Real-time simulation of water splitting on rutile TiO_2(110) by photo-generated hole

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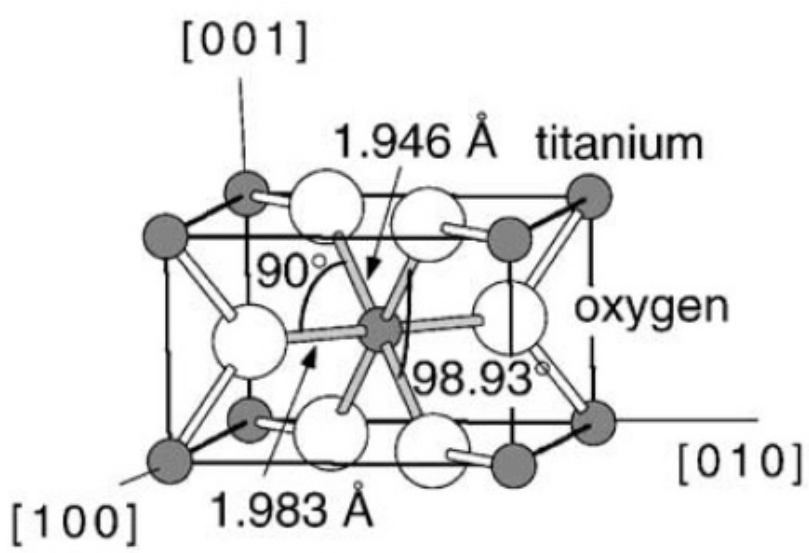
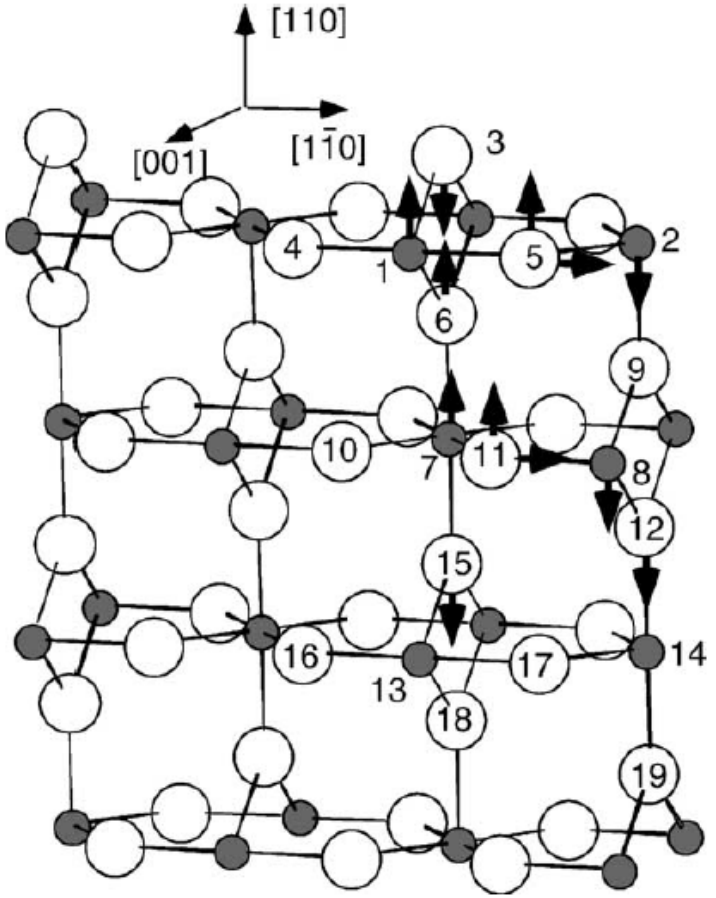
Rutile TiO_2 (110) – a model photocatalyst

Titania (TiO_2) – one of the most widely studied materials for photocatalysis [1]



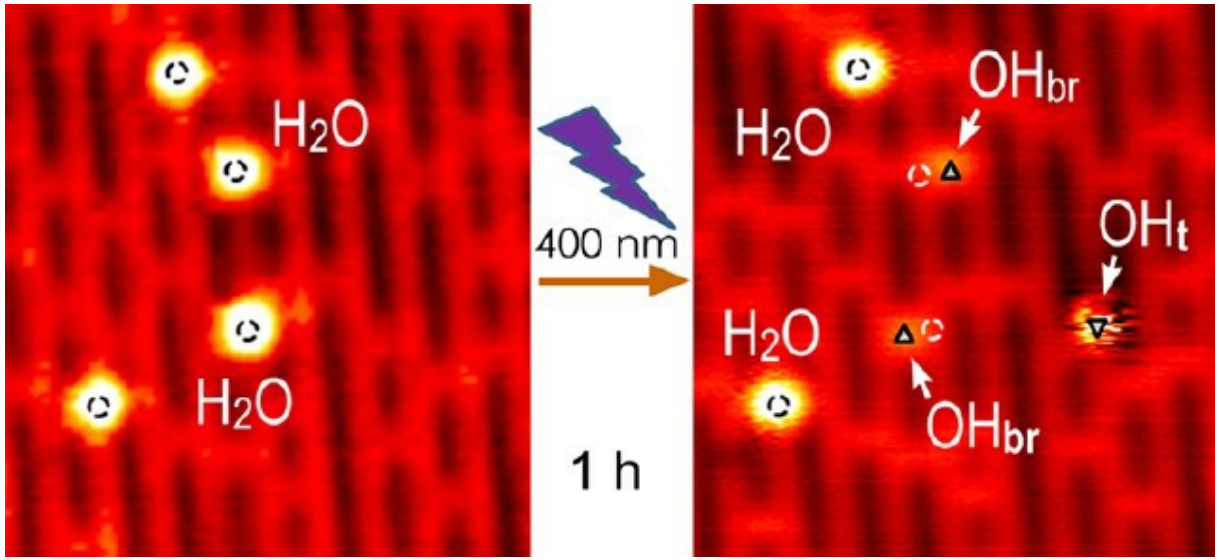


Rutile bulk crystal structure (top),
Model of the (110) surface (left) [2]

1- A. Fujishima, K. Honda. Nature, 238:37-38 (1972)
2- U. Diebold, Surf. Sci. Rep., 48:53-229 (2003)

Experimental evidence for water photooxidation

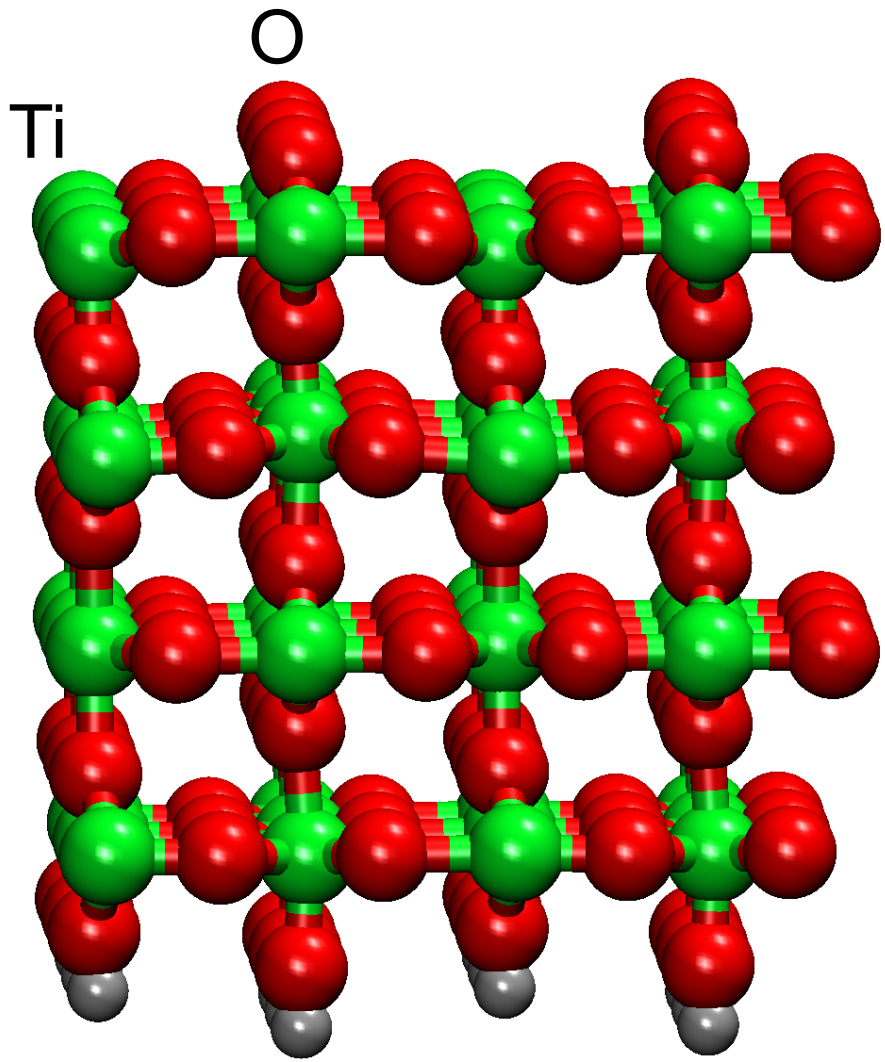
Water can undergo photodissociation, as shown in ultra-high vacuum study [1].



Goal of the present work – real-time simulation of the first step of the water photooxidation.

1 – S. Tan et al., JACS. 134:9978-9985 (2012)

Simulation methodology



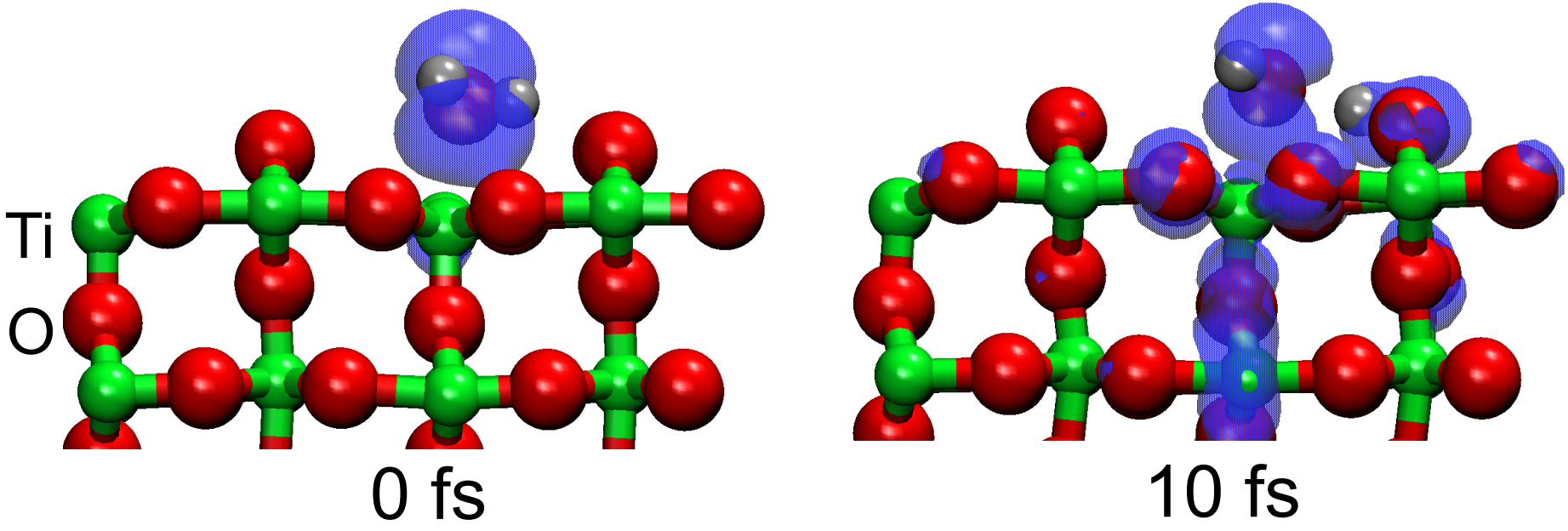
- Simulation slab 4 layers thick
- DFT: GGA-PBE, GPAW code [1], Including DFT+U correction
- ΔSCF approach for simulation of excitation
- Ehrenfest dynamics for time propagation

1 – J. Enkovaara et al., J. Phys. Cond. Mat. 22:253202 (2010)

Dynamics of electron–hole pair on clean (110) surface

Hole on water non-bonding orbital

Excitation energy 9.3 eV

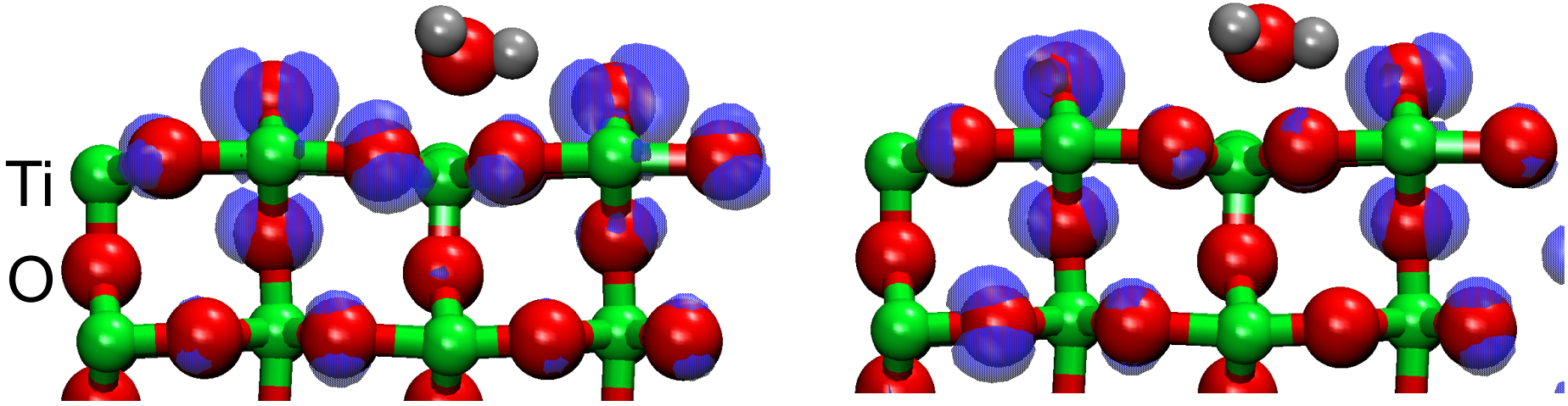


WATER SPLITS!

Dynamics of electron–hole pair on clean (110) surface

Hole on surface localized slab eigenstate

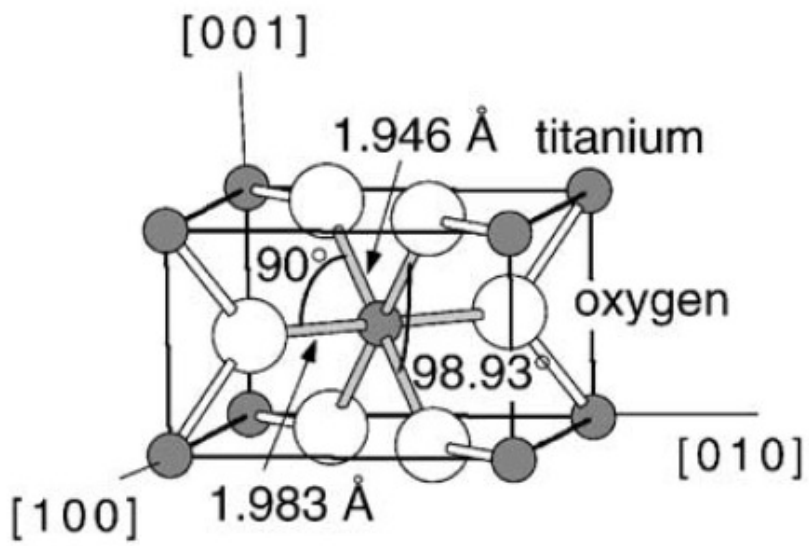
Excitation energy 3.5 eV

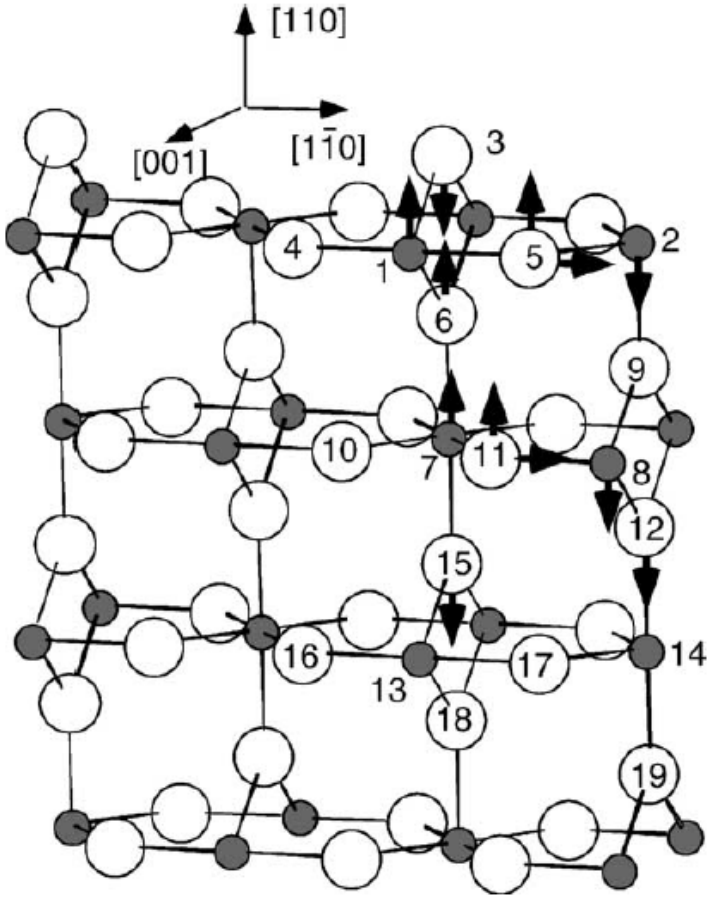


NO SPLITTING

Rutile TiO_2 (110) – a model photocatalyst

Oxygen – 3 sigma bonds, 1 “lone pair”





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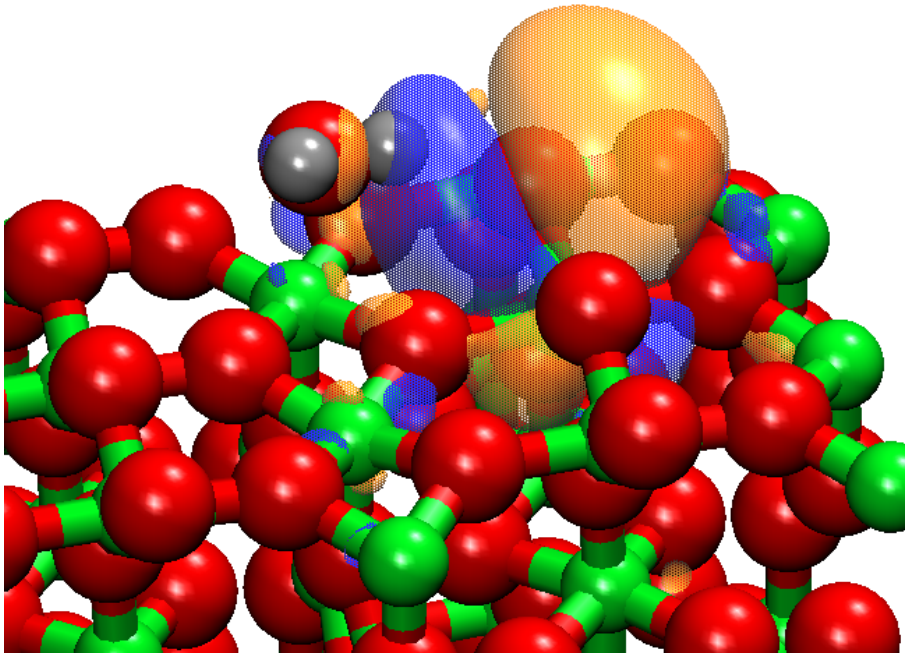
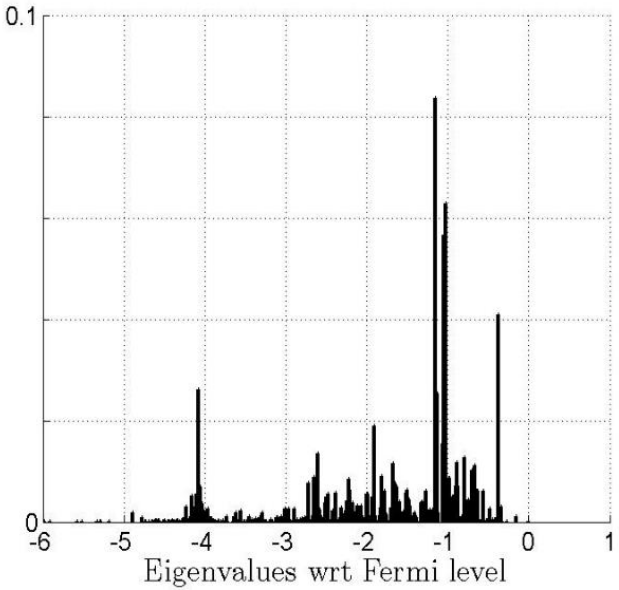
Dynamics of electron–hole pair on clean (110) surface

Hole on a MLWF

Excitation energy 3.8 eV

Maximally Localized Wannier Functions, computed using the *Wannier90* code [1]



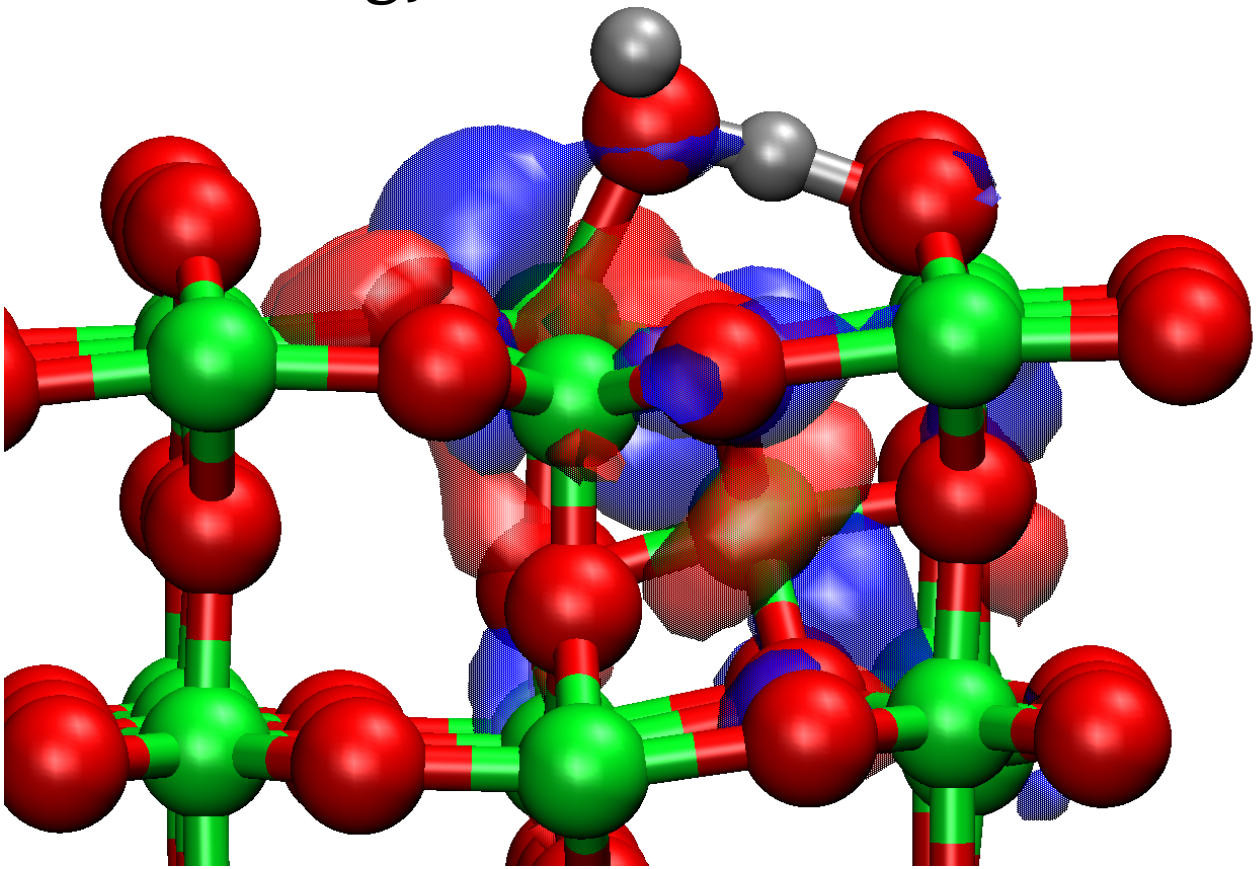


1 – A. Mostofi et al. Comput. Phys. Commun. 178:685 (2008)

Interstitial titanium atom defect level

Hole on interstitial defect level

Excitation energy 1.7 eV



Conclusions and outlook

Behind the scenes: Dozens of simulations with varying initial conditions:

Hole localization

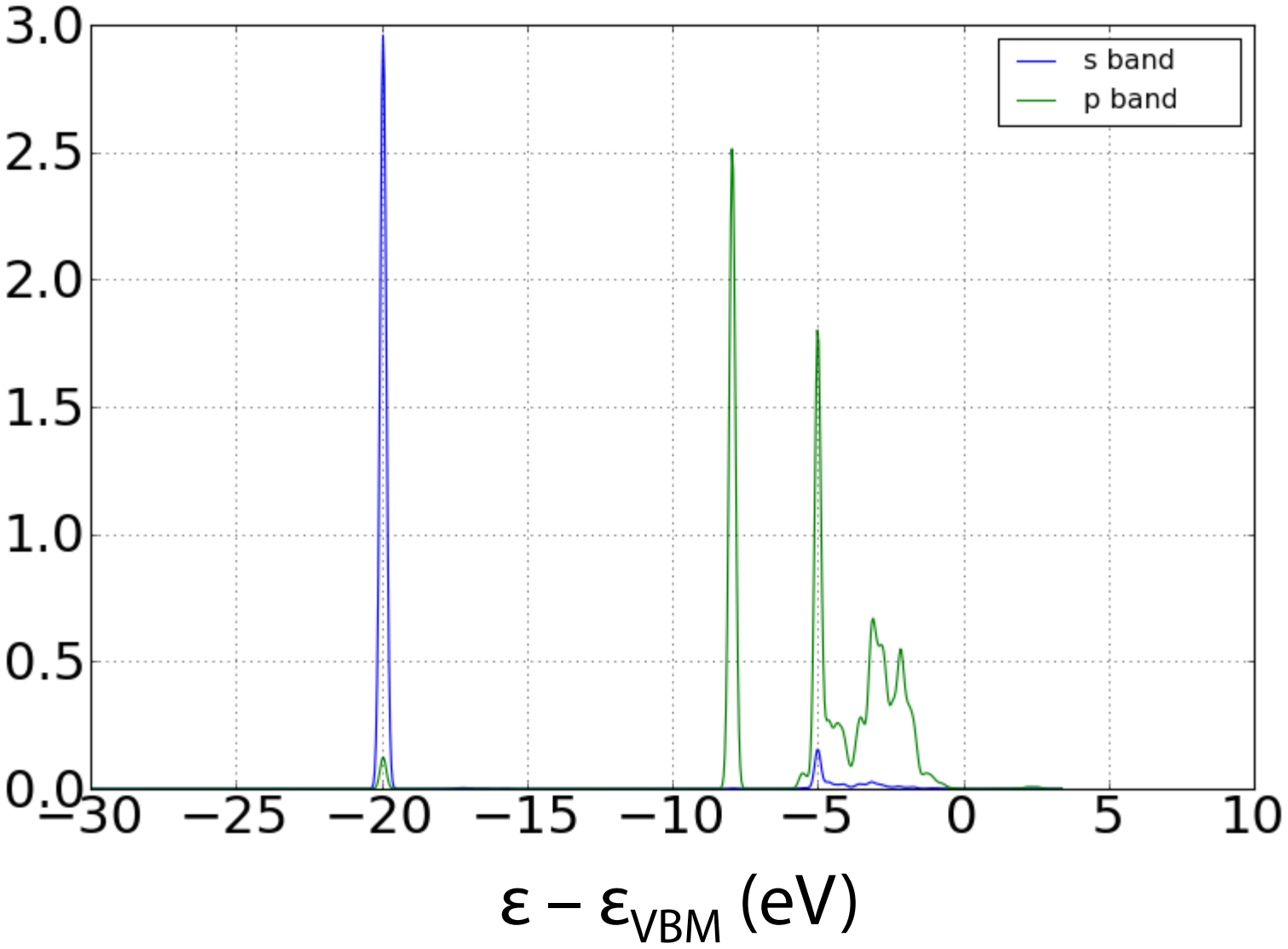
Geometry

Initial velocities of nuclei, etc

The situation under consideration is complex, and full understanding can be achieved upon expanding the model to include:

- Complex adsorbate – adsorbate interactions
- Presence of the macroscopic amount of water and changes in the dielectric constant of the environment
- Presence of another type of defects, or complex interplay between defects of different types
- Consideration of more reactive sites, surfaces, or phases of titania

Density of states and the contribution of water O atom



Nudged elastic band calculation