Δ-Self-Consistent-Field Calculations of Core Electron Binding Energies in Solids and Surface Species

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A quick recap

- For molecules, we can calculate core electron binding energies directly as

$$E_B = E_{N-1,\text{core hole}} - E_N$$

Total energy of the final state with a core hole, obtained from a DFT calculation with non-Aufbau-principle Occupation numbers

Ground state total energy

What is different in solids?

What is different in solids?

- Energy referencing!
  - In gas phase XPS, core electron binding energies are referenced to the vacuum level
  - In solids and surface species, they are not
  - Instead, the **Fermi level of the sample is typically used as the zero of the binding energy scale**

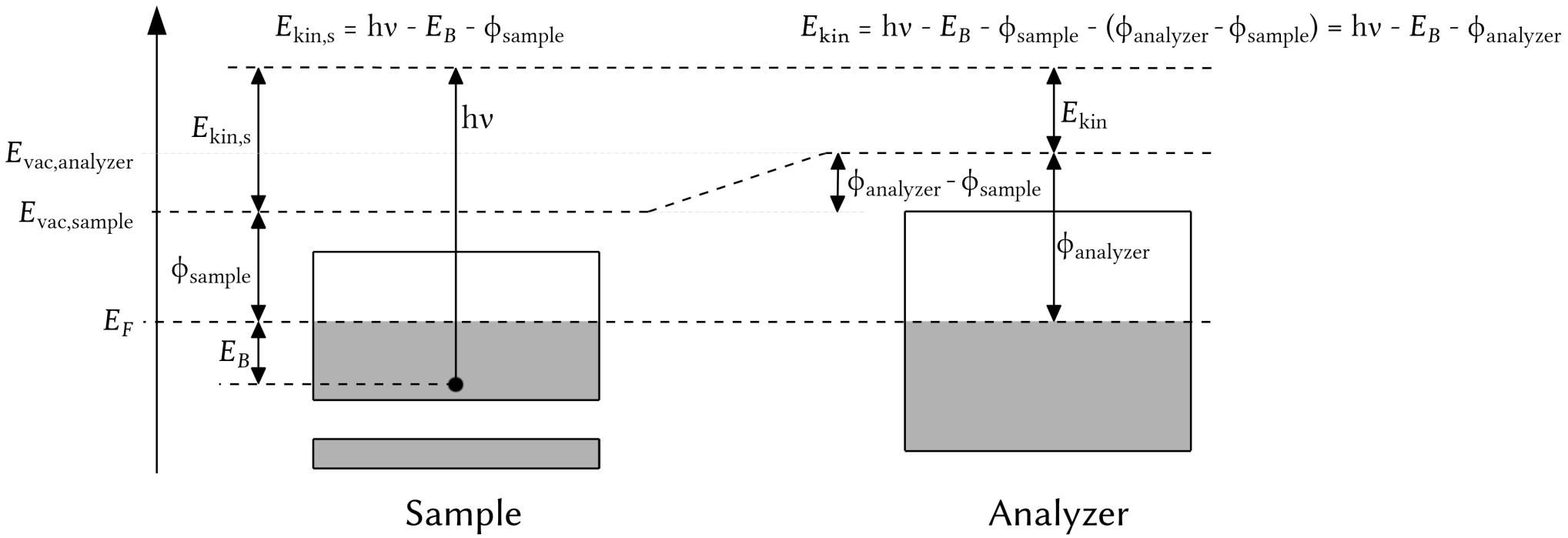


Figure 2.4 The alignment of energy levels during a photoemission experiment.

Energy referencing

- In a calculation, the Fermi level is also a good point of reference for metals
- But in an insulator, the Fermi level could be anywhere within the band gap!
  - We need a well defined point of reference
  - Use the VBM as the zero of the binding energy scale
  - Comparison to experiment is only possible, if the experimental data can also be referenced to the VBM

ΔSCF method for solids

- Calculate the difference between core electron binding energy, and first ionization energy instead
- Core B.E. – 1st I.E. =

  $=(E_{N-1(core)} - E_N) - (E_{N-1(VBM)} - E_N)=$ (Eqn. 1)

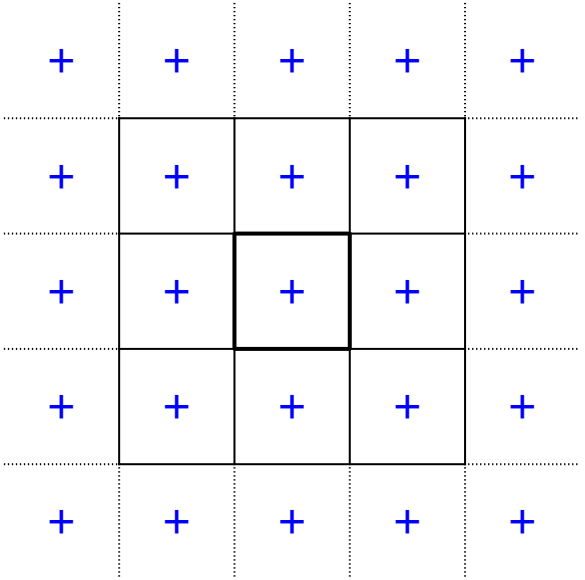
  $= E_{N-1(core)} - E_{N-1(VBM)}$
- Ground state total energy cancels out

ΔSCF method for solids

- In metals:
  - Obtain E_B referenced to the Fermi level
- In insulators:
  - Obtain E_B referenced to the VBM

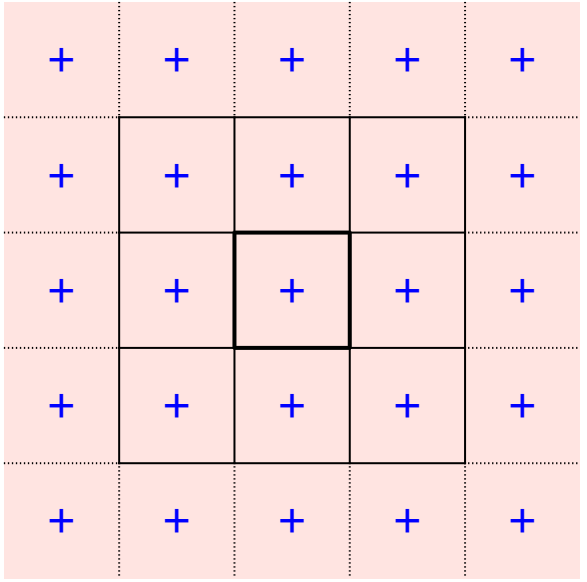
What else is different for solids?

- The system with a core hole is charged
- In a periodic calculation, this must be compensated



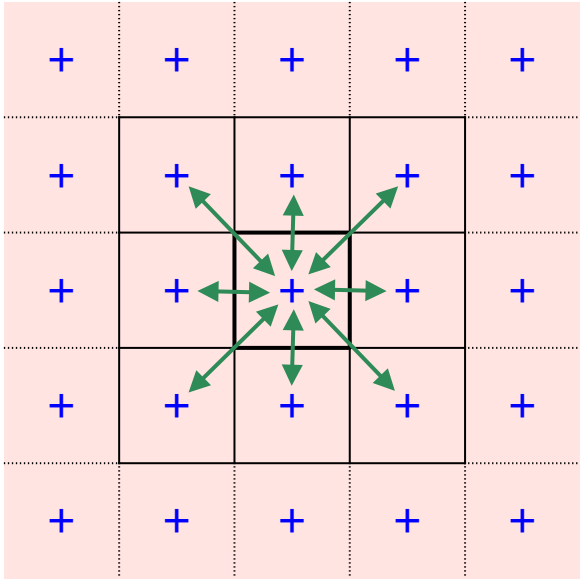
Periodic core hole calculations

- The system with a core hole is charged
- In a periodic calculation, this must be compensated



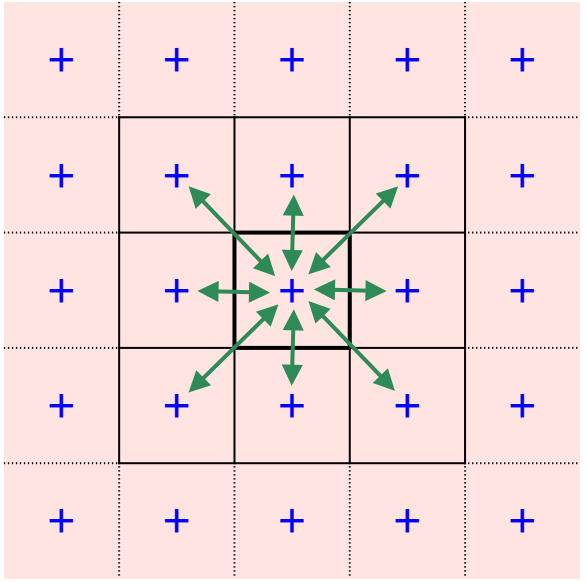
Periodic core hole calculations

- Even with a compensating background charge, the localized core hole is still interacting with its periodic copies



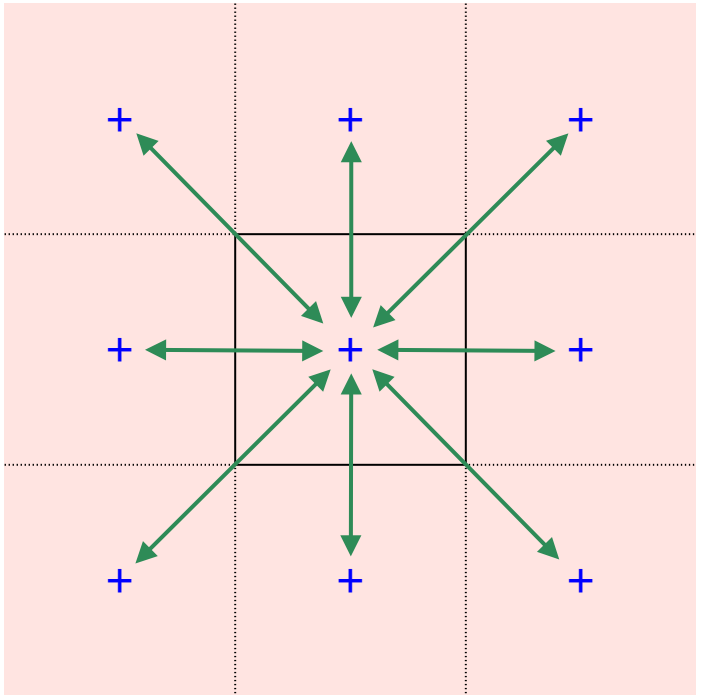
Periodic core hole calculations

- In a real experiment – the concentration of core holes is very low. Interactions between core holes usually negligible



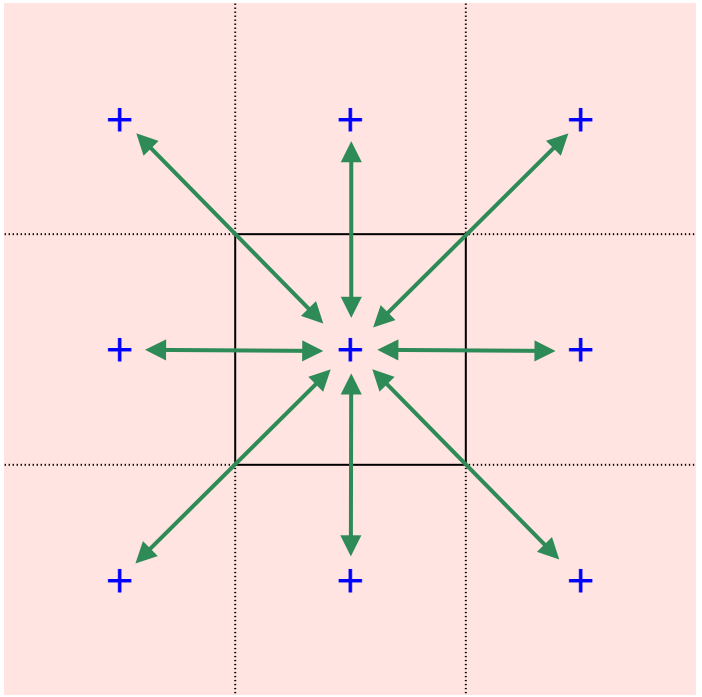
Periodic core hole calculations

- In a calculation, we can reduce the interactions between periodic copies of the core hole by building supercells



Periodic core hole calculations

- And by extrapolating to the infinite supercell limit



Example: C 1s in β-SiC

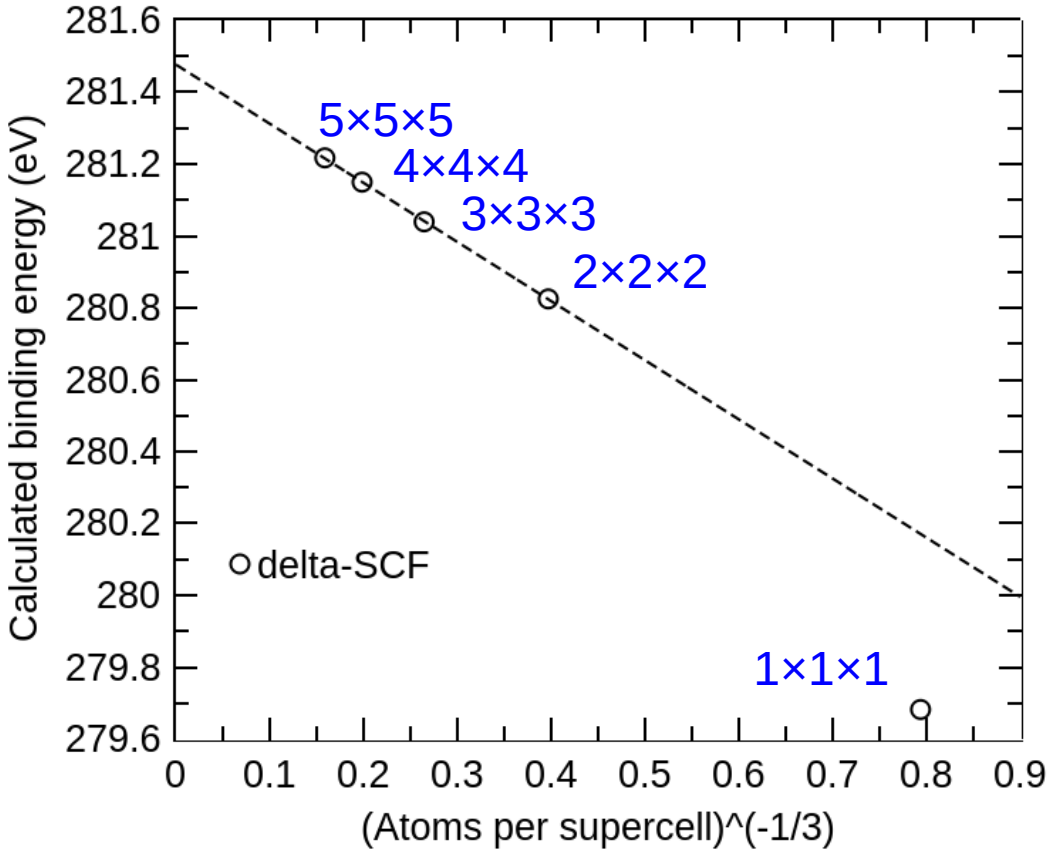
- Coulomb interactions scale as 1/r. Plot energy against

  1/lattice-vector

  or equivalently

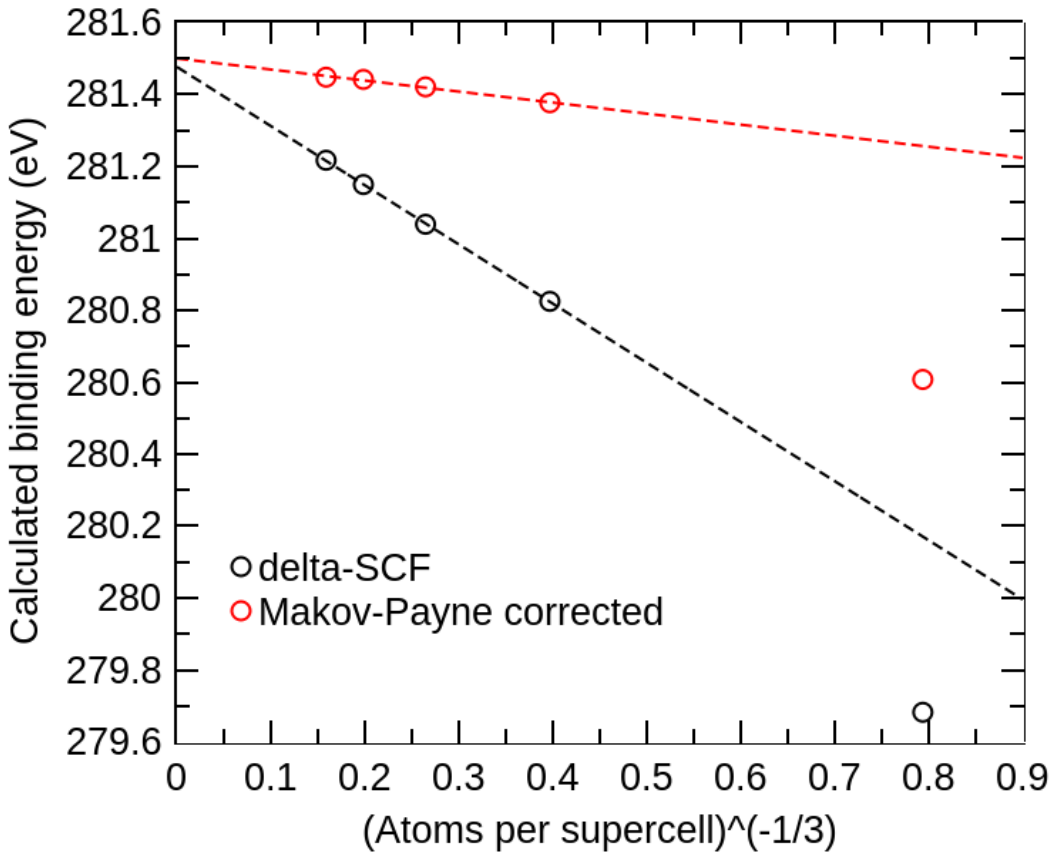
  $1/(\text{atoms-per-supercell})^{1/3}$

- Infinite size limit at y-axis crossing
- Ignore datapoint for unit cell – core holes on adjacent atoms



Example: C 1s in β-SiC

- A localized core hole in a solid is analogous to a charged defect
- We can use the finite size correction schemes developed for calculations of charged defects



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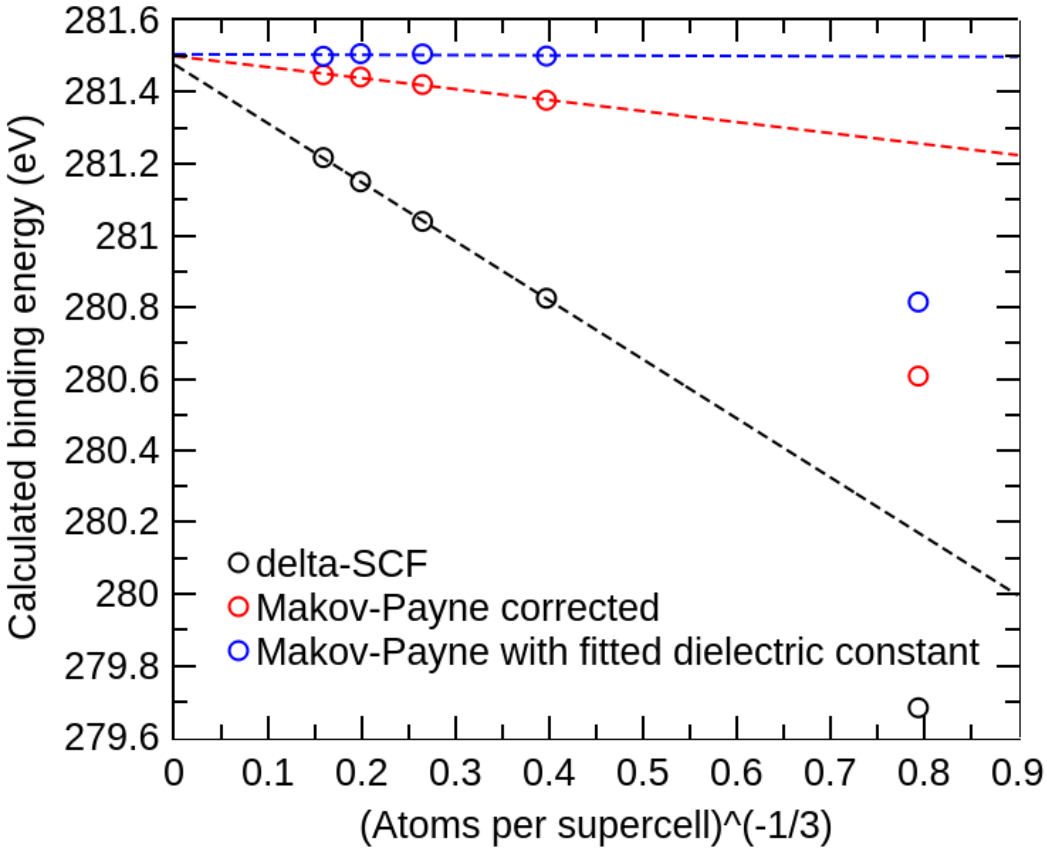
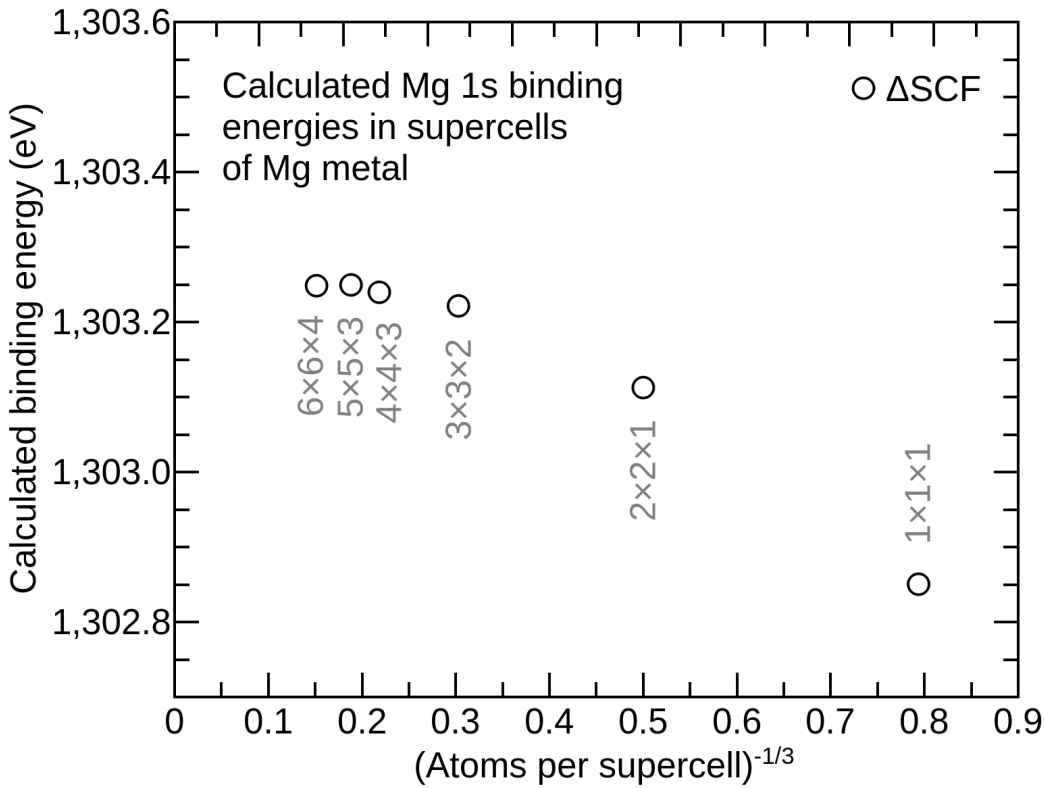


Example: Mg 1s in metallic magnesium

- Effective screening of the interaction between periodic images of the core hole
- For large enough supercells, the binding energy converges



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				

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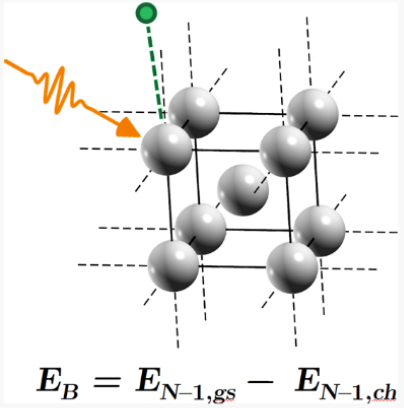
Core Electron Binding Energies in Solids from Periodic All-Electron Δ-Self-Consistent-Field Calculations

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

Cite This: *J. Phys. Chem. Lett.* 2021, 12, 9353−9359 Read Online

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.



The ΔSCF expression for solids

$$\text{Core B.E.} - \text{1st I.E.} = E_{N-1(\text{core})} - E_{N-1(\text{VBM})}$$

- We can modify this equation by taking advantage of an important result from computational solid state physics

This is the total energy of the supercell with one electron removed from the highest occupied state

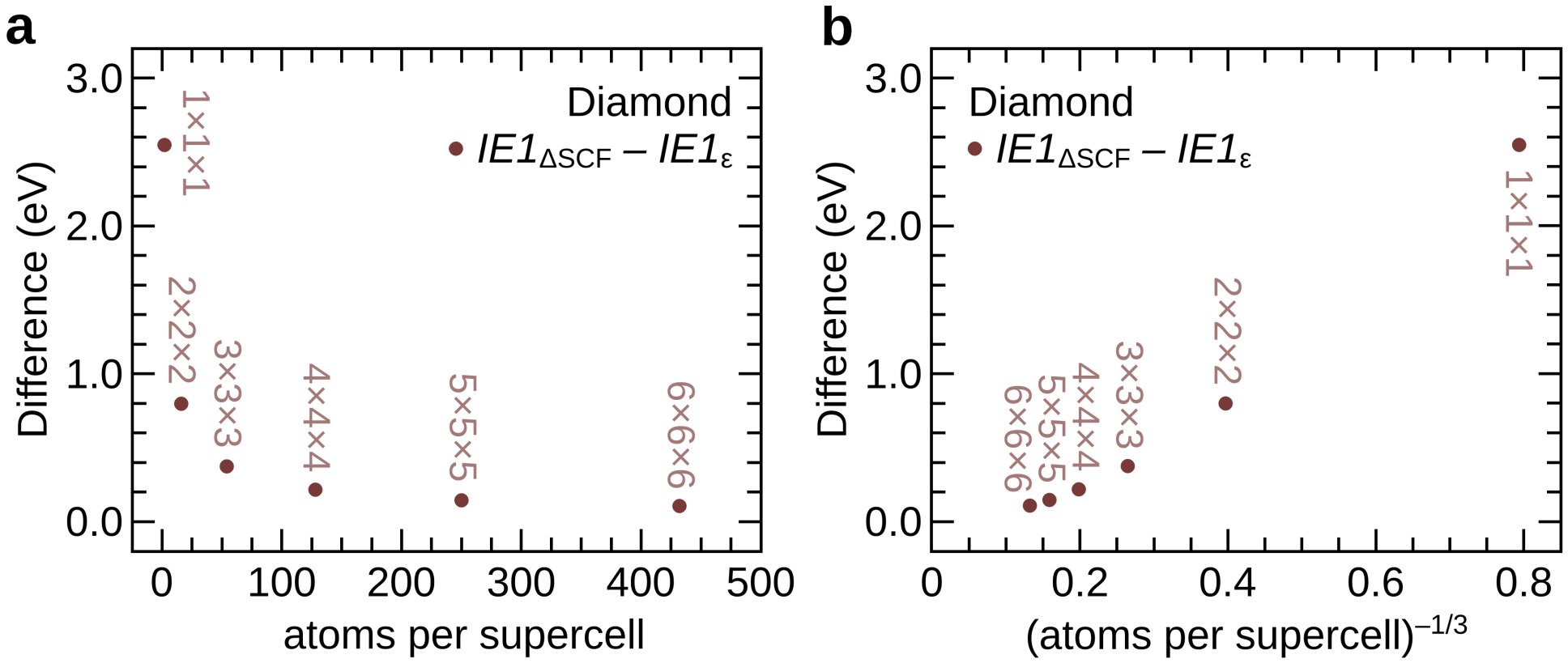
The ΔSCF expression for solids

- At the limit of infinite supercell size, in DFT with practical exchange-correlation functionals

$$\lim_{n \to \infty} (E_{N-1(VBM)} - E_N) = -\epsilon_{VBM}$$

- i.e. the ΔSCF result for the 1st ionization energy simply convergees to the VBM eigenvalue at the limit of infinite supercell size

The ΔSCF expression for solids



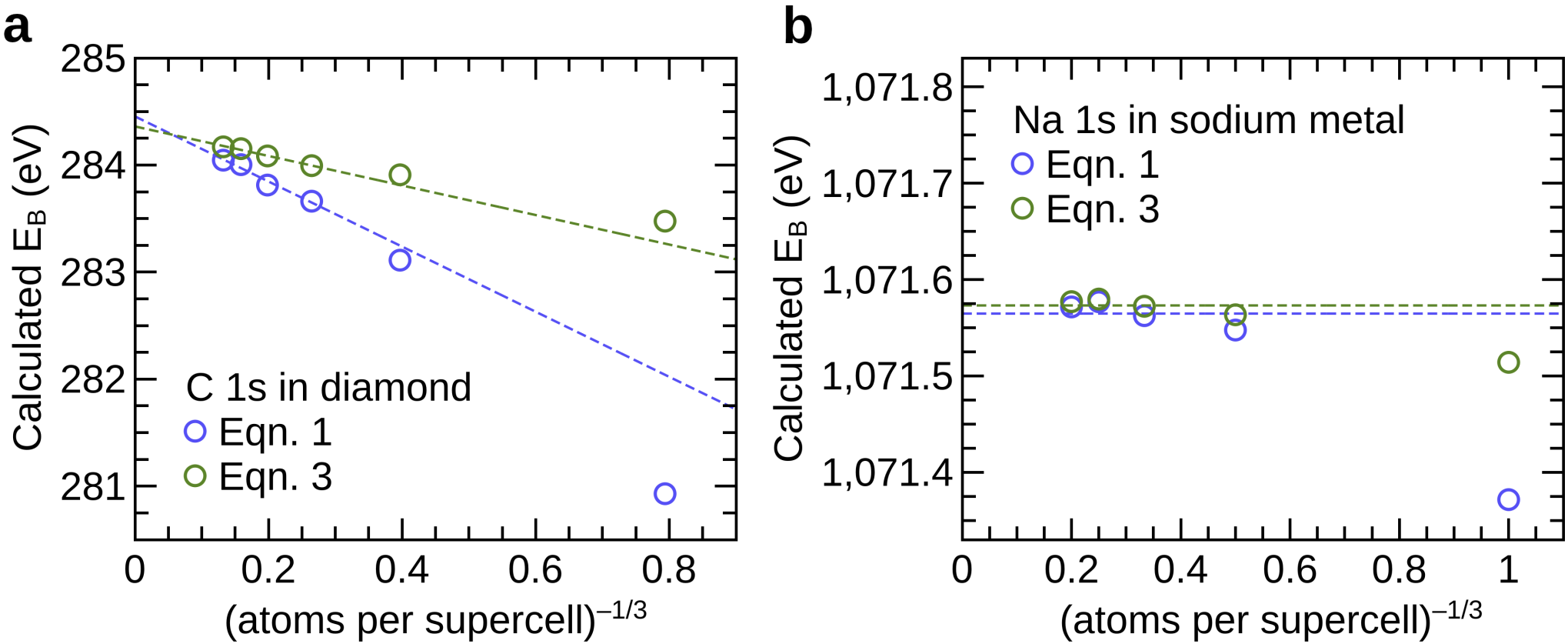
The ΔSCF expression for solids

- This allows us to rewrite the expression for the core electron binding energy as follows

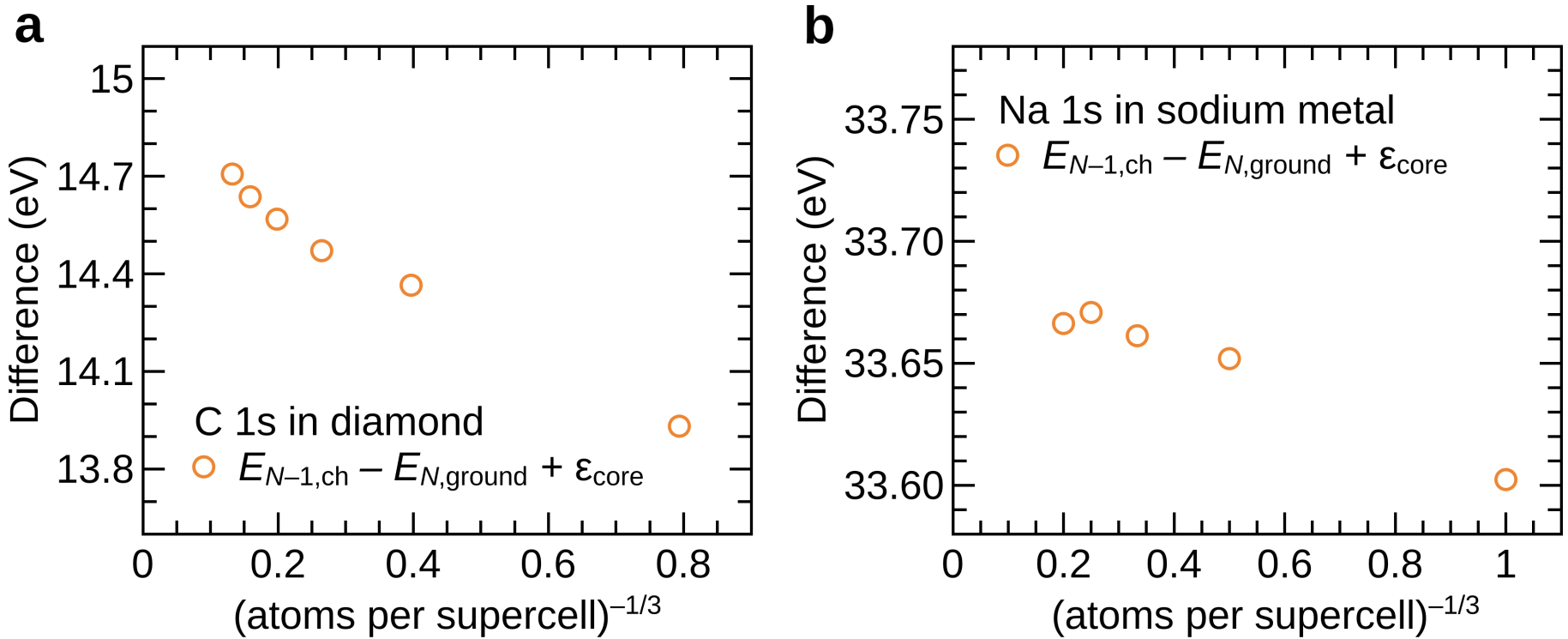
$$\text{Core B.E.} - \text{1st I.E.} = E_{N-1(\text{core})} - E_N + \epsilon_{VBM} \qquad \text{(Eqn. 3)}$$

- At the limit of infinite supercell size, this expression gives identical results to the previous expression

The ΔSCF expression for solids



- NB! The ΔSCF result for the core electron binding energy does NOT converge to the core orbital's eigenvalue



Why is Eqn. 3 interesting?

$$\text{Core B.E.} - \text{1st I.E.} = E_{N-1(\text{core})} - E_N + \epsilon_{VBM}$$

- It exposes how the calculated binding energy depends on the DFT eigenvalue at the VBM
- But we know that DFT has a band gap problem: calculated band gaps are typically too small
  - Errors in both VBM and CBM energies

Solid	Core level	Theor E_B (eV)	Expt E_B (eV)	Error (eV)
Li	Li 1s	54.88	54.85	0.03
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Position of the VBM

- In Eqn. 3, the binding energy depends on the DFT eigenvalue at the VBM

$$E_B = E_{N-1,\ \text{core hole}} - E_{N,\ \text{ground state}} + \epsilon_{VBM} \qquad (3)$$

- 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 $\epsilon_{VBM} = \epsilon_{VBM,\ DFT}$ + quasiparticle correction

The ΔSCF method: solids

- Try:

$$E_B = E_{N-1,\ \text{core hole}} - E_{N,\ \text{ground state}} + \epsilon_{VBM,DFT} + \Delta\epsilon_{VBM,G_0W_0}$$

- Problem: the accuracy becomes much worse!
- All binding energies underestimated:
  - ME = –0.56 eV (c.f. 0.17 eV without correction)
  - MAE = 0.56 eV (c.f. 0.24 eV)

Why isn't G_0W_0 an improvement?

- G_0W_0 gives accurate band gaps
  - But absolute positions of the band edges may be underestimated
  - Schmidt, Patrick, Thygesen, "Simple Vertex Correction Improves GW Band Energies of Bulk and Two-Dimensional Crystals", Phys Rev B 96, 205206 (2017)

Why isn't G_0W_0 an improvement?

- Schmidt et al. introduce $G_0W_0\Gamma$
  - G_0W_0 with vertex corrections
  - Band gaps mostly unaffected
  - "The most striking effect of the vertex is that it raises the absolute QP energies from G_0W_0 by around 0.5 eV"
- Maybe we should use $G_0W_0\Gamma$ to correct the position of the VBM instead?

Solid	Core level	Theor E_B (eV)	Expt E_B (eV)	Error (eV)
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	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
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Mean absolute error = 0.19 eV				

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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 Read Online

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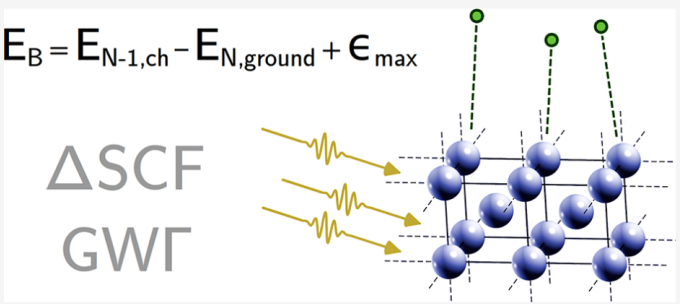
ABSTRACT: For the computational prediction of core electron binding energies in solids, two distinct kinds of modeling strategies have been pursued: the Δ-Self-Consistent-Field method based on density functional theory (DFT), and the GW method. In this study, we examine the formal relationship between 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.



What about surface species?

- Two possible strategies to model adsorbates on a surface:
  1) Represent the substrate as a finite cluster
  2) Represent the substrate using periodic slabs

Surface species via cluster models

- Advantages:
  - No need for a compensating background charge
  - No spurious interactions between periodic copies of the core hole
- Disadvantages:
  - Finite size effects in the band structure of the substrate
  - Large finite size effect in final state screening for insulators

Example: adsorbates on Cu(111)

For adsorbed H_2O on Cu(111), the calculated O 1s binding energy is not very strongly dependent on cluster size

Species	Calculated O 1s E_B (eV)
H_2O on Cu_{42}	532.97
H_2O on Cu_{88}	532.85
H_2O on Cu_{163}	532.95
H_2O on Cu_{292}	532.84

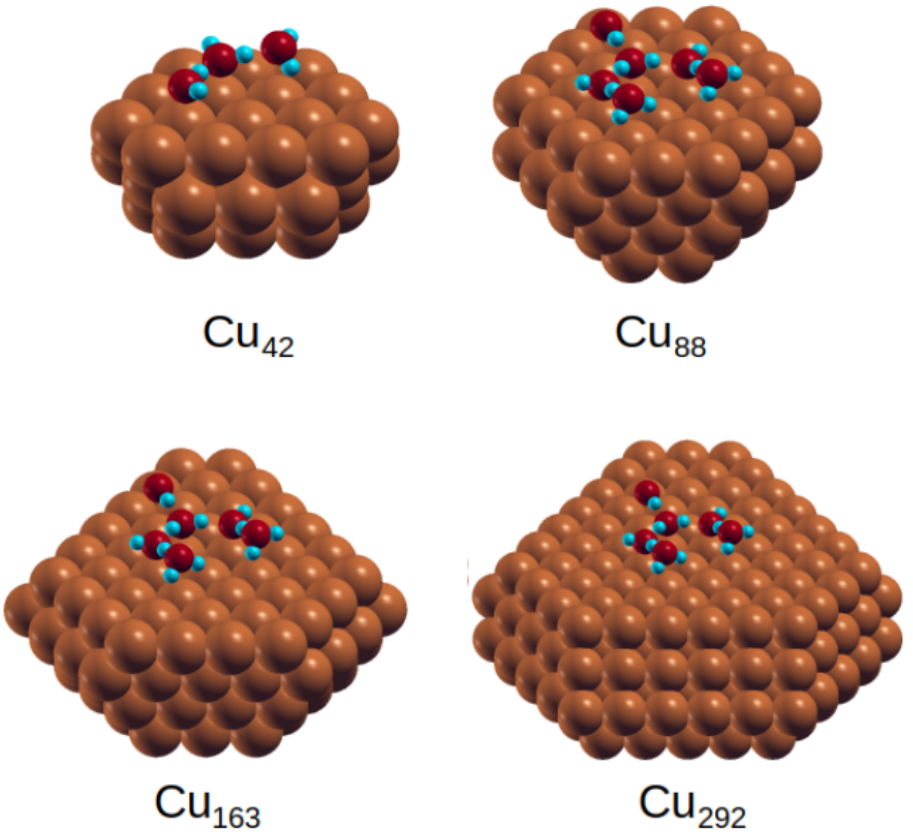
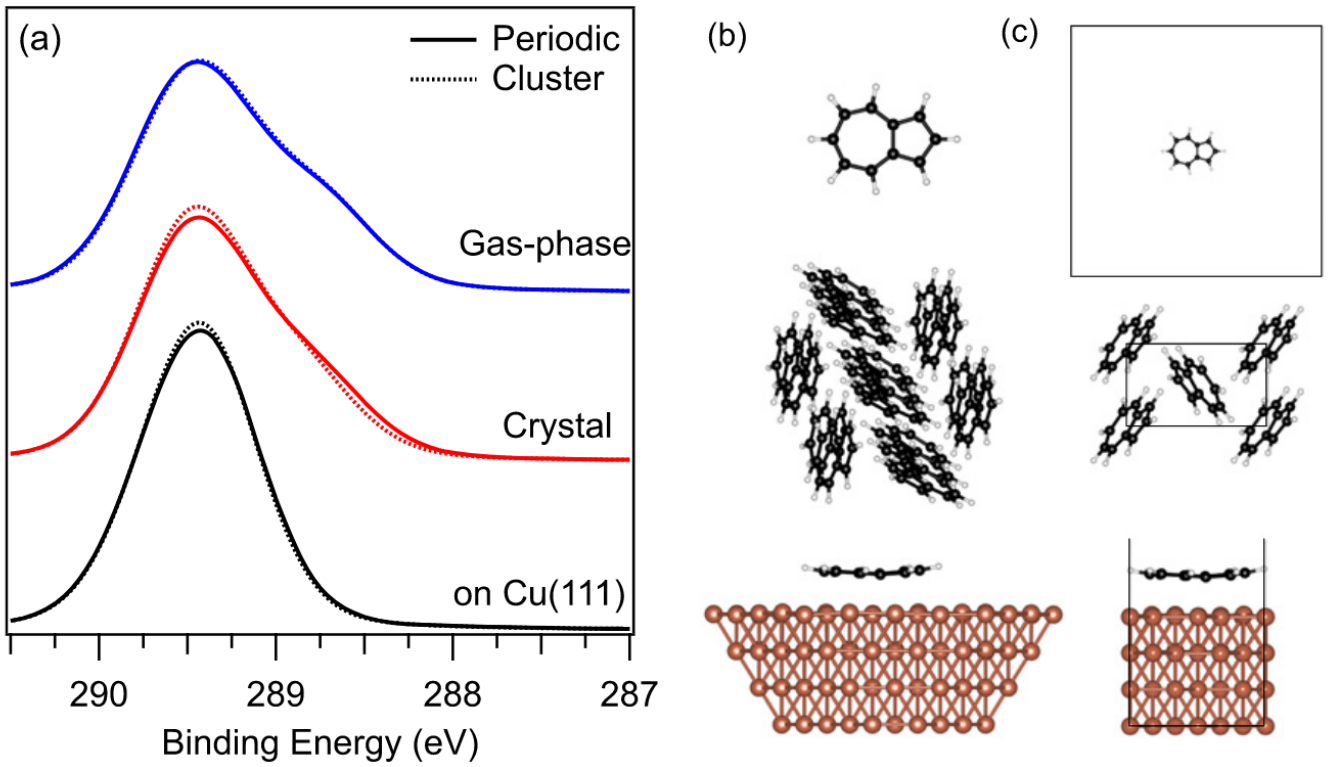


TABLE III. A comparison of experimental and calculated core-electron binding energies for adsorbates on Cu(111).

Core level	Theor. E_B (eV)	Expt. E_B (eV)	
H_2O O 1s	532.95	533.0	[56]
		532.4	[57]
OH O 1s	531.15	531.50	[58]
CO C 1s	285.70	286.1	[59]
		286.2	[58]
CO O 1s	532.52	531.5	[59]
		533.4	[58]
HCOO C 1s	286.82	287.3	[57]
		288.2	[60]
		289.75	[61]
HCOO O 1s	531.25	531.5	[60]

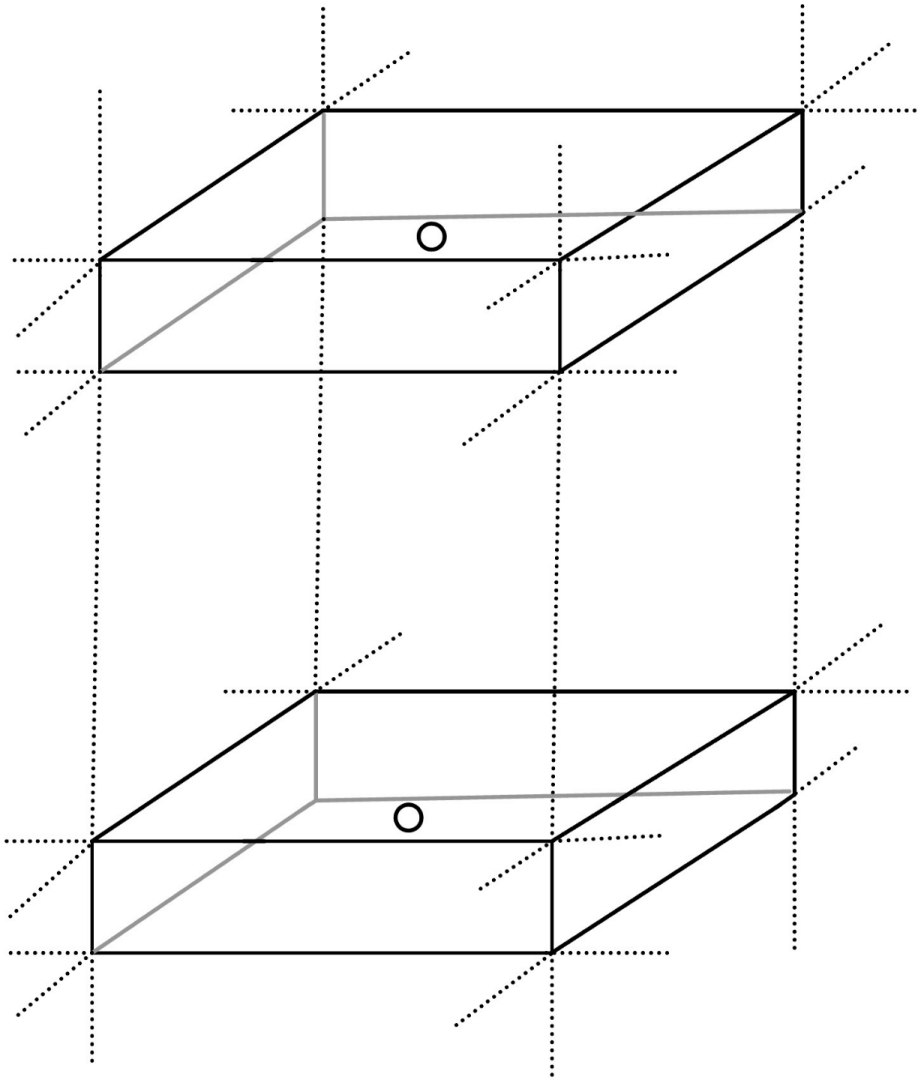
Periodic vs. cluster models



Klein et al., J. Phys.: Condens. Matter 33, 154005 (2021)

Surface species via periodic models

- Surface modelled as an infinite array of infinite 2D slabs, separated by a vacuum region



Surface species via periodic models

- Advantages:
  - In principle, possible to eliminate finite size effects via extrapolation
- Disadvantages:
  - In practice, performing this extrapolation is difficult (may require calculations of very large supercells)
  - You can’t just have one surface – the slab must also have the other exposed surface – this may be a nuisance
  - Finite size correction schemes are also more complex than for bulk solids

The Z+1 approximation

- Instead of removing a unit of negative charge, could we add a unit of positive charge to the nucleus?
- Core electron binding energy shifts are well approximated by the relative energy change upon replacing an element with the next one in the periodic table

The Z+1 approximation

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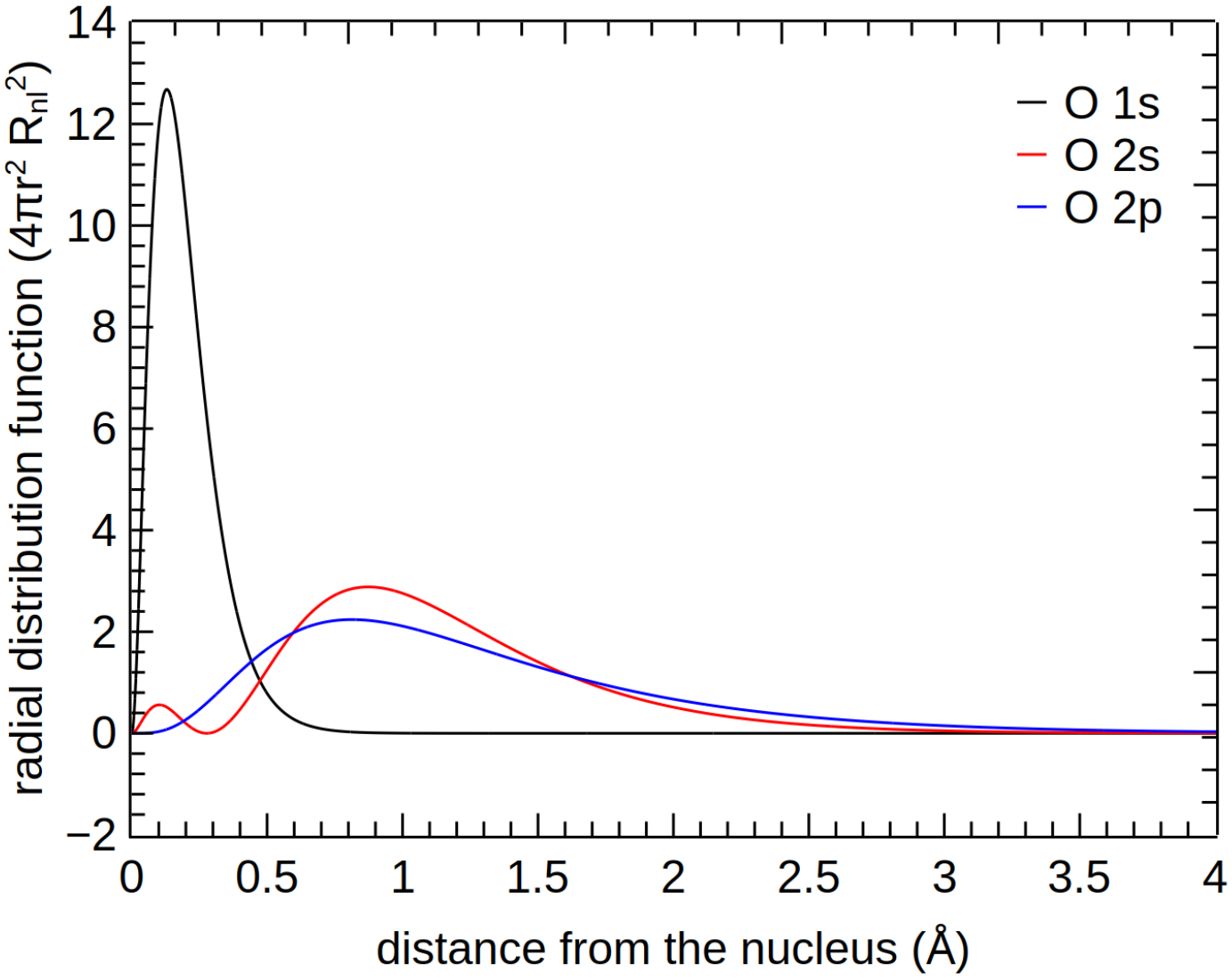
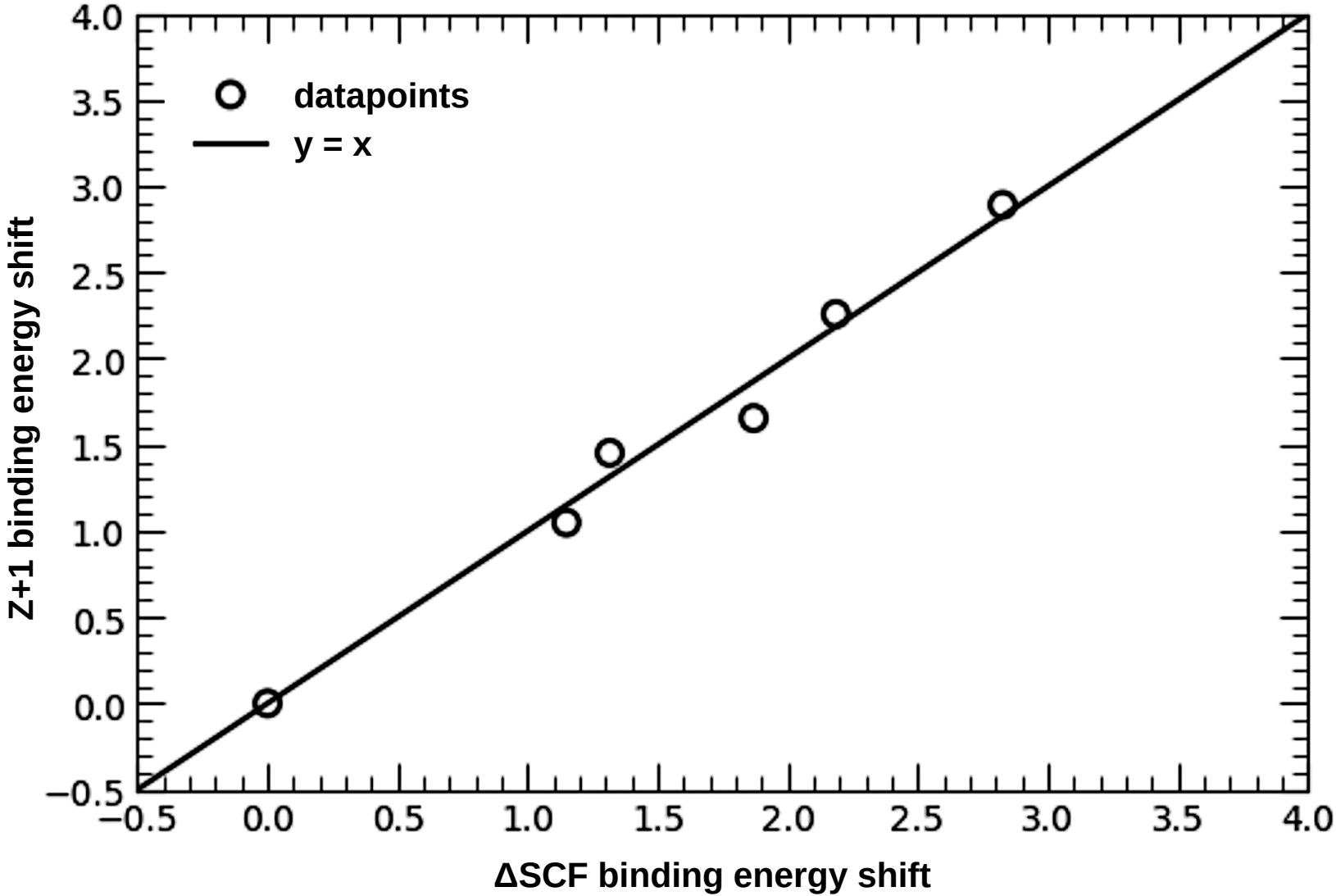

O 1s
O 2s
O 2p
radial distribution function (4πr² R_nl²)
distance from the nucleus (Å)
14
12
10
8
6
4
2
0
−2
0
0.5
1
1.5
2
2.5
3
3.5
4

Calculated O 1s binding energy shifts in small oxygen containing molecules



Ongoing work and future directions

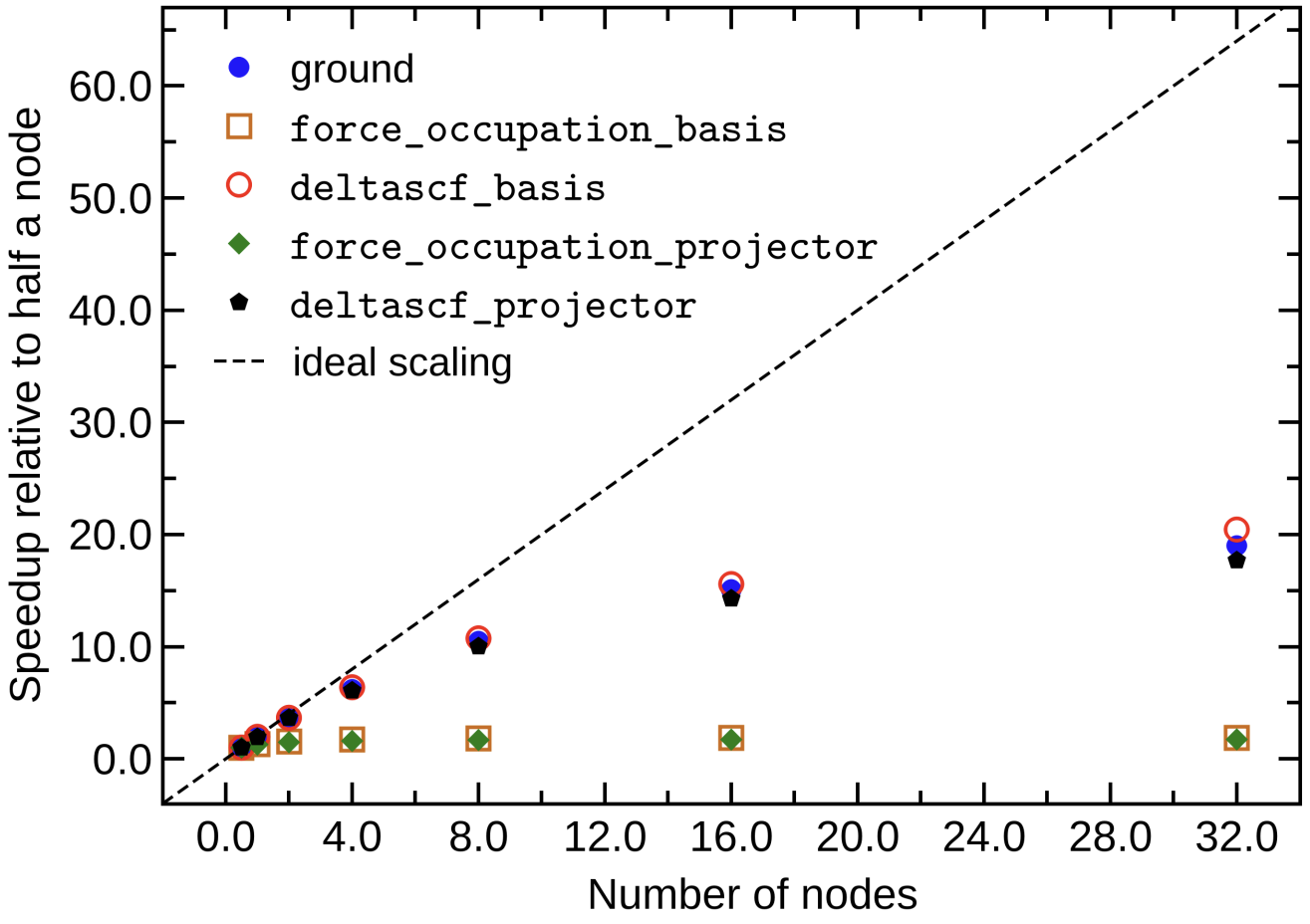
- Once you have a structural model, calculating a core electron binding energy shouldn’t be too difficult
  - Scalability
  - Usability

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	✗	✓

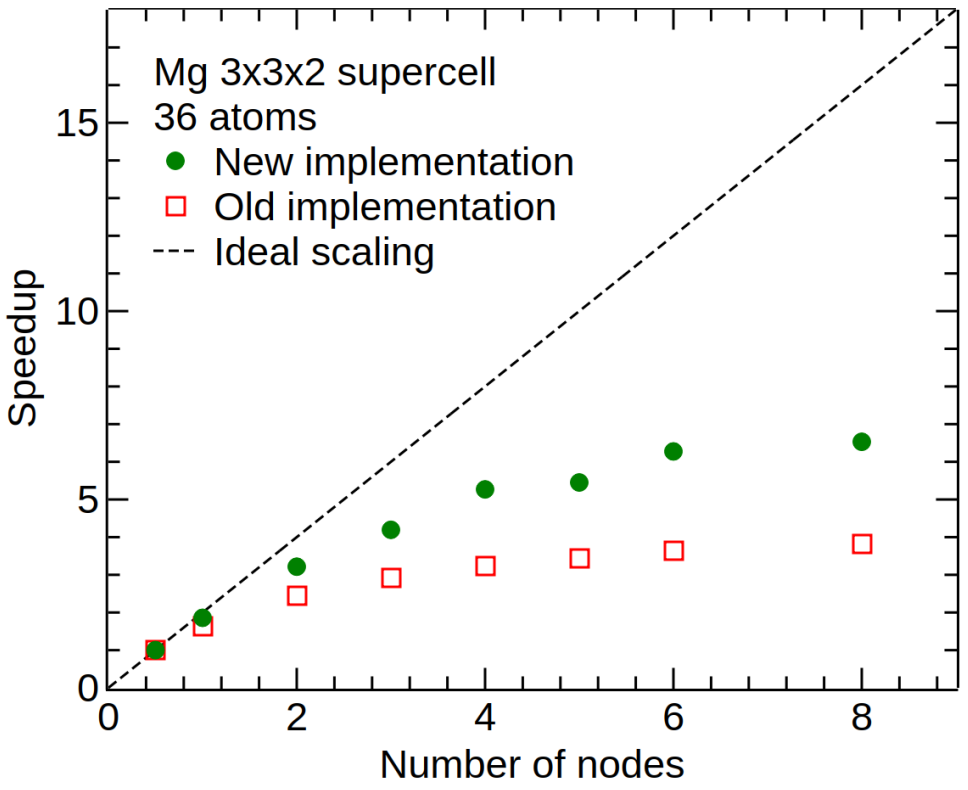
* only with collect_eigenvectors = .true.

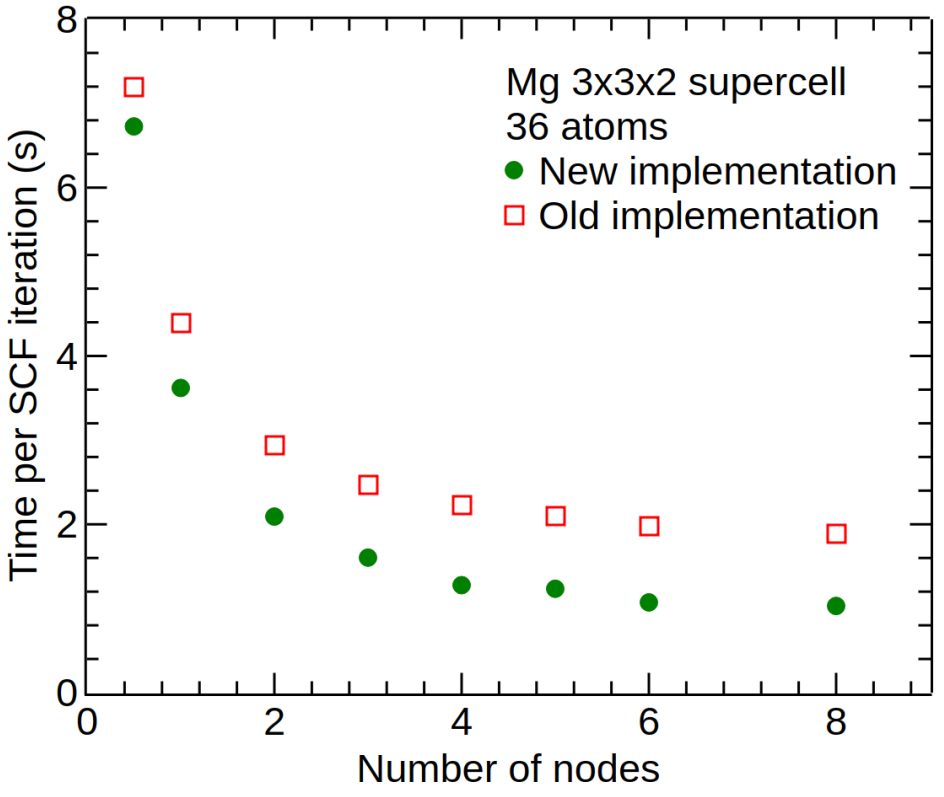
Scalability: aperiodic systems



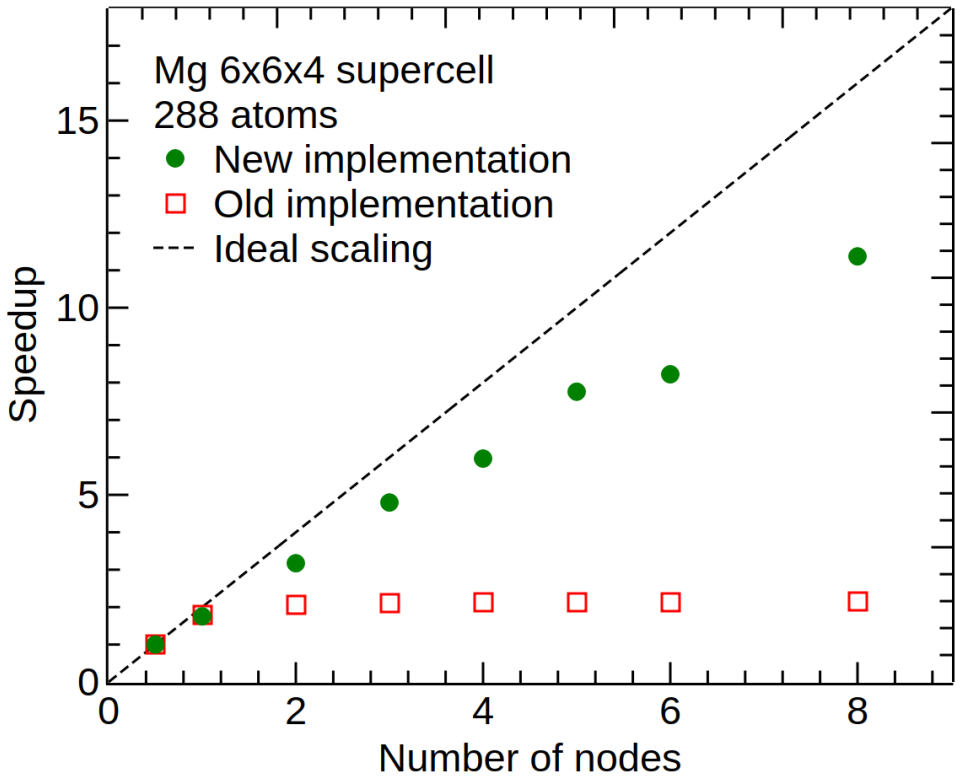
Peroxide-terminated diamond cluster containing 205 atoms

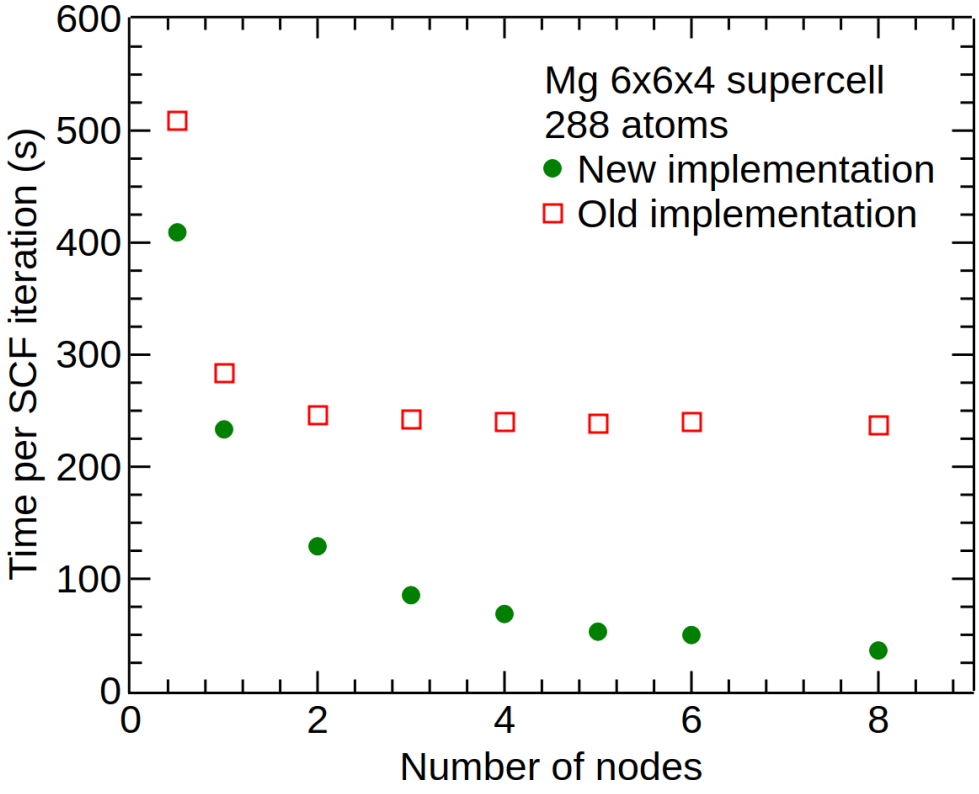
Scalability: periodic systems





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

Summary

- The ΔSCF method can also be readily applied to periodic systems
  - Though there are additional complications
- The prediction of binding energy shifts within the same structure is well established
- Absolute binding energies (needed for comparing results between different systems) can be calculated, but less work has been done thus far, especially for surface species