Ab initio calculations of core-level XPS spectra

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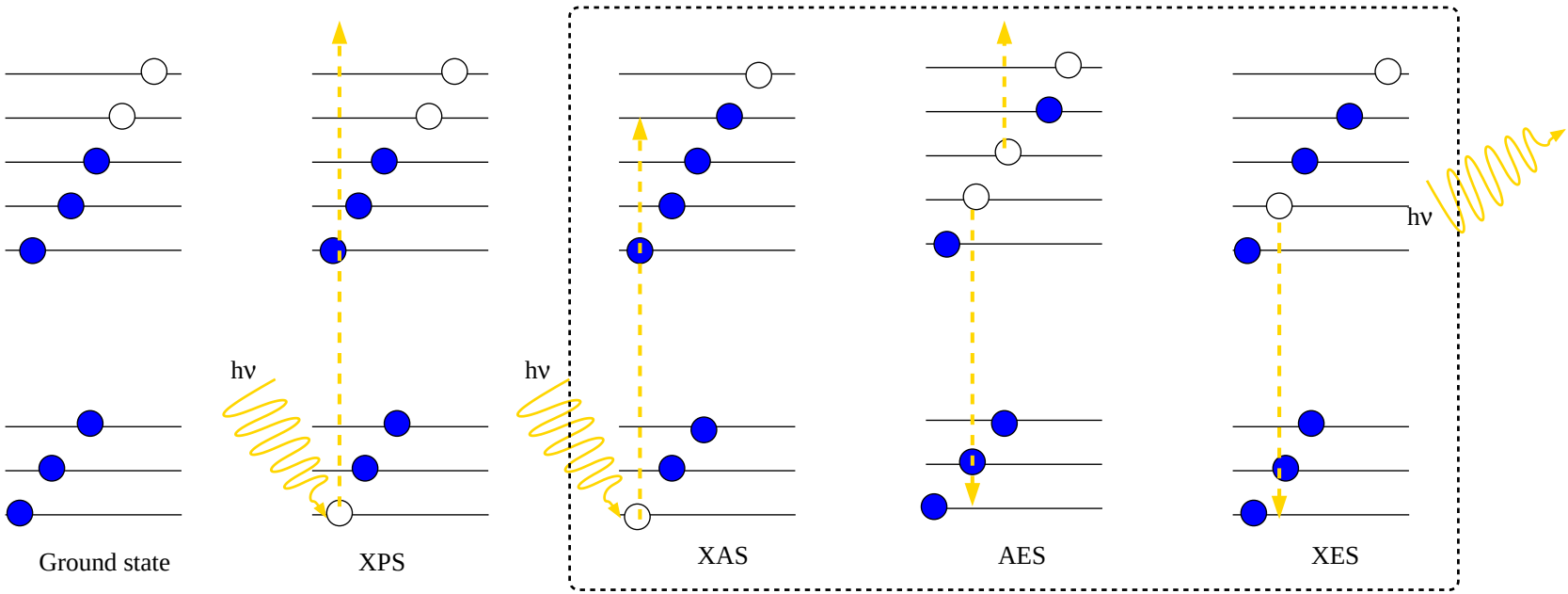
Core-level X-ray spectroscopies

Core-level spectroscopies are used as local probe to investigate the electronic structure, but also the atomic structure, phase transitions...



A very long story...

- From Röntgen in 1895, and Einstein in 1905...
- ...going through Mahan, Nozières and DeDominicis at the end of the sixties (the edge singularity, the so-called "MND problem", see Ref.[1])...
- ...to the implementation of XAS[2] and XES[3] in ABINIT...
- ...and the implementation of core-level XPS in a FLAPW code[4].

Aim: implement this latter method, able to provide a full XPS spectrum. Other methods, less demanding in computational cost, are available if we are only interested in the core-level shift.

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[1] K. Ohtaka and Y. Tanabe, RMP **62**, 929 (1990).

[2] S. Mazevet and G. Zérah, PRL **101**, 155001 (2008). V. Recoules and S. Mazevet, PRB **80**, 064110 (2009).

[3] S.M. Vinko *et al.*, PRL **104**, 225001 (2010).

[4] M. Takahashi, J.-I. Igarashi and N. Hamada, PRB **78**, 155108 (2008). M. Takahashi and J.-I. Igarashi, PRB **81**, 035118 (2010).

1. Theoretical background
   - *The MND problem*
   - *Final states*
   - *Overlap integral*
2. Implementation in the ABINIT code
   - *How to create a core-hole?*
   - *The PAW approach*
   - *Methodology – Flow chart*
3. Results
   - *Application to the 3s core-level of iron*
4. Conclusions

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The MND problem

Let us define the initial (i) and final (f) wavefunctions, Ψ^i and Ψ^f respectively, as Slater determinants:

Wave functions of the ground and final states

$$\left|\Psi^i\right\rangle = |\psi^i, \Psi^i_N|$$

$$\left|\Psi^f\right\rangle = |\psi^f, \Psi^f_N|$$

For an x-ray photon with energy $h\nu$, the probability to detect a photoelectron (ϵ, σ) is:

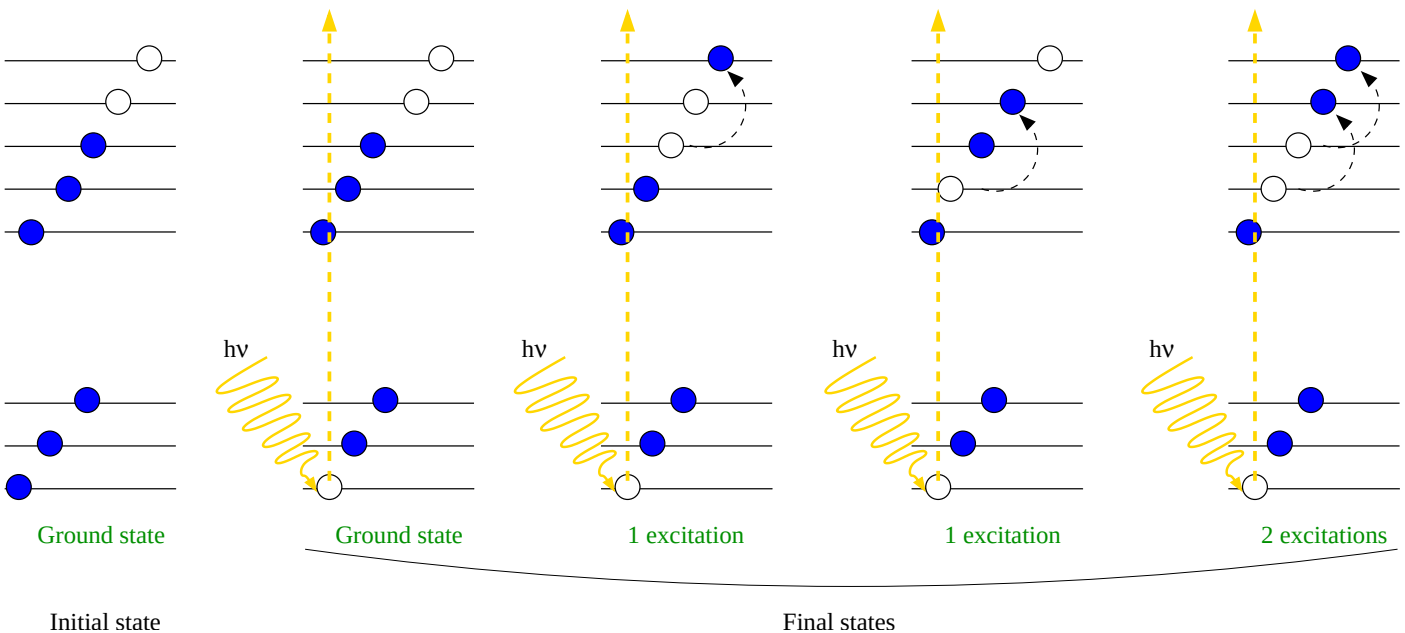
XPS intensity

$$I_\sigma^{XPS}(h\nu - \epsilon) = 2\pi |\left\langle \psi^f \left| \mathcal{O}_\sigma \right| \psi^i \right\rangle|^2 \sum_f |\langle \Psi^f_N | \Psi^i_N \rangle|^2 \delta(h\nu - \epsilon + E_i - E_f)$$

with $\mathcal{O}_\sigma$ the annihilation operator.

Final states: terminology about excitations

- initial (ground) state i with no core-electron removed.
- final (ground and excited) states f with an electron removed from an inner-shell.
  Some "valence excitations" can also occur in the upper shells $\rightarrow$ satellites (shake-up processes) and we have to sum over all these final states f:



Overlap integral: ground state of the final state

In order to compute the overlap $\langle \Psi_N^f | \Psi_N^i \rangle$, we can define[5] an operator $\mathcal{A}$ such as:

Without any excitation

$$\langle \Psi^f | \Psi^i \rangle = det\mathcal{A} = \Delta = \begin{vmatrix} a_{11} & a_{12} & \dots & a_{1N} \\ a_{21} & a_{22} & \dots & a_{2N} \\ \vdots & \vdots & \ddots & \vdots \\ a_{N1} & a_{N2} & \dots & a_{NN} \end{vmatrix}$$

with $(\mathcal{A})_{\alpha\alpha'} = a_{\alpha\alpha'} = \langle \psi_\alpha | \psi_{\alpha'} \rangle$. The subscript α replaces the **k**-point, spin and band indices.

[5] K. Ohtaka and Y. Tanabe, RMP **62**, 929 (1990)

Overlap integral: ground state of the final state

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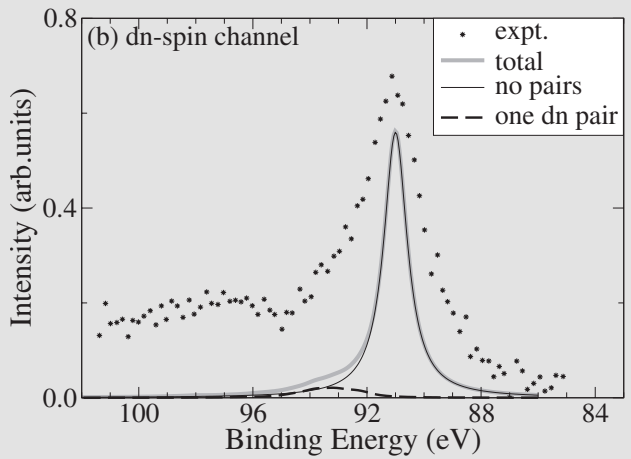


Without any valence excitations, the XPS spectrum is reduced to its main peak, with Δ its intensity.

[5] K. Ohtaka and Y. Tanabe, RMP **62**, 929 (1990)

Overlap integral: one excitation

For an excitation $f = (\mu;\gamma)$, from the occupied state μ to the empty one γ, the overlap becomes:

For only one excitation

$$\Delta(\mu;\gamma) = \begin{vmatrix} a_{11} & \dots & a_{1N} \\ \vdots & & \vdots \\ a_{\gamma 1} & \dots & a_{\gamma N} \\ \vdots & & \vdots \\ a_{N1} & \dots & a_{NN} \end{vmatrix}$$

- Here, we replace the μth row by $(a_{\gamma 1}, a_{\gamma 2}, \dots, a_{\gamma N})$.
- We have to compute such a determinant for all the excitations going from an occupied state (1 among $\mathrm{N_{occ}} = N$) to an unoccuppied one (1 among $\mathrm{N_{unocc}}$)
  $\longrightarrow N_{\mathrm{occ}} \times N_{\mathrm{unocc}}$ determinants.

Overlap integral: two excitations

For an excitation $f = (\mu_1, \mu_2; \gamma_1, \gamma_2)$, from the states μ_1 and μ_2 to the states γ_1 and γ_2:

For two excitations

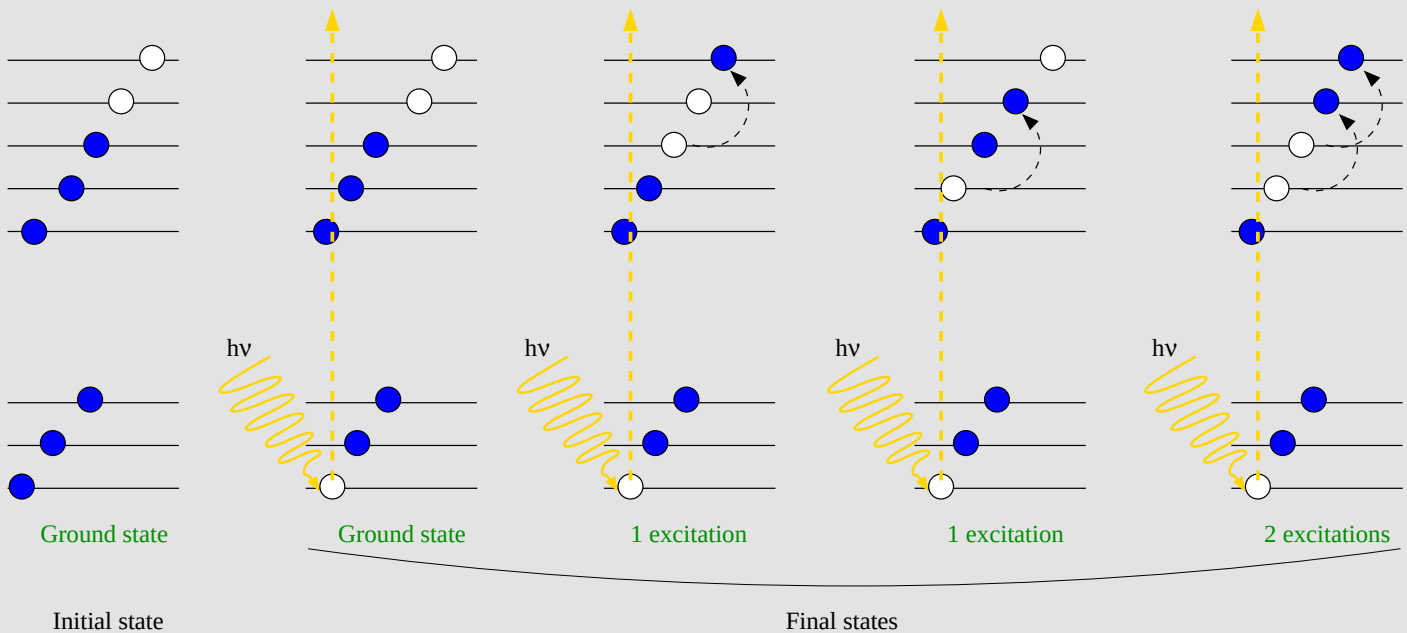
$$\Delta(\mu_1,\mu_2;\gamma_1,\gamma_2) = \begin{vmatrix} a_{11} & \dots & a_{1N} \\ \vdots & & \vdots \\ a_{\gamma_1 1} & \dots & a_{\gamma_1 N} \\ \vdots & & \vdots \\ a_{\gamma_2 1} & \dots & a_{\gamma_2 N} \\ \vdots & & \vdots \\ a_{N1} & \dots & a_{NN} \end{vmatrix} \rightarrow \Delta \begin{vmatrix} \frac{\Delta(\mu_1;\gamma_1)}{\Delta} & \frac{\Delta(\mu_1;\gamma_2)}{\Delta} \\ \frac{\Delta(\mu_2;\gamma_1)}{\Delta} & \frac{\Delta(\mu_2;\gamma_2)}{\Delta} \end{vmatrix}$$

... thanks to Jacobi's identity.

Overlap integral: two excitations

For two excitations

- Due to the anti-symetrization of the wave functions (Slater determinants), the electrons and their excitations are indiscernible. For instance, the two permutations $f = (\mu_1, \mu_2; \gamma_1, \gamma_2)$ and $f = (\mu_2, \mu_1; \gamma_1, \gamma_2)$ are taken into account in the previous overlap integral $\Delta(\mu_1, \mu_2; \gamma_1, \gamma_2)$.



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- The number of determinants to compute is : $C^2_{\rm occ} \times C^2_{\rm unocc} = \frac{N_{\rm occ} \times (N_{\rm occ}-1) \times N_{\rm unocc}(N_{\rm unocc}-1)}{2 \times 2}$.
- These excitations have to be performed for the two spin channels.

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How to create a core-hole?

Two methods are possible:

1. The first one, which is currently employed:
   1. Generate[6] a pseudopotential with a core-hole (define a level occupied by $(n-1)$ electrons rather than n).
   2. Introduce this one in the calculation and consider it as an impurity (perform a convergence with respect to the size of the supercell).
   3. Force the neutrality of the system and add one electron at the top of the valence band[7].

   Drawback: the spin of the electron removed during the generation process is not specified. It could be important when the screening of the core-hole by the valence electrons depends on the spin value of the electron removed.

[6] Natalie A. W. Holzwarth and Marc Torrent, see `http://pwpaw.wfu.edu`

[7] If you can't deal with charged systems in periodic calculations.

How to create a core-hole?

Two methods are possible:

1. The first one, which is currently employed:
2. The second one, adopted in the following procedure:
   1. Generate[6] a pseudopotential with the core-levels in the valence.
   2. Create the core-hole self-consistently ("on the fly") by removing the lowest state during the electronic minimization.

   Bonus: we also take into account of the relaxation of the core-level, feature not included in the previous method since the core-level was frozen within the pseudopotential.

[6] Natalie A. W. Holzwarth and Marc Torrent, see `http://pwpaw.wfu.edu`

PAW: background

In the PAW method[7], the true monoelectronic wave function ψ_α is obtained starting from the PS (pseudo) one $\tilde{\psi}_\alpha$ by using a linear transformation:

PAW transformation

$$\mathcal{T} = \mathcal{I}d + \sum_k (|\phi_k\rangle - |\tilde{\phi}_k\rangle)\langle\tilde{p}_k|$$

When this transformation $\mathcal{T}$ is applied to the PS wave function $|\tilde{\psi}_\alpha\rangle$, we obtain:

$$\begin{aligned} |\psi_\alpha\rangle &= \mathcal{T}|\tilde{\psi}_\alpha\rangle \\ &= |\tilde{\psi}_\alpha\rangle + \sum_k (|\phi_k\rangle - |\tilde{\phi}_k\rangle)\langle\tilde{p}_k|\tilde{\psi}_\alpha\rangle \end{aligned}$$

[7] P. E. Blöchl, PRB 50 (1994) 17953. M. Torrent, F. Jollet, F. Bottin, G. Zérah, X. Gonze, CMS 42, 337 (2008).

PAW: background

Operators

The same transformation applied to an operator $\mathcal{A}$ gives:

$$\begin{aligned}\tilde{\mathcal{A}} &= \mathcal{T}^{\dagger}\mathcal{A}\mathcal{T} \\ &= \mathcal{A} + \sum_{kl} \left|\tilde{p}_k\right\rangle \left(\left\langle\phi_k|\mathcal{A}|\phi_l\right\rangle - \left\langle\tilde{\phi}_k|\mathcal{A}|\tilde{\phi}_l\right\rangle\right) \left\langle\tilde{p}_l\right| + \Delta\mathcal{A}\end{aligned}$$

with $\Delta\mathcal{A}$ equals to zero for local or quasi-local operator.

PAW: expectation value and scalar product

Expectation value and scalar product

$$\begin{aligned}\langle\tilde{\psi}_\alpha|\tilde{\mathcal{A}}|\tilde{\psi}_\alpha\rangle &= \langle\tilde{\psi}_\alpha|\mathcal{A}|\tilde{\psi}_\alpha\rangle \\ &+ \sum_{kl}\langle\tilde{\psi}_\alpha|\tilde{p}_k\rangle\left(\langle\phi_k|\mathcal{A}|\phi_l\rangle - \langle\tilde{\phi}_k|\mathcal{A}|\tilde{\phi}_l\rangle\right)\langle\tilde{p}_l|\tilde{\psi}_\alpha\rangle\end{aligned}$$

- This kind of formulation is already used in large number of PAW implementations in ABINIT: LDA+U, spin-orbit, exact exchange, XAS, XES... At now, for these implementations, only the second term is coded (assume that all the relevant features are included in the sphere).
- Here we choose to implement the three terms. For iron, the modification of the electronic structure outside the PAW sphere, in order to screen the core-hole, may be significant.
- In our case $\mathcal{A} = \mathcal{I}d$, since we only want to compute an overlap.

PAW: expectation value with two PAW basis set

On the atom site with the core-hole, we generally have an atomic data with a basis set ϕ_k^f different of the one used to compute the ground state ϕ_k^i. It can be demonstrated that the previous equation remain valid:

Overlap integral in PAW

$$\langle \psi_\alpha^f | \psi_\alpha^i \rangle = \langle \tilde{\psi}_\alpha^f | \tilde{\psi}_\alpha^i \rangle + \sum_{kl} \langle \tilde{\psi}_\alpha^f | \tilde{p}_k^f \rangle \left(\langle \phi_k^f | \phi_l^i \rangle - \langle \tilde{\phi}_k^f | \tilde{\phi}_l^i \rangle \right) \langle \tilde{p}_l^i | \tilde{\psi}_\alpha^i \rangle$$

- The PAW radius of the partial waves without or with core-levels, ϕ_l^i and ϕ_l^f respectively, have to be equals.
- We can compute the $\langle \phi_k^f | \phi_l^i \rangle$ and $\langle \tilde{\phi}_k^f | \tilde{\phi}_l^i \rangle$ integrals more easily (without any spline) if their meshes are identical.

Methodology – Flow chart

Overlap integral

Using the `kgb` parallelisation[a] (over spin/**k**-points/PWs).

1. Compute the initial state and write the wave functions $\left|\tilde{\psi}^i_\alpha\right\rangle$.
2. Compute the ground state of the final state (with the core-hole) and store the wave functions $\left|\tilde{\psi}^f_\alpha\right\rangle$.
3. Read the initial state wave functions $\left|\tilde{\psi}^i_\alpha\right\rangle$ (in MPI-IO since this one could be huge – supercell calculation).

[a] F. Bottin, S. Leroux, A. Knyazev and G. Zérah, CMS 42, 329 (2008).

Overlap integral in PAW

$$\langle\psi^f_\alpha|\psi^i_\alpha\rangle = \langle\tilde{\psi}^f_\alpha|\tilde{\psi}^i_\alpha\rangle + \sum_{kl}\langle\tilde{\psi}^f_\alpha|\tilde{p}^f_k\rangle\left(\langle\phi^f_k|\phi^i_l\rangle - \langle\tilde{\phi}^f_k|\tilde{\phi}^i_l\rangle\right)\langle\tilde{p}^i_l|\tilde{\psi}^i_\alpha\rangle$$

Methodology – Flow chart

Overlap integral

Using the `kgb` parallelisation[a] (over spin/**k**-points/PWs).

4. Calculation of the PW scalar product $\langle\tilde{\psi}^f_\alpha|\tilde{\psi}^i_\alpha\rangle$.
5. Calculation of associated projectors $\langle\tilde{p}^{i/f}_l|\tilde{\psi}^{i/f}_\alpha\rangle$ (`ctocproj`).
6. Calculation of on-site terms $(\langle\phi^f_k|\phi^f_l\rangle - \langle\tilde{\phi}^i_k|\tilde{\phi}^i_l\rangle)$.
7. Calculation of the summation $\sum_{kl}$ over atom for each $\alpha = (\sigma, n, \mathbf{k})$.

[a] F. Bottin, S. Leroux, A. Knyazev and G. Zérah, CMS 42, 329 (2008).

Overlap integral in PAW

$$\langle\psi^f_\alpha|\psi^i_\alpha\rangle = \langle\tilde{\psi}^f_\alpha|\tilde{\psi}^i_\alpha\rangle + \sum_{kl}\langle\tilde{\psi}^f_\alpha|\tilde{p}^f_k\rangle\left(\langle\phi^f_k|\phi^i_l\rangle - \langle\tilde{\phi}^f_k|\tilde{\phi}^i_l\rangle\right)\langle\tilde{p}^i_l|\tilde{\psi}^i_\alpha\rangle$$

Methodology – Flow chart

Determinants – Matrix elements – Intensity

Using the `kgb` parallelisation[a] (over spin/**k**-points/combinations).

8. Compute the determinants $\langle\Psi^f|\Psi^i\rangle$ with 0, 1, 2... excitations.
9. ... the matrix elements $|\langle\Psi^f|\Psi^i\rangle|^2 = |\langle\Psi^f_\uparrow|\Psi^i_\uparrow\rangle\langle\Psi^f_\downarrow|\Psi^i_\downarrow\rangle|^2$.
10. ... the binding energy $E_i - E_f$ using KS eigenvalues [b].
11. Convolute δ with a lorentzian (FWHM: Γ=1.0 eV).

[a] F. Bottin, S. Leroux, A. Knyazev and G. Zérah, CMS 42, 329 (2008).
[b] At this time, we don't take into account any (GW) correction.

XPS intensity

$$I_\sigma^{XPS}(h\nu - \epsilon) = 2\pi|\langle\psi^f|\mathcal{O}_\sigma|\psi^i\rangle|^2 \sum_f |\langle\Psi^f|\Psi^i\rangle|^2 \delta(h\nu - \epsilon + E_i - E_f)$$

Methodology – Flow chart

Simplification

1. Proceed step by step. Begin by a small number of excitations (`mnd_mexcit`=1 or 2) then increase.
2. Do not use combinations with a too small overlap integral when computing the matrix elements (hard coded).
3. Do not consider the excitations above a cutoff energy (`mnd_maxene`=10 eV, more or less).

Some of these simplifications are already used in TDDFT.

Computational time

System with 100 atoms, 1000 bands (occupied & unoccupied 10 eV above the Fermi level), 10 **k**-points and spin-polarisation: 1-2 hours for each DFT calculation (i & f) and 1-2 hours for the XPS spectrum (with 2 excitations) over 2000 processors.

$3s$ core-level XPS spectra of iron

Reference calculation

Calculations[a] performed using a FLAPW code.

- Iron in its bcc phase.
- Supercell with 27 atoms.
- DFT calculations with a [???] MP mesh, Γ-point spectrum.

[a] M. Takahashi, J.-I. Igarashi and N. Hamada, PRB **78**, 155108 (2008). M. Takahashi and J.-I. Igarashi, PRB **81**, 035118 (2010).

3s core-level XPS spectra of iron

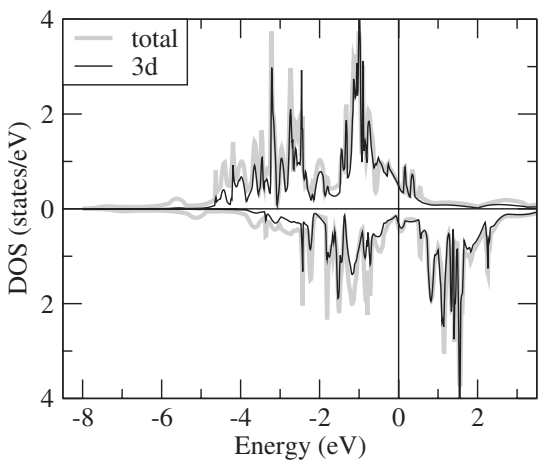
Reference calculation

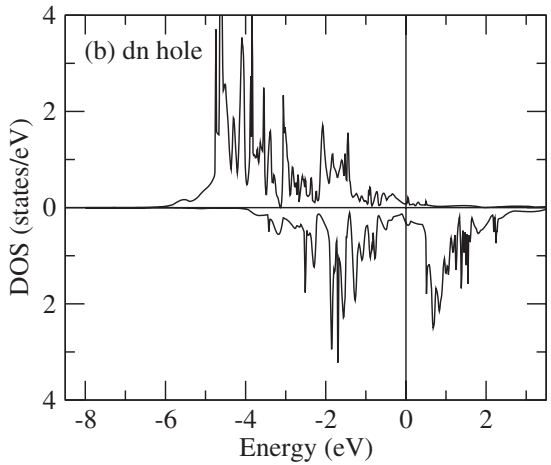
Calculations[a] performed using a FLAPW code.

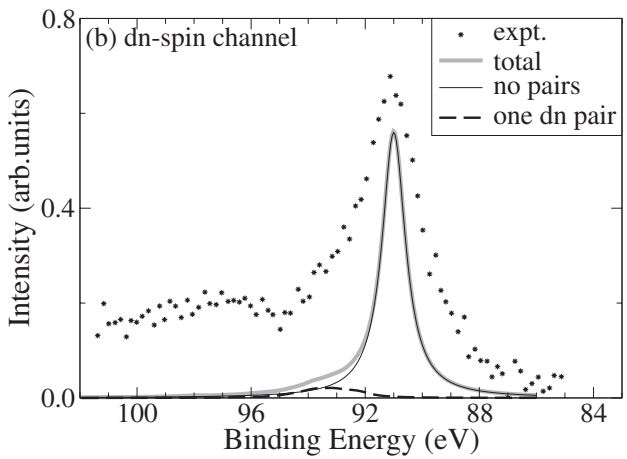
- No modification of the up- or down-spin channel.
- Unoccupied final states $\perp$ ocupied initial ones.
- Neither up- nor down-excitations are possible.

[a] M. Takahashi, J.-I. Igarashi and N. Hamada, PRB **78**, 155108 (2008). M. Takahashi and J.-I. Igarashi, PRB **81**, 035118 (2010).

i f I







3s core-level XPS spectra of iron

Reference calculation

Calculations[a] performed using a FLAPW code.

- Unitary transformation within the majority spin channel.
- Strong modifications within the minority one.
- So only down excitations would be efficient.

[a] M. Takahashi, J.-I. Igarashi and N. Hamada, PRB **78**, 155108 (2008). M. Takahashi and J.-I. Igarashi, PRB **81**, 035118 (2010).

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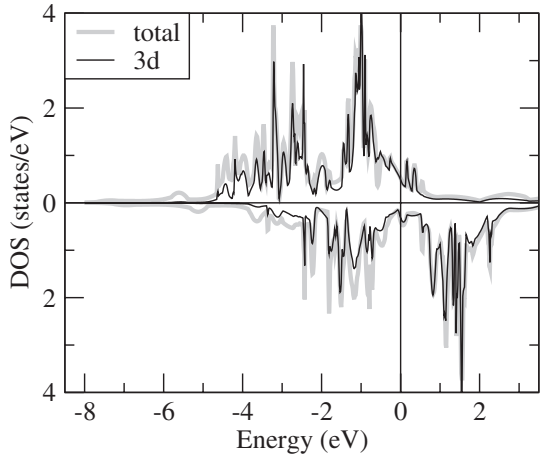

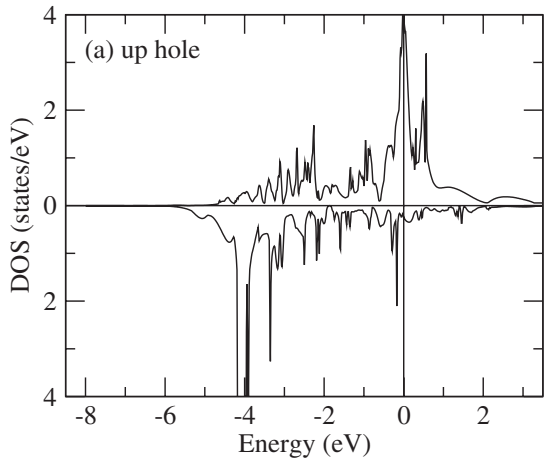

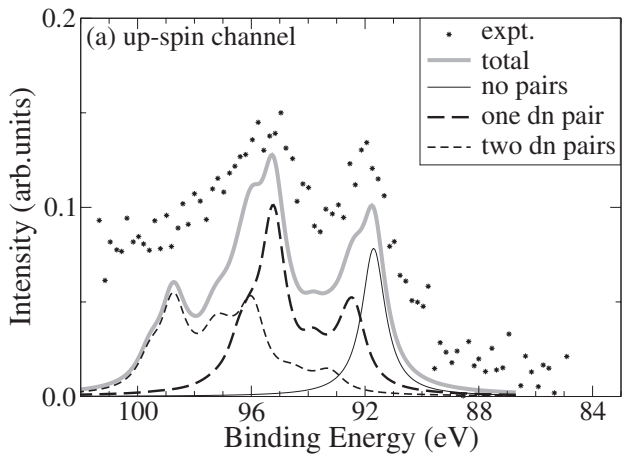

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Calculations performed using ABINIT in the PAW framework.

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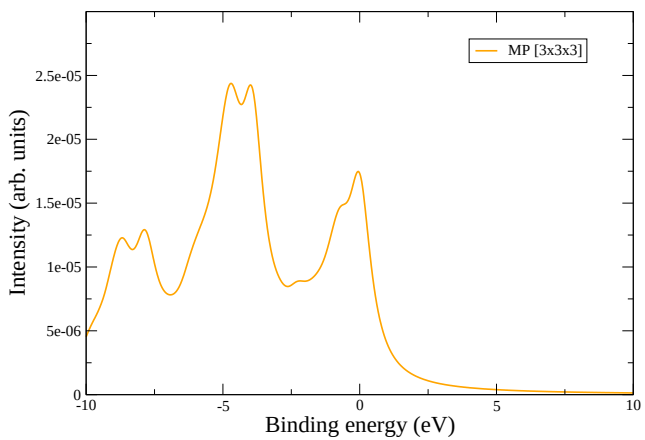
- DFT calculations with a [333] MP mesh, Γ-point spectrum.

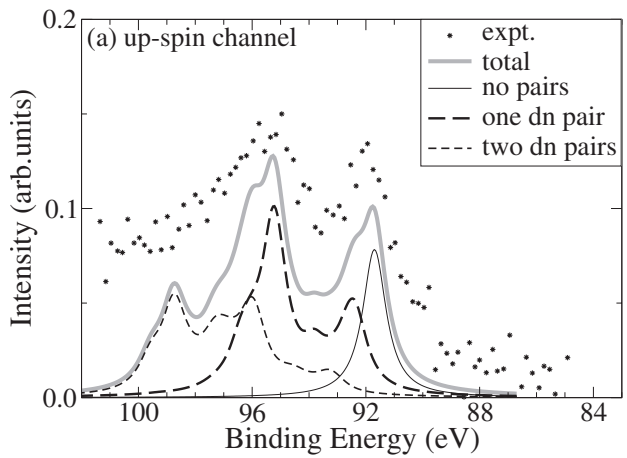
$3s$ core-level XPS spectra of iron

This work

Calculations performed using ABINIT in the PAW framework.

- DFT calculations with a [333] MP mesh, Γ-point spectrum.
- Good agreement (energy and number of excitation peaks).
- $I^{XPS}_{\uparrow}$ does not converge wrt. the number of **k**-points.





$3s$ core-level XPS spectra of iron

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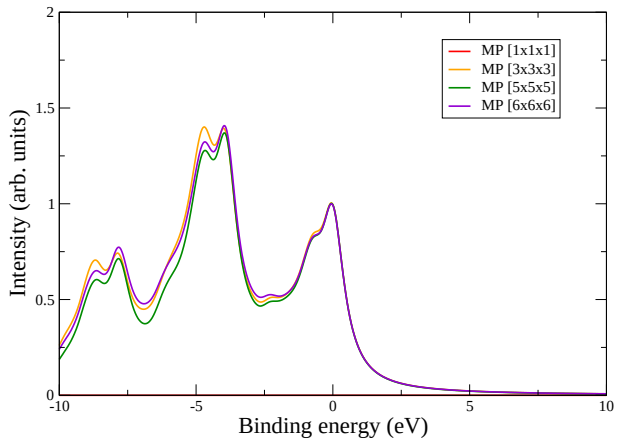
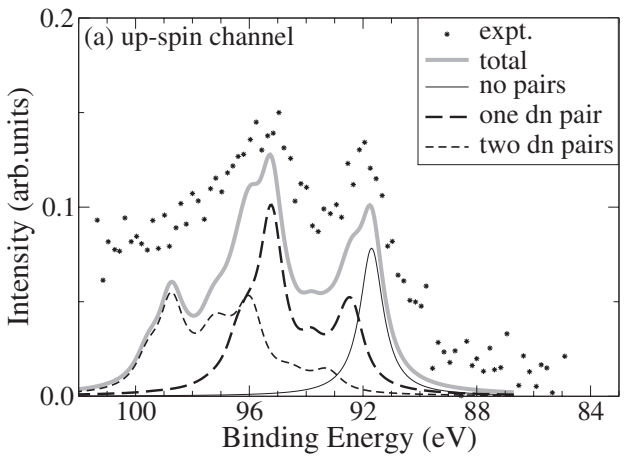
Calculations performed using ABINIT in the PAW framework.

- DFT calculations with a [xxx] MP mesh, Γ-point spectrum.
- If we rescale the threshold intensity: convergence of the shape.
- But not with respect to the number of atoms.



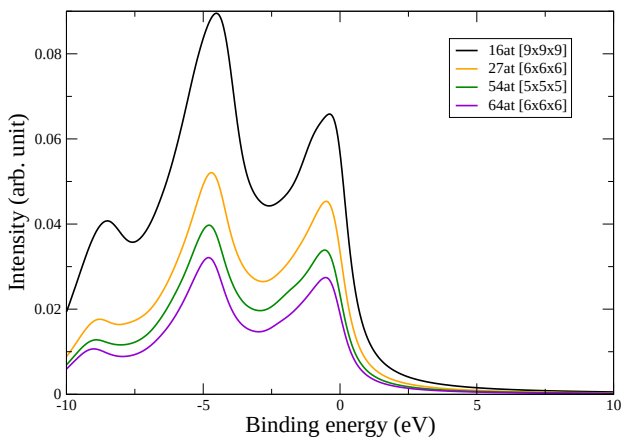


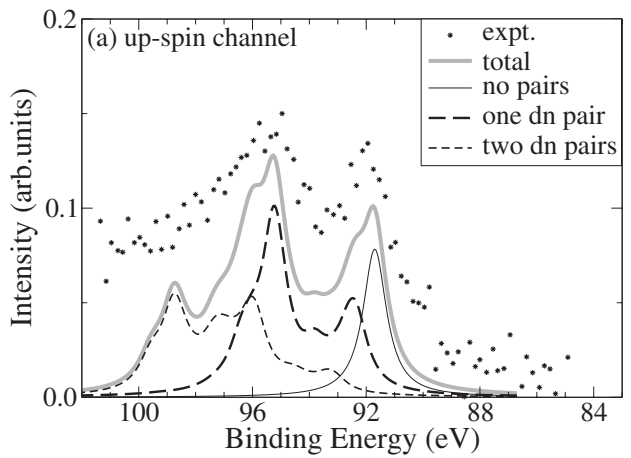
$3s$ core-level XPS spectra of iron

This work

Calculations performed using ABINIT in the PAW framework.

- DFT calculations with a [xxx] MP mesh, [xxx] full spectrum.
- $I_{\uparrow}^{XPS}$ does not converge wrt. the number of atoms.
- If we rescale again, the shape is converged for $N_{at} \geq 27$.





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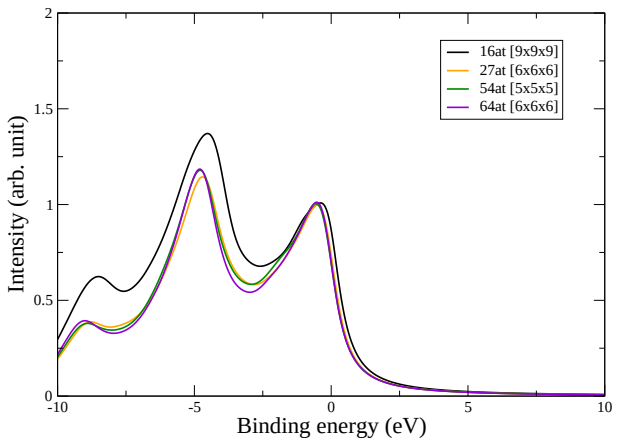

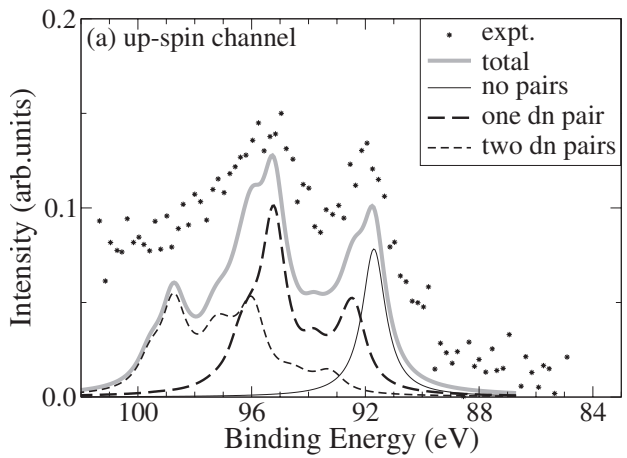

Discussion

Restrictions – Improvement

- The inclusion of a net charge during DFT calculations. First attempts show no effect on spectra.
- How to perform core-level XPS calculations with fractionnal occupations?
- How to take into account the relaxation of a level occupied after a valence excitation?

Conclusions

- We implement a method to compute the core-level XPS spectra by means of PAW *ab initio* calculations.
- We are able to be spin-resolved and to take into account the core relaxation with valence excitations.
- Our spectra are equal to the ones obtained by Takahashi *et al.* but the overall intensities don't converge wrt. the number of **k**-points or atoms.

Perspectives

- Apply this method to surfaces (able to deal with 100 or 200 atoms).
- Introduce spin-orbit within the XPS calculation in order to include multiplet effects.
- Take into account the overlap between the (N-1) electrons remaining in the system, and their shake-up, within XAS, NXES, RIXS... calculations.

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