Modelling Core Level XPS using the Δ-Self-Consistent-Field Approach

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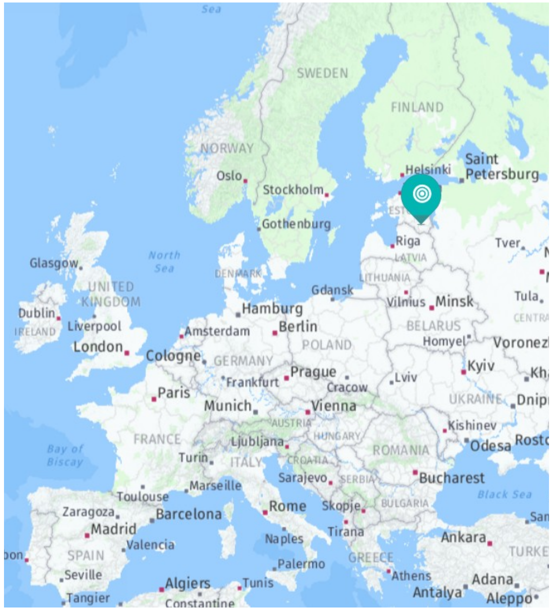
for Research & Innovation

FHI-aims
The ab initio materials simulation package

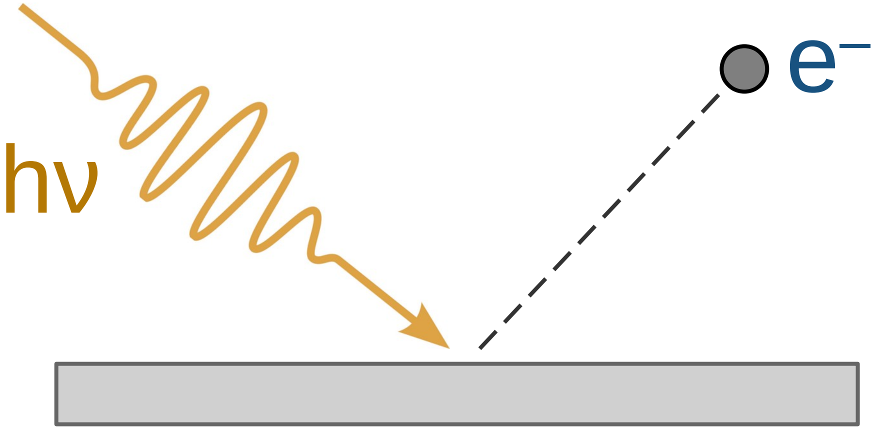
GPAW!

TARTU ÜLIKOOL
UNIVERSITAS TARTUENSIS
1632



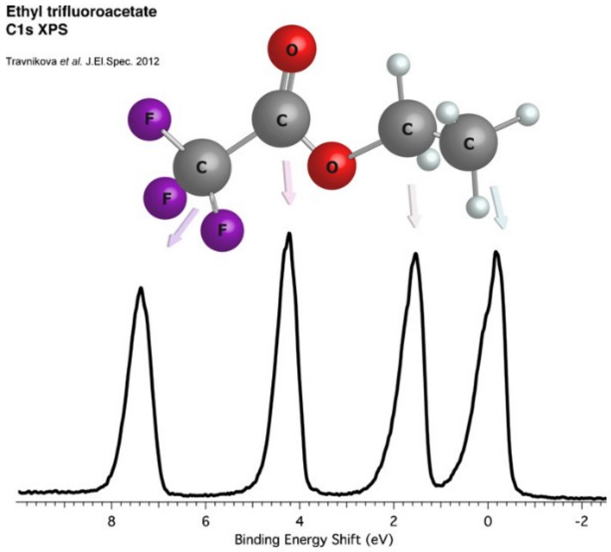
Core Level XPS

- X-ray Photoelectron Spectroscopy
- Photon in => electron out



$$\underset{\text{Photon energy}}{h\nu} = \underbrace{E_B + \varphi}_{\text{Energy required to remove the electron from the sample}} + \underset{\text{Kinetic energy of the photoelectron}}{E_k}$$

XPS: the ideal scenario

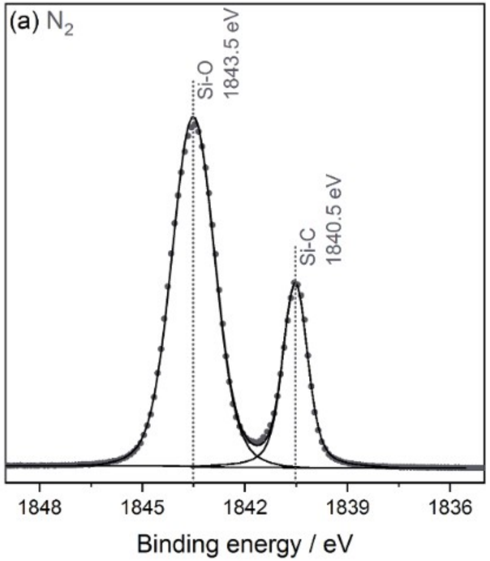


Ethyl trifluoroacetate
C1s XPS

Travnikova *et al.* J.El.Spec. 2012

The “ESCA molecule” – four carbon environments, four C 1s peaks

Travnikova et al., *J. Electron Spectrosc. Relat. Phenomena* **185**, 191 (2021)



Si 1s core level spectra of a SiC/SiO_2 heterostructure

Berens et al., *J. Phys.: Energy* **2**, 035001 (2020)

XPS: binding energies from the literature

- HCOO on Cu(111), C 1s – 287.3 eV, 288.2 eV, 289.75 eV
- HCOO on Cu(poly), C 1s – 287.3 eV, 288.1 eV
- CO on Cu(111), O 1s – 531.5 eV, 533.4 eV
- In contrast, shifts as small as 0.2-0.3 eV are sometimes used for chemical state identification

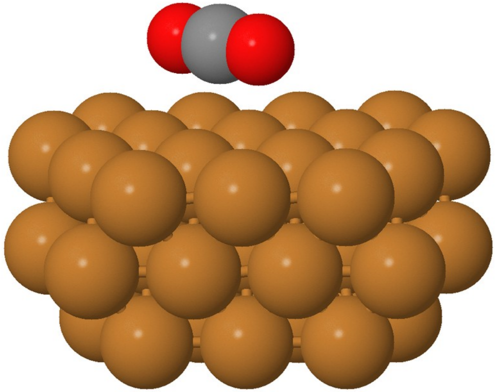
Calculating core electron binding energies

- Given a structural model, can we predict
  - Relative core electron binding energies (shifts)?
  - Absolute binding energies from first principles?
- DFT eigenvalues are a poor approximation
  - No final state screening!

Calculating core electron binding energies

$O{=}C{=}O$

Free CO_2



Physisorbed CO_2

C 1s eigenvalue	278.35 eV	278.11 eV
C 1s calculated B.E. (ΔSCF)	297.69 eV	294.64 eV

NB! Experimental B.E. for adsorbed CO_2 would be reported relative to E_F

Calculating core electron binding energies

- DFT eigenvalues are a poor approximation
  - May give ok results when very similar systems are compared, but fail badly in other situations
  - Hybrid functionals, Koopmans corrected functionals, etc. do not address the main issue

Calculating core electron binding energies

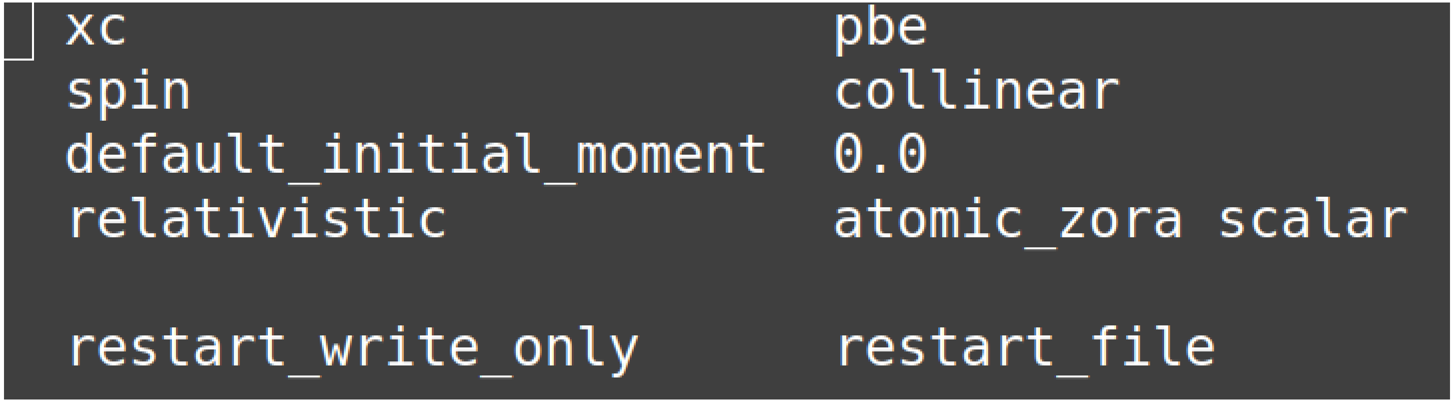
- Two “real” methods to tackle the problem
  - Δ-methods (explicitly calculate E_N and $E_{N-1,\text{core hole}}$)
  - Response theory methods (GW, EOM-IP-CCSD, ...)
- Δ-methods: how to calculate final state total energy? Model an excited state of a charged radical?? ~~CIS, TDDFT, EOM-CCSD(T)~~

Calculating core electron binding energies

- Δ-Self-Consistent-Field (ΔSCF) approach:
  - E_N: ground state total energy from DFT
  - E_{N-1},core hole:
    - Enforce a non-Aufbau-principle occupancy of the Kohn-Sham eigenstates
    - Converge the self-consistent field in the presence of the core hole
    - All other electrons are allowed to fully relax in the presence of the core hole

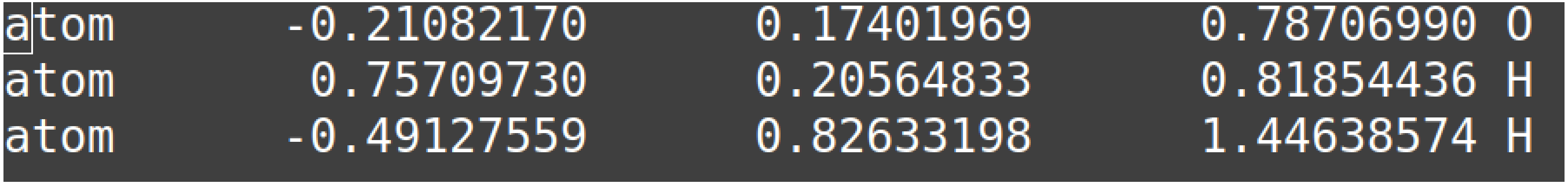
A simple ΔSCF calculation in FHI-aims

- O 1s in H_2O – ground state calculation



```
xc                      pbe
spin                    collinear
default_initial_moment  0.0
relativistic            atomic_zora scalar

restart_write_only      restart_file
```

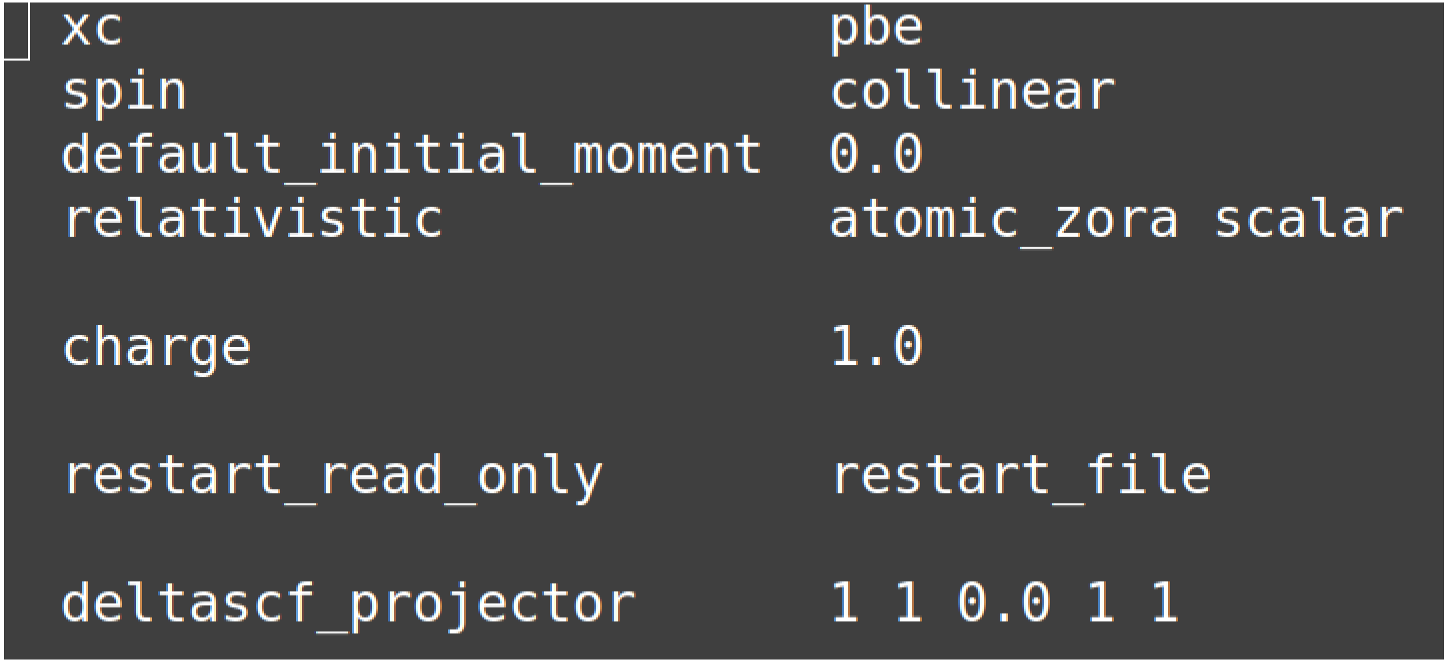
default “tight” species definitions



```
atom      -0.21082170      0.17401969      0.78706990 O
atom       0.75709730      0.20564833      0.81854436 H
atom      -0.49127559      0.82633198      1.44638574 H
```

A simple ΔSCF calculation in FHI-aims

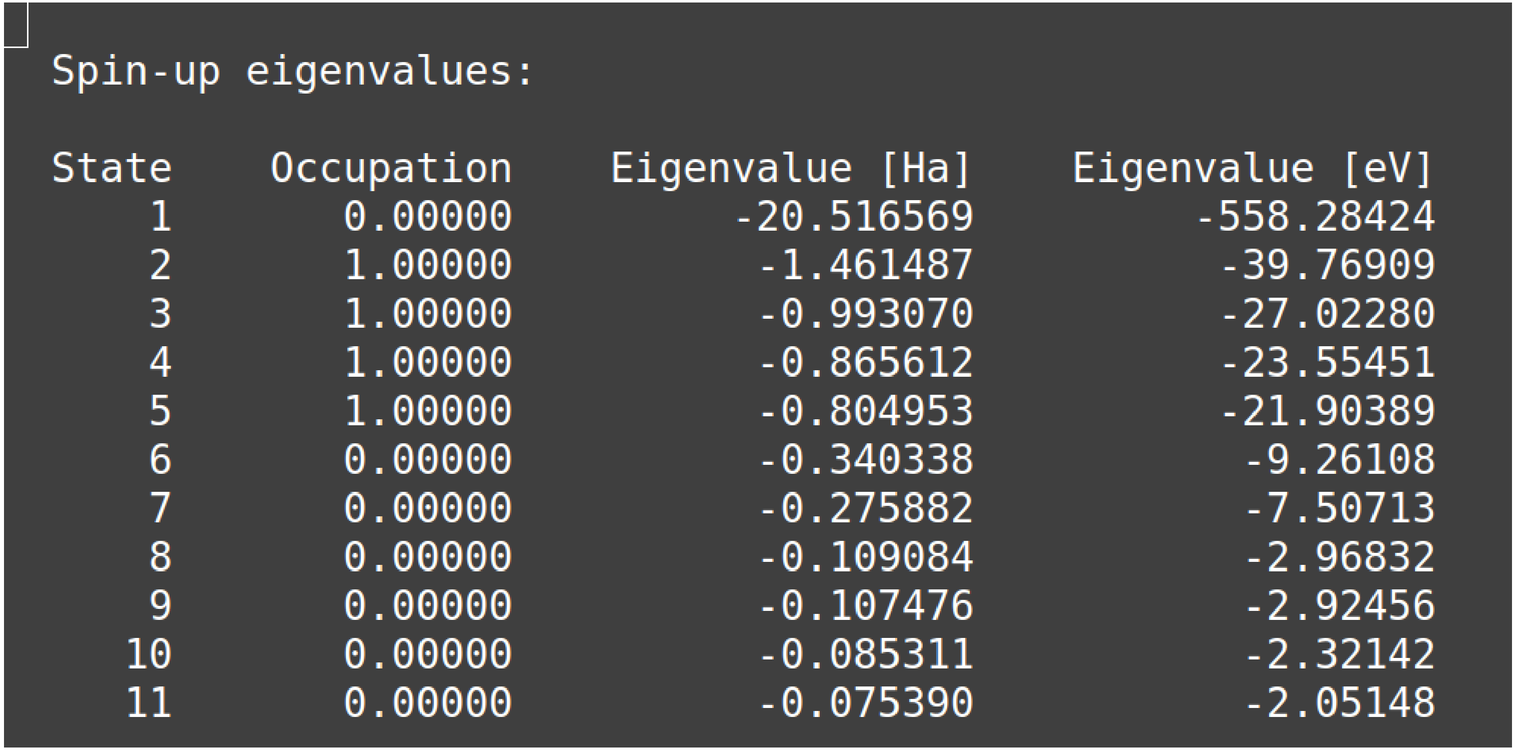
- O 1s in H_2O – core hole calculation



```
xc                      pbe
spin                    collinear
default_initial_moment  0.0
relativistic            atomic_zora scalar

charge                  1.0

restart_read_only       restart_file

deltascf_projector      1 1 0.0 1 1
```

A simple ΔSCF calculation in FHI-aims

- O 1s in H_2O – core hole calculation



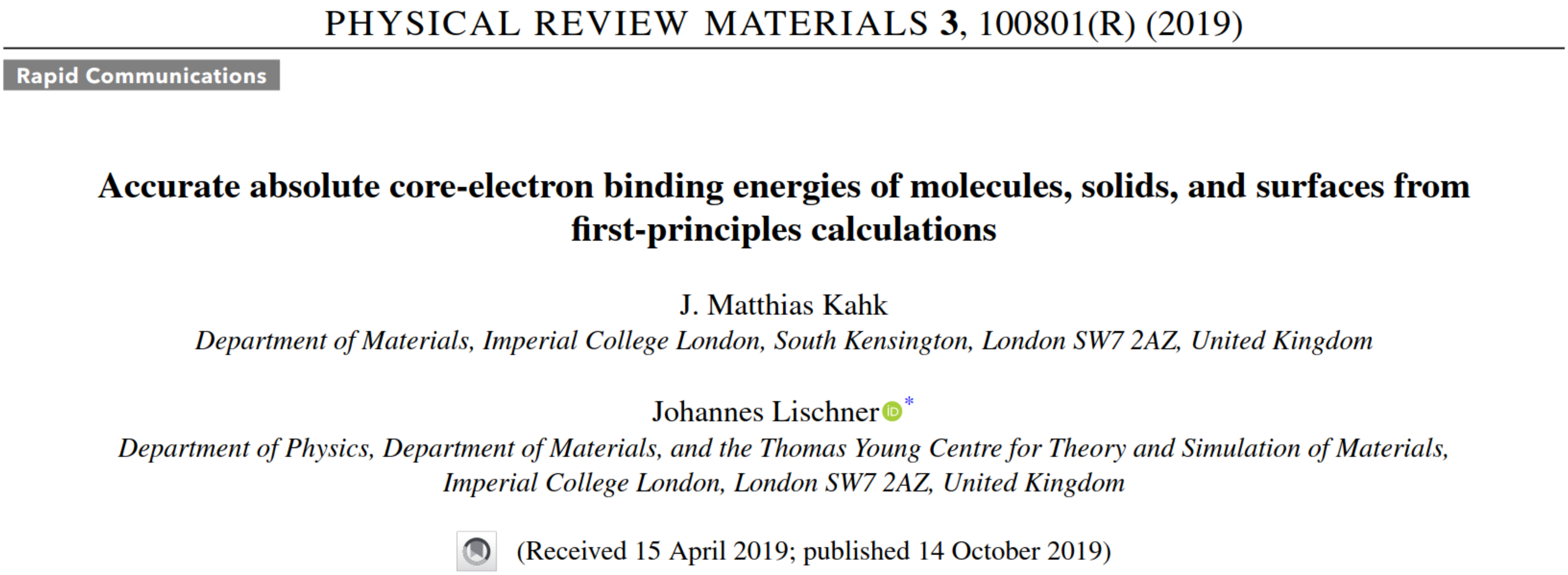
```
Spin-up eigenvalues:

State     Occupation     Eigenvalue [Ha]     Eigenvalue [eV]
    1        0.00000          -20.516569          -558.28424
    2        1.00000           -1.461487           -39.76909
    3        1.00000           -0.993070           -27.02280
    4        1.00000           -0.865612           -23.55451
    5        1.00000           -0.804953           -21.90389
    6        0.00000           -0.340338            -9.26108
    7        0.00000           -0.275882            -7.50713
    8        0.00000           -0.109084            -2.96832
    9        0.00000           -0.107476            -2.92456
   10        0.00000           -0.085311            -2.32142
   11        0.00000           -0.075390            -2.05148
```

A simple ΔSCF calculation in FHI-aims

- Ground state Etot: -2080.96 eV
- Final state Etot: -1540.42 eV
- ΔSCF: 540.54 eV
- Expt. B.E. from gas phase XPS: 539.9 eV

- Simple ΔSCF calculation with default settings
  - Relative binding energies (~ shifts) ✓
  - Absolute binding energies ✗
- For accurate absolute core electron binding energies need to consider
  - Basis sets
  - Relativistic effects
  - Functional

Calculating absolute core electron BE-s



PHYSICAL REVIEW MATERIALS **3**, 100801(R) (2019)

Rapid Communications

Accurate absolute core-electron binding energies of molecules, solids, and surfaces from first-principles calculations

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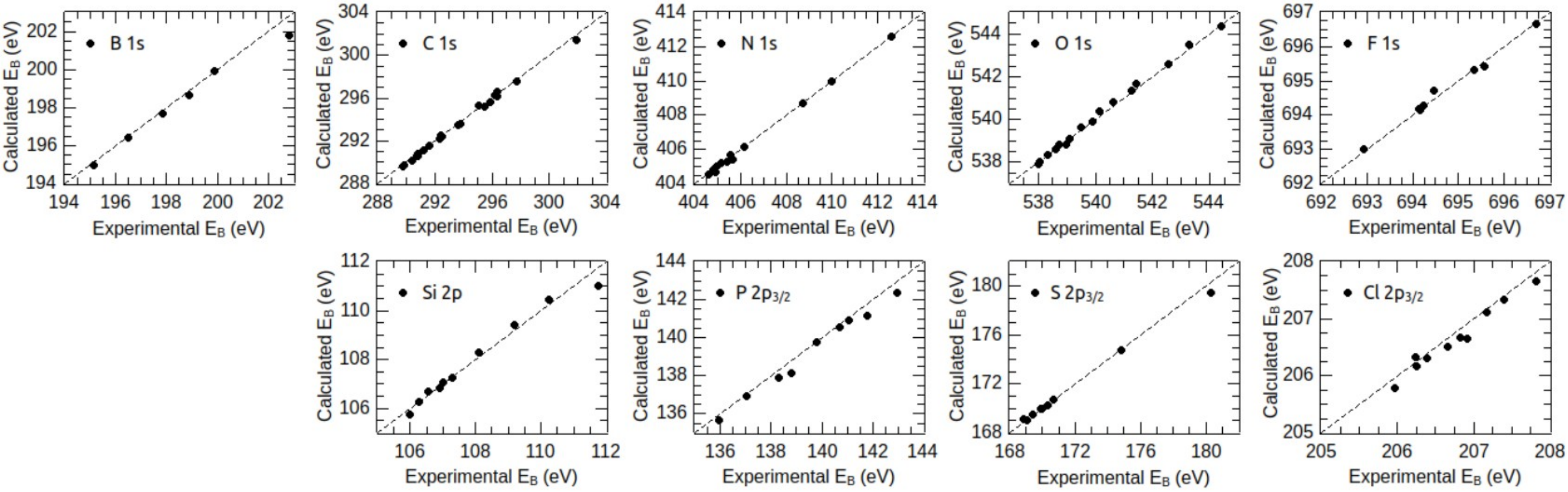
(Received 15 April 2019; published 14 October 2019)

Calculating absolute core electron BE-s

- DFT with the SCAN functional
- Scaled ZORA treatment of relativistic effects
- Basis sets that permit the relaxation of the remaining core and valence electrons in the presence of the core hole
- $2p_{3/2}$ levels – get “2p” binding energy from a scalar relativistic calculation, subtract 1/3 spin-orbit splitting for $2p_{3/2}$



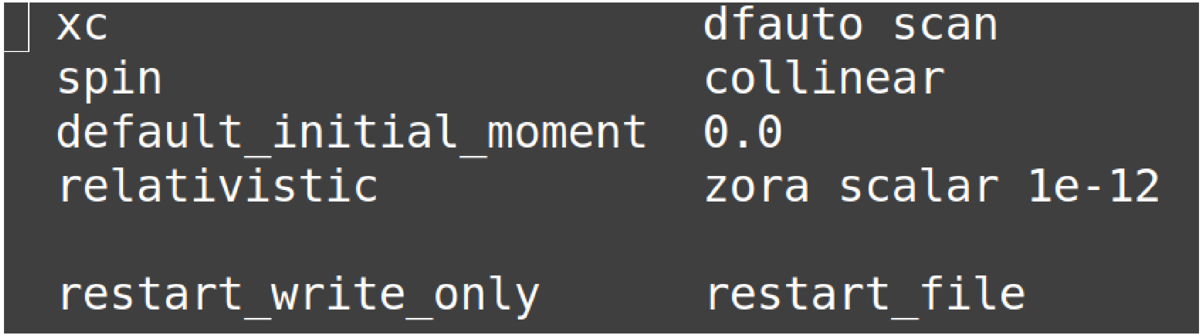
MAE = 0.16 eV for 103 binding energies from gas phase XPS

Kahk et al., Phys. Rev. Materials 3, 100801(R) (2019)

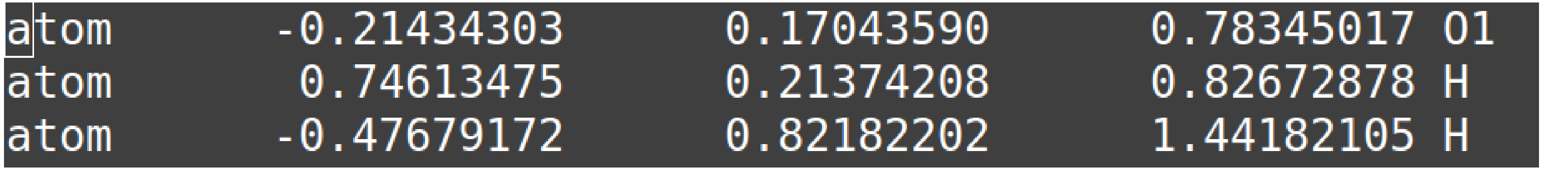
Works for 1s levels of Li...Mg, $2p_{3/2}$ levels of Na...Ar

ΔSCF in FHI-aims: example 2

- O 1s in H_2O, with the recipe from Phys. Rev. Materials 3, 100801(R) (2019)



```
  xc                        dfauto scan
  spin                      collinear
  default_initial_moment    0.0
  relativistic              zora scalar 1e-12

  restart_write_only        restart_file
```



```
atom      -0.21434303      0.17043590      0.78345017 O1
atom       0.74613475      0.21374208      0.82672878 H
atom      -0.47679172      0.82182202      1.44182105 H
```

ΔSCF in FHI-aims: example 2

- O 1s in H_2O, with the recipe from Phys. Rev. Materials 3, 100801(R) (2019)

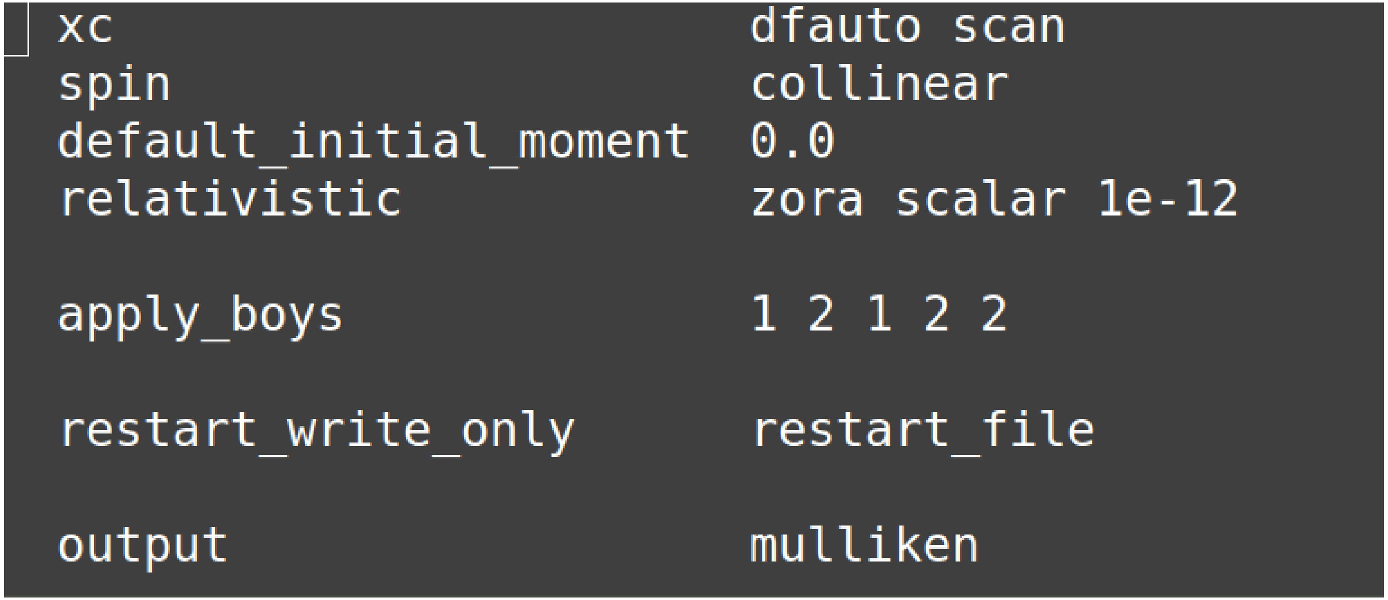
```
# additional basis functions for atom with a core hole
     hydro 1 s 12.0
     hydro 1 s 10.0
     hydro 1 s 6.0
     hydro 2 s 10.0
     hydro 2 p 8.0
     hydro 2 p 6.0
     hydro 3 d 8.0
```

ΔSCF in FHI-aims: example 2

- Ground state Etot: -2081.55 eV
- Final state Etot: -1541.67 eV
- ΔSCF: 539.88 eV
- Expt. B.E. from gas phase XPS: 539.9 eV

Example 3: O 1s in CO_2

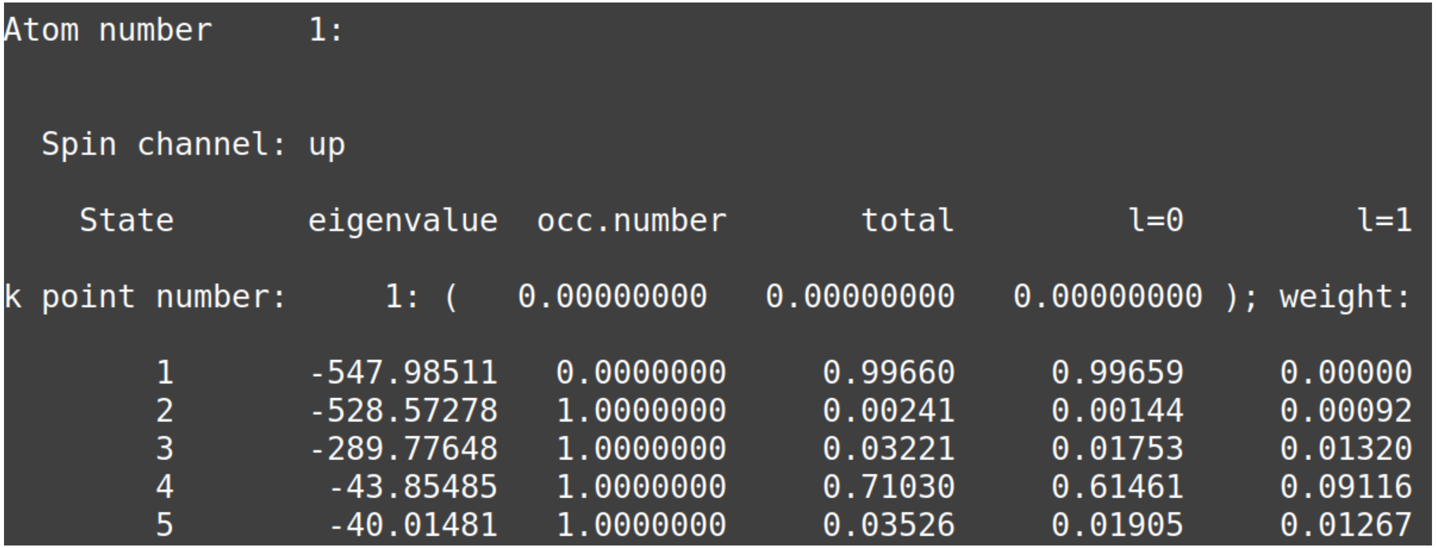
- In symmetrical molecules it is important to localize the core hole!



```
xc                        dfauto scan
spin                      collinear
default_initial_moment    0.0
relativistic              zora scalar 1e-12

apply_boys                1 2 1 2 2

restart_write_only        restart_file

output                    mulliken
```

Example 3: O 1s in CO_2

- Check Mulliken.out to verify localization of the core hole on the correct atom



```
Atom number     1:


  Spin channel: up

    State       eigenvalue  occ.number      total         l=0         l=1

k point number:     1: (   0.00000000   0.00000000   0.00000000 ); weight:

        1       -547.98511   0.0000000     0.99660     0.99659     0.00000
        2       -528.57278   1.0000000     0.00241     0.00144     0.00092
        3       -289.77648   1.0000000     0.03221     0.01753     0.01320
        4        -43.85485   1.0000000     0.71030     0.61461     0.09116
        5        -40.01481   1.0000000     0.03526     0.01905     0.01267
```

Example 3: O 1s in CO_2

- ΔSCF: 541.35 eV
- Expt. B.E. from gas phase XPS: 541.3 eV

Some practical aspects

- Wavefunction based restart files are (currently) required
  - Cannot use ELSI-restart
  - May need to specify “density_update_method orbital”
  - Only serial eigensolver for periodic systems

Heavier elements

DOI: 10.1039/D1FD00103E (Paper) *Faraday Discuss.*, 2022, **236**, 364-373

Predicting core electron binding energies in elements of the first transition series using the Δ-self-consistent-field method†

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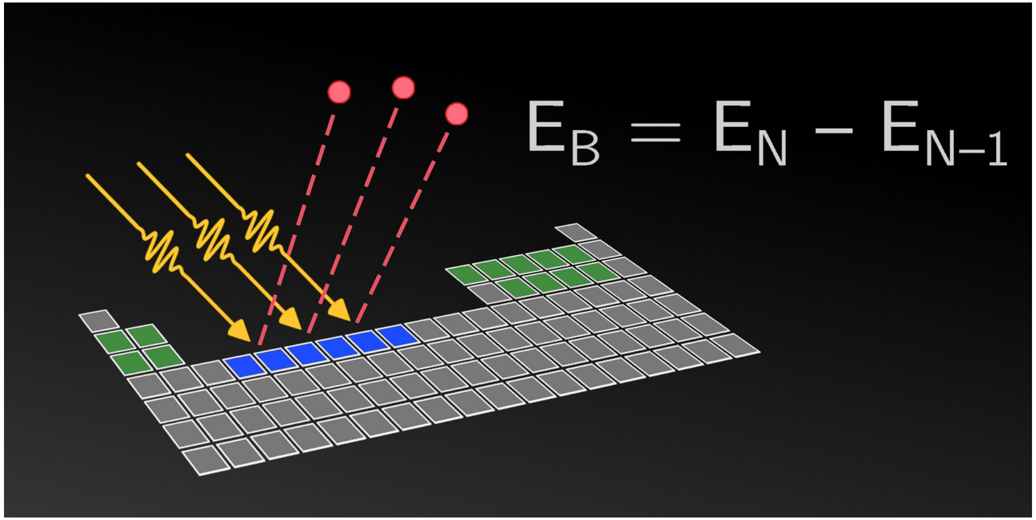
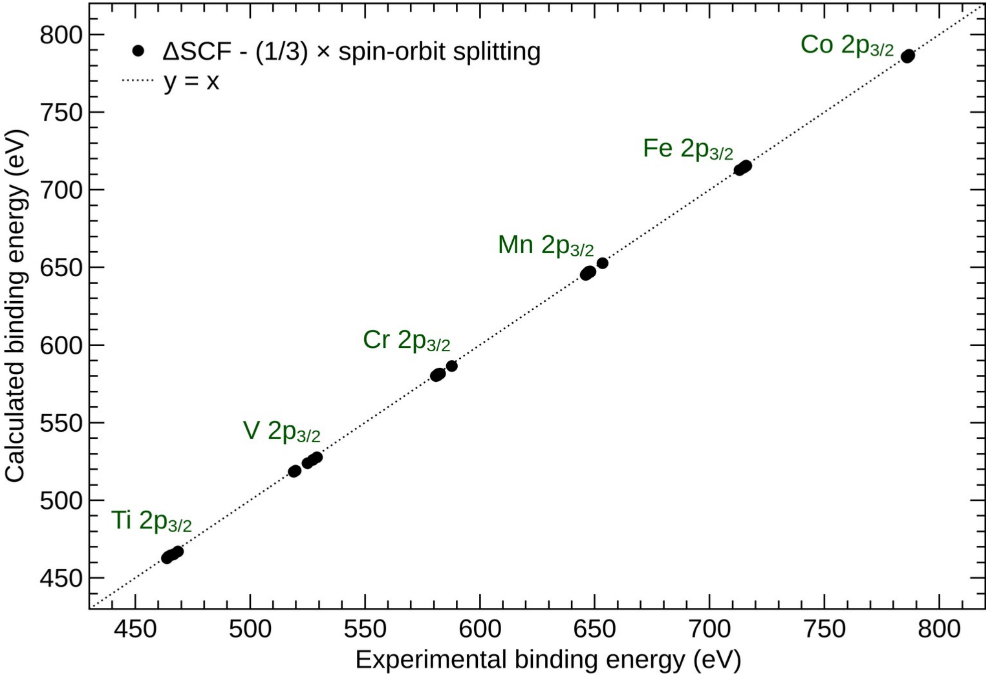
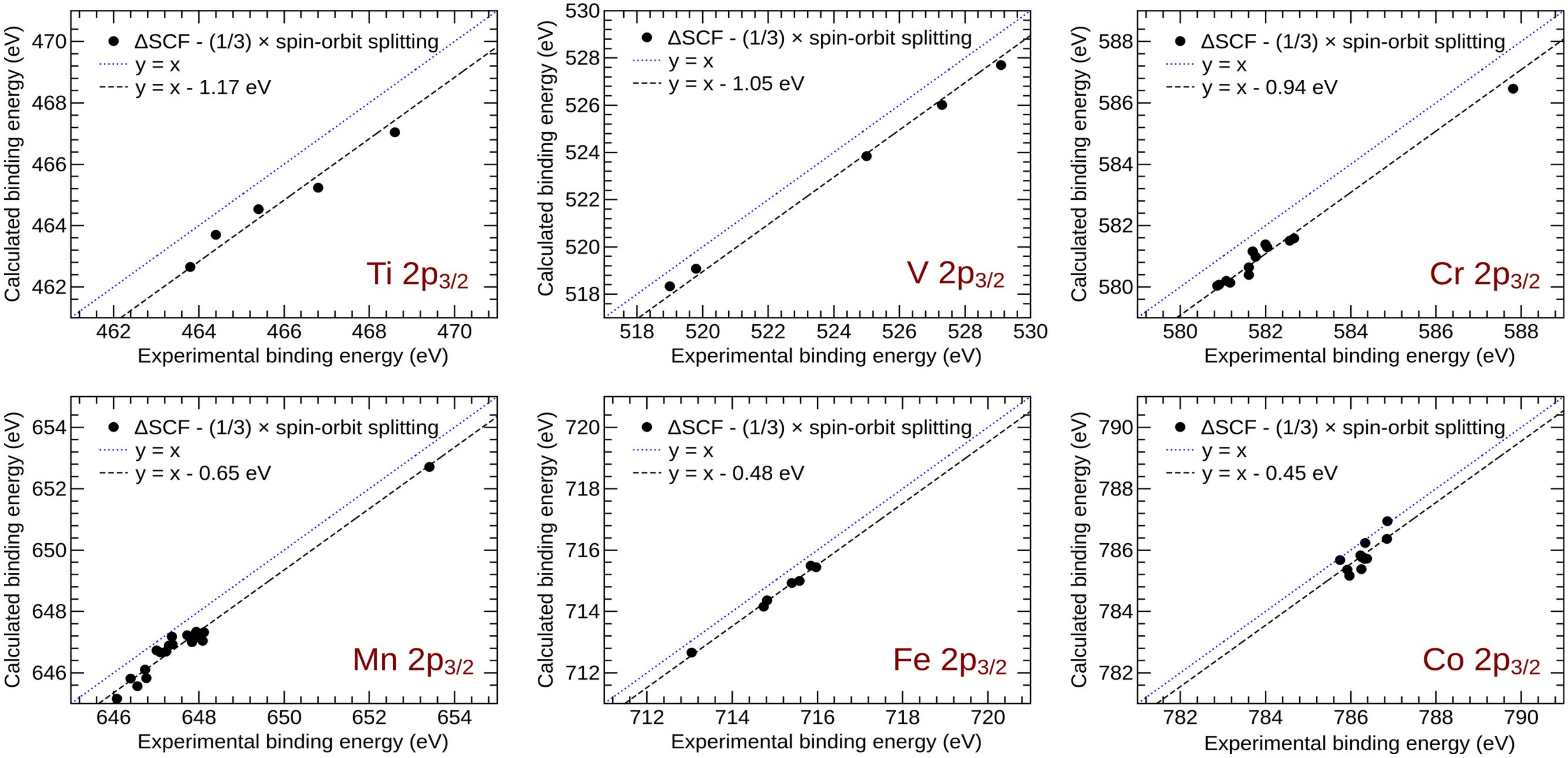
[b] *Department of Materials, and the Thomas Young Centre for Theory and Simulation of Materials, Imperial College London, London SW7 2AZ, UK*

Heavier elements

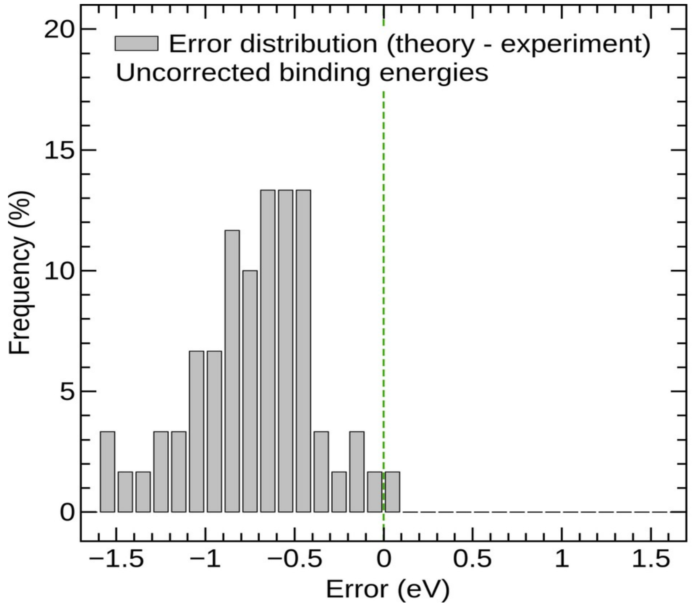


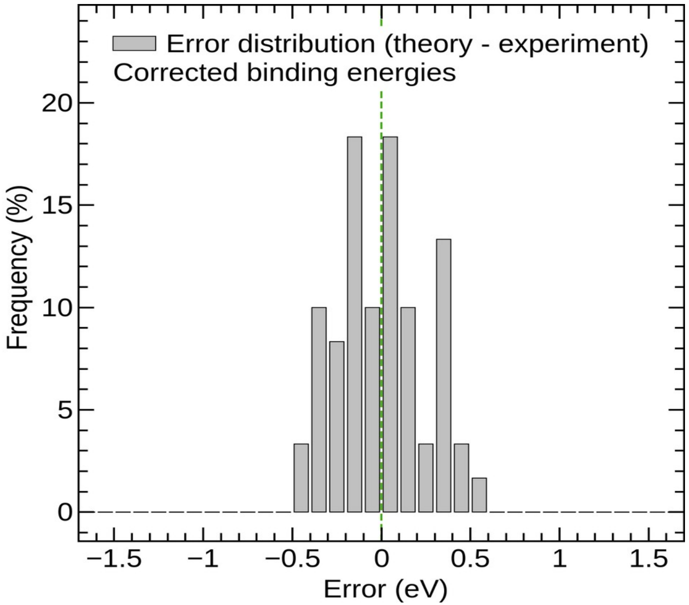


Heavier elements



	Ti $2p_{3/2}$	V $2p_{3/2}$	Cr $2p_{3/2}$	Mn $2p_{3/2}$	Fe $2p_{3/2}$	Co $2p_{3/2}$	Entire Dataset
Number of molecules	5	5	13	19	7	11	60
Mean Error (uncorrected)	-1.17	-1.05	-0.92	-0.65	-0.48	-0.45	-0.73
Mean Absolute Error (uncorrected)	1.17	1.05	0.92	0.65	0.48	0.47	0.73
Mean Absolute Error (corrected)	0.32	0.28	0.19	0.20	0.07	0.24	0.20





Calculating core electron binding energies

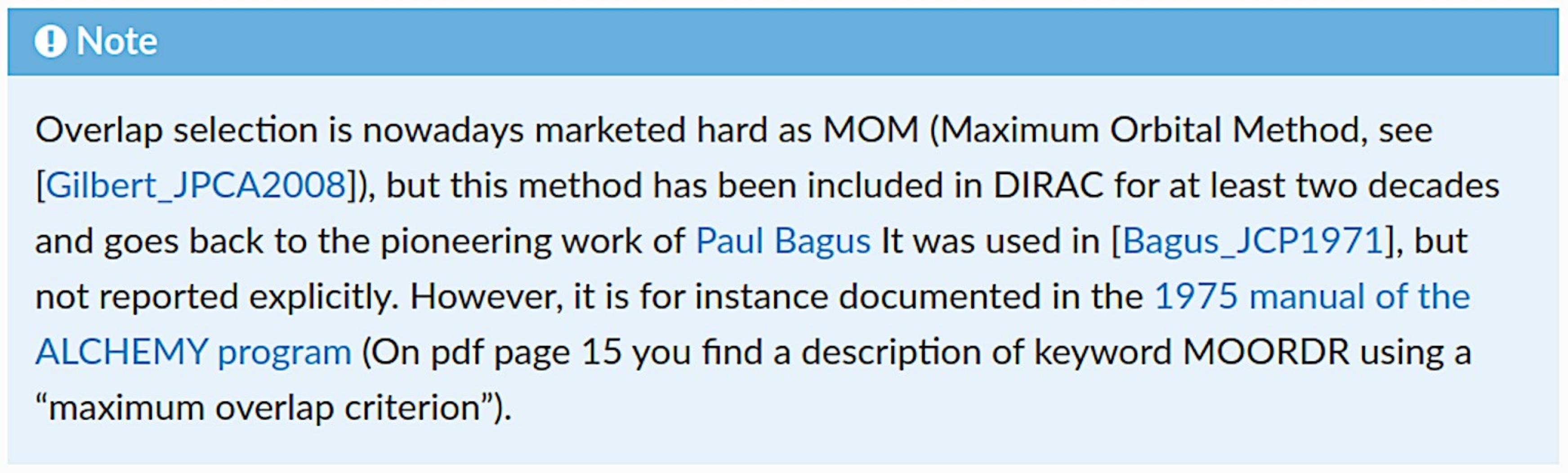
- Δ-methods vs response theory in the coupled cluster approximation
  - Martinez et al., PCCP 24, 20728 (2022)
  - ΔCCSD (much) more accurate than EOM-IP-CCSD for core excitations
  - Expressing the relaxation of the remaining electrons in terms of the ground state orbitals inefficient (?)

Excited states from ground state DFT?

- How to prevent “variational collapse” of the SCF to the ground state?
  - Gilbert et al., “Self-Consistent Field Calculations of Excited States Using the Maximum Overlap Method (MOM)”, J. Phys. Chem. A 112, 13164 (2008)
  - Also implemented in FHI-aims (deltascf_projector, force_occupation_projector (legacy))

Excited states from ground state DFT?

- A note in the manual of DIRAC23



Note

Overlap selection is nowadays marketed hard as MOM (Maximum Orbital Method, see [Gilbert_JPCA2008]), but this method has been included in DIRAC for at least two decades and goes back to the pioneering work of Paul Bagus It was used in [Bagus_JCP1971], but not reported explicitly. However, it is for instance documented in the 1975 manual of the ALCHEMY program (On pdf page 15 you find a description of keyword MOORDR using a “maximum overlap criterion”).

Preventing variational collapse

- The maximum overlap method sometimes fails
- Newer, more robust algorithms for preventing variational collapse
  - Initial maximum overlap method (IMOM)
  - Square gradient minimization (SGM)
  - State targetted energy projection (STEP)
  - …
- MOM generally sufficient for creating a core hole

Excited states from ground state DFT?

- The idea is not new, e.g.
  - Perdew & Levy, “Extrema of the density functional for the energy: Excited states from the ground-state theory”, PRB 31, 6264 (1985)
- Modern considerations: topology of the electron energy landscape in orbital parametrization space
  - Global minimum => electronic ground state
  - Local minima or saddle points => excited states

ΔSCF method – general considerations

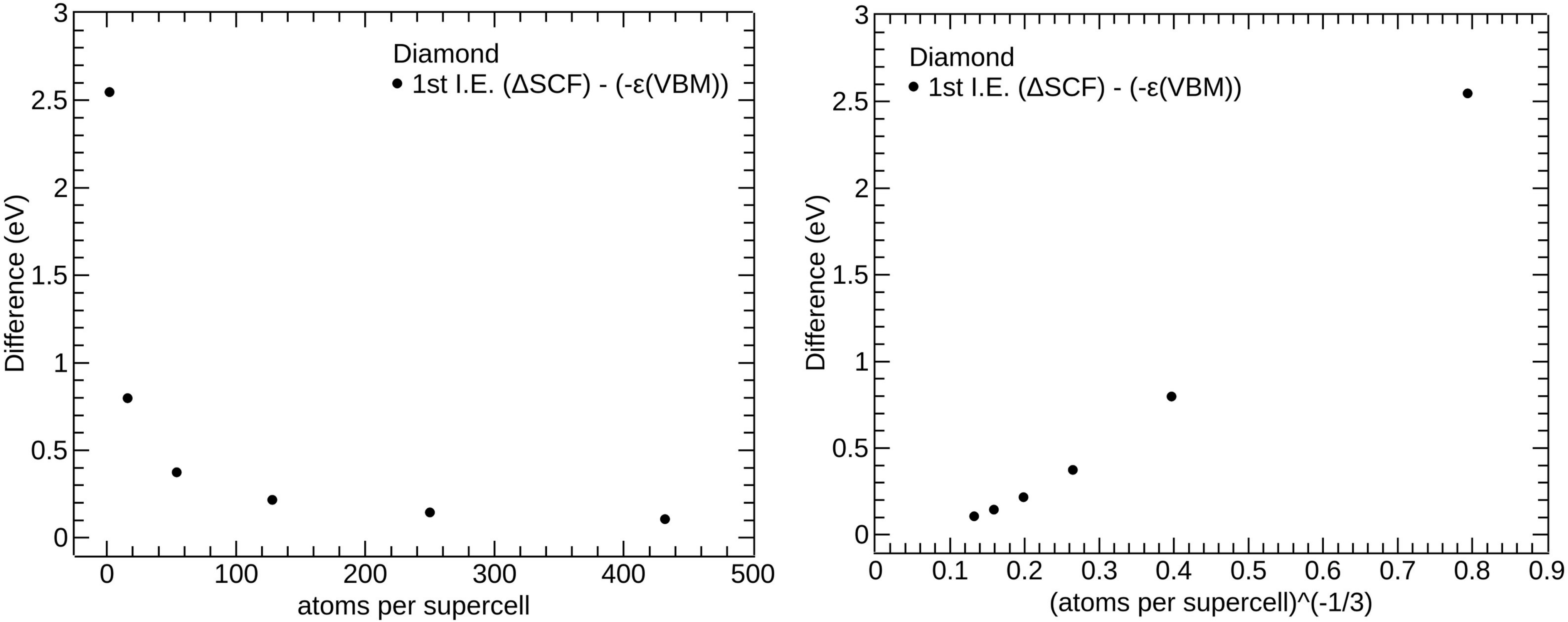
- “OO-DFT” – Hait, Head-Gordon (Q-Chem)
- Orbital-optimized Density Functional Theory for Excited States
  - Core binding energies
  - Neutral excitations (XAS)
  - Core excitations in radicals
  - Valence excitations, incl. doubly excited states
  - …
- PhD thesis of Diptarka Hait

ΔSCF method – effects of system size

- The ΔSCF approach fails for calculating the first ionization energies of large systems
- E.g. in solids, at the limit of infinite supercell size, $E_{N,\,\mathrm{ground}} - E_{N-1,\mathrm{ground}}$ converges to the VBM eigenvalue

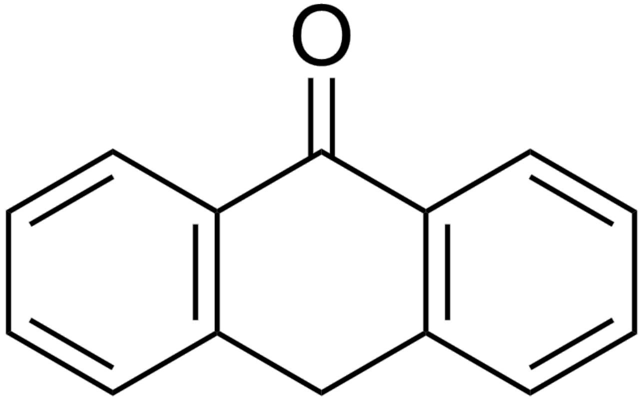
$$E_{N,\,\mathrm{ground}} - E_{N-1,\mathrm{ground}} = \epsilon_{\mathrm{VBM}}$$

VBM: ΔSCF vs eigenvalue

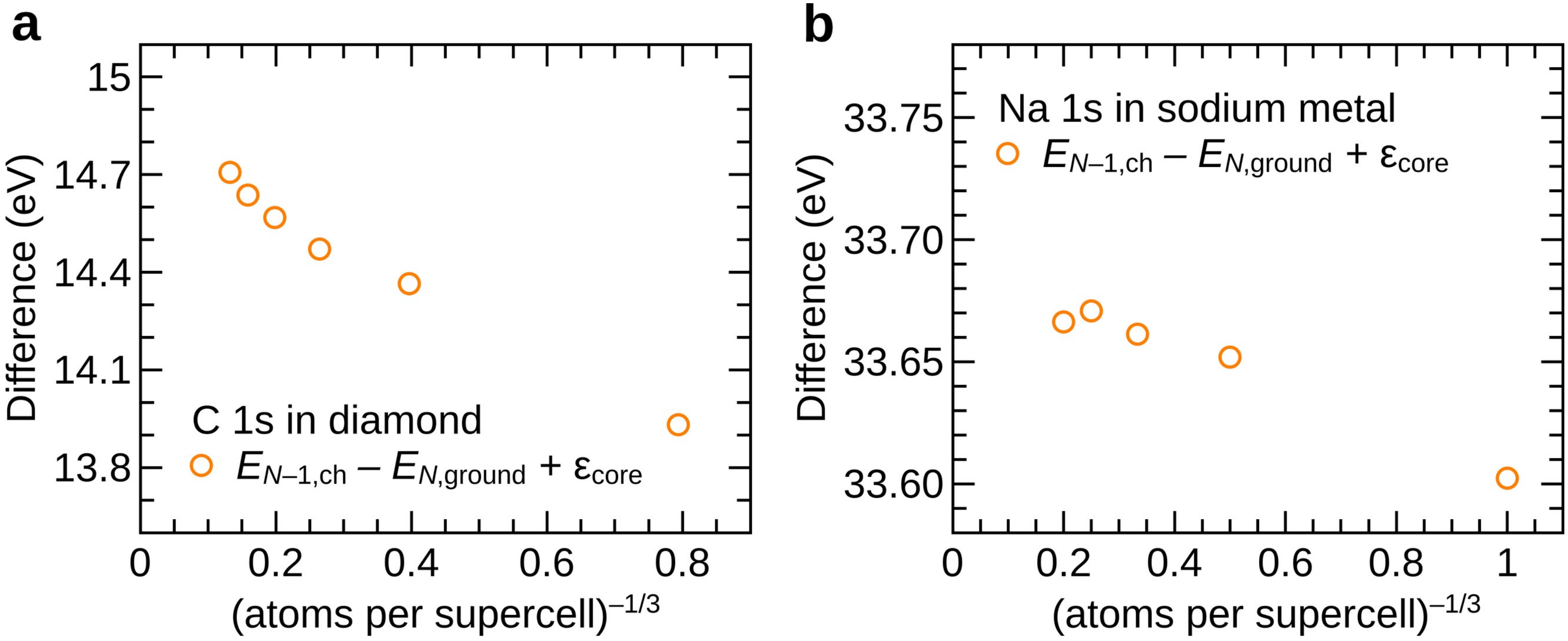


ΔSCF method – effects of system size

- Empirical evidence: core electron BE-s from ΔSCF method become increasingly inaccurate for larger molecules
- Errors > 1.0 eV reported for C 1s and O 1s binding energies in anthrone

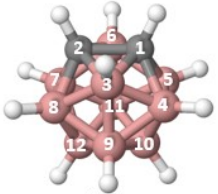


- However, core electron BE-s from ΔSCF calculations do not converge towards the core orbital eigenvalue for large supercells!

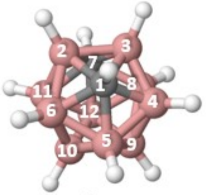


ΔSCF method – bigger molecules

- Remeasured gas phase XPS of anthrone at FinEstBeAMS beamline at MAX-IV synchrotron
- New ΔSCF calculations: SCAN + scaled ZORA

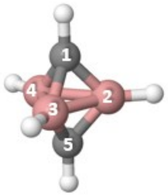


o-Carborane
$1,2\text{-}C_2B_{10}H_{12}$



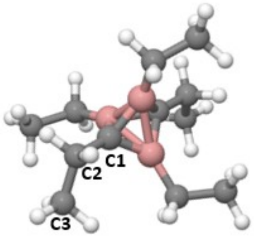
m-Carborane
$1,7\text{-}C_2B_{10}H_{12}$

$2,3\text{-}C_2B_4H_8$

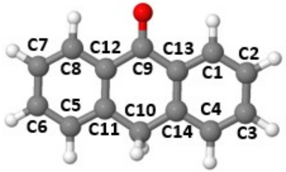


$1,5\text{-}C_2B_3H_5$

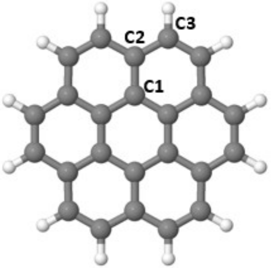
$2,4\text{-}C_2B_5H_7$



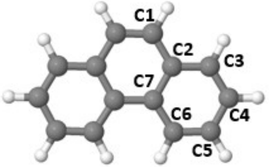
$1,5\text{-}C_2B_3(C_2H_5)_5$



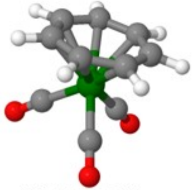
Anthrone
$C_{14}H_{10}O$



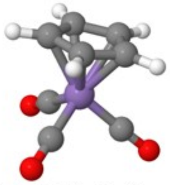
Coronene
$C_{24}H_{12}$



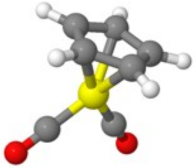
Phenanthrene
$C_{14}H_{10}$



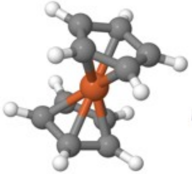
$V(CO)_3C_7H_7$



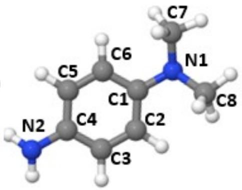
$Mn(CO)_3C_5H_5$



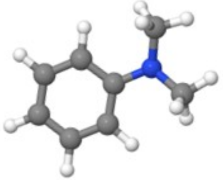
$Co(CO)_2C_5H_5$



$Fe(C_5H_5)_2$



N,N-dimethyl-p-phenylenediamine
$C_8H_{12}N_2$



N,N-dimethylaniline
$C_8H_{11}N$

44 binding energies: mean absolute error = 0.20 eV

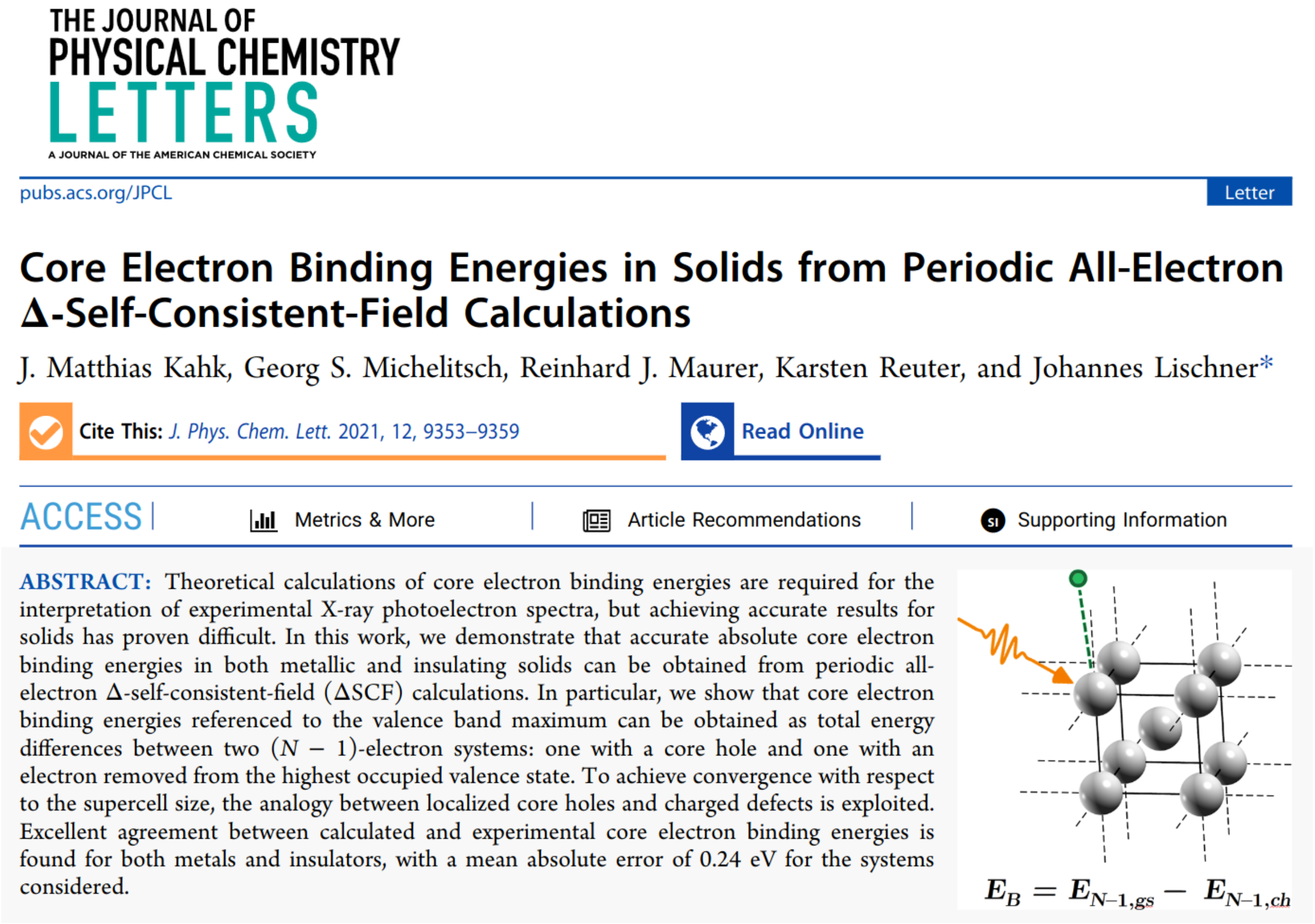
(unpublished data: J.M. Kahk and M. Berholts)

ΔSCF calculations – periodic solids

- Experimental binding energies in solids are typically reported relative to the Fermi level
- For calculated values
  - In metals, the Fermi level is a good point of reference
  - In insulators, the position of the Fermi level within the band gap is not known *a priori*
  - Instead, use the VBM as the point of reference

ΔSCF calculations – periodic solids

- $E_B = E_{N-1,\text{ core hole}} - E_{N-1,\text{ ground state}}$
- Use a uniform compensating background charge in both calculations
- A localized core hole is analogous to a charged defect in a solid
  - Converge core electron binding energy to the limit of infinite supercell size



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Letter

Core Electron Binding Energies in Solids from Periodic All-Electron Δ-Self-Consistent-Field Calculations

J. Matthias Kahk, Georg S. Michelitsch, Reinhard J. Maurer, Karsten Reuter, and Johannes Lischner*

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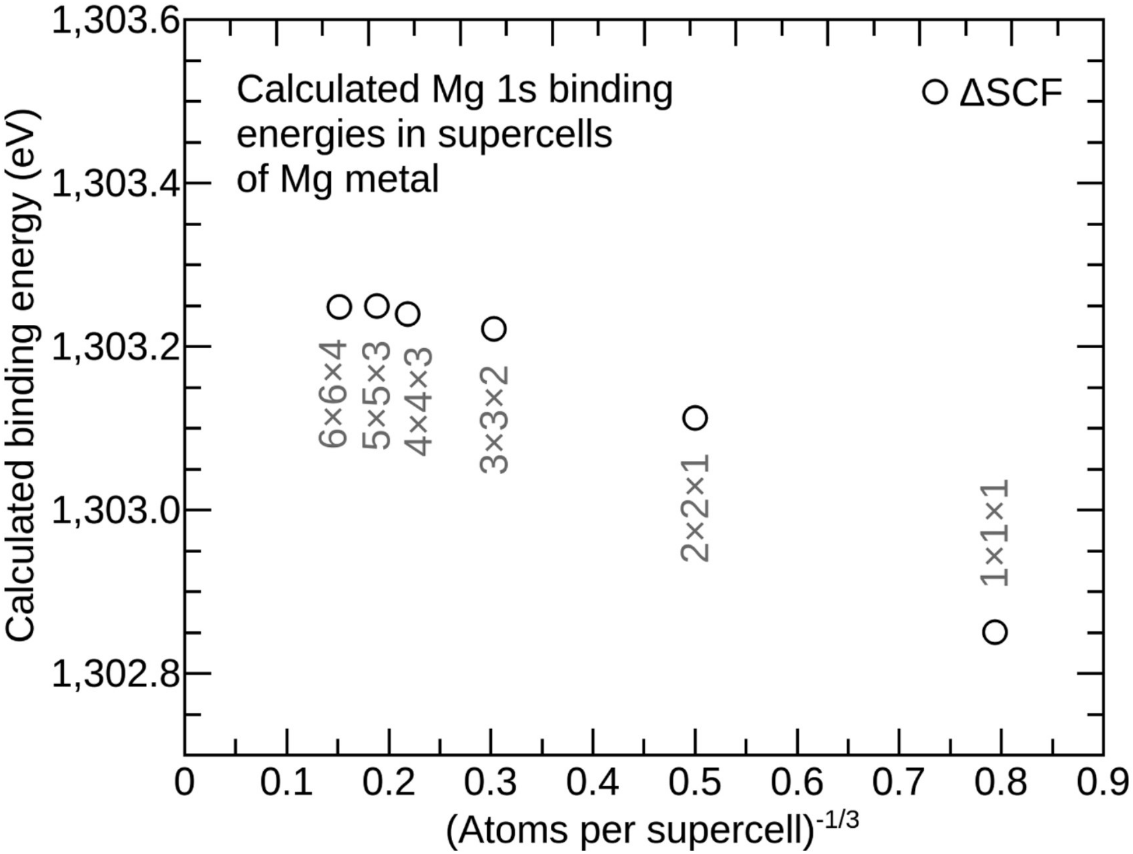
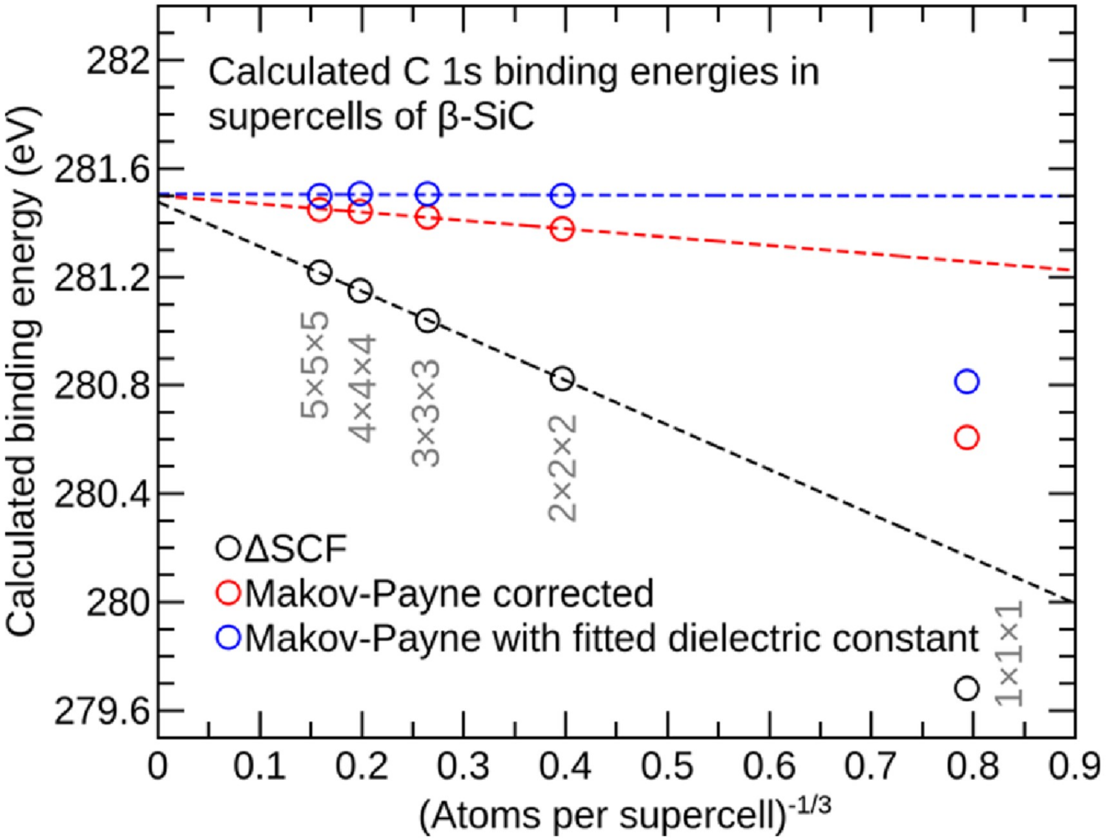
ABSTRACT: Theoretical calculations of core electron binding energies are required for the interpretation of experimental X-ray photoelectron spectra, but achieving accurate results for solids has proven difficult. In this work, we demonstrate that accurate absolute core electron binding energies in both metallic and insulating solids can be obtained from periodic all-electron Δ-self-consistent-field (ΔSCF) calculations. In particular, we show that core electron binding energies referenced to the valence band maximum can be obtained as total energy differences between two $(N-1)$-electron systems: one with a core hole and one with an electron removed from the highest occupied valence state. To achieve convergence with respect to the supercell size, the analogy between localized core holes and charged defects is exploited. Excellent agreement between calculated and experimental core electron binding energies is found for both metals and insulators, with a mean absolute error of 0.24 eV for the systems considered.

$$E_B = E_{N-1,gs} - E_{N-1,ch}$$

The ΔSCF method: metallic solids



The ΔSCF method: insulating solids



Solid	Core level	Theor E_B (eV)	Expt E_B (eV)	Error (eV)
Li	Li 1s	54.88	54.85	0.03
Be	Be 1s	111.88	111.85	0.03
Na	Na 1s	1071.56	1071.75	-0.19
	Na 2p	30.65	30.51	0.14
Mg	Mg 1s	1303.25	1303.24	0.01
	Mg 2p	49.69	49.79	-0.10
Graphite	C 1s	284.44	284.41	0.03
BeO	Be 1s	110.79	110.00	0.79
	O 1s	528.86	527.70	1.16
hex-BN	B 1s	188.42	188.35	0.07
	N 1s	396.39	396.00	0.39
Diamond	C 1s	284.43	284.04	0.39
beta-SiC	Si 2p	99.24	99.20	0.04
	C 1s	281.48	281.55	-0.07
Si	Si 2p	99.17	99.03	0.14
Mean absolute error = 0.24 eV				

The ΔSCF method: solids

- At the limit of infinite supercell size, the total energy difference $E_{N,\ \mathrm{ground}} - E_{N-1,\mathrm{ground}}$ converges to the VBM eigenvalue

$$E_{N,\ \mathrm{ground}} - E_{N-1,\mathrm{ground}} = \epsilon_{\mathrm{VBM}}$$

- This has been discussed in detail in
  - Corsetti & Mostofi, Phys. Rev. B 84, 035209 (2011)
  - Persson et al., Phys. Rev. B 72, 035211 (2005)

The ΔSCF method: solids

- We can therefore write two different equations for the core electron binding energy

$$E_B = E_{N-1,\text{ core hole}} - E_{N-1,\text{ ground state}} \qquad (1)$$

$$E_B = E_{N-1,\text{ core hole}} - E_{N,\text{ ground state}} + \epsilon_{\text{VBM, ground}} \qquad (2)$$

- At the limit of infinite supercell size, (1) and (2) should give the same result

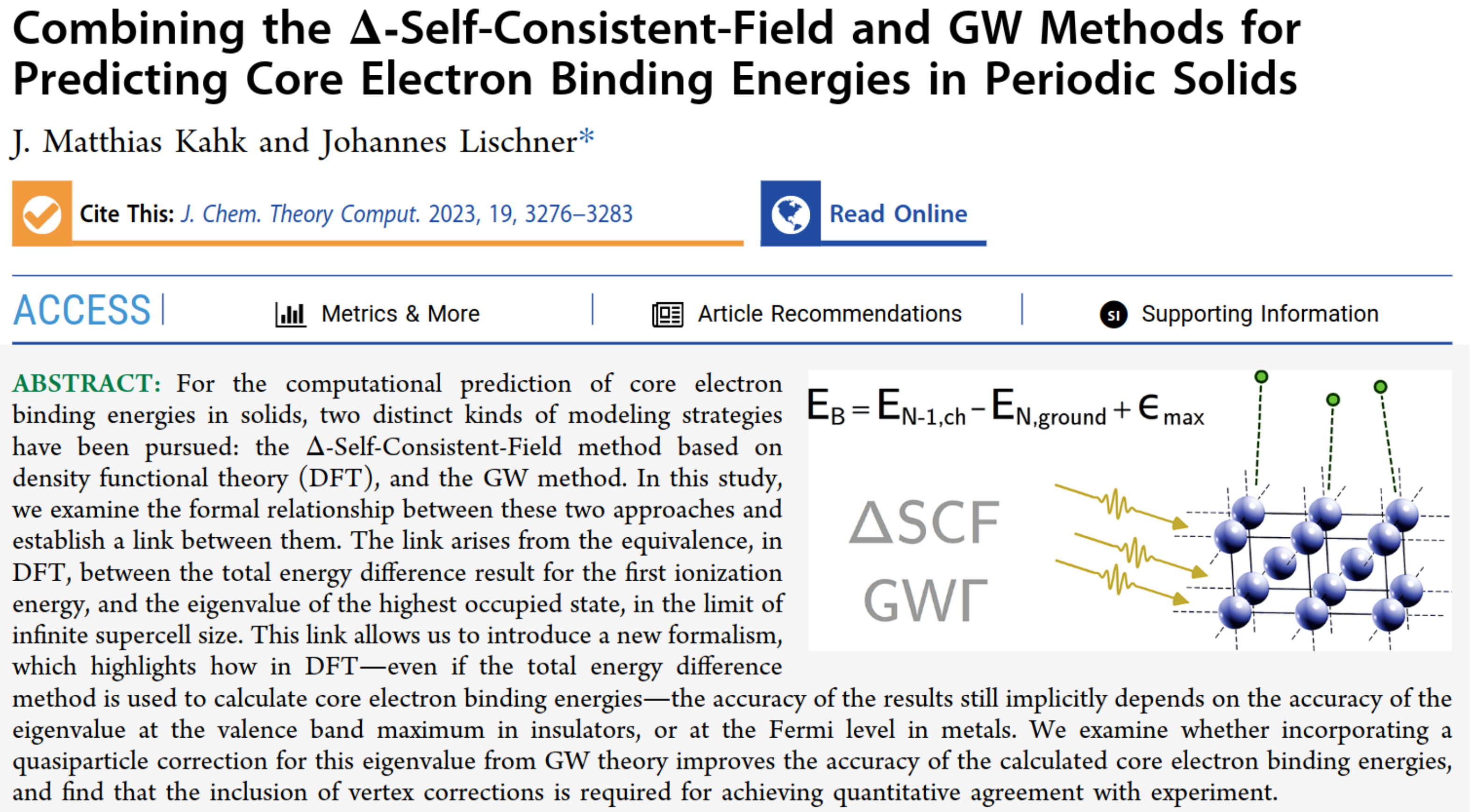
Position of the VBM

- In Eqn. 2, the binding energy depends on the DFT eigenvalue at the VBM

$$E_B = E_{N-1,\text{ core hole}} - E_{N,\text{ ground state}} + \epsilon_{VBM} \qquad (2)$$

- Could we improve the accuracy of the calculated binding energies by obtaining ϵ_{VBM} from a more accurate theory, e.g. GW?
  - i.e. by using $\epsilon_{VBM} = \epsilon_{VBM,\text{ DFT}}$ + quasiparticle correction

Core BEs with VBM corrected by $G_0W_0\Gamma$



Combining the Δ-Self-Consistent-Field and GW Methods for Predicting Core Electron Binding Energies in Periodic Solids

J. Matthias Kahk and Johannes Lischner*

Cite This: *J. Chem. Theory Comput.* 2023, 19, 3276–3283

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ABSTRACT: For the computational prediction of core electron binding energies in solids, two distinct kinds of modeling strategies have been pursued: the Δ-Self-Consistent-Field method based on density functional theory (DFT), and the GW method. In this study, we examine the formal relationship between these two approaches and establish a link between them. The link arises from the equivalence, in DFT, between the total energy difference result for the first ionization energy, and the eigenvalue of the highest occupied state, in the limit of infinite supercell size. This link allows us to introduce a new formalism, which highlights how in DFT—even if the total energy difference method is used to calculate core electron binding energies—the accuracy of the results still implicitly depends on the accuracy of the eigenvalue at the valence band maximum in insulators, or at the Fermi level in metals. We examine whether incorporating a quasiparticle correction for this eigenvalue from GW theory improves the accuracy of the calculated core electron binding energies, and find that the inclusion of vertex corrections is required for achieving quantitative agreement with experiment.

$$E_B = E_{N-1,ch} - E_{N,ground} + \epsilon_{max}$$

Core BEs with VBM corrected by $G_0W_0\Gamma$

- MAE = 0.19 eV (vs. 0.24 eV without correction)
- Major improvements for BeO and diamond
- Dataset is too small for a definitive assessment

Solid	Core level	Theor E_B (eV)	Expt E_B (eV)	Error (eV)
Li	Li 1s	54.85	54.85	0.00
Be	Be 1s	112.34	111.85	0.49
Na	Na 1s	1071.70	1071.75	-0.05
	Na 2p	30.77	30.51	0.26
Mg	Mg 1s	1303.48	1303.24	0.24
	Mg 2p	49.96	49.79	0.17
Graphite	C 1s	284.53	284.41	0.12
BeO	Be 1s	109.54	110.00	-0.46
	O 1s	527.59	527.70	-0.11
hex-BN	B 1s	188.02	188.35	-0.33
	N 1s	395.94	396.00	-0.06
Diamond	C 1s	284.08	284.04	0.04
beta-SiC	Si 2p	99.11	99.20	-0.09
	C 1s	281.36	281.55	-0.19
Si	Si 2p	99.36	99.03	0.33
Mean absolute error = 0.19 eV				

What is still difficult?

- SCF-convergence!
  - Sometimes the total energy converges faster than the change in charge density
  - In FHI-aims, turn off the Kerker preconditioner
- Basis sets
  - Current (numerical) basis sets for atoms with a core hole are accurate, but very inefficient

What is still difficult?

- Periodic calculations
  - In FHI-aims, only KS_method serial can be currently used in periodic calculations with deltascf_projector (or force_occupation_projector)
  - “Tricks” required for creating a localized core hole
- Heavier elements
  - Creating core holes in p, d, or f-orbitals in scalar relativistic calculations is conceptually problematic
  - Also bad for SCF-convergence, core hole can “hop around” between the degenerate orbitals

Other important things

- Neutral excitations => XAS
- Spin-orbit splitting in core levels – fully relativistic ΔSCF calculations. Restricted open-shell Kohn-Sham (ROKS) required (?)
- All-electron schemes (~ FHI-aims) vs pseudopotentials with a core hole
- GW calculations of core electron binding energies in FHI-aims (D. Golze et al.)

Summary

1) Peak-assignment problems in core level XPS as something that seriously limits our overall ability to characterize complex surfaces
2) Orbital-optimized DFT for excited states, especially for core-excitations
3) FHI-aims as the best available code for all-electron ΔSCF calculations of realistic systems