The Δ-Self-Consistent-Field Method

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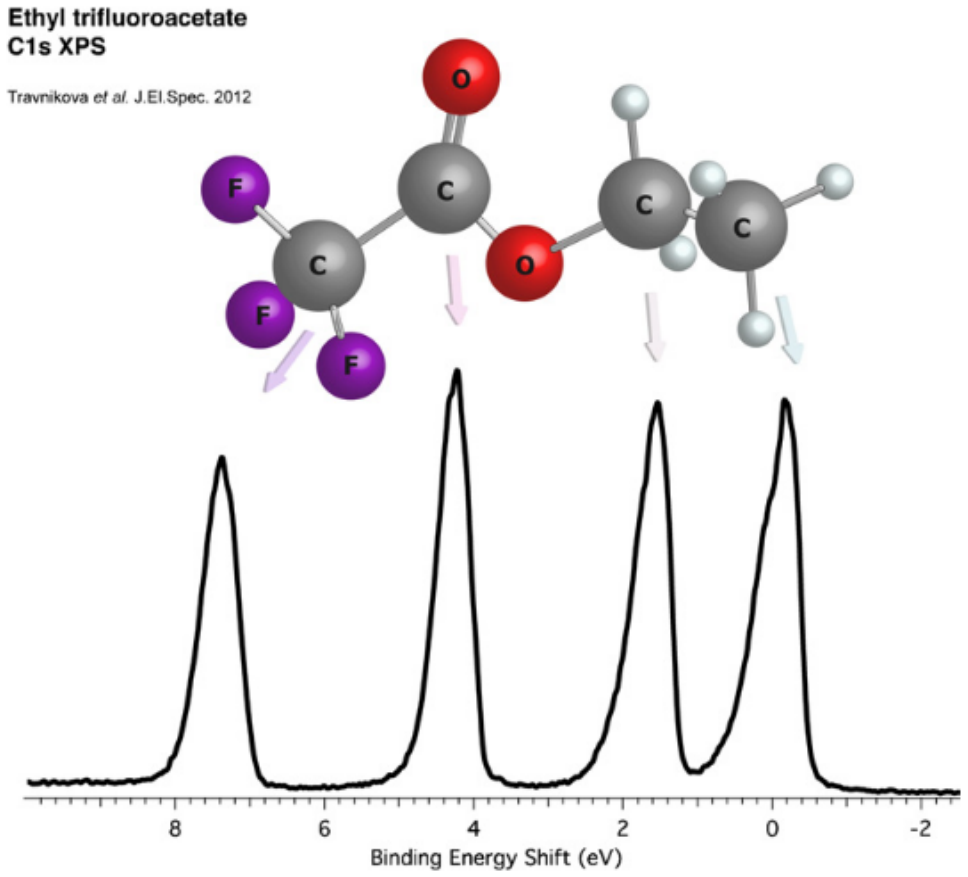
Core Electron Binding Energies

- How much work do we need to do, to remove a core electron from a given atom?
- E.g. the C 1s binding energy in gaseous CH_4 is 290.9 eV
- Measure experimentally, and find out about
  - Elemental composition of the sample
  - Chemical composition (?)

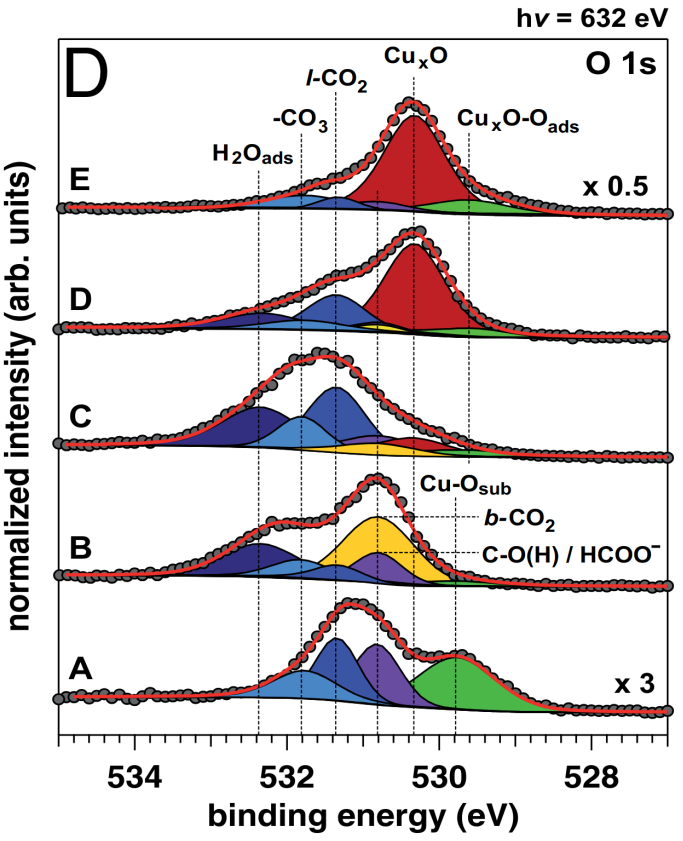
Core electron binding energies

- 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)

Why do we need theory?

- Let’s say we’ve measured a spectrum, but we are not sure, what the peaks mean.
- Can we work in the opposite direction?
  - Start with a structural model
  - Calculate, what the spectrum should look like
  - Then see, if the measured spectrum is consistent with our theoretical result

A computational approach to core level XPS

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

Core electron binding energy

Total energy of the N–1 electron final state with a core hole

Total energy of the N electron ground state

How to calculate E_B?

- Several approaches are possible
  - Koopmans' theorem and related methods
  - "Response" theories: GW, IP-CCSD, …
  - Total energy difference methods

How to calculate E_B?

- Koopmans' theorem
  - If all other electrons remain frozen, when one electron is removed from a system, then

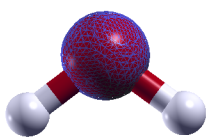
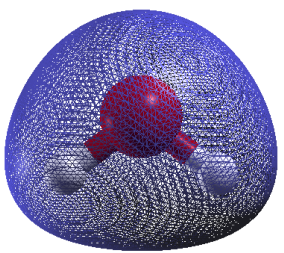
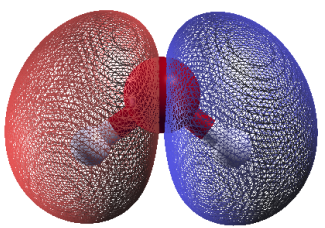
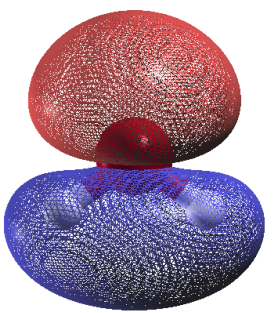
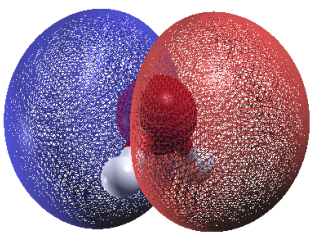
$$E_{N-1} - E_N = -\epsilon_k$$

$$E_B = -\epsilon_k$$

Orbital eigenvalue of the relevant core orbital from Hartree-Fock theory

Hartree-Fock theory: H_2O

- 10 electrons, 5 occupied orbitals

#	1	2	3	4	5
label	$1a_1$	$2a_1$	$1b_1$	$3a_1$	$1b_2$
ϵ (eV)	-560.24	-37.11	-19.94	-15.93	-13.94
χ					

Koopmans' theorem: H_2O

- H_2O: orbital eigenvalues vs binding energies from photoelectron spectroscopy
- Sources of error: correlations, neglect of orbital relaxation.

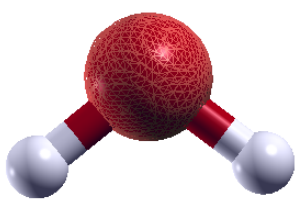
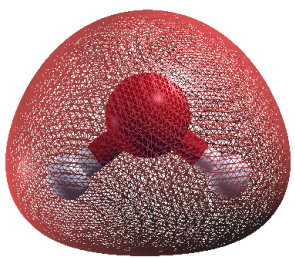
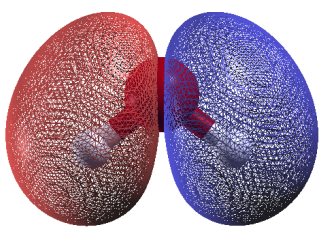
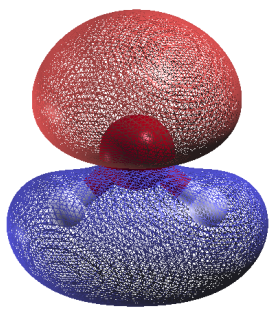
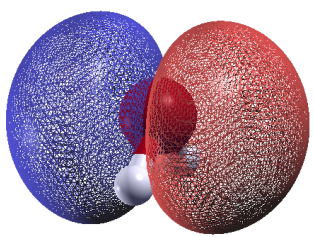
Orbital	$1a_1$	$2a_1$	$1b_1$	$3a_1$	$1b_2$
$-\epsilon$ (eV)	560.24	37.11	19.94	15.93	13.94
I.E. (eV)	539.9	32.2	18.5	14.7	12.6

Could we use orbital eigenvalues from DFT instead of Hartree-Fock theory?

Strictly, Koopmans' theorem does not hold for DFT, but we can still try...

Kohn-Sham DFT: H_2O

(using PBE xc functional)

#	1	2	3	4	5
label	$1a_1$	$2a_1$	$1b_1$	$3a_1$	$1b_2$
-ϵ (eV)	511.21	25.26	13.07	9.31	7.20
B.E. (expt.)	539.9	32.2	18.5	14.7	12.6
χ					

How to calculate E_B?

- Several approaches are possible
  - ~~Koopmans' theorem and related methods~~
  - "Response" theories: GW, IP-CCSD, …
  - Total energy difference methods

The remaining electrons do NOT remain frozen when a core electron is removed

Sometimes, Koopmans' theorem gives accurate binding energy shifts, but sometimes it doesn't (e.g. when final state screening is important)

How to calculate E_B?

- Several approaches are possible
  - Koopmans' theorem and related methods

    Cheap, but unreliable
  - "Response" theories: GW, IP-CCSD, …

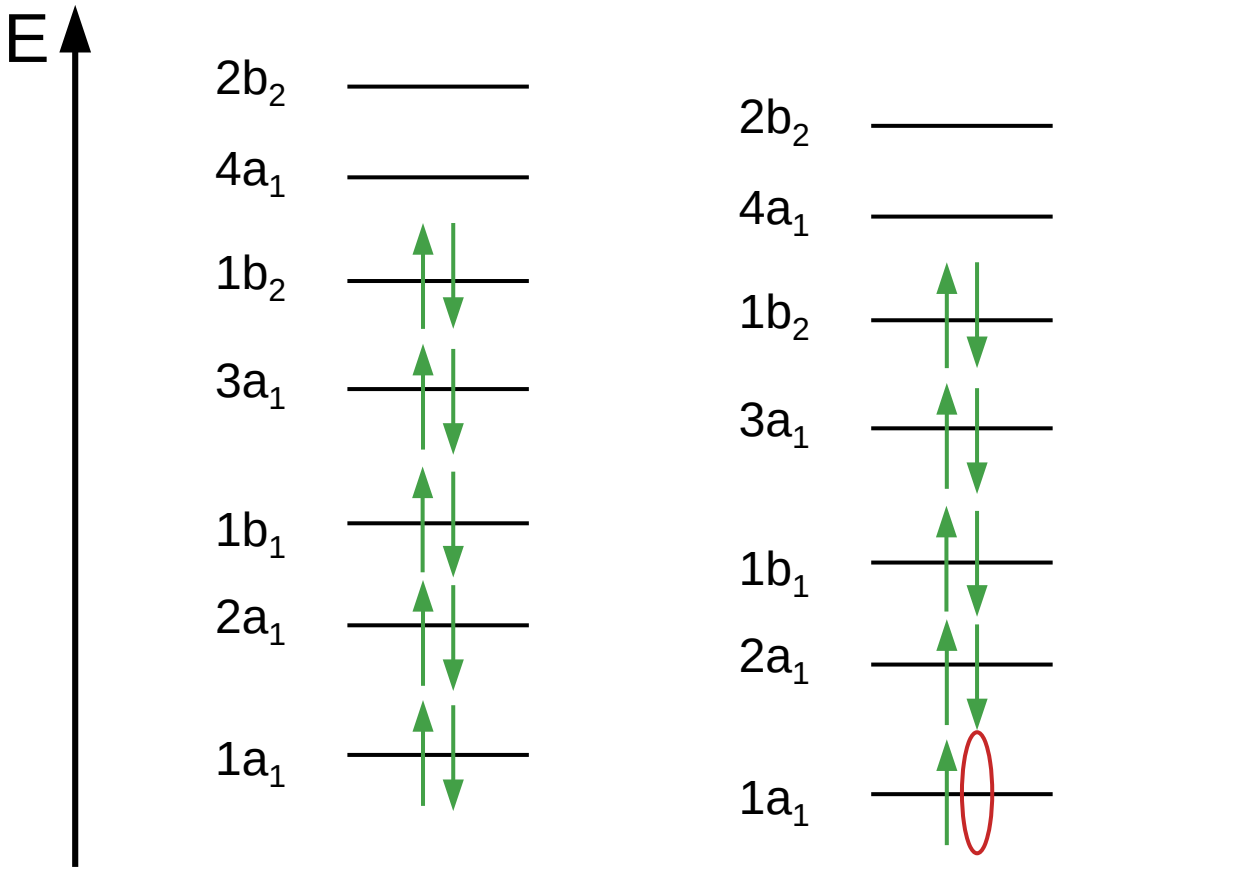
    In principle accurate, but expensive
  - Total energy difference methods

    The main topic of this talk

The Δ-Self-Consistent-Field method

- Evaluate $E_B = E_{N-1} - E_N$ by “brute force”, i.e. calculate E_N and E_{N-1} directly
- E_N is simply the ground state total energy
- How to calculate E_{N-1}?

ΔSCF method: H_2O example



Ground state

Final state with a core hole

The final state with a core hole is a

- high energy excited state
- of a radical cation ($H_2O^{+\bullet}$)

It would be challenging to calculate its energy using conventional excited state methods, e.g. CIS, TDDFT, EOM-CCSD, ...

Calculating E_{N-1}

For the core-hole state, we can instead perform

a self-consistent field calculation

with an excited electronic configuration

P.S. Bagus, *Phys. Rev.* **139**, A619 (1965)

Calculating E_{N-1}

For the core-hole state, we can instead perform

a self-consistent field calculation — DFT or Hartree-Fock

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Calculating E_{N-1}

For the core-hole state, we can instead perform

a self-consistent field calculation

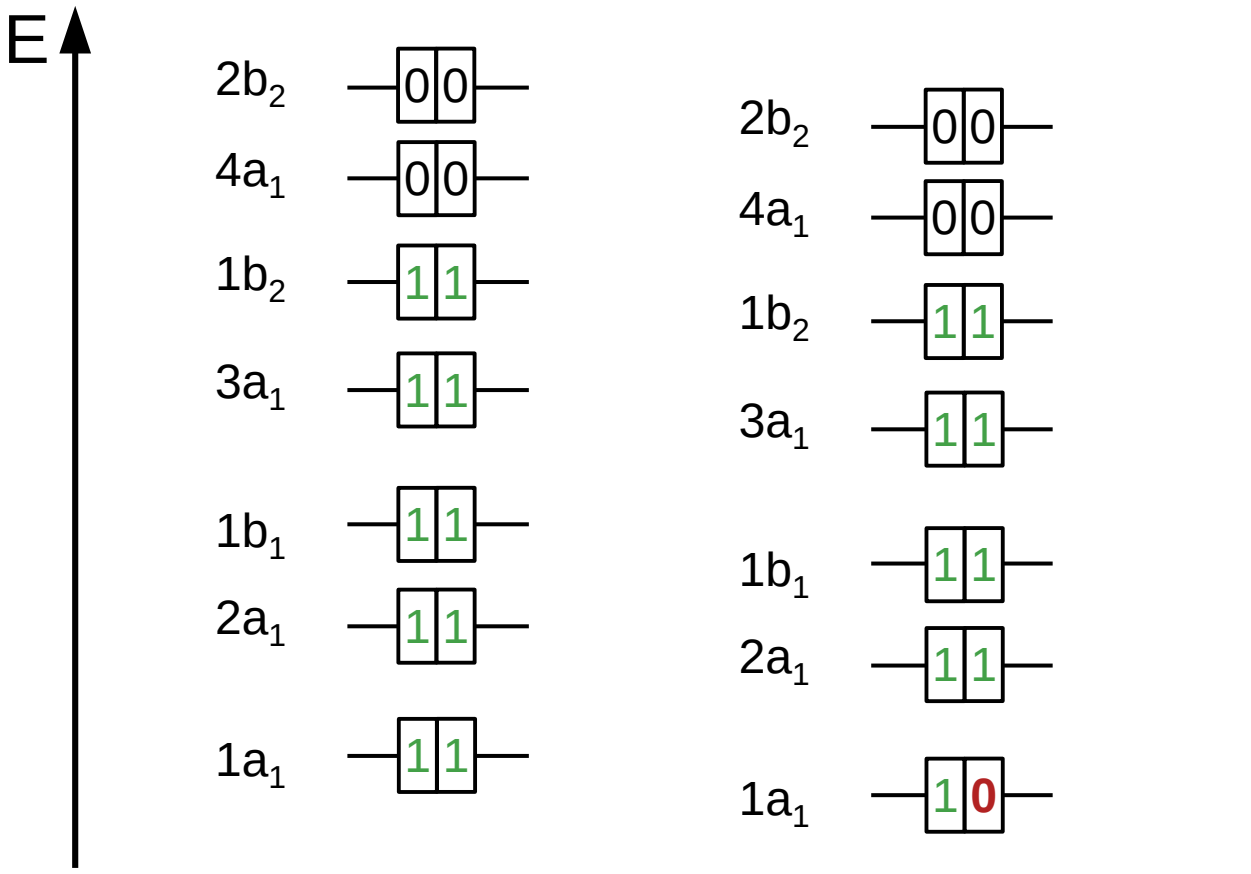
DFT or
Hartree-Fock

with an excited electronic configuration

i.e. non-Aufbau-principle
occupation numbers

P.S. Bagus, *Phys. Rev.* **139**, A619 (1965)

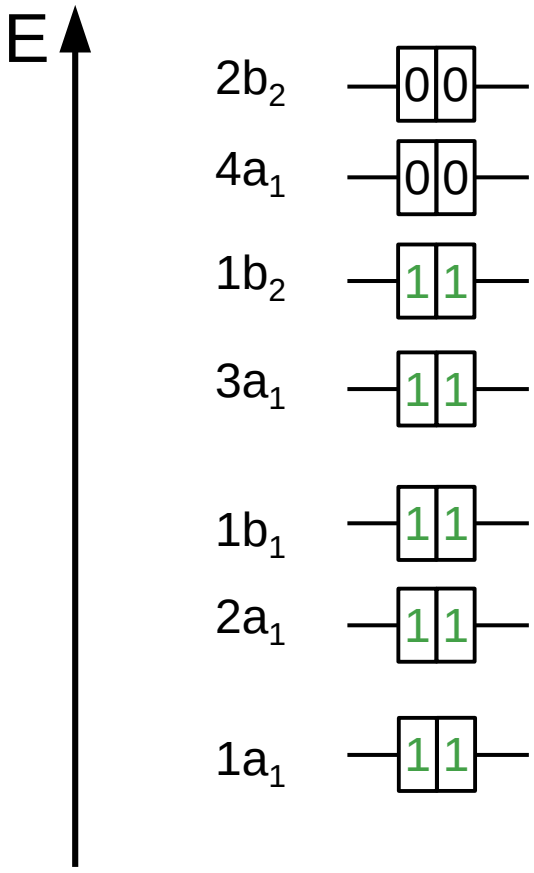
ΔSCF method: H_2O example



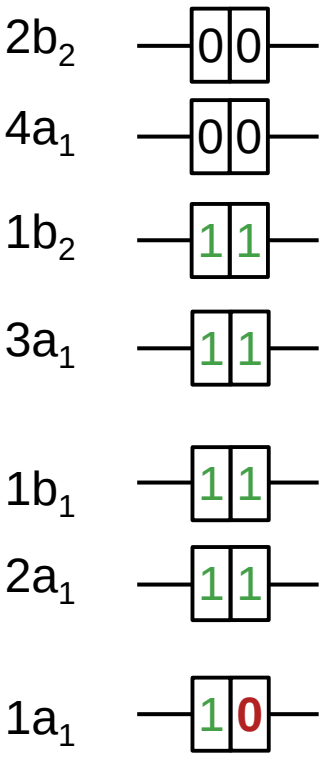
Ground state

Final state with a core hole

ΔSCF method: H_2O example



Ground state



Final state with a core hole

These values depend on the specific numerical settings: more on that later

Ground state E_{tot}: -2081.54 eV

Final state E_{tot}: -1541.72 eV

ΔSCF: 539.82 eV

Experimental B.E.: 539.9 eV

ΔSCF method

- Calculate core electron binding energies at the cost of 1 ground state DFT calculation per core level
  - How to run these calculations?
  - How well does it work?
  - Is it justified?

ΔSCF method

- Calculate core electron binding energies at the cost of 1 ground state DFT calculation per core level
  - How to run these calculations?
  - How well does it work?
  - Is it justified?
- This lecture: molecules (~ aperiodic systems)
- Tomorrow: solids and surfaces

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 method: H_2O example

- A number of DFT codes could be used, but the examples I will show are run in FHI-aims
  - All electron DFT with numerical atom-centered basis functions
  - Academic license: full source code distributed to all license holders, license fee can be reduced / waived upon request

www.fhi-aims.org

FHI-aims
The ab initio materials simulation package

ΔSCF method: H_2O example

- Try 1:
  - “Textbook” nonrelativistic Hamiltonian
  - PBE exchange-correlation functional
  - Default “tight” numerical basis functions

ΔSCF method: H_2O example

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ΔSCF method: H_2O example

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ΔSCF method: H_2O example

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- Ground state E_{tot}: -2078.63 eV
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- ΔSCF: 539.67 eV

ΔSCF method: H_2O example

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- Ground state E_{tot}: -2078.63 eV
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- ΔSCF: 539.67 eV

This is already quite close to the experimental value of 539.9 eV, but right now we are a bit lucky with error cancellation

ΔSCF method: H_2O example

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  - "Textbook" nonrelativistic Hamiltonian
  - PBE exchange-correlation functional
  - Default "tight" numerical basis functions
- Ground state E_{tot}: -2078.63 eV
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- ΔSCF: 539.67 eV

Close to the nucleus, electrons travel at speeds approaching the speed of light – for core electrons, relativistic effects matter even for light elements

ΔSCF method: H_2O example

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  - “Textbook” nonrelativistic Hamiltonian
  - PBE exchange-correlation functional
  - Default “tight” numerical basis functions
- Ground state E_{tot}: -2078.63 eV
- Final state E_{tot}: -1538.95 eV
- ΔSCF: 539.67 eV

The default basis set for O only has one basis function for the 1s orbital. This is optimized for the neutral O atom, not the O atom with a core hole.

ΔSCF method: H_2O example

- Try 2:
  - Relativistic effects via the “scaled ZORA” approximation
  - PBE exchange-correlation functional
  - Default “tight” basis for ground state, core-hole optimized basis for the final state
- Ground state E_{tot}: -2080.14 eV
- Final state E_{tot}: -1541.25 eV
- ΔSCF: 538.88 eV

ΔSCF method: H_2O example

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But now we are further from the experimental value of 539.9 eV!

ΔSCF method: H_2O example

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- Ground state E_{tot}: -2080.14 eV
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We could try using a different exchange-correlation functional

But now we are further from the experimental value of 539.9 eV!

ΔSCF method: H_2O example

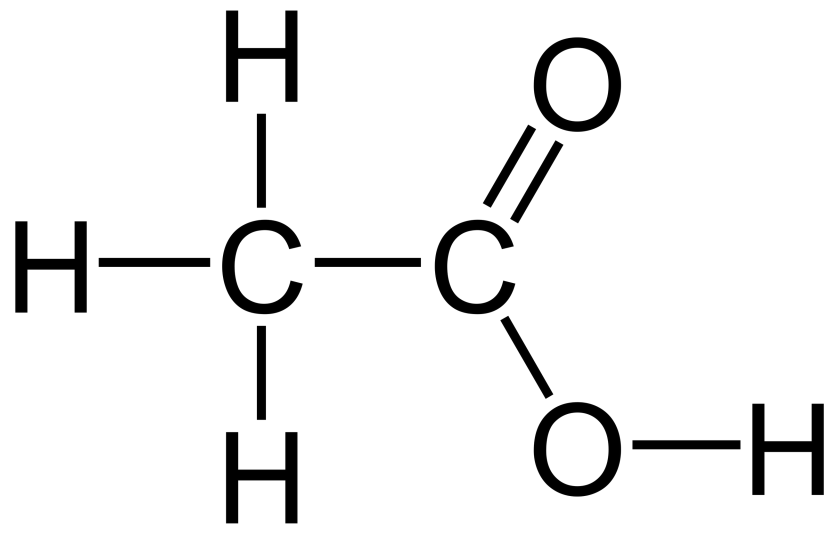
- With proper basis sets, and an adequate treatment of relativity, we get:
  - E_B = 538.88 eV (PBE)
  - E_B = 539.82 eV (SCAN)
  - E_B = 539.73 eV (B3LYP)
  - …
- C.f. experimental binding energy of 539.9 eV

ΔSCF method: H_2O example

- All reasonable functionals should give us relatively accurate binding energy shifts
  - But only some of them will give us accurate absolute binding energies
  - (And even then, probably not for all core levels of all elements)

ΔSCF method: CH_3COOH example

- Now we have two different C atoms. Let’s look at the molecular orbitals.



State	Occupation	Eigenvalue [Ha]	Eigenvalue [eV]	
1	2.00000	-19.027015	-517.75142	O 1s
2	2.00000	-18.967546	-516.13318	
3	2.00000	-10.182338	-277.07550	C 1s
4	2.00000	-10.056128	-273.64117	
5	2.00000	-1.079301	-29.36928	
6	2.00000	-0.991741	-26.98665	
7	2.00000	-0.732408	-19.92983	
8	2.00000	-0.581211	-15.81557	
9	2.00000	-0.463889	-12.62306	
10	2.00000	-0.450621	-12.26202	
11	2.00000	-0.444231	-12.08815	
12	2.00000	-0.387741	-10.55097	
13	2.00000	-0.371018	-10.09590	
14	2.00000	-0.367246	-9.99327	
15	2.00000	-0.301673	-8.20893	
16	2.00000	-0.251573	-6.84566	
17	0.00000	-0.028707	-0.78117	HOMO
18	0.00000	0.009953	0.27083	LUMO

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But which is $-CH_3$ and which $-COOH$?

ΔSCF method: CH_3COOH example

- To find the C 1s orbital for the -CH_3 group, we can
  - Visualize the orbitals themselves
  - Use Mulliken analysis (which basis functions contribute to which state)

State	Occupation	Eigenvalue [Ha]	Eigenvalue [eV]	
1	2.00000	-19.027015	-517.75142	O 1s
2	2.00000	-18.967546	-516.13318	O 1s
3	2.00000	-10.182338	-277.07550	C 1s (-COOH)
4	2.00000	-10.056128	-273.64117	C 1s ($-CH_3$)
5	2.00000	-1.079301	-29.36928	
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ΔSCF method: CH_3COOH example

- Let’s run a calculation with a core hole in the fourth eigenstate. (-CH_3 C 1s)

ΔSCF method: CH_3COOH example

- Let’s run a calculation with a core hole in the fourth eigenstate. (-CH_3 C 1s)
- ΔSCF result = 291.52 eV
- Experimental B.E. = 291.6 eV

- Look at eigenvalues just in case:

```
Spin-up eigenvalues:

State    Occupation    Eigenvalue [Ha]    Eigenvalue [eV]
    1       1.00000         -19.235958         -523.43705
    2       1.00000         -19.190978         -522.21307
    3       0.00000         -10.882778         -296.13545
    4       1.00000         -10.455453         -284.50736
```

- Missing electron in eigenstate number 3!

- Look at eigenvalues just in case:

```
Spin-up eigenvalues:

State    Occupation    Eigenvalue [Ha]    Eigenvalue [eV]
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```

- Missing electron in eigenstate number 3!
- Maximum Overlap Method (MOM) was used to keep track of the core hole.

Keeping track of the core hole

- FHI-aims provides two keywords for specifying the eigenstate, whose occupation number you want to constrain

Keeping track of the core hole

- FHI-aims provides two keywords for specifying the eigenstate, whose occupation number you want to constrain
- `deltascf_projector`
  - Provide initial orbitals (e.g. from a ground state calculation)
  - Specify the index of the constrained state
  - Keep track of that orbital throughout the SCF cycle using the maximum overlap method

Keeping track of the core hole

- FHI-aims provides two keywords for specifying the eigenstate, whose occupation number you want to constrain
- `deltascf_basis`
  - Specify a particular basis function, e.g. an atomic “1s” basis function on a specific C atom
  - During each SCF iteration, the occupation constraint is applied to the Kohn-Sham orbital with the highest contribution from that basis function

ΔSCF method: CH_3COOH example

- ΔSCF: 291.52 eV (-CH_3), 295.21 eV (-COOH)
- Experiment: = 291.6 eV (-CH_3), 295.5 eV (-COOH)

ΔSCF method: N_2 example

- Proceed as before:
  - Ground state calculation: write wavefunction to disk
  - Core hole calculation: load wavefunction from disk, create hole in the lowest eigenstate, and keep track of the core hole using the MOM
  - ΔSCF result = 404.76 eV
  - Experimental N 1s B.E. = 409.9 eV
  - What went wrong?

ΔSCF method: N_2 example

- What went wrong?
  - Check Mulliken analysis => the core hole is delocalized across the two N atoms
  - We need to localize the core hole. Breaking the symmetry is usually enough – e.g. by using a core-hole adaped basis set on only one atom
  - Now: Calculated B.E. = 409.97 eV, c.f. experimental B.E. = 409.9 eV

ΔSCF method: core hole localization

- In a ΔSCF calculation, the core hole must always be localized on one atom to get meaningful results
- In almost all systems, this is also physically the correct picture
- However, ironically, in N_2, the core hole is probably actually delocalized: see Ueda et al., *Eur. Phys. J. Special Topics* **169**, 95 (2009)

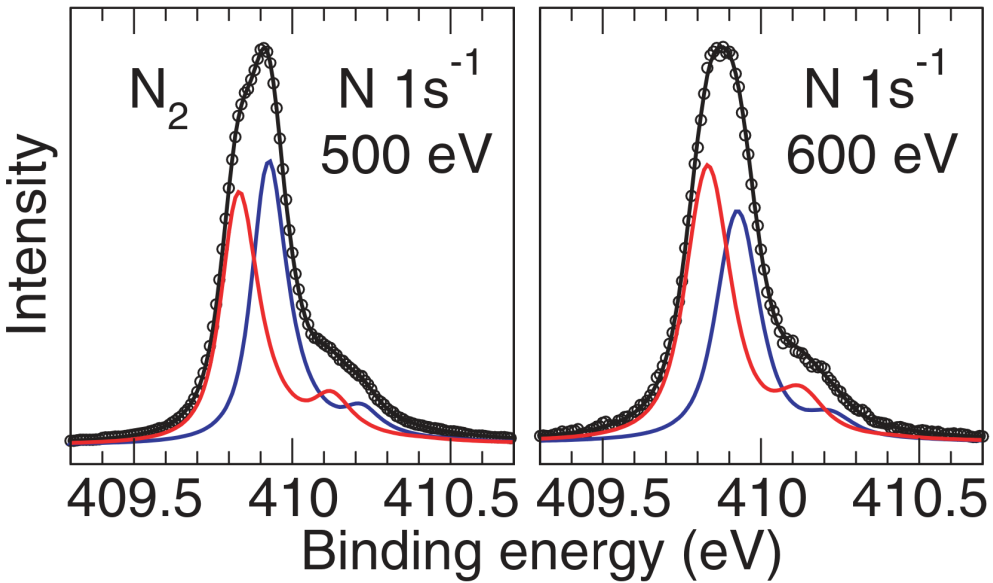


Fig. 2. N 1*s* photoelectron spectra of N_2 recorded at photon energies of 500 eV and 600 eV. The solid lines through the data points represent the fit results. The blue and red subspectra indicate the contributions from the $1\sigma_g$ and $1\sigma_g$ components, respectively.

Figure 2 from Ueda et al., Eur. Phys. J. Special Topics 169, 95 (2009)

ΔSCF method: core hole localization

- ΔSCF – final state wavefunction is a single Slater determinant
- Real life – delocalized core hole in N_2 correctly described using configuration interaction theory
- In this case, the need for localization stems from a limitation of the ΔSCF approach
- In most real systems, vibrations decouple core orbitals – core holes really are localized

ΔSCF method: H_2S example

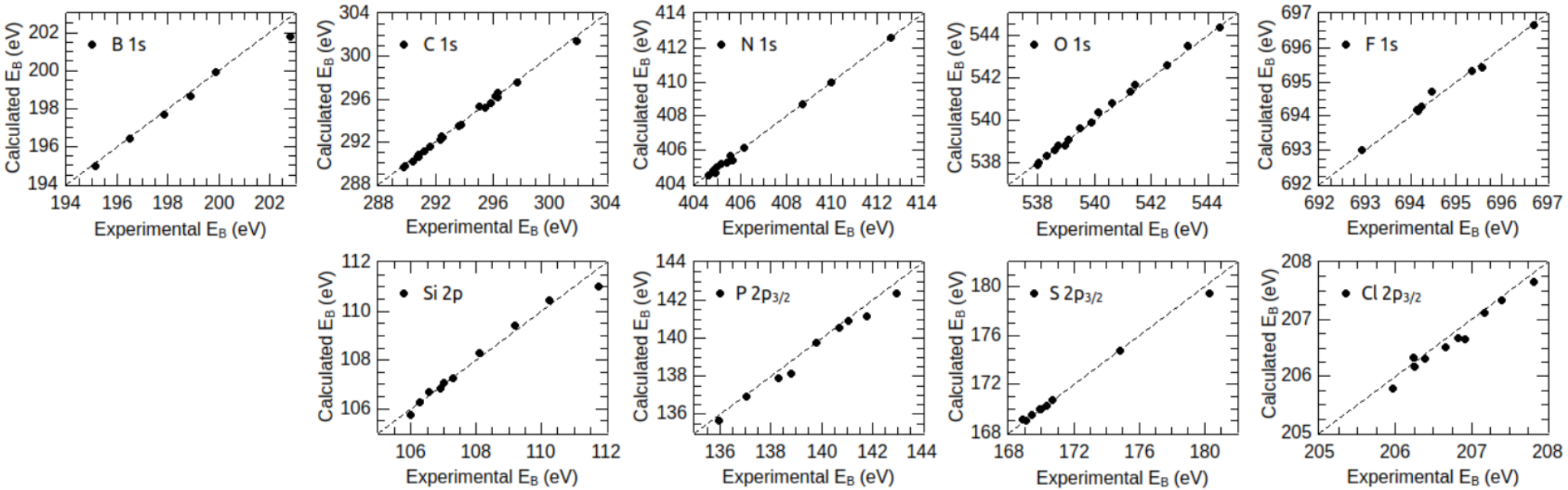
- Experimentally reported S $2p_{3/2}$ binding energy 170.32 eV
- Most codes (incl. FHI-aims) only permit scalar-relativistic ΔSCF calculations
- Workaround: calculate scalar relativistic 2p binding energy, then subtract 1/3 of the splitting to get theoretical $2p_{3/2}$ result

Spin-orbit splitting of S 2p core level, i.e. separation between the $2p_{3/2}$ and $2p_{1/2}$ peaks is 1.16 eV

ΔSCF method: performance

- Numerical settings used for benchmarking:
  - SCAN
  - scaled ZORA relativity
  - FHI-aims with core-enhanced numerical basis sets for the atoms with a core hole

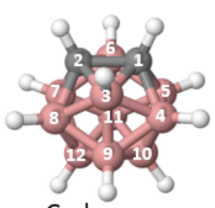
Performance – small molecules



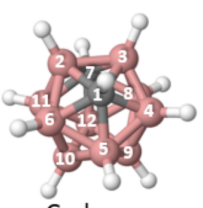
MAE = 0.16 eV for 103 binding energies from gas phase XPS

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

Performance – slightly bigger molecules

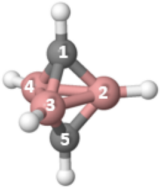


o-Carborane
$1,2\text{-}C_2B_{10}H_{12}$

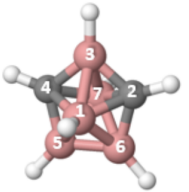


m-Carborane
$1,7\text{-}C_2B_{10}H_{12}$

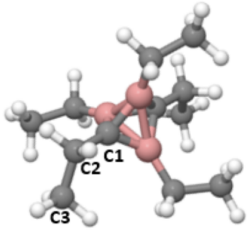
$2,3\text{-}C_2B_4H_8$



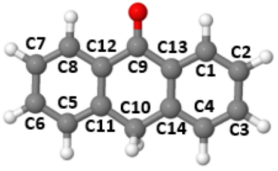
$1,5\text{-}C_2B_3H_5$



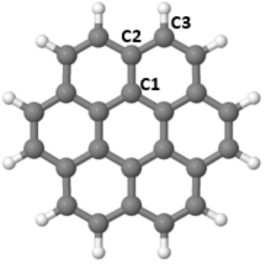
$2,4\text{-}C_2B_5H_7$



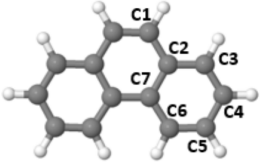
$1,5\text{-}C_2B_3(C_2H_5)_5$



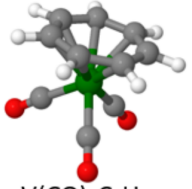
Anthrone
$C_{14}H_{10}O$



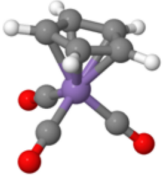
Coronene
$C_{24}H_{12}$



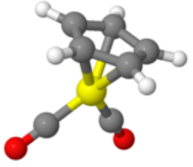
Phenanthrene
$C_{14}H_{10}$



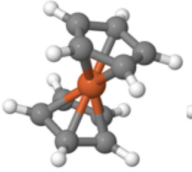
$V(CO)_3C_7H_7$



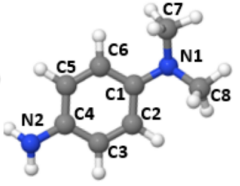
$Mn(CO)_3C_5H_5$



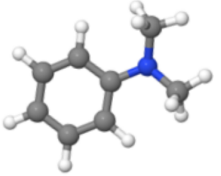
$Co(CO)_2C_5H_5$



$Fe(C_5H_5)_2$



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

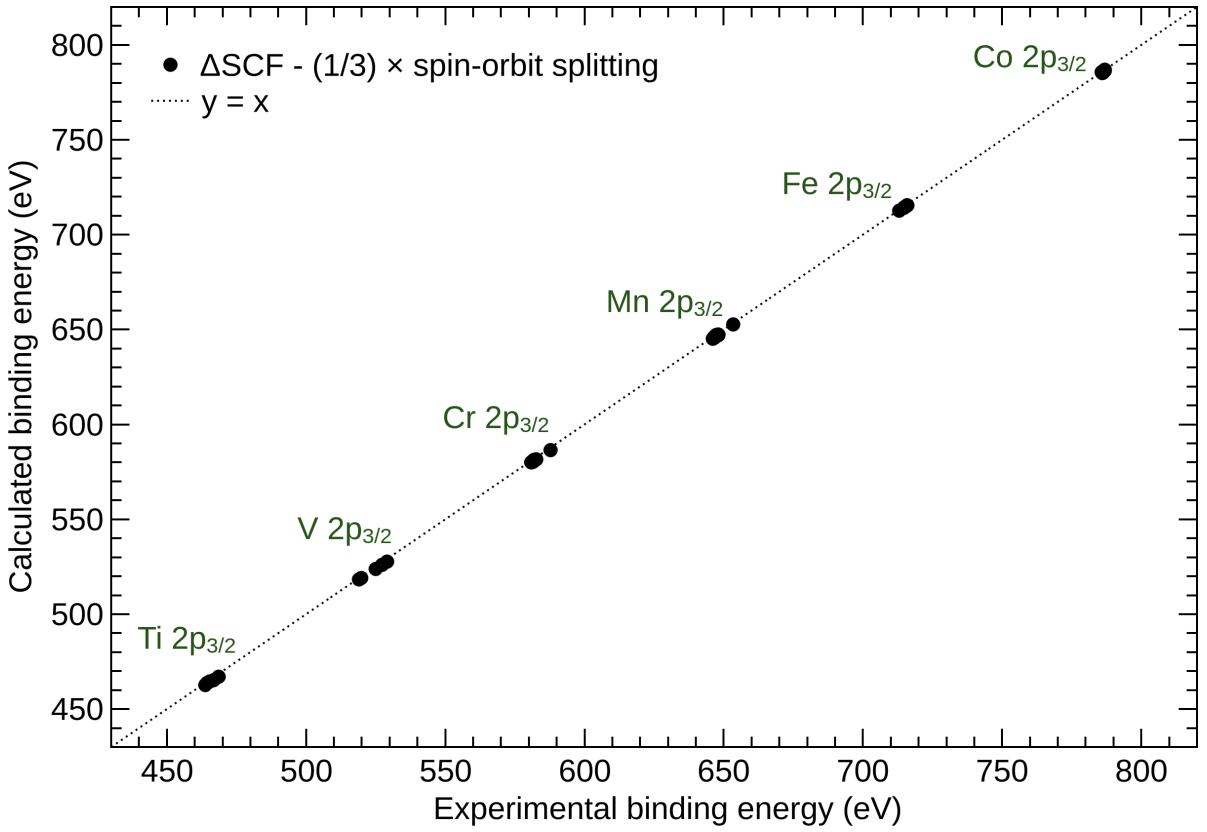


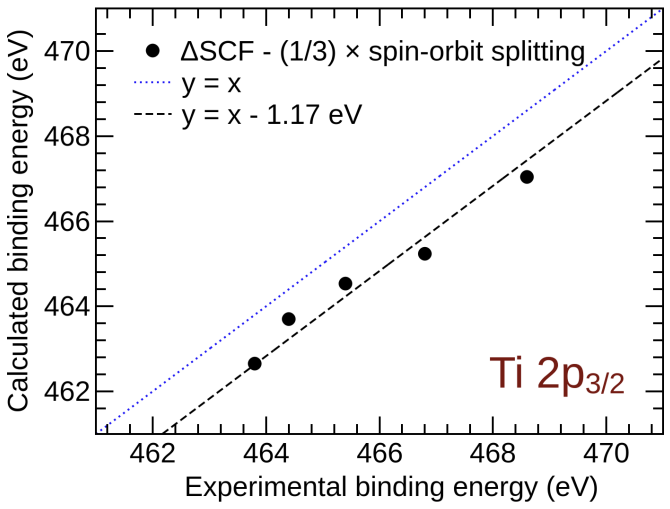
N,N-dimethylaniline
$C_8H_{11}N$

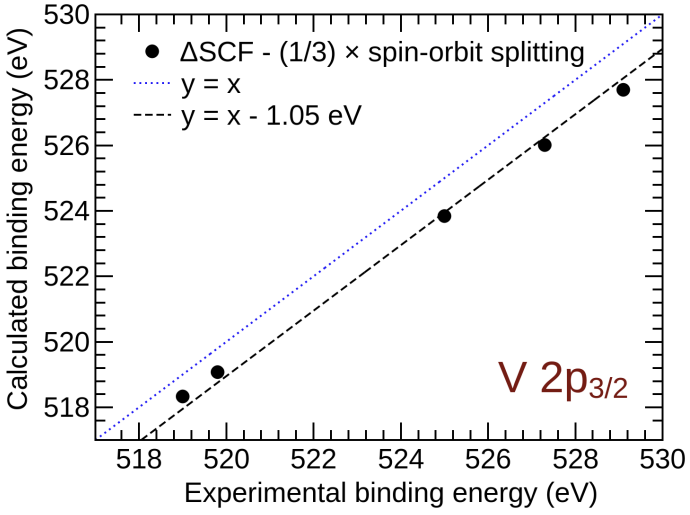
Performance – slightly bigger molecules

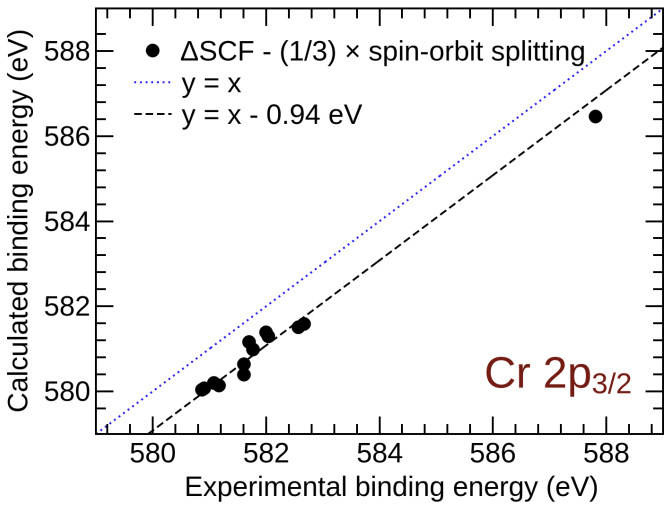
- Mean absolute error (SCAN) = 0.19 eV
- Mean error (SCAN) = -0.05 eV
- Mean absolute error (B3LYP) = 0.19 eV
- Mean error (B3LYP) = 0.06 eV

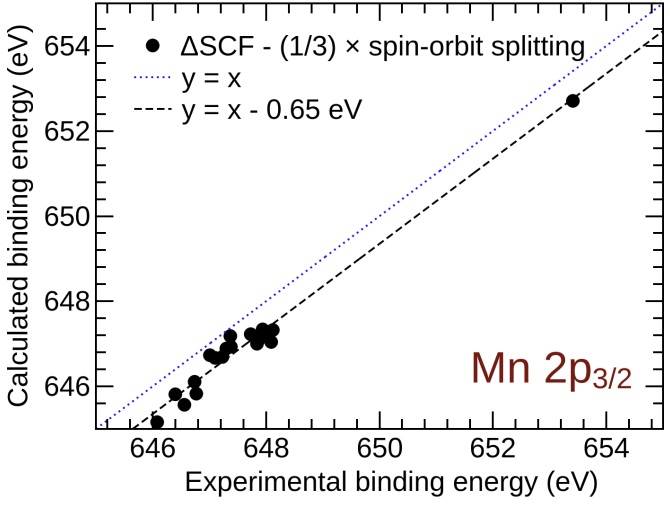
Performance – small molecules, heavier elements

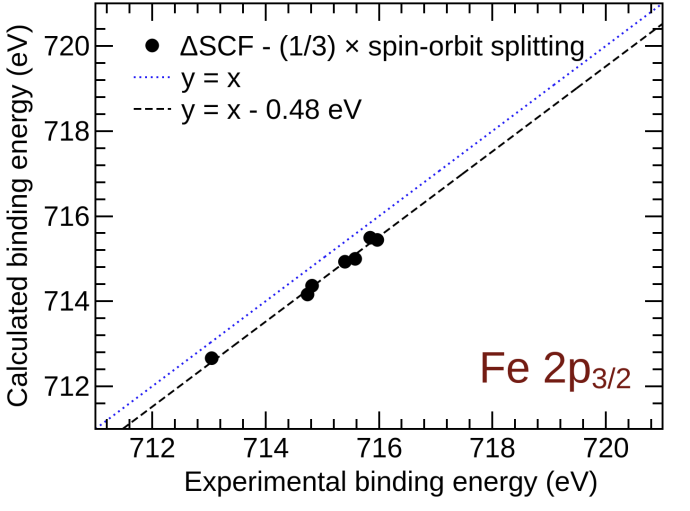


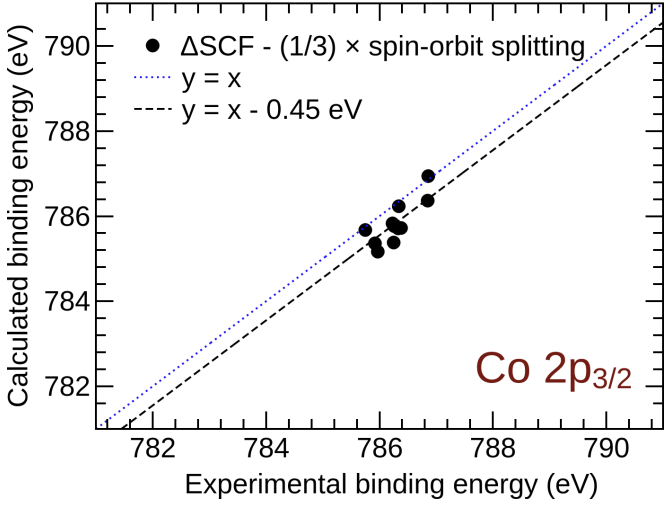

ΔSCF - (1/3) × spin-orbit splitting
y = x
y = x - 1.17 eV
Ti 2p3/2
Calculated binding energy (eV)
Experimental binding energy (eV)
462
464
466
468
470

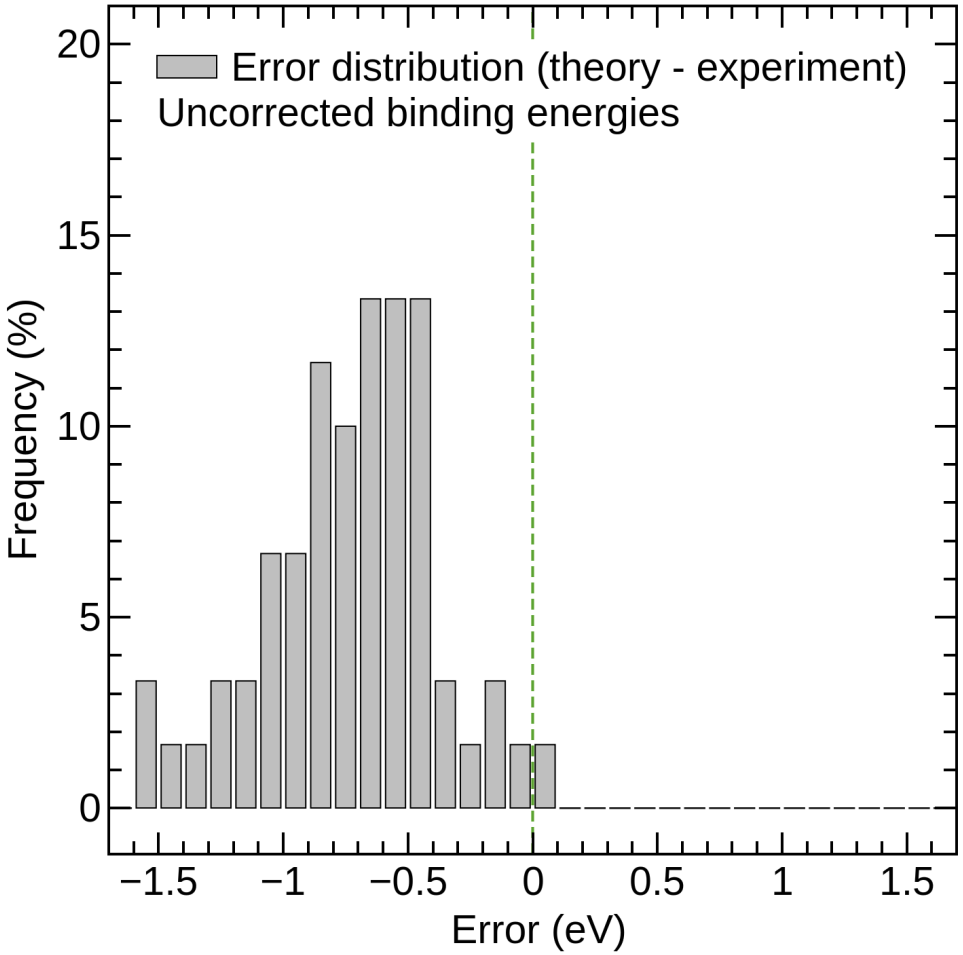

ΔSCF - (1/3) × spin-orbit splitting
y = x
y = x - 1.05 eV
V 2p3/2
Calculated binding energy (eV)
Experimental binding energy (eV)
518
520
522
524
526
528
530

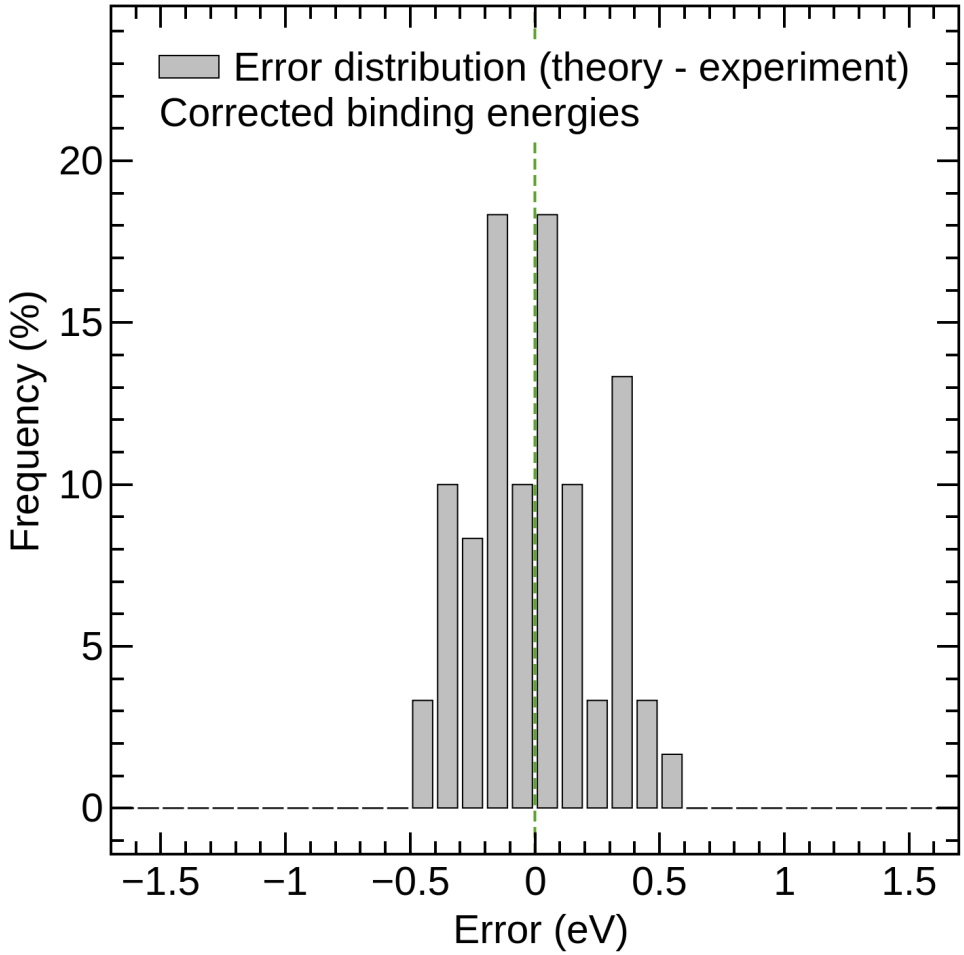

ΔSCF - (1/3) × spin-orbit splitting
y = x
y = x - 0.94 eV
Cr 2p3/2
Calculated binding energy (eV)
Experimental binding energy (eV)
580
582
584
586
588


ΔSCF - (1/3) × spin-orbit splitting
y = x
y = x - 0.65 eV
Mn 2p3/2
Calculated binding energy (eV)
Experimental binding energy (eV)
646
648
650
652
654


ΔSCF - (1/3) × spin-orbit splitting
y = x
y = x - 0.48 eV
Fe 2p3/2
Calculated binding energy (eV)
Experimental binding energy (eV)
712
714
716
718
720


ΔSCF - (1/3) × spin-orbit splitting
y = x
y = x - 0.45 eV
Co 2p3/2
Calculated binding energy (eV)
Experimental binding energy (eV)
782
784
786
788
790


Error distribution (theory - experiment)
Uncorrected binding energies
Frequency (%)
Error (eV)
0
5
10
15
20
−1.5
−1
−0.5
0
0.5
1
1.5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Corrected binding energies
Frequency (%)
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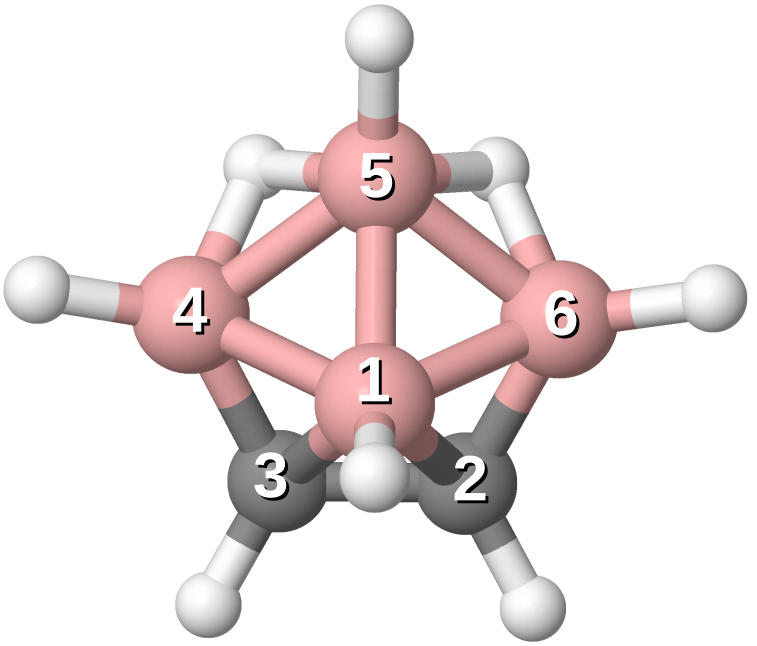
0
5
10
15
20
−1.5
−1
−0.5
0
0.5
1
1.5

Molecules – some interesting results

Core electron binding energies in 2,3-$C_2B_4H_8$			
Core level	Theory	Experiment*	Error
B 1s (1)	195.47	196.0	-0.53
B 1s (5)	195.92	195.7	0.22
B 1s (4, 6)	195.17	195.2	-0.03
C 1s	290.83	290.9	-0.07



* Allison et al., *J. Electron Spectrosc. Relat. Phenom.* **1**, 269 (1972)

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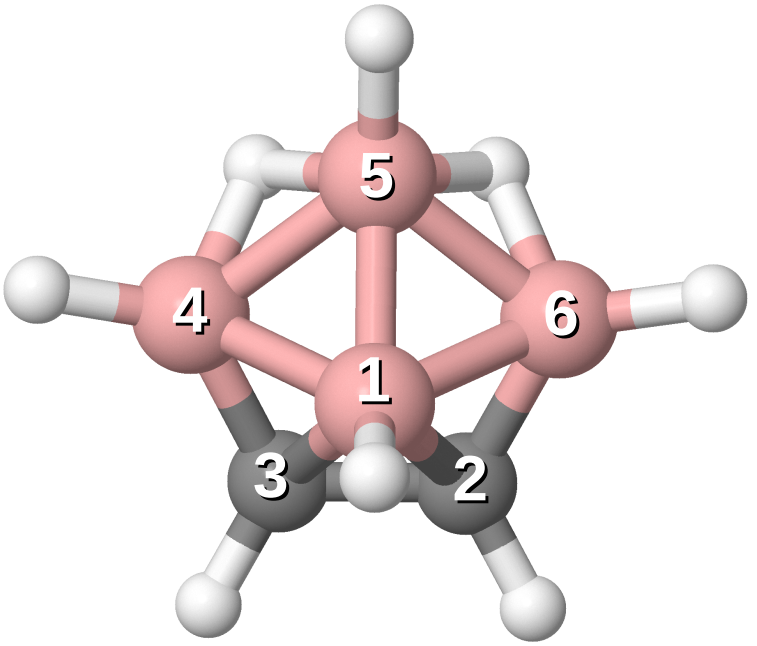

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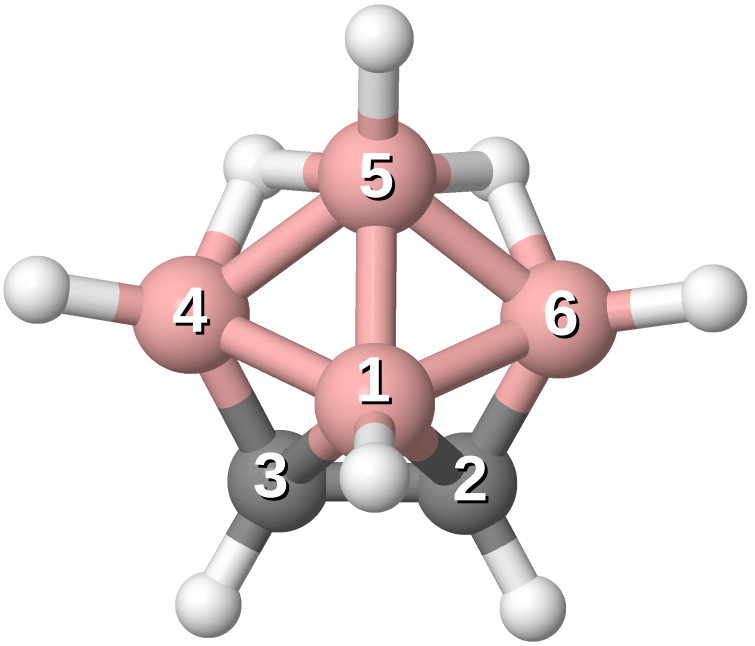
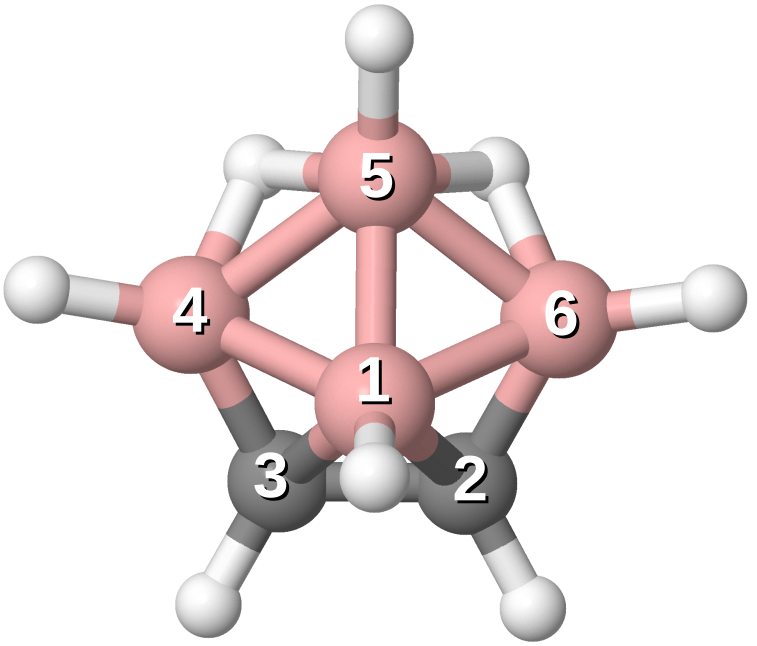


* Allison et al., *J. Electron Spectrosc. Relat. Phenom.* **1**, 269 (1972)

Molecules – some interesting results

Core electron binding energies in 2,3-$C_2B_4H_8$			
Core level	Theory	Experiment*	Error
B 1s (1)	195.47	195.7	-0.23
B 1s (5)	195.92	196.0	-0.08
B 1s (4, 6)	195.17	195.2	-0.03
C 1s	290.83	290.9	-0.07



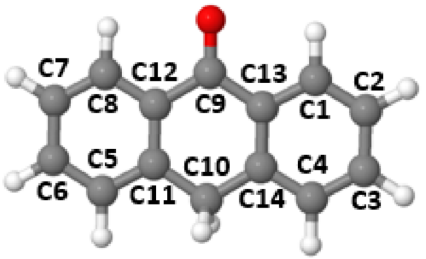
* Allison et al., *J. Electron Spectrosc. Relat. Phenom.* **1**, 269 (1972)

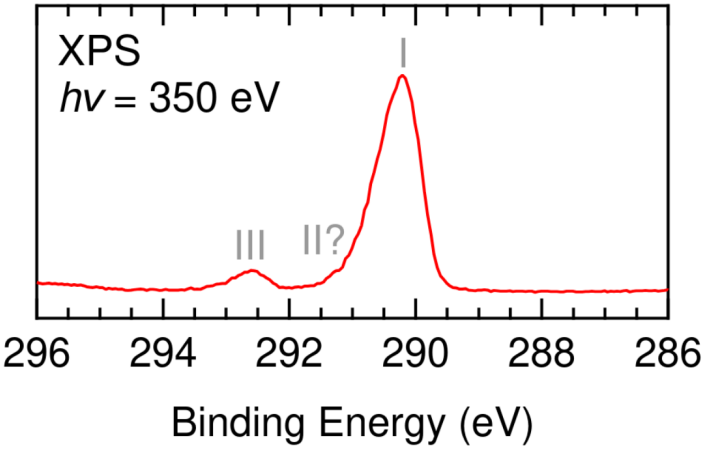
Molecules – some interesting results

- Errors of > 1 eV reported for calculated C 1s and O 1s binding energies in anthrone.
  - *J. Chem. Theory Comput.* **14**, 4856 (2018)
- “For medium-sized to large molecules, the accuracy of ΔSCF can quickly reduce by an order of magnitude”
  - *J. Phys. Chem. Lett.* **11**, 1840 (2020)

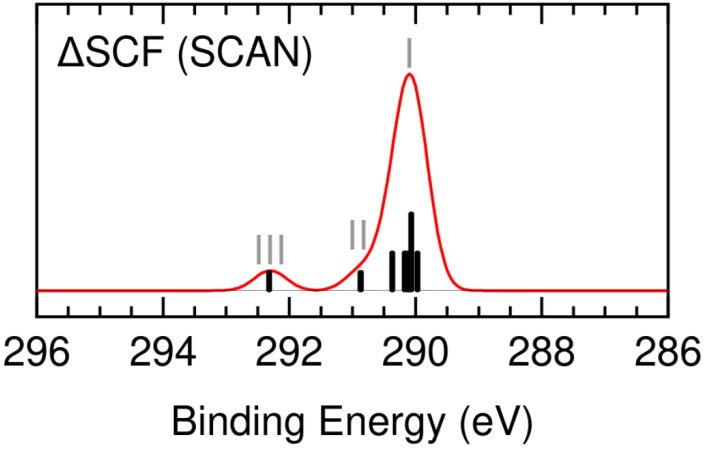
Molecules – some interesting results

Remeasured gas phase XPS on anthrone at FinEstBeAMS





Core level	Theory	Experiment	Error
C 1s (1-8, 11-14)	290.11	290.3	-0.19
C 1s (10)	290.85	290.9	-0.05
C 1s (9)	292.28	292.7	-0.42
O 1s	536.25	536.6	-0.35



Summary - molecules

- Calculate core electron binding energies at the cost of two ground state DFT calculations
- Binding energy shifts: relatively easy
- Absolute binding energies: possible
  - 1s core level in 2nd row elements, 2$p_{3/2}$ in 3rd row elements
  - Heavier elements – so far only if an element- and method-specific empirical correction is known
- Localization of the core hole onto the correct atom is critical
- Very little work thus far on “strongly correlated” systems