Calculating Core Electron Binding Energies for Atoms at the Surfaces of Insulators

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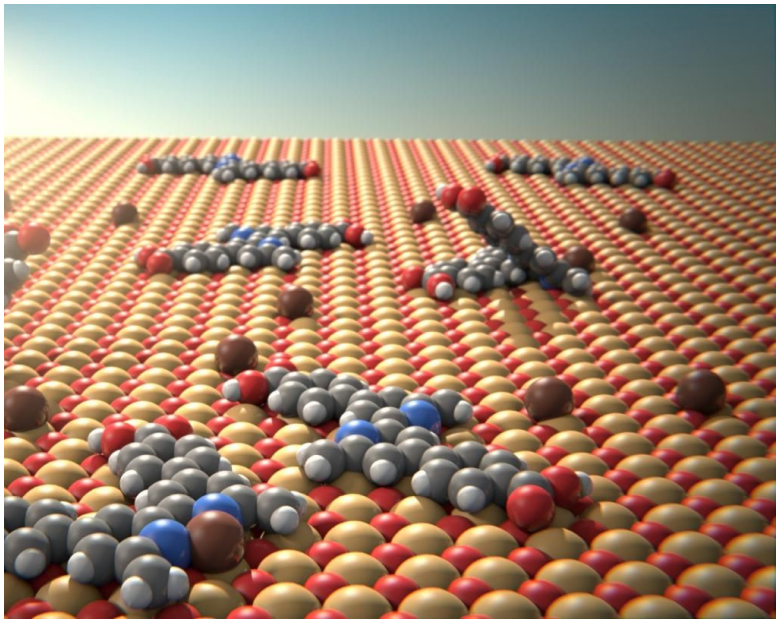
How to determine the chemical composition of a surface?

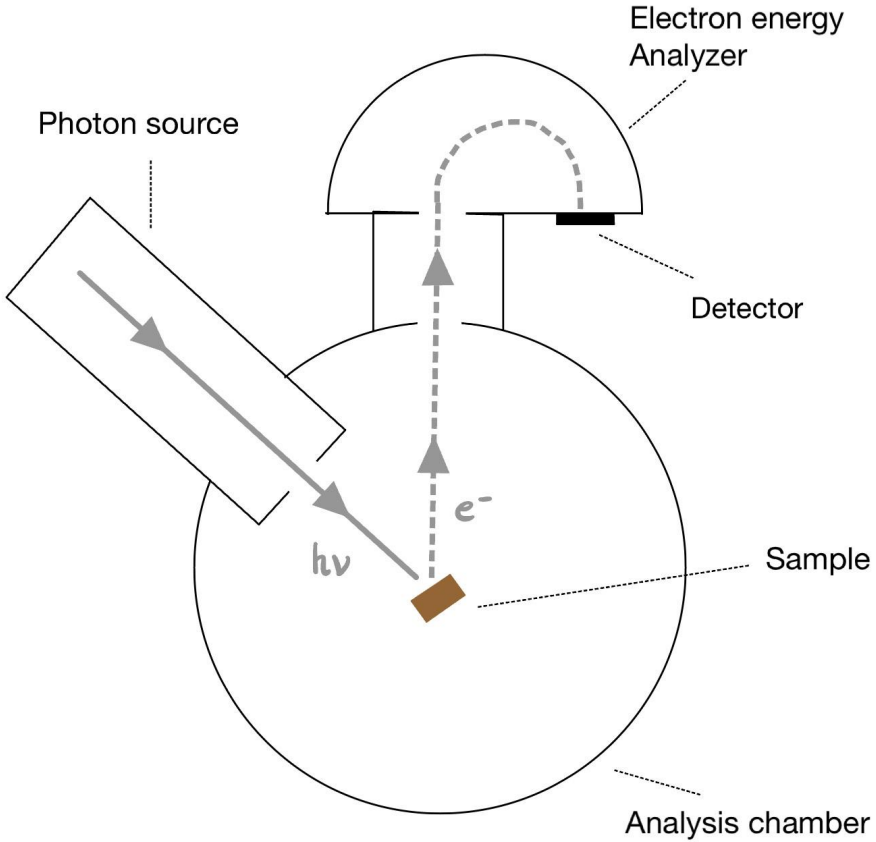
- Only extremely surface sensitive methods can be used
- Most common is X-ray Photoelectron Spectroscopy (XPS)



X-ray electron spectroscopy

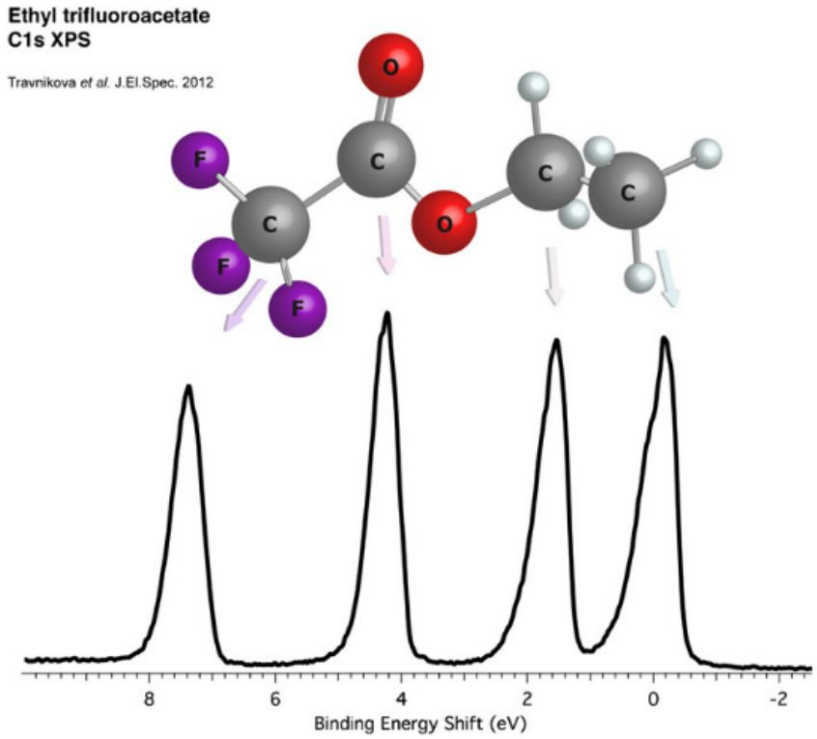
- Projecting x-ray photons at surface
- Exiting electron energies are measured

$$h\nu = E_k + E_B + \phi$$



Core level XPS

- Able to determine elemental composition of a surface
- Observe characteristic binding energies of atomic core electrons
- Determine even the chemical composition of surface



The problem

- How to interpret the found XPS spectrum
- What does each peak correspond to?
- Usually literature data from previous measurements is used
- But there are many inconsistencies
- Could we calculate the binding energies instead?

Previous work

- Delta self-consistent field method (ΔSCF)

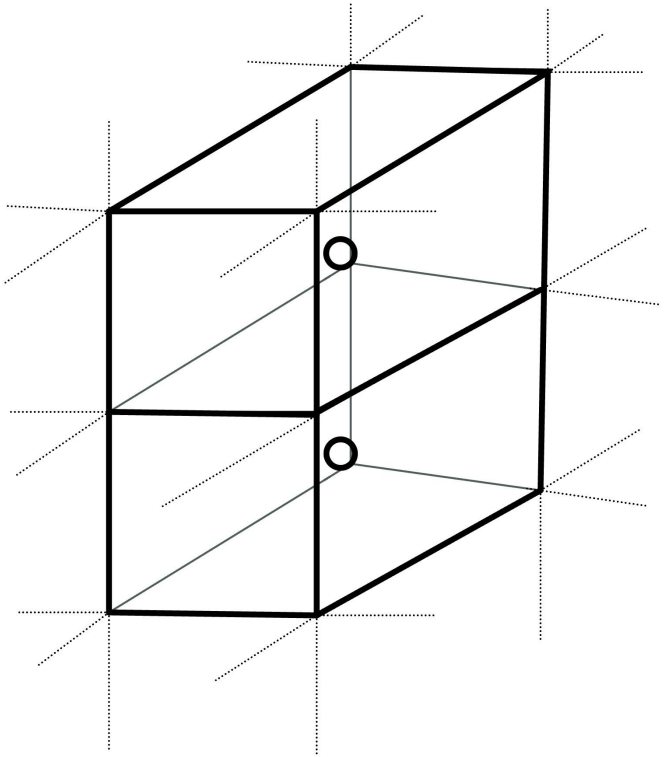
$$E_B = E_{N-1} - E_N$$

Using ΔSCF method:

- calculations of free molecules
- calculations of bulk solids
- calculations of surface species on metals using cluster models

Central problem

- Bulk solids are typically modelled as an infinite periodic system
- A core hole is created in each periodic cell
- We aim to remove the influence of interactions between holes on the calculation results



Material as periodic cells

The aim of the project

- Previous work looked at free molecules and bulk solids
- But experimentally XPS is mostly used to study surfaces
- So how can we calculate binding energies for surfaces?
- How can we eliminate finite size effects?

Objective

1. Computational method for calculating absolute core electron binding energies for atoms at the surfaces of insulators

2. Demonstrate the convergence of calculations with respect to cell size

Methods

- Calculations with DFT
- Functional used was PBE
- ΔSCF core hole and Z+1 methods were applied
- The program used for calculations was FHI-aims

ΔSCF method

- Method for finding binding energies
- Difference between excited state and ground state
- Accounts for orbital relaxation
- Need for a core hole calculation

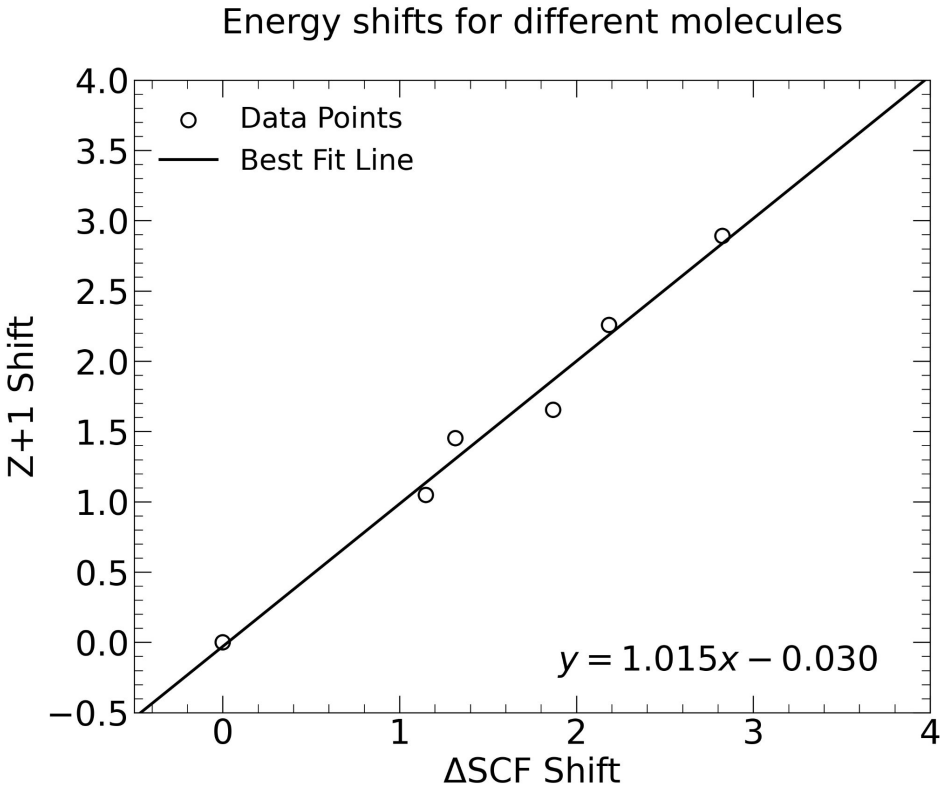
$$E_B = E_{N-1} - E_N$$

Z+1 method

- Also known as equivalent cores approximation
- Variation of the ΔSCF method
- Instead of removing an electron the nuclear charge is increased
- No need for core hole calculation
- Doesn’t give absolute binding energies

Z+1 method justification

- Core electron binding energy calculations for 6 oxygen containing compounds
- Difference between Z+1 method and core hole calculations graphed
- Best-fit line with slope of one



Computational approach

Bulk calculations

Surface calculations of same solid

For a core hole in the middle layer of the slab,

do the two models converge to the same result?

TiO2 as the test material

- Structural isomer - rutile
- Good amount of experimental data
- Wide practical applications
- Insulator

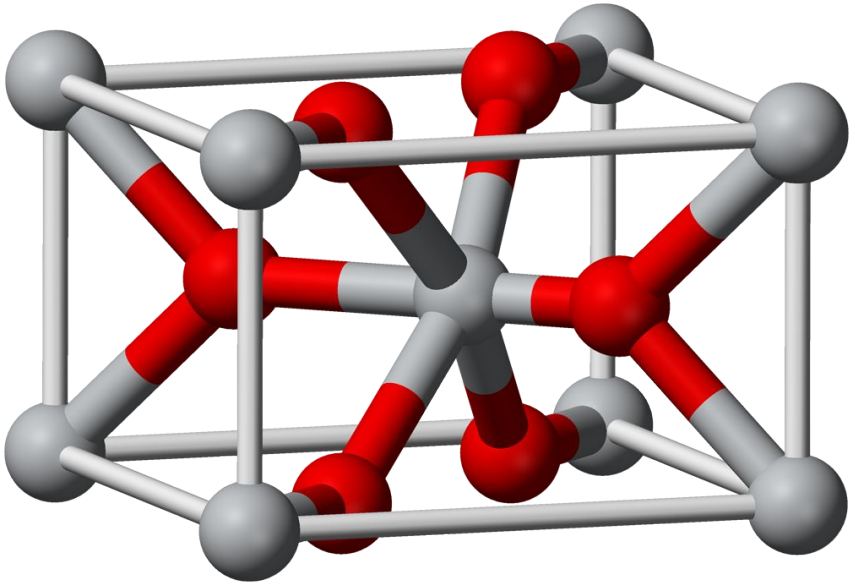
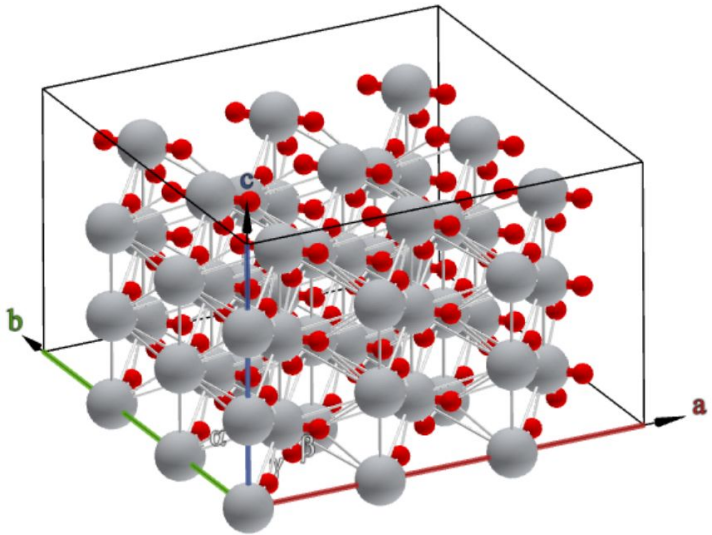


Figure 1. Rutile unit cell [1]

How we do calculations

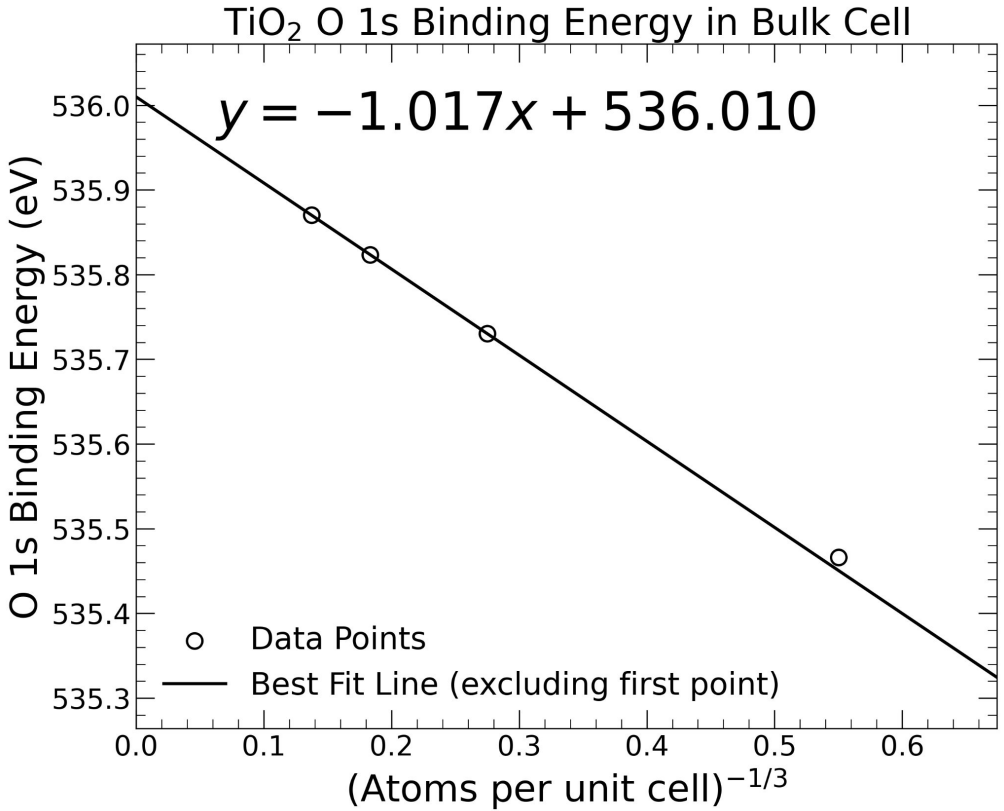
- Geometry relaxation
- ΔSCF calculations for unit cell
- And next four supercells
- Supercells scaled proportionally
- Binding energy is referenced to the middle of the band gap rather than absolute zero



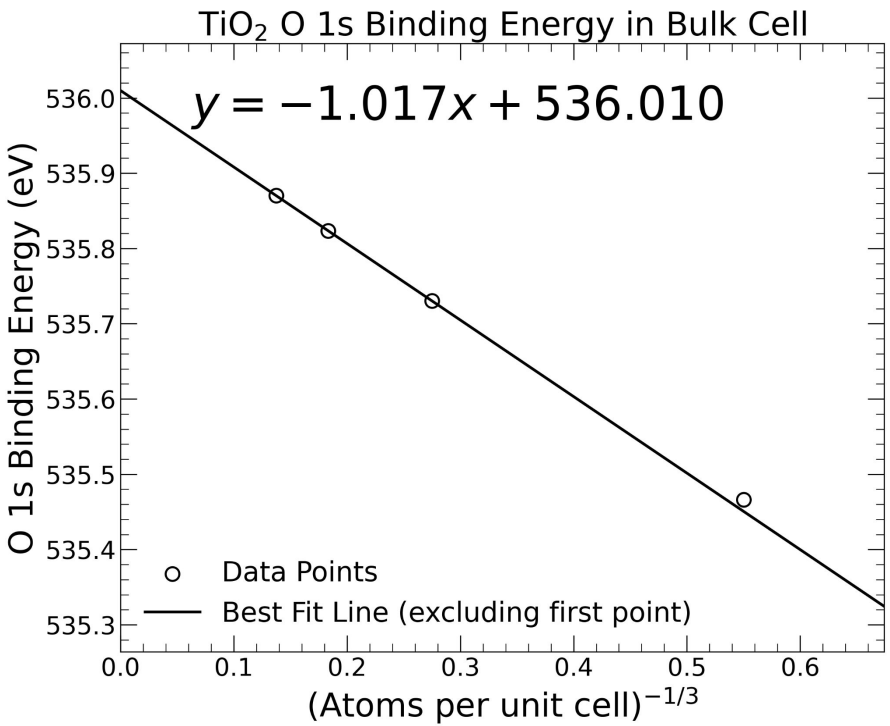
Rutile 3x3 supercell

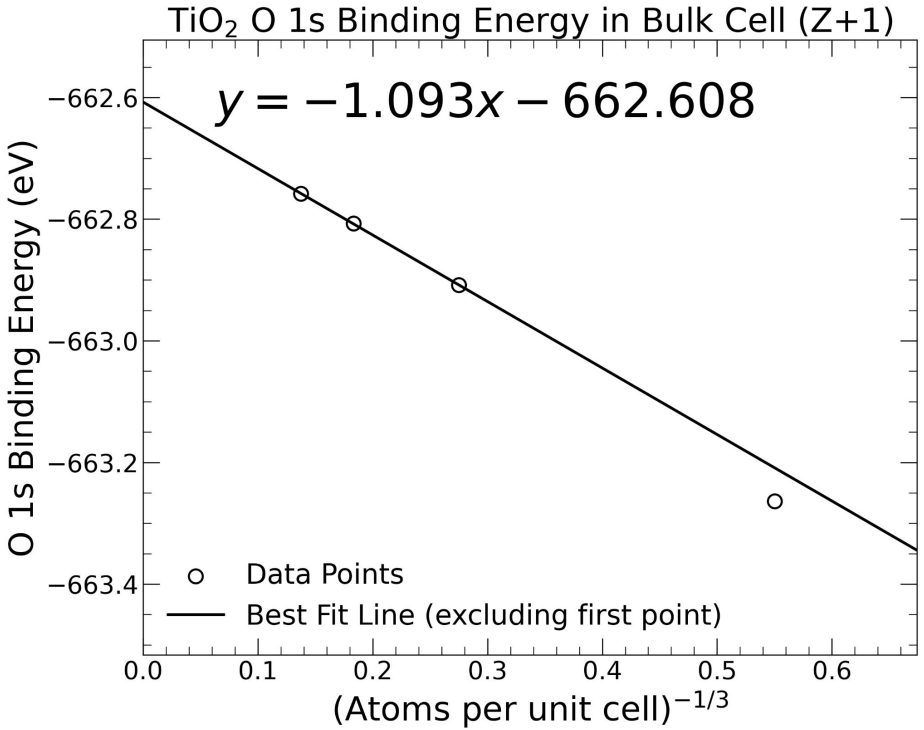
Graphing results

- y-axis: binding energy
- x-axis: inverse of cell side length
- Best-fit line
- Disregarding first unit cell datapoint
- y-intercept gives binding energy value for infinite size cell



Calculations for bulk model

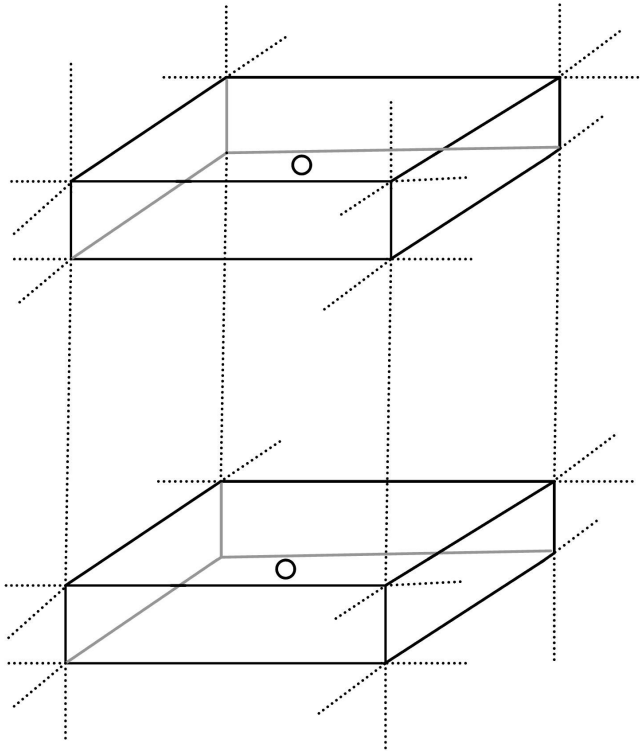




Slab calculations

- Periodic in each direction
- Vacuum layer between two slabs
- Core hole in the middle layer

  … or on the surface
- Scaling cells equally in each direction



110 (1x1) surface

- Most stable rutile surface
- Two types of oxygens on the surface
- Under-coordinated atoms

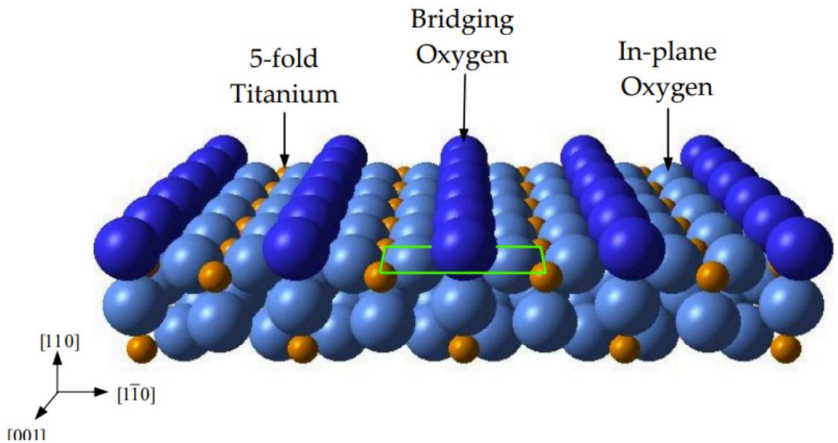
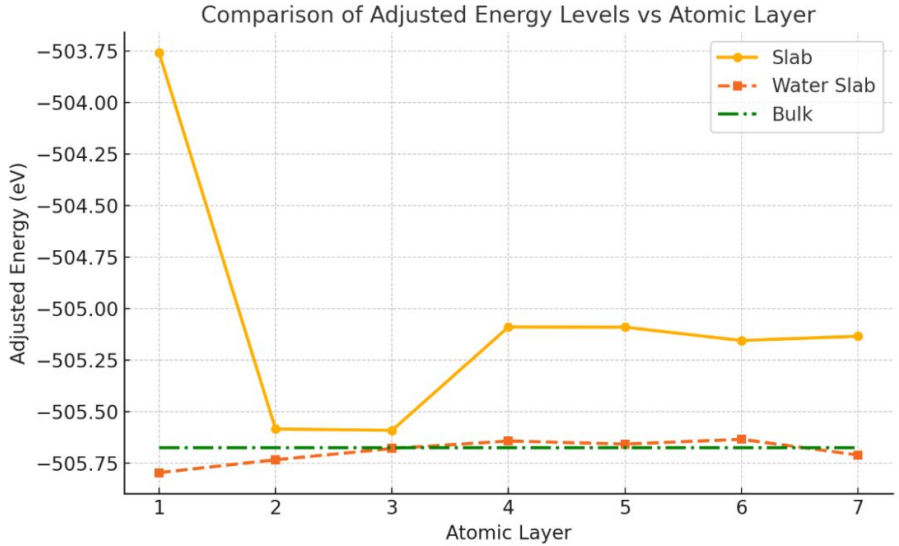
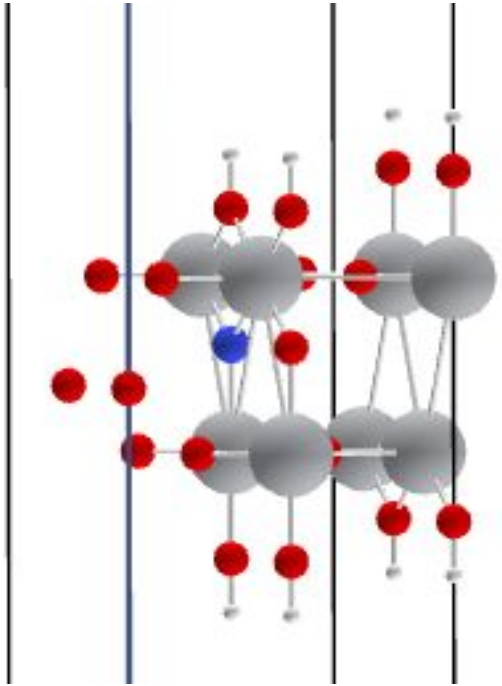


Figure 2. Rutile 110 surface [2]

Problem with this approach

- Binding energies too different between layers
- Wouldn’t work with our extrapolation method
- Thus passivating the surface, adding water





Z+1 binding energy results

Bulk: 670.4285211 eV

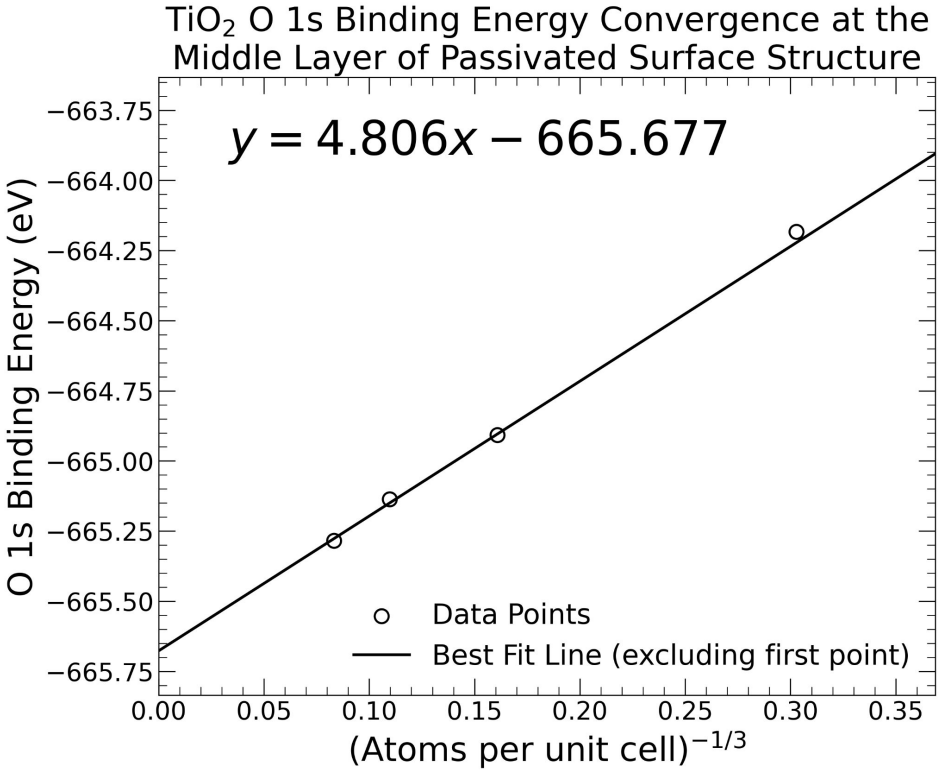
slab: 670.7774163 eV

passivated slab: 670.4165438 eV

Difference from bulk model:

slab model: **0.3488952 eV**

passivated slab model: **0.011977275 eV**



Z+1 calculation results for different TiO2 models

Energy shift compared to bulk solid

Bare 110 surface

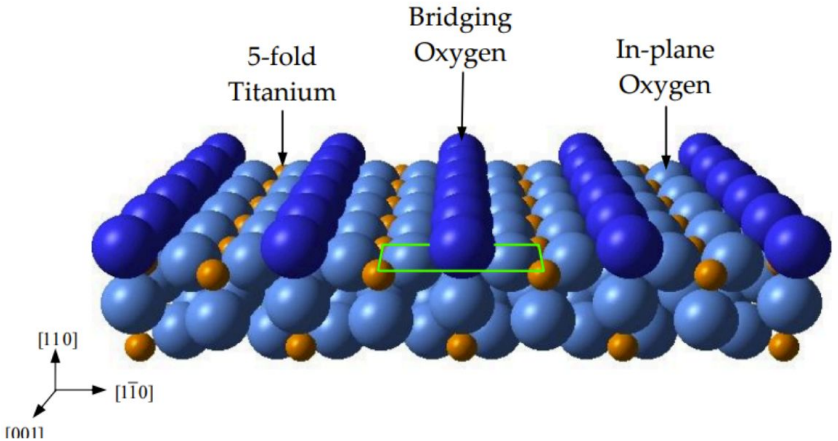
In-plane oxygen: 0.555 eV

Bridging oxygen: 2.765 eV

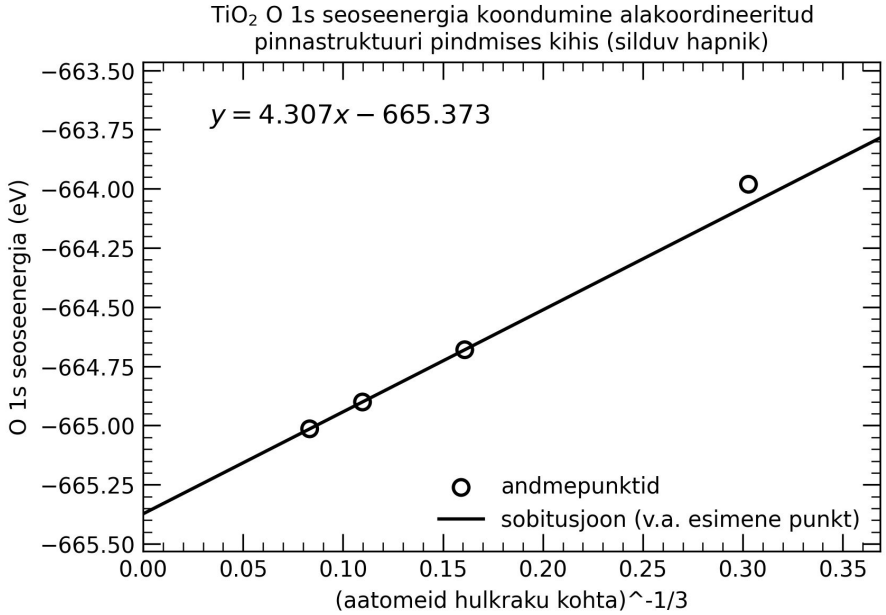
Passivated surface

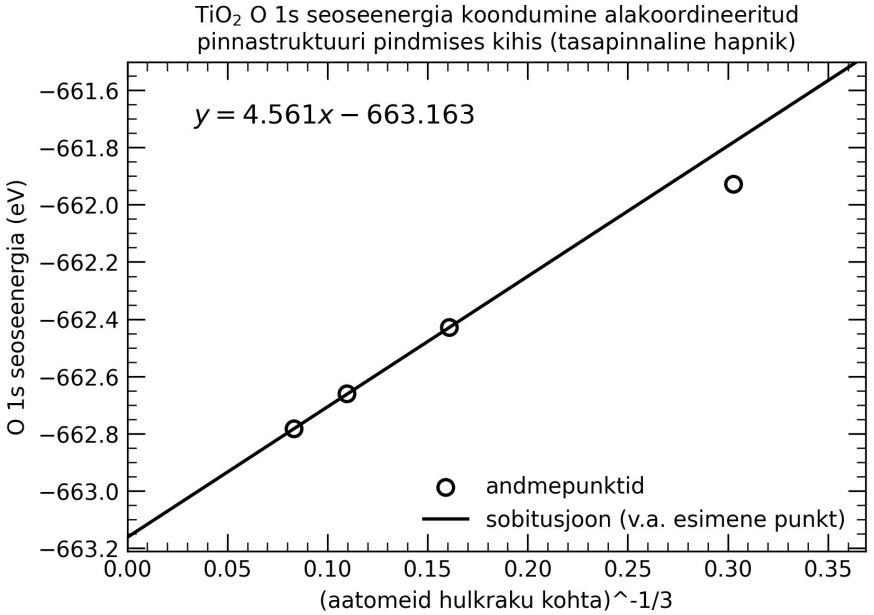
In-plane oxygen: 0.570 eV

Bridging oxygen: 3.302 eV

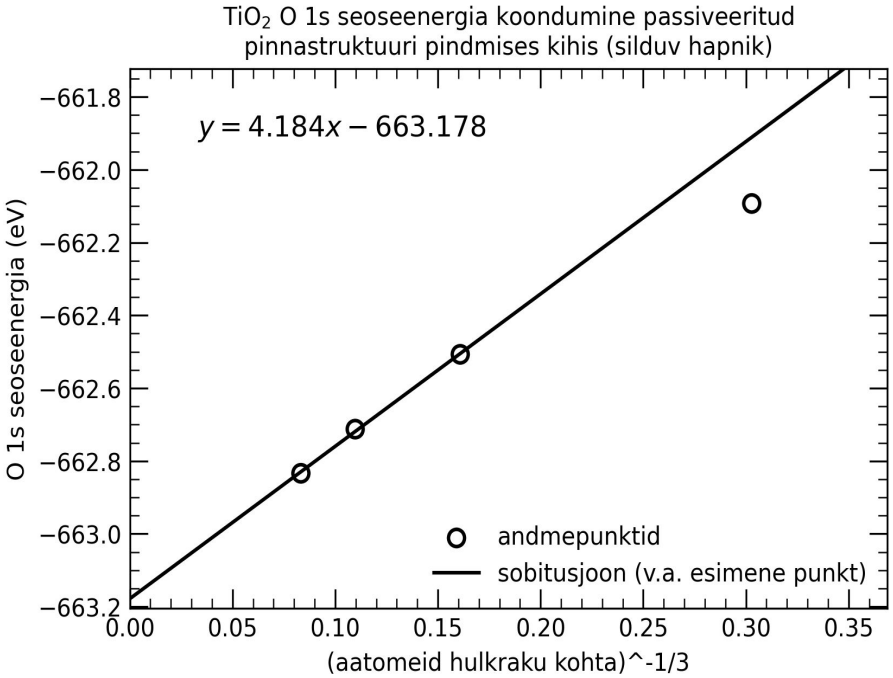


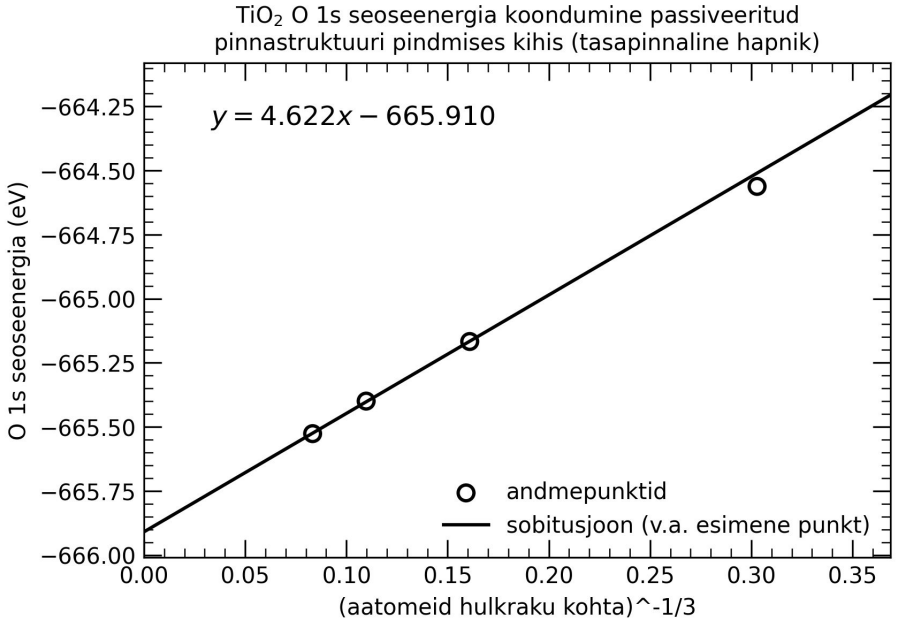
Bare 110 surface





Passivated surface





Summary

- Use of Z+1 method is justified
- Slab model with passivated surface gives better results
- Binding energy value converges into same place for slab and bulk model
- Extrapolation method works for surface defect models
- Core electron binding energy shifts found between bulk and slab models

Further developments

- Verify findings with alternative methods
- Finding binding energies for other materials using this method
- Comparing findings to experimental data

Thank you for your attention!

Sources

[1] - Ben Mills. Rutile Unit Cell 3D Balls. Public Domain Image. 2007. url: https://commons.wikimedia.org/wiki/File:Rutile-unit-cell-3D-balls.png.

[2] - Wutthikrai Busayaporn. ”TiO(110) Surface Structure“. PhD thesis. University of Manchester, School of Materials, 2010.