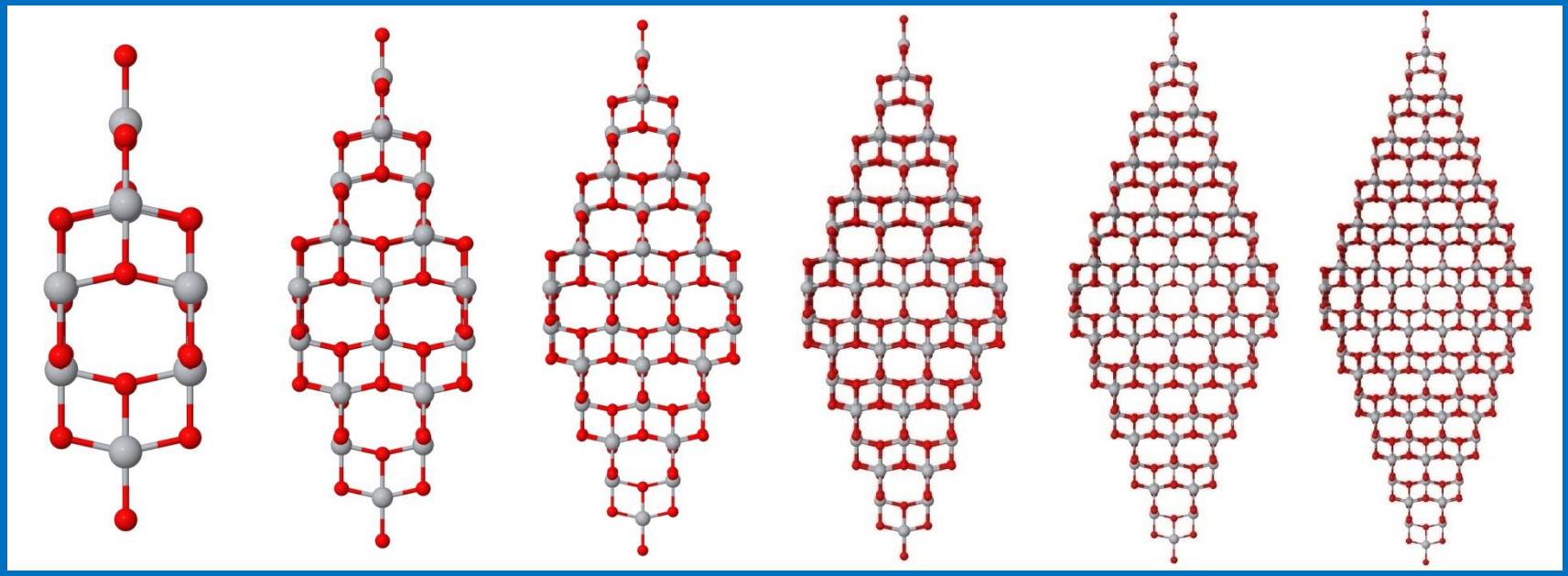
Shape?

Doping?



Electronic structure of realistic TiO_2 nanoparticles

$(TiO_2)_{10}$ $(TiO_2)_{35}$ $(TiO_2)_{84}$ $(TiO_2)_{165}$ $(TiO_2)_{286}$ $(TiO_2)_{455}$



From Wulff construction

Covering subnm to 4-6 nm scale

Not only huge computational resources needed

Efficient highly parallel code too

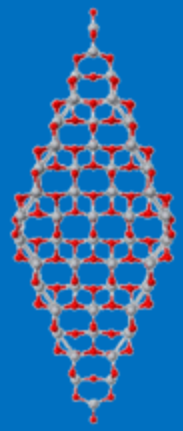
FHI-AIMS chosen

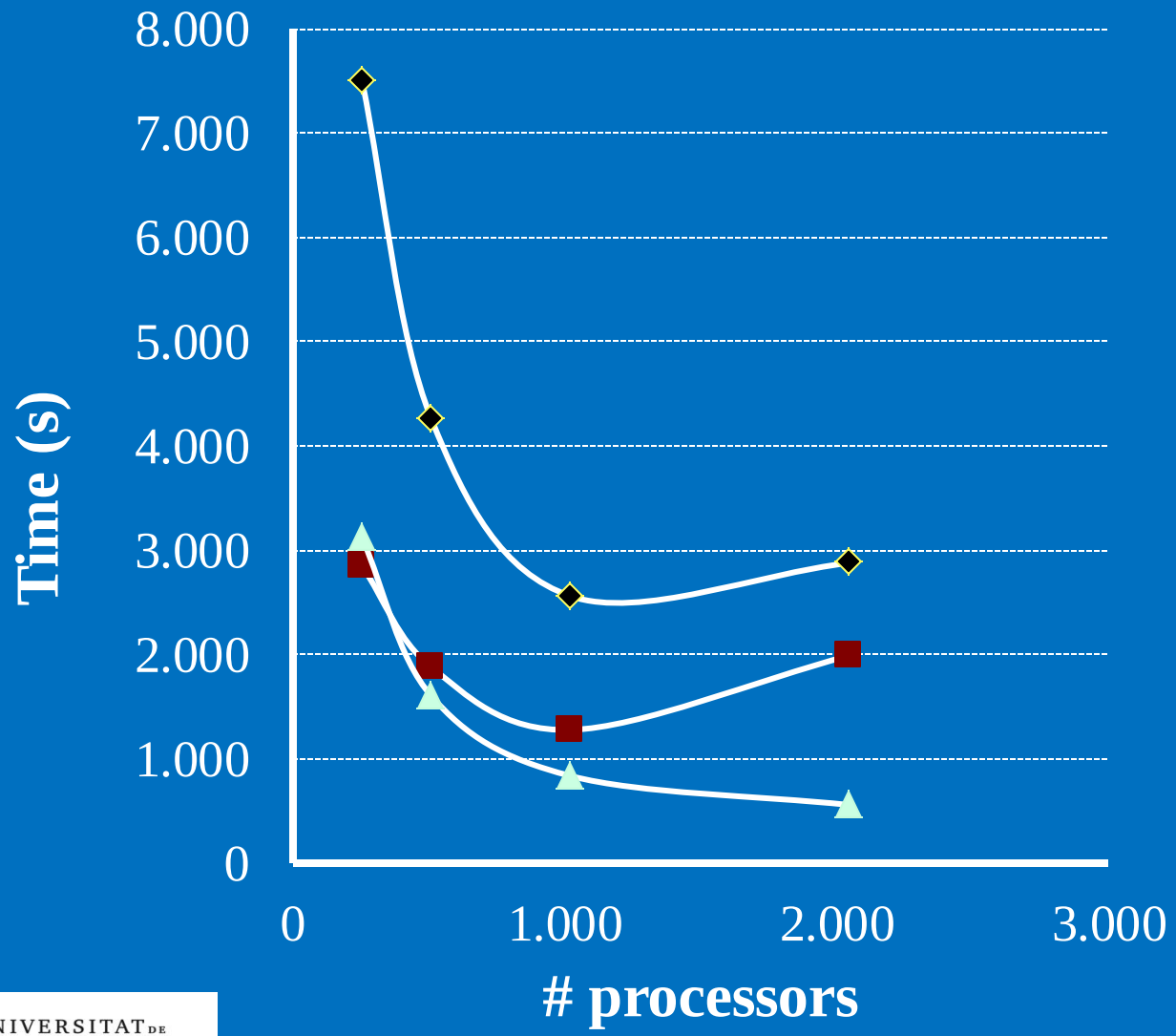
An accurate AE electronic structure code package for computational materials science

Numerical basis

Standard GGA and hybrid functionals

Scaling test for $(TiO_2)_{165}$ with tight tier 2 basis set

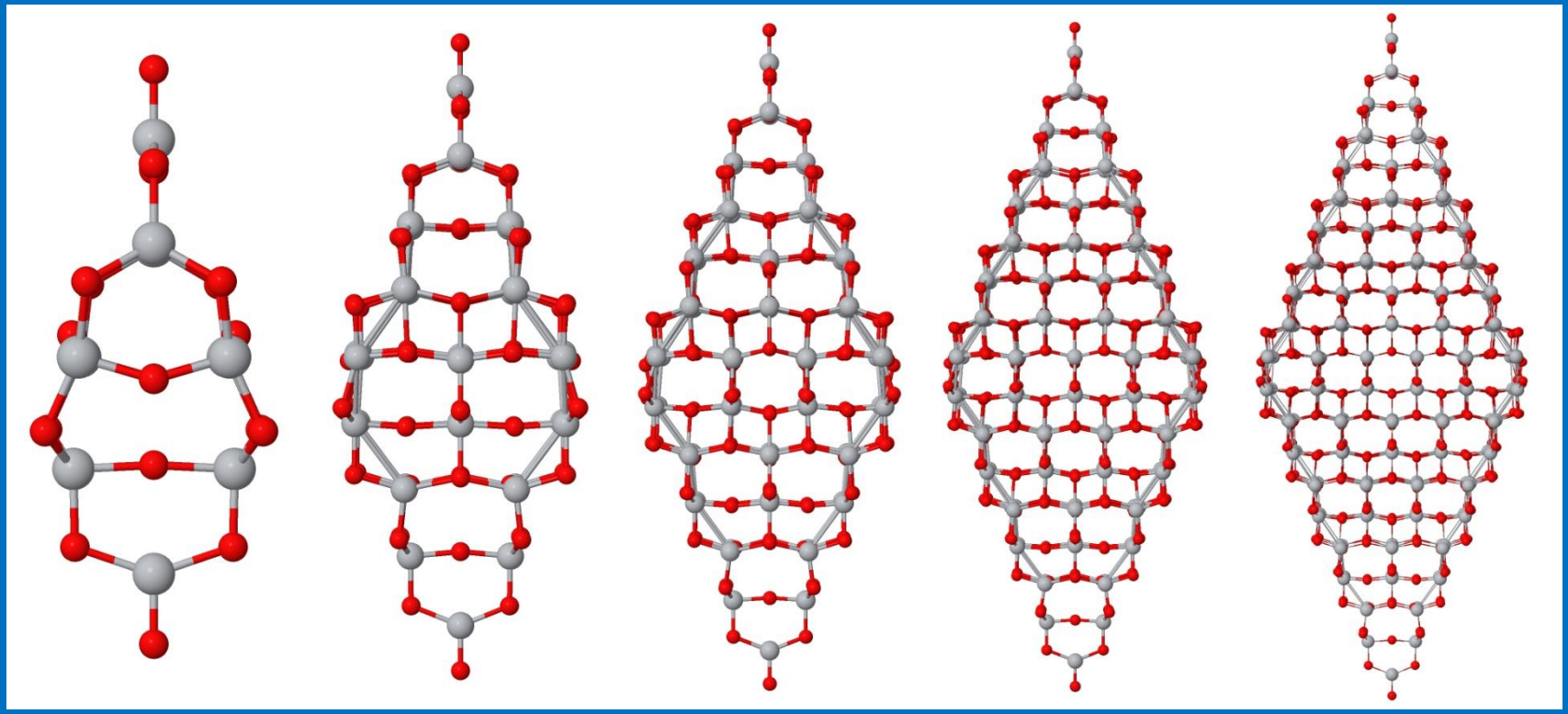




- ✓ Excellent scaling up to 1000 cores
- ✓ Better scaling expected for larger particles
- ✓ Memory problems to be solved
- ✓ Work in progress with developers

PBE optimized nanoparticles

$(TiO_2)_{10}$ $(TiO_2)_{35}$ $(TiO_2)_{84}$ $(TiO_2)_{165}$ $(TiO_2)_{286}$



Structure of corner atoms as in bulk

PBE optimized nanoparticles

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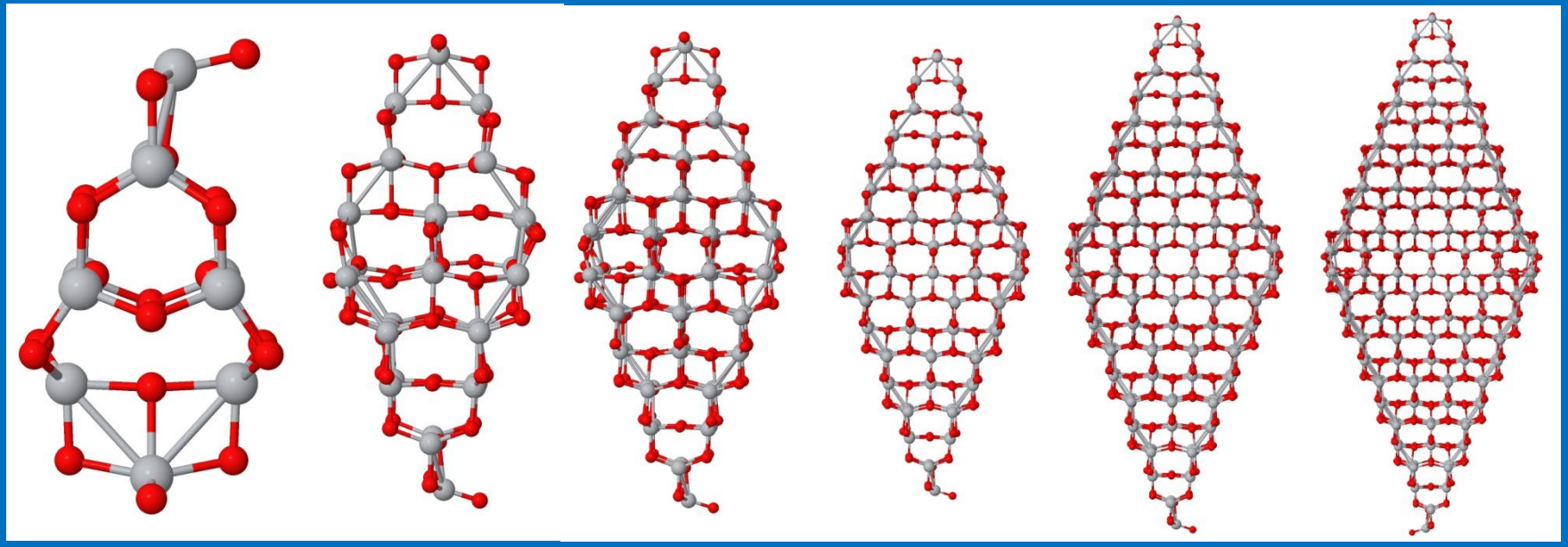
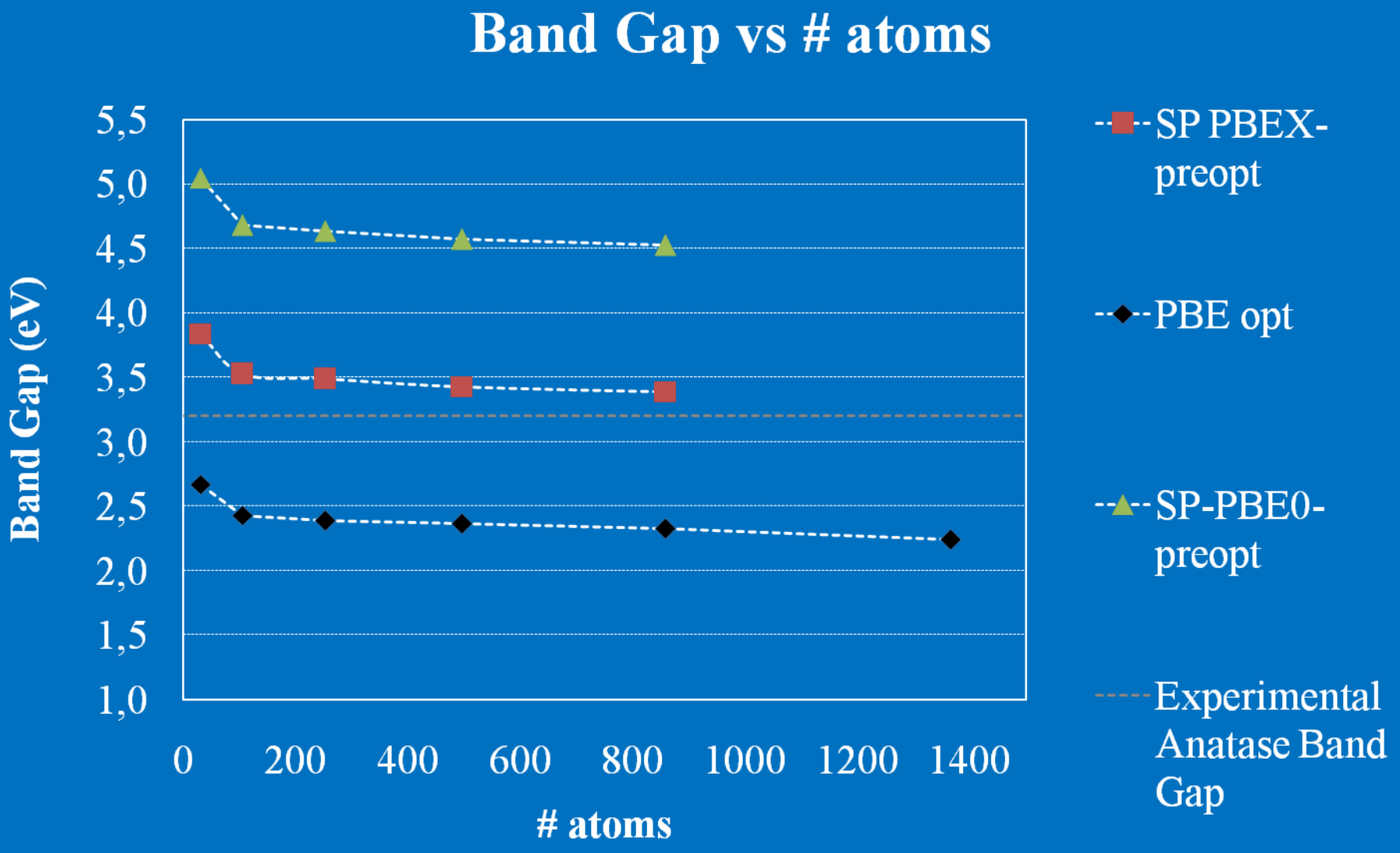
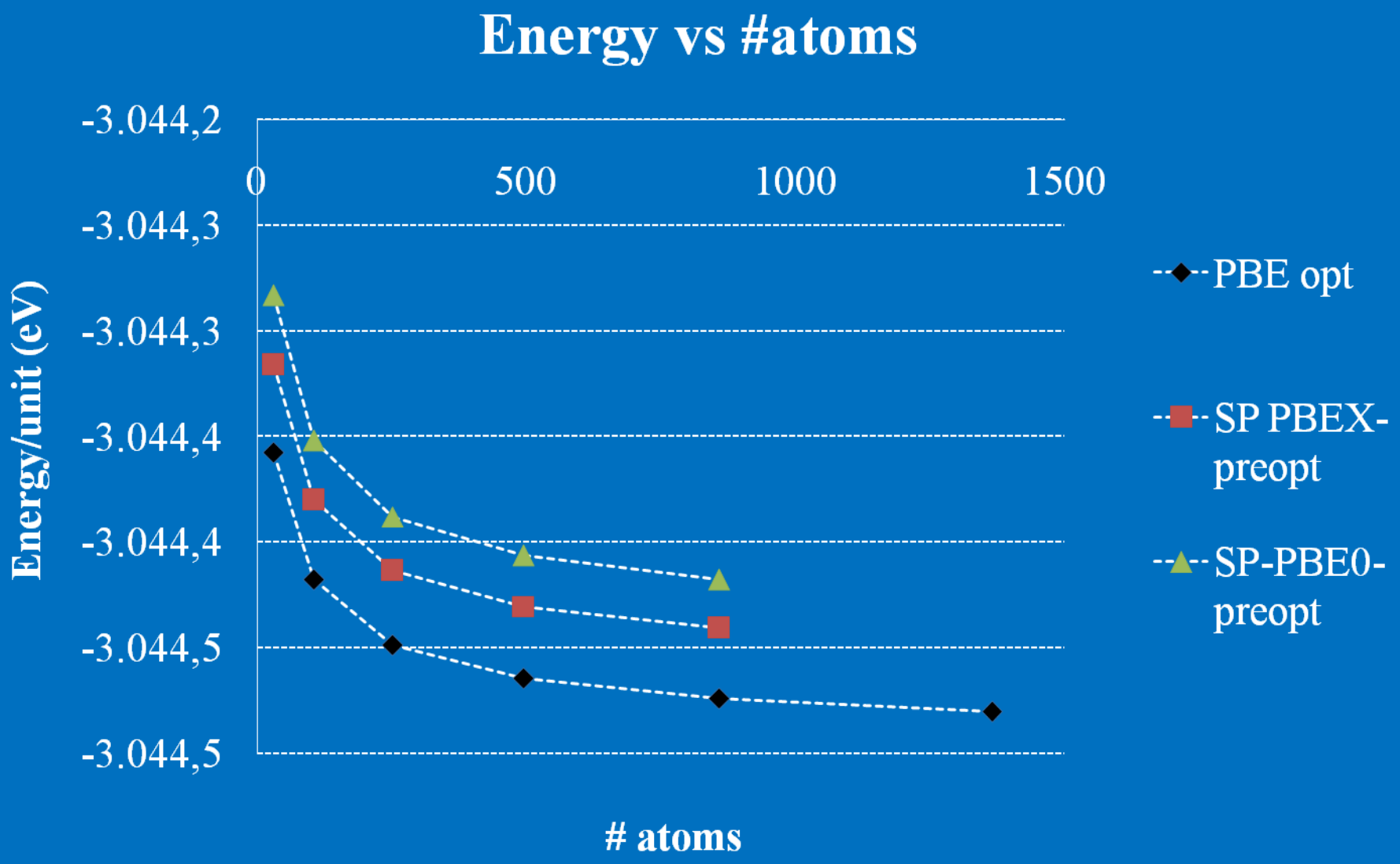


Structure of corner atoms bent

Initial trends on electronic structure



Initial trends on stability (energy(eV) /unit)



Structure of corner atoms as in bulk

Similar results for bent structures

What we learn?

- ✓ First principles calculations on realistic particles with nanometer dimensions are possible
- ✓ Excellent performance of FHI-AIMS
- ✓ Electronic structure seems to converge fast with particle size
- ✓ Energy per unit shows asymptotic behavior

What's next

- ✓ Shape, composition and solvent effects
- ✓ Scalable versus non scalable regime about to be accurately defined for the first time
- ✓ Dynamics of ground and excited states for both nuclei and electrons
- ✓ Huge amount of data to analyze

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