Scalable Δ-Self-Consistent-Field Calculations of Core Electron Binding Energies in Periodic and Aperiodic Systems

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Core level XPS

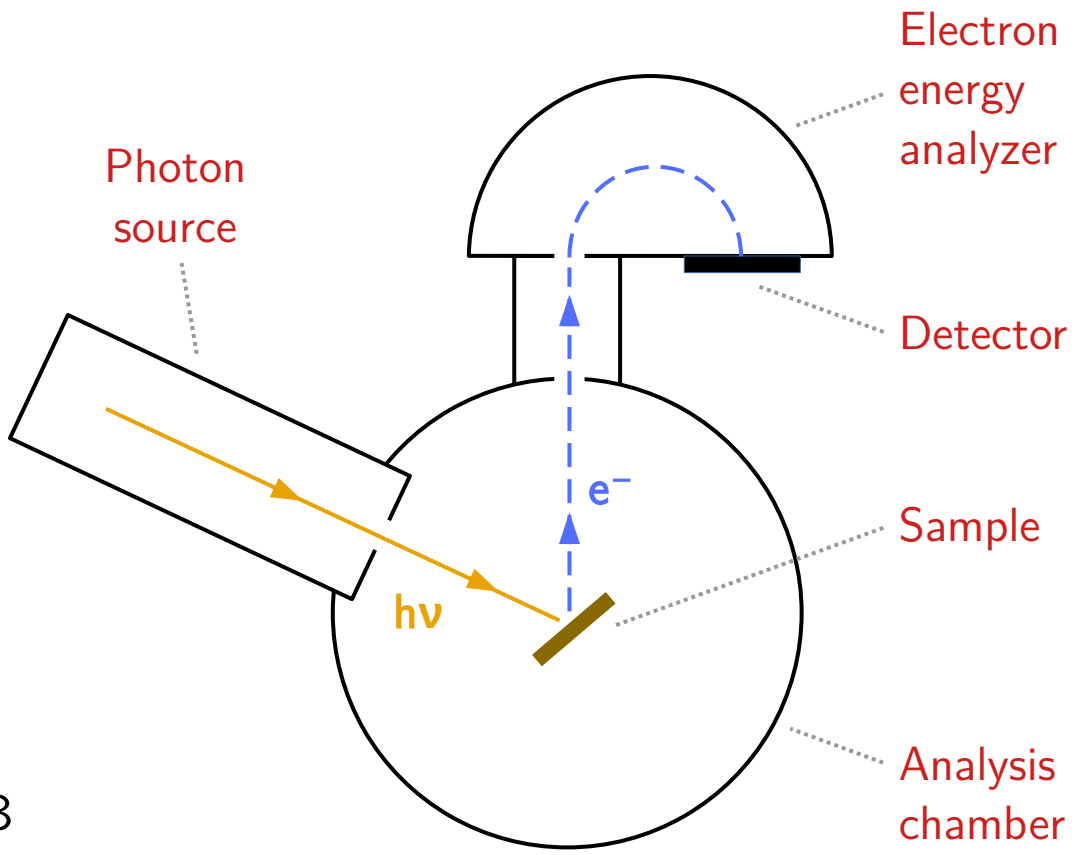
XPS

Photon in =>

electron out

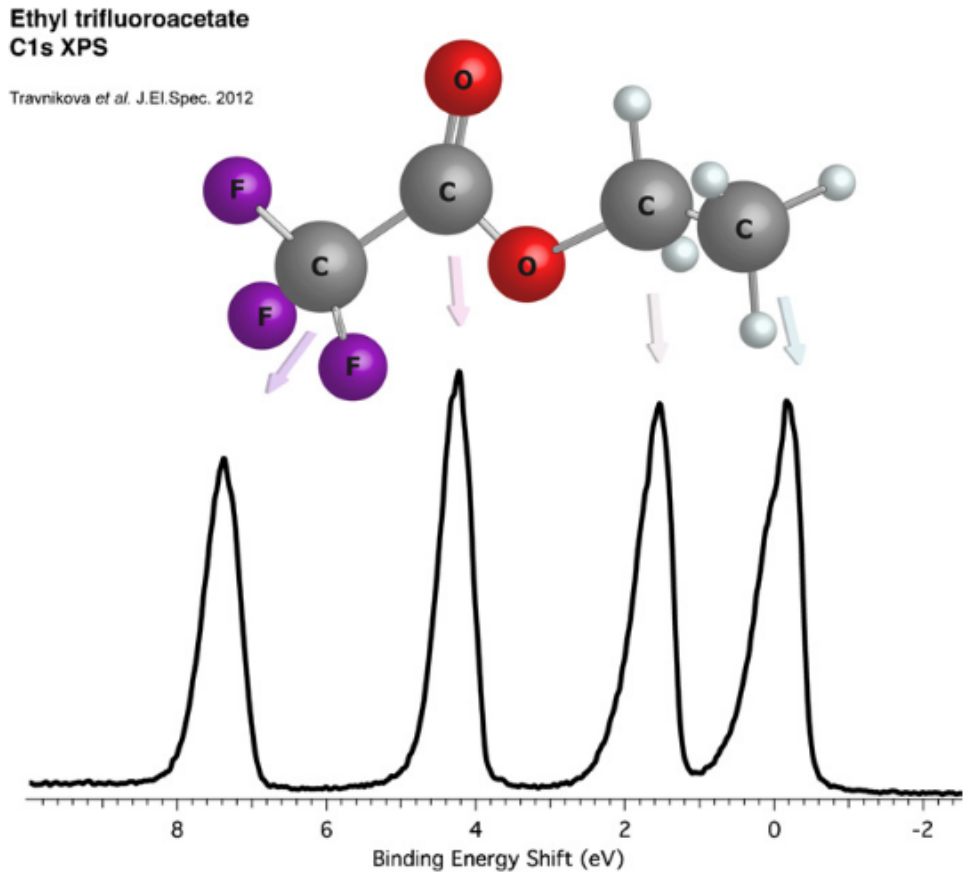
$$h\nu = E_{kin} + E_B + \varphi$$

Measure E_{kin}, determine E_B



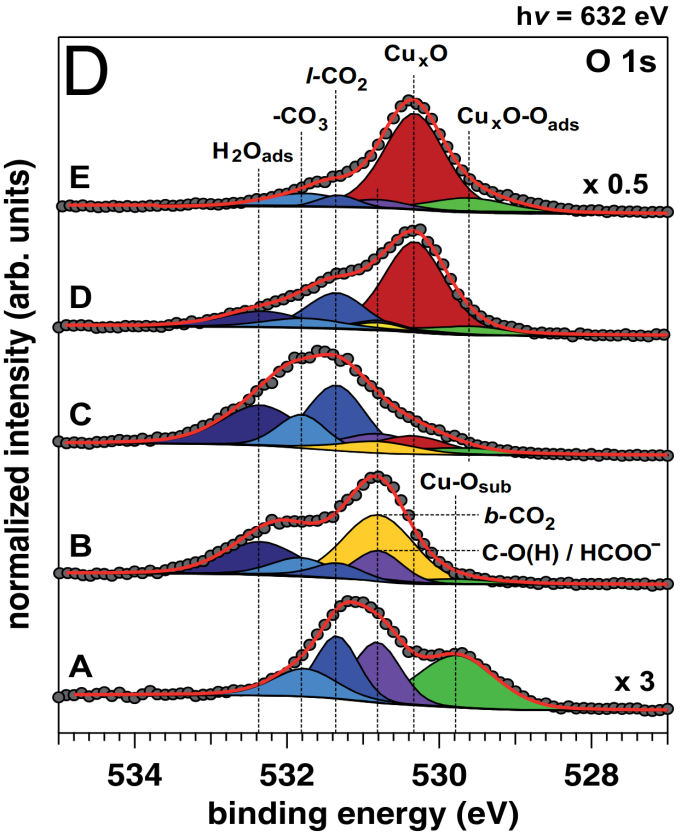
Core electron binding energies

- Small “chemical shifts” depending on the local environment of the atom
- XPS is used to study the chemical composition of the sample



The peak-assignment problem

- Real spectra look messy
- How to disentangle the overlapping peaks?
- Reference data?



Reproduced from Favaro et al., PNAS 144, 6706 (2017)

The peak-assignment problem

Volume 39, Issue 2
March 2021

INTRODUCTION | FEBRUARY 05 2021

Introduction to topical collection: Reproducibility challenges and solutions with a focus on guides to XPS analysis FREE

Donald R. Baer; Gary E. McGuire; Kateryna Artyushkova; Christopher D. Easton; Mark H. Engelhard; Alexander G. Shard

Check for updates

+ Author & Article Information

J. Vac. Sci. Technol. A 39, 021601 (2021)
https://doi.org/10.1116/6.0000873 **Article history**

Topics

Epitaxy, Atomic layer deposition, Semiconductor materials, Surface analysis techniques, X-ray photoelectron spectroscopy, Nanoparticle, Catalysts and Catalysis, Editorials

Reproducibility Challenges and Solutions II with a Focus on Surface and Interface Analysis

Reliability and reproducibility of data and analysis issues impact most areas of modern science, including those of importance to the AVS. In 2020, *JVST A* published a special topic collection on Reproducibility Challenges and Solutions with a Focus on XPS. As a follow up to the first collection of papers, this collection expands into other areas of surface analysis.

This special topic collection includes issues related to AES, SIMS, LEIS, Ellipsometry and Scanning Probe methods, as well as XPS topics not fully covered in the first collection. The intent is to present papers that identify important challenges faced by analysts that often lead to incomplete or erroneous results and to identify useful protocols and other solutions.

Guest Editors

- Don Baer, Pacific Northwest National Laboratory (emeritus) (USA)
- Ian Gilmore, National Physical Laboratory (UK)

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TUTORIAL | NOVEMBER 20 2020

Assessment of the frequency and nature of erroneous x-ray photoelectron spectroscopy analyses in the scientific literature FREE

Special Collection: Special Topic Collection: Reproducibility Challenges and Solutions

George H. Major; Tahereh G. Avval; Behnam Moeini; Gabriele Pinto; Dhruv Shah; Varun Jain; Victoria Carver; William Skinner; Thomas R. Gengenbach; Christopher D. Easton; Alberto Herrera-Gomez; Tim S. Nunney; Donald R. Baer; Matthew R. Linford

Check for updates

+ Author & Article Information

J. Vac. Sci. Technol. A 38, 061204 (2020)

https://doi.org/10.1116/6.0000685 **Article history**

"experienced XPS analysts reviewed these spectra and found that peak fitting was a common source of significant errors"

Volume 26, Issue 1
1 February 2020

Next >

JOURNAL ARTICLE

Proliferation of Faulty Materials Data Analysis in the Literature

Matthew R Linford, Vincent S Smentkowski ✉, John T Grant, C Richard Brundle, Peter MA Sherwood, Mark C Biesinger, Jeff Terry, Kateryna Artyushkova, Alberto Herrera-Gómez, Sven Tougaard, William Skinner, Jean-Jacques Pireaux, Christopher F McConville, Christopher D Easton, Thomas R Gengenbach, George H Major, Paul Dietrich, Andreas Thissen, Mark Engelhard, Cedric J Powell, Karen J Gaskell, Donald R Baer

Microscopy and Microanalysis, Volume 26, Issue 1, 1 February 2020, Pages 1–2, https://doi.org/10.1017/S1431927619015332

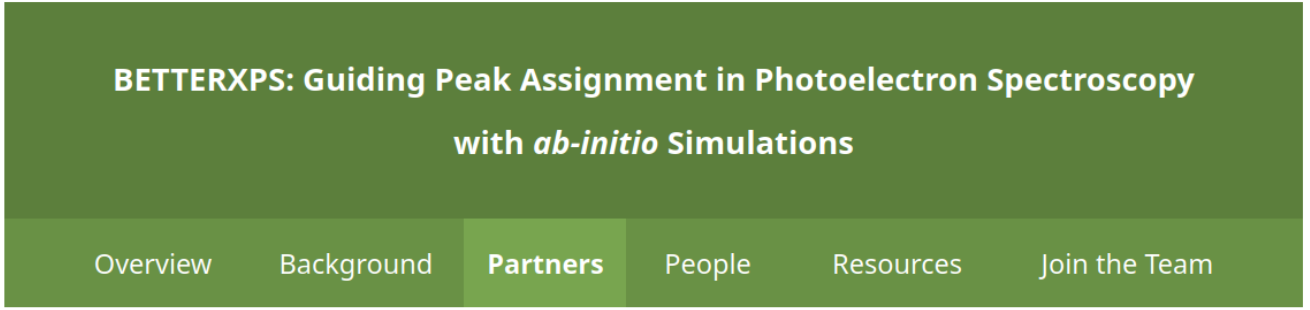
Published: 01 February 2020 **Article history** ▾

Extract

As a group of subject-matter experts in X-ray photoelectron spectroscopy (XPS) and other material characterization techniques from different countries and institutions, we write this document to raise awareness of an epidemic of poor and incorrect materials data analysis in the literature. This issue is a growing

BETTERXPS

- Horizon Europe Staff Exchanges project
  - Method development
  - Case studies
  - Workshops
- 11 partners from 7 countries
- xps.ut.ee/betterxps



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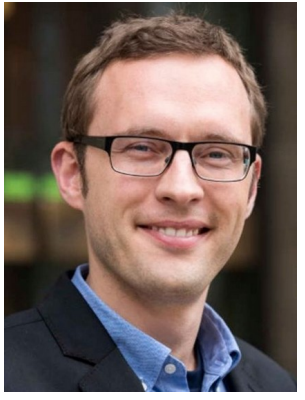
University of Vienna
(previously Warwick)

Dylan Morgan
University of Warwick

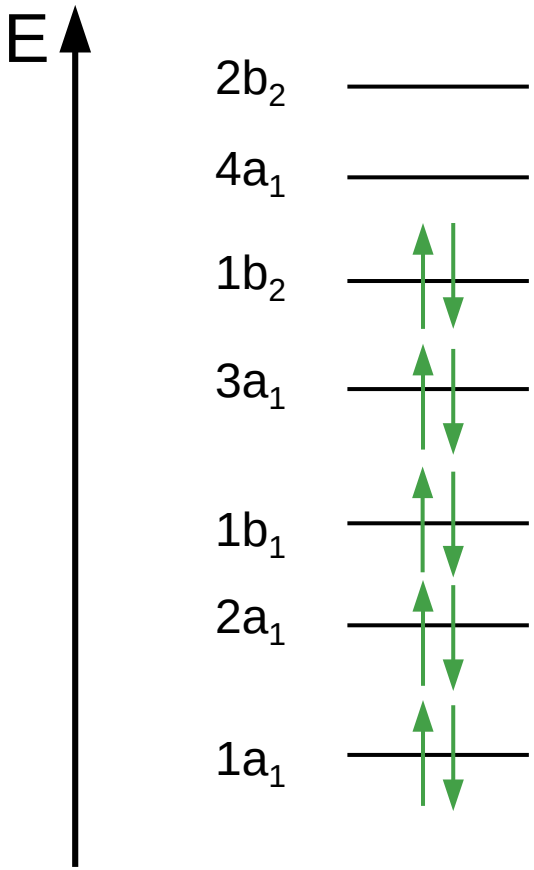


Prof. Johannes Lischner
Imperial College London

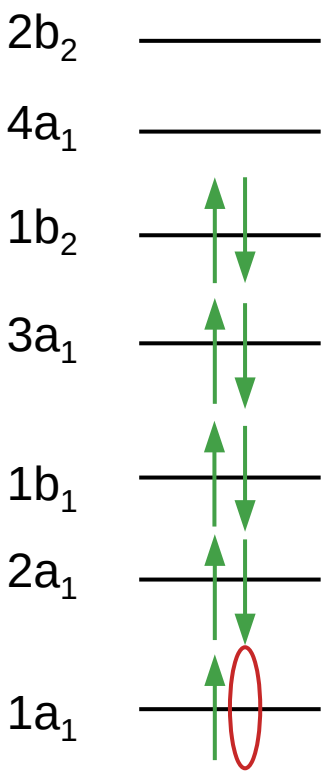
The ΔSCF method

- ΔSCF = ΔSelf-Consistent Field
- $E_B = E_N - E_{N-1}$
  - E_N - ground state total energy
  - E_{N-1} - total energy of the final state with a core hole
- P.S. Bagus, Phys. Rev. 139, A619 (1965)

ΔSCF method: H_2O example



Ground state



Final state with a core hole

DFT with SCAN, scaled ZORA treatment of relativistic effects, numerical atom-centred basis functions as implemented in FHI-aims

Ground state E_{tot}: -2081.55 eV

Final state E_{tot}: -1541.67 eV

ΔSCF: 539.88 eV

Experimental B.E.: 539.9 eV

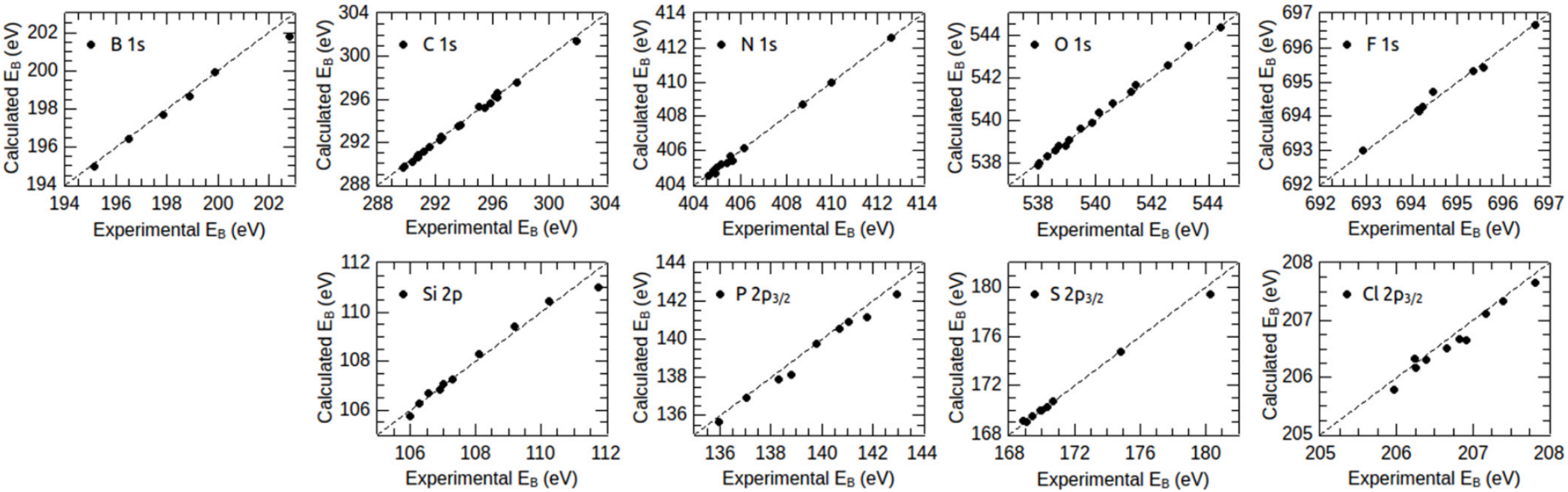
How can this be justified?

- W. Yang and P.W. Ayers, “Foundation for the ΔSCF Approach in Density Functional Theory”, arXiv:2403.04604
- The Hohenberg-Kohn theorem does not hold for excited states but, they show that equivalent and exact excited state theories can be formulated in terms of
  - The excitation quantum number and the noninteracting potential
  - The noninteracting wave function
  - The noninteracting one-electron reduced density matrix

How can this be justified?

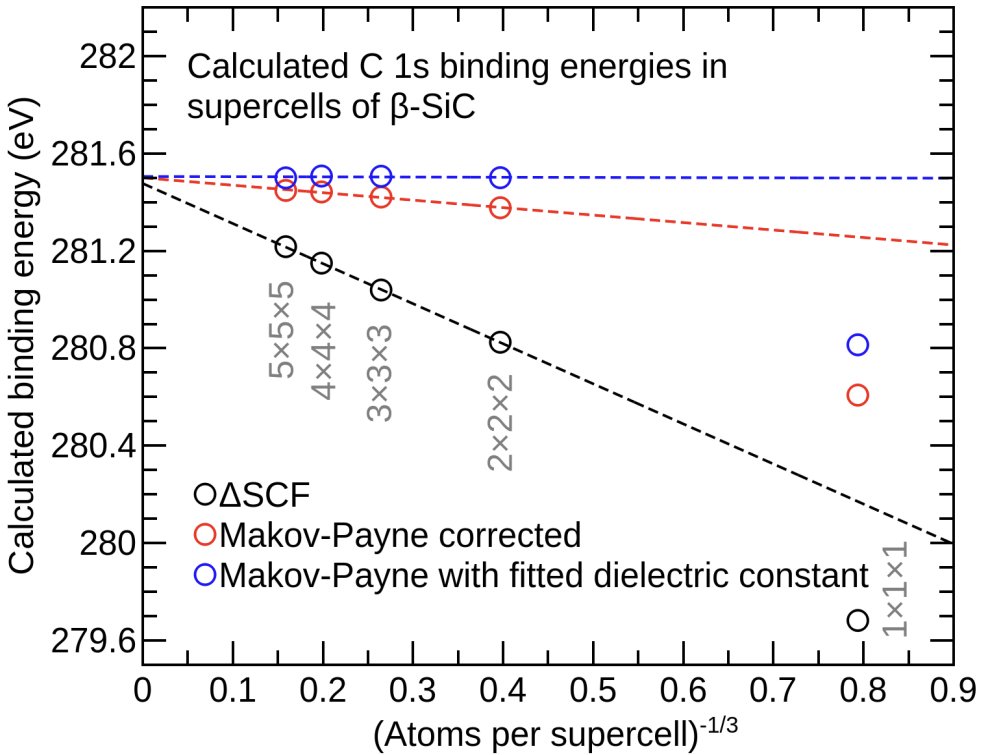
- W. Yang and P.W. Ayers, "Foundation for the ΔSCF Approach in Density Functional Theory", arXiv:2403.04604
- Importantly, the ground and excited-state exchange-correlation energy use the same universal functional
- Using approximate ground state functionals for excited states ($\sim$ non-Aufbau electronic configurations) might not be such a bad idea

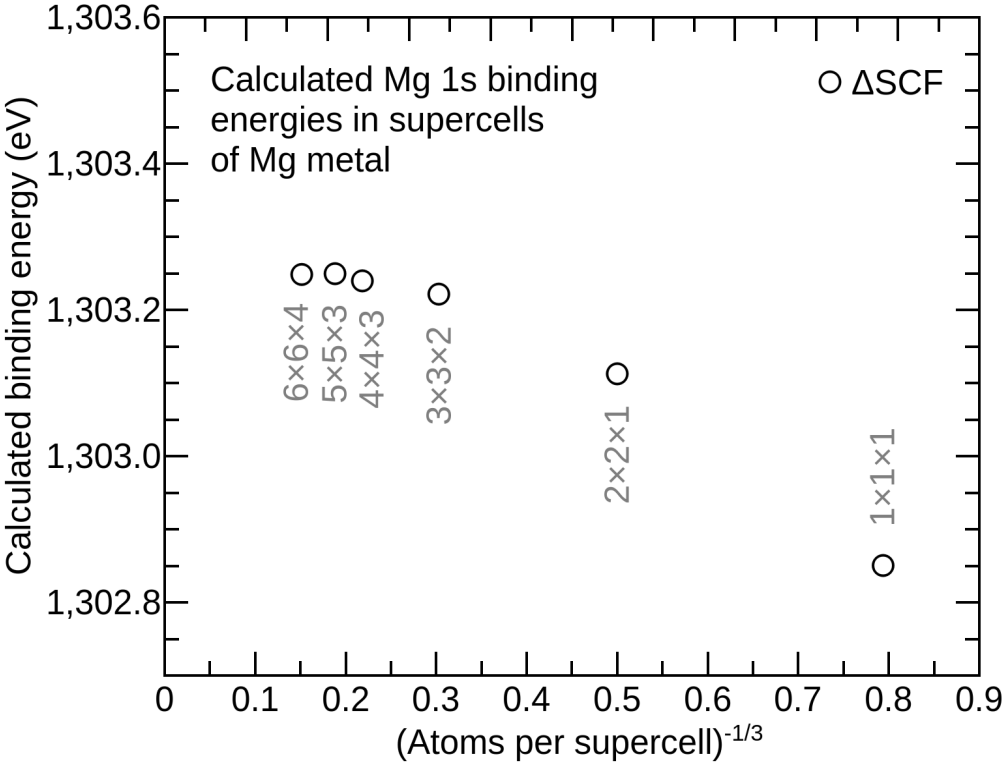
ΔSCF – previous results



MAE = 0.16 eV for dataset of 103 core levels

Kahk & Lischner, Phys. Rev. Materials 3, 100801(R) (2019)





Convergence of the ΔSCF result with respect to supercell size in insulators (left) and metals (right). MAE = 0.24 eV (15 datapoints for solids)

Kahk et al., J. Phys. Chem. Lett. 12, 9353 (2021)

Core level	Experimental B.E. (eV)	Calculated B.E. (eV)	Error (eV)
Sodium Na 2p	30.6	30.65	0.05
Magnesium Mg 2p	49.6	49.7	0.1
Lithium Li 1s	54.9	54.88	-0.02
beta-SiC Si 2p	99.2	99.25	0.05
BeO Be 1s	109.8	110.81	1.01
Beryllium Be 1s	111.82	112.1	0.28
hexBN B 1s	188.4	188.49	0.09
beta-SiC C 1s	281.38	281.5	0.12
Diamond C 1s	283.9	284.43	0.53
Graphite C 1s	284.4	284.44	0.04
hexBN N 1s	396.1	396.43	0.33
BeO O 1s	527.7	528.82	1.12
Sodium Na 1s	1071.4	1071.57	0.17
Magnesium Mg 1s	1303.2	1303.25	0.05
		Mean absolute error	0.28 eV

ΔSCF calculations in FHI-aims

- How to request non-Aufbau-principle occupation numbers?
- Old methods/keywords:
  - `force_occupation_projector`
  - `force_occupation_basis`
- New methods/keywords:
  - `deltascf_projector`
  - `deltascf_basis`

ΔSCF calculations in FHI-aims

- `deltascf_projector`

1) Provide initial orbitals (e.g. from a ground state calculation)
2) Specify the orbital, whose occupation number you want to change
3) Keep track of that orbital throughout the SCF cycle using the Maximum Overlap Method

ΔSCF calculations in FHI-aims

- `deltascf_basis`

1) Specify a particular basis function, e.g. an atomic “1s” basis function on a specific C atom
2) During each SCF iteration, the occupation constraint is applied to the Kohn-Sham orbital with the highest contribution from that basis function

ΔSCF calculations in FHI-aims

- `deltascf_basis`

1) Specify a particular basis function, e.g. an atomic “1s” basis function on a specific C atom
2) During each SCF iteration, the occupation constraint is applied to the Kohn-Sham orbital with the highest contribution from that basis function

In both cases – occupation constraint(s) is(are) passed on to ELSI

Table 4.1: A summary of the currently supported types of ΔSCF calculations in FHI-aims.

Geometry	Kohn-Sham eigensolver	`deltascf_projector`	`deltascf_basis`
Aperiodic	Serial	✓	✓
	Parallel	✓	✓
Periodic (Γ-point only)	Serial	✓	✗
	Parallel	✓	✗
Periodic (multiple k-points)	Serial	✓	✗
	Parallel	✗	✗

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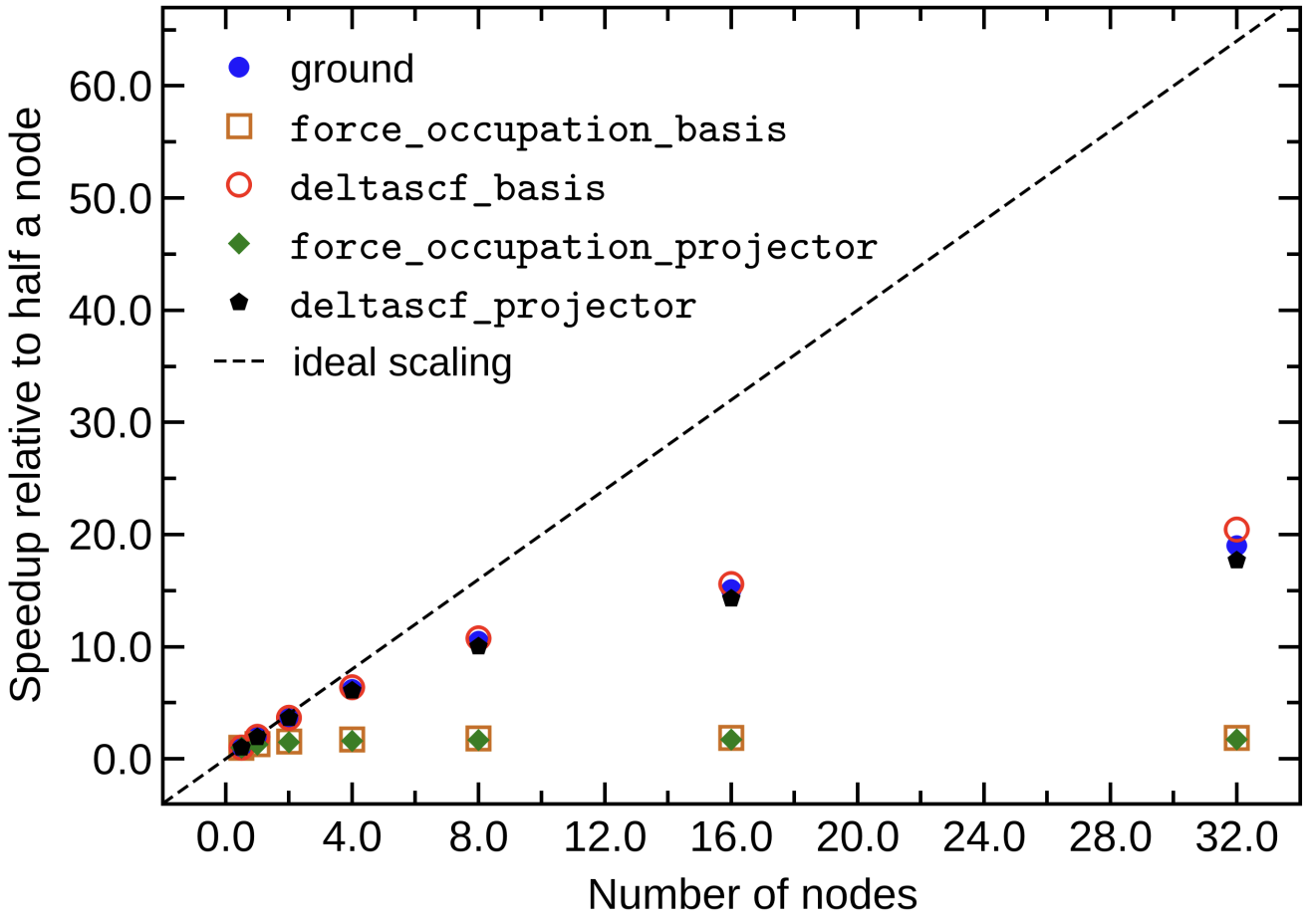
Periodic (multiple k-points)	Serial	✓	✓
	Parallel	✗	✓

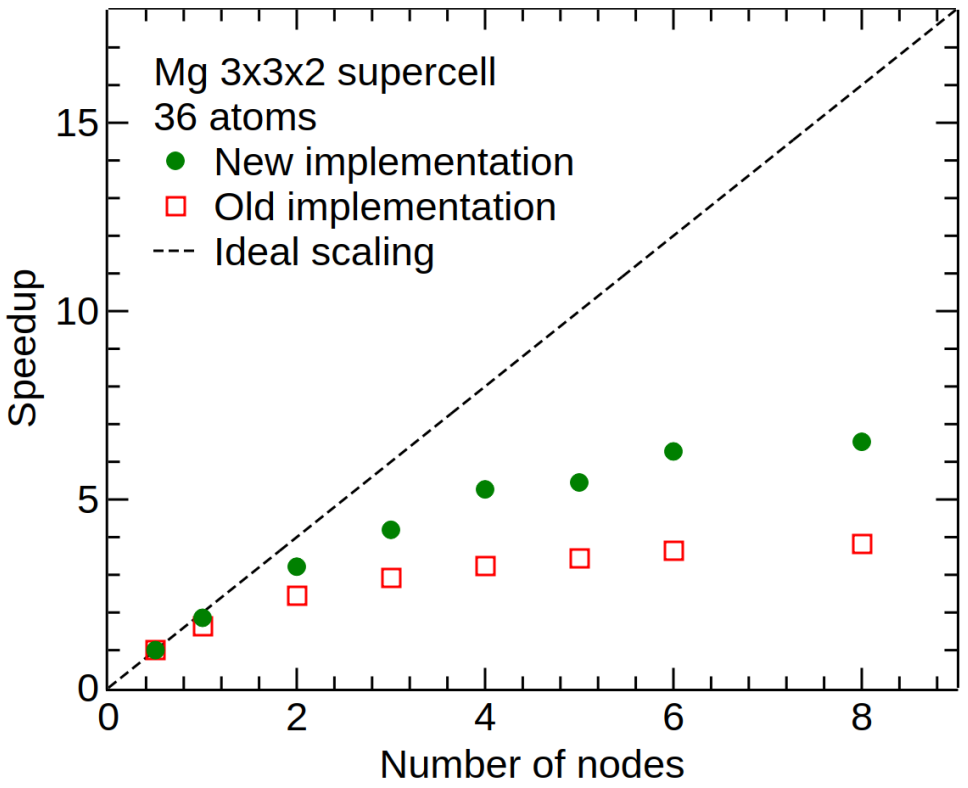
* only with collect_eigenvectors = .true.

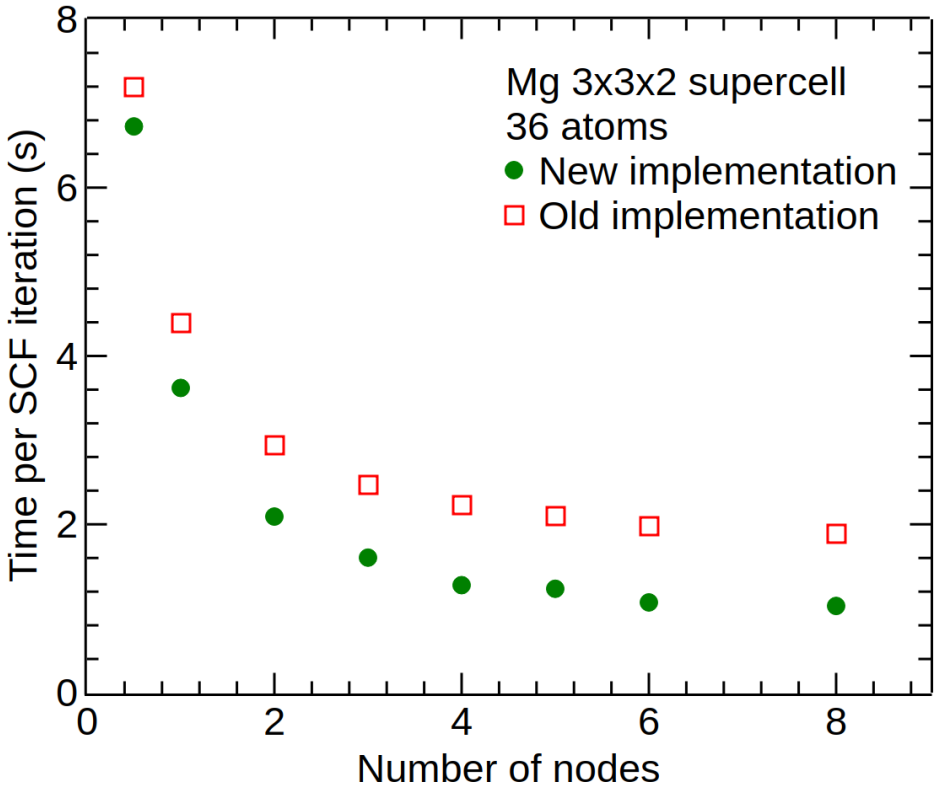
Scalability: aperiodic systems



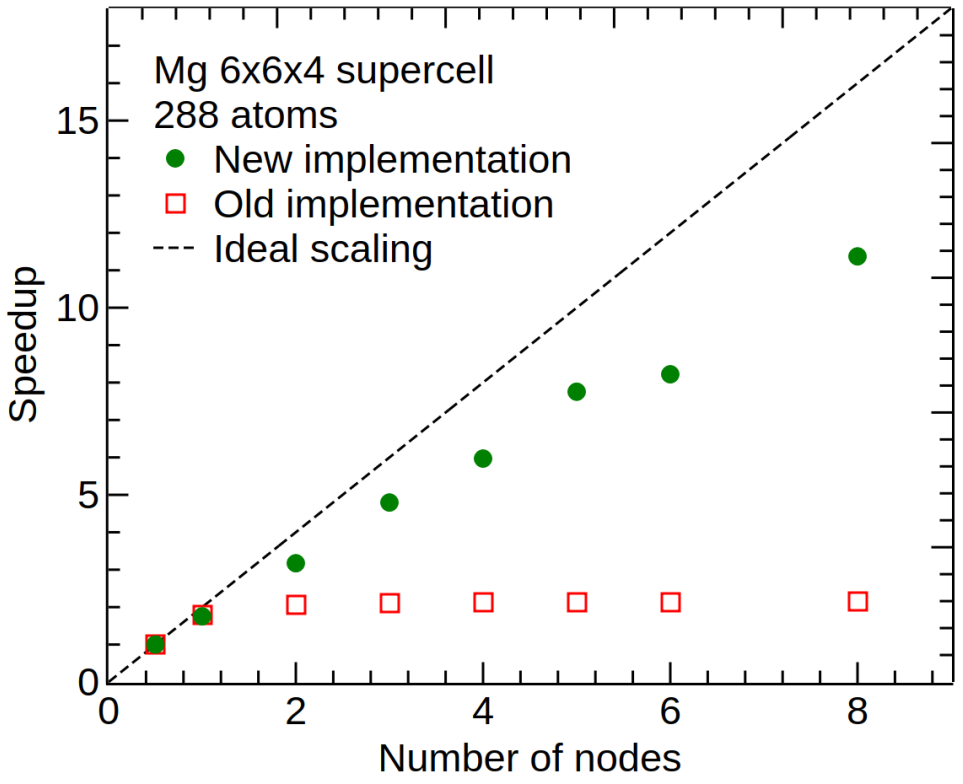
Peroxide-terminated diamond cluster containing 205 atoms

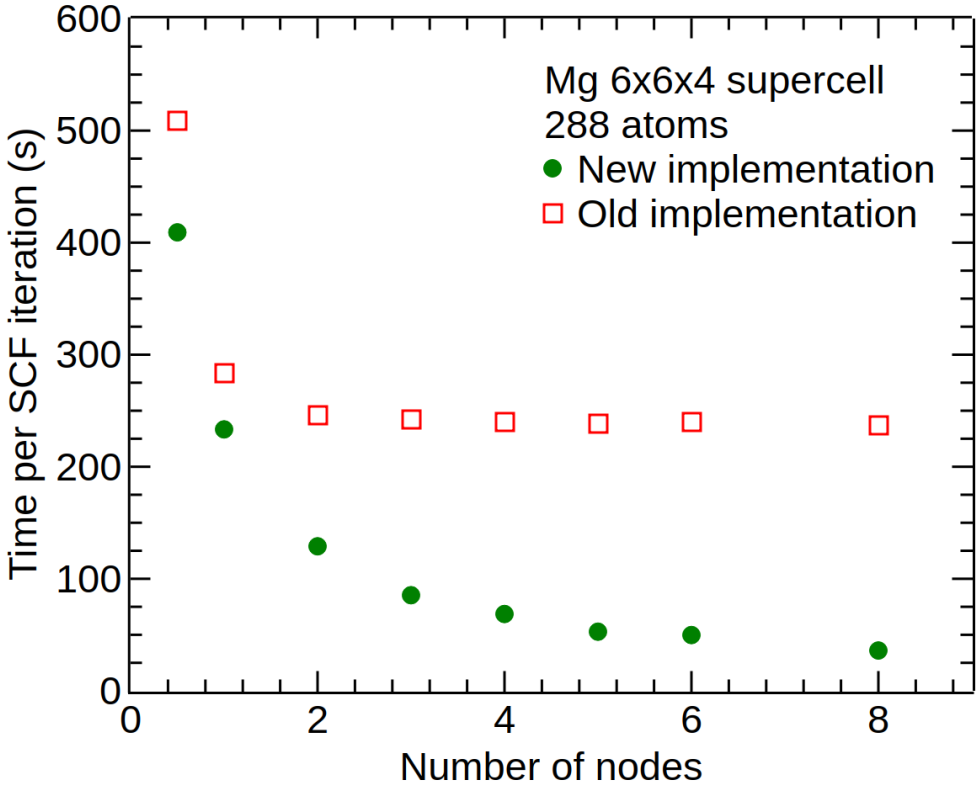
Scalability: periodic systems





Scalability: periodic systems





Example: 8x8x8 supercell of diamond

- 1024 atoms
- 2x2x2 k-point grid
- FHI-aims default “tight” basis
- C 1s hole (missing spin-up electron) on one atom
- Runs at 950 seconds per scf iteration on 1024 parallel tasks
- Still bottlenecked by “collect_eigenvectors”
- ΔSCF result: 284.24 (experimental value, referenced to the VBM is 284.0 eV)

ΔSCF calculations in FHI-aims

- Automatic generation of core-hole adapted basis sets
  - Basis sets in FHI-aims: "minimal basis" (= atomic orbitals) + additional basis functions.
  - Automatic generation of the minimal basis for atoms with a core hole* now implemented

* Spherically symmetric, non-spin-polarized

species **sub-tag:** `core_shell_occ` (control.in)

Usage: `core_shell_occ n l occupation`

Purpose: Specifies a non-standard occupation number for a core shell in the non-spinpolarized free atom that defines the minimal basis.

`n` is the (integer) radial quantum number.
`l` is a character, specifying the angular momentum (*s*, *p*, *d*, *f*, ...).
`occupation` is the number of electrons in the specified core shell of the given species.

This keyword can be used to introduce a non-spinpolarized, radially symmetric core hole into a species definition. The minimal basis functions for this species will then be generated in the presence of the core hole.

Example:

```
core_shell_occ 2 p 5.0
```

specifies the occupation of the 2*p* core shell with 5 electrons instead of the usual 6. Whenever `core_shell_occ` is used, the occupation of the valence levels must be adjusted accordingly using the keyword `valence` , to keep the free atom neutral.

Note that this keyword only affects the behaviour of the atomic solver. It does *not* modify the occupation of the core levels in the actual FHI-aims calculation - for that, one can use `deltascf_basis` or `deltascf_projector` .

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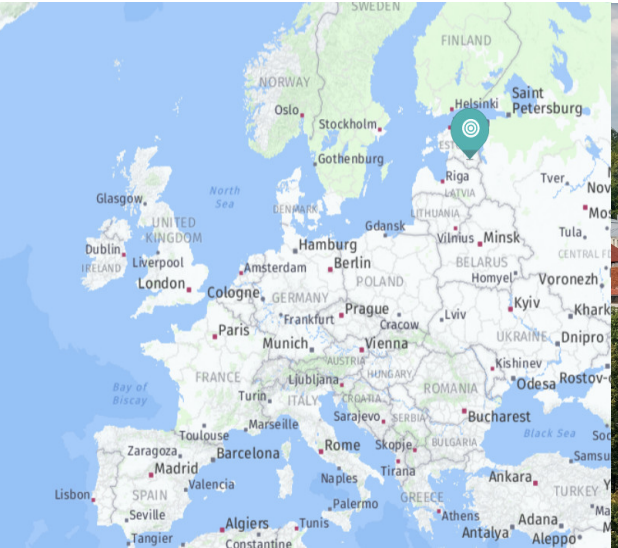

Summary

- ΔSCF calculations give accurate core electron binding energies in solids, surface species, and molecules
- FHI-aims permits true "all-electron" ΔSCF calculations with an explicit, spin-polarized core hole
  - Periodic and aperiodic systems
  - New implementation provides simpler workflow (only one calculation for the core-hole state), and scalability up to thousands of CPU cores and systems containing > 1000 atoms.