Chemical analysis of surfaces

Ondřej Šipr

XII.

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Outline

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Energy levels and spectroscopy

Chemical analysis with core level spectroscopy

Core level shifts calculations

Technicalities (lifetime, surface sensitivity, . . .)

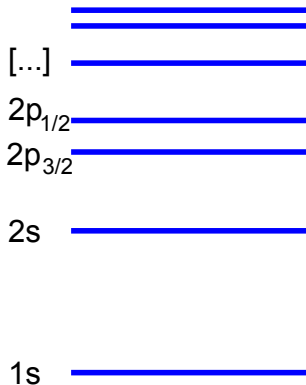# Outline

Energy levels and spectroscopy

Chemical analysis with core level spectroscopy

Core level shifts calculations

Technicalities (lifetime, surface sensitivity, . . .)

Outline

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Energy levels

- ▶ Quantum mechanics: discrete energy levels
- ▶ Energy levels are characteristic for each system

[...] ────────

$2p_{1/2}$ ────────

$2p_{3/2}$ ────────
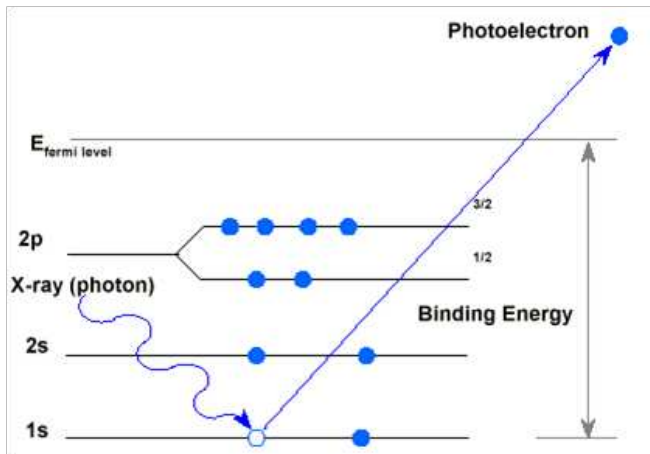
2s ────────

1s ────────

Spectroscopy: way to probe energy levels

▶ Absorbed or excited energy equals the difference between
  energy levels
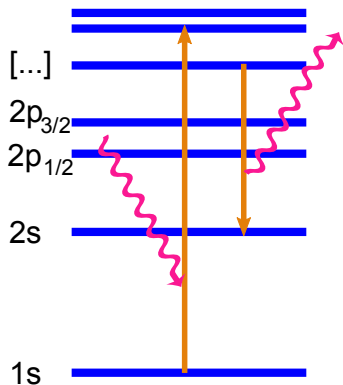
X-ray photoelectron spectroscopy: scheme

Measuring binding energy associated with core levels.

X-ray photoelectron spectroscopy: real life

Electron Energy Analyzer (0-1.5 kV)

X-Rays (~1.5kV)

Electron (Count) Detector

Electrons (<1.5 kV)

Sample
(~10^(-8) mbar)

O (1s)
O (3s)

Photoelectric Effect
(A. Einstein Nobel Price 1921)
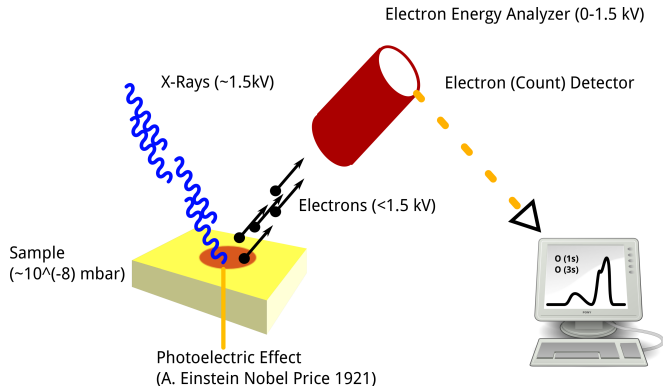
Auger electron spectroscopy
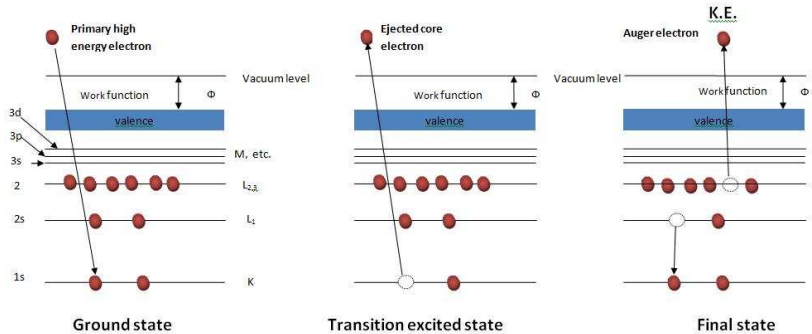
One hole in the initial state, two holes in the final state.

$$E_{\mathrm{kin}} \approx E_K - E_{L_1} - E_{L_{2,3}}$$

Core levels, valence levels
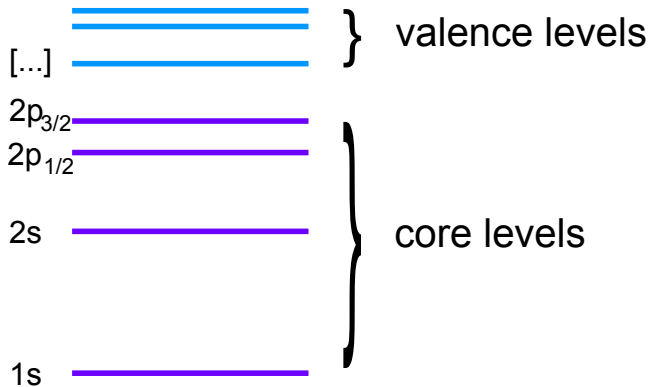
Core levels, valence levels

- Some levels are more prone to disturbance by the environment than the others

Elemental analysis

- ▶ Characteristic spectrum — core levels
- ▶ Tells us which elements are present (and possibly in which quantity).
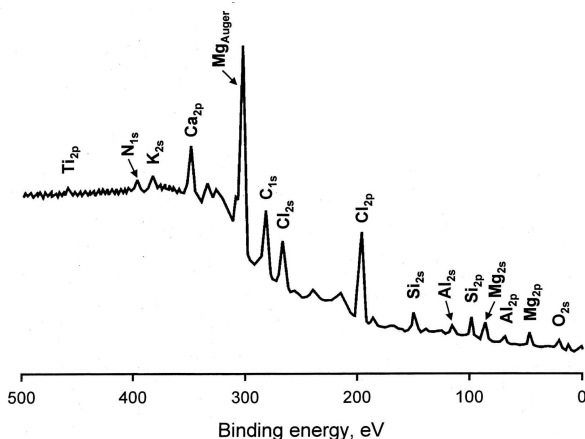
XPS spectrum of a soil particle [Soil Sci. Soc. Am. J. **66**, 1526 (2001)]

Beyond elemental analysis

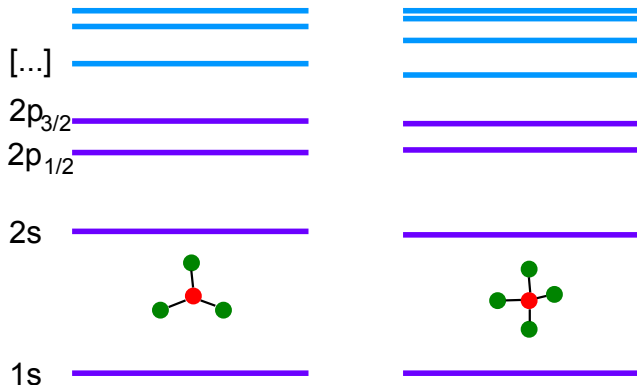Can we do better than just to determine which elements are there (and in which quantities)?

Can we find also something about the environment in which given elements occurs in the material we are interested in?

Because knowing more about the environment of an atom means knowing more about its chemical properties, the area is called "chemical analysis".

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Which levels are useful for chemical analysis?
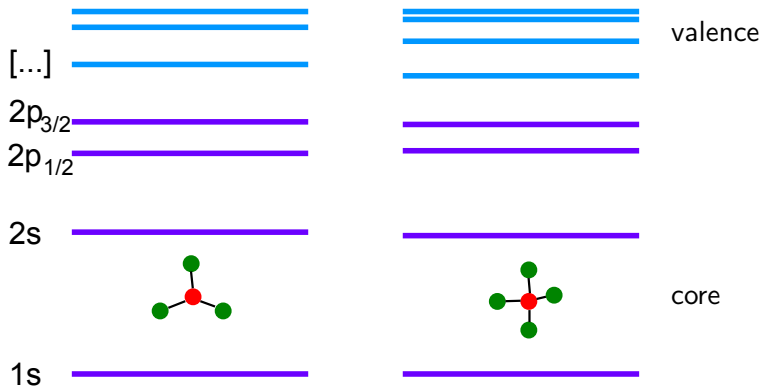
Valence levels are (much) more sensitive to the chemistry than core levels.

Valence levels (1)

- Valence levels are strongly affected by the bonding
- Fine variations of the environment cause large changes in the spectra
  - Great if we are interested in details...
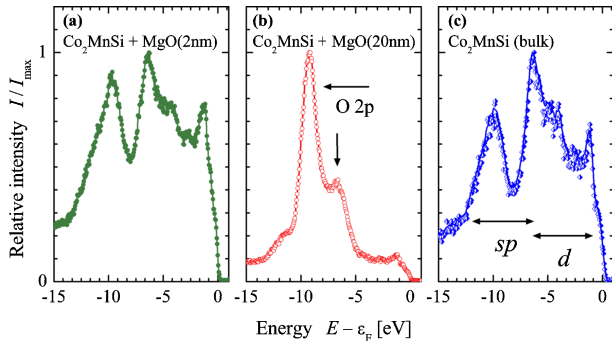
Valence band of Co_2MnSi in three different environments [Fecher *et al.* APL **92**, 193513 (2008)]

Valence levels (2)
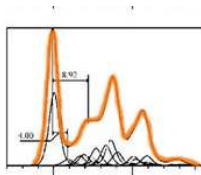
Calculated X-ray photoelectron valence band spectra of model compounds containing carbon hexagons and C-O bonds

[http://what-when-how.com]
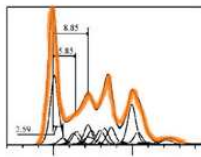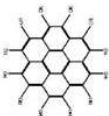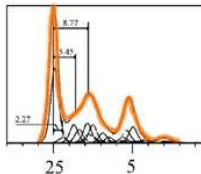
Valence levels (3)

- If we are interested in nearest environment only (CH_4, CO_2, CO, CN . . .), valence-band spectroscopy is not so great

  - Valence-band spectra sensitive not only to nearest-neighbor coordination but also to what's going on further down

  - It contains too much information, it is difficult to extract from it the information we are interested in

- Valence band spectroscopy might be useful if we know something about the system already and want to improve our knowledge by adding finer details (recall lecture about valence-band photoemission)

Core levels

- Only little affected by the nearest neighborhood and practically *not at all* affected by more distant environment

- Core level spectra contain only limited information — but it is the piece of information we are often interested in !

Core level shifts: surface

- ▶ Change in bonding causes a shift of the core level energy

- ▶ This change can be due to different location of the atom: surface core level shifts
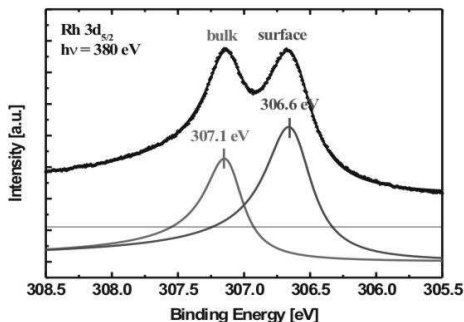
Atoms at the surface have different number of neighbors than atoms in the bulk.

Core level shifts: chemistry

- The change can be also due to different environment: chemical core level shifts
  - By measuring the core level shifts, information about bonding environment can be obtained

$^c/200s$

SULFUR 2p (MgKα)

$\begin{bmatrix} & O & \\ & | & \\ O-S-S & \\ & | & \\ & O & \end{bmatrix}^{2-}$

central   ligand

COUNTING RATE

1000

500

1080   1085   1090   1095 eV
KINETIC ENERGY

eV   170   165   160   155
BINDING ENERGY

[http://www.nb.uw.edu, K. Siegbahn (1967),...]

Core level shifts: chemistry

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poly(ethylene terephthalate) (PET) C_{1s} Spectrum

[http://www.nb.uw.edu, K. Siegbahn (1967),...]
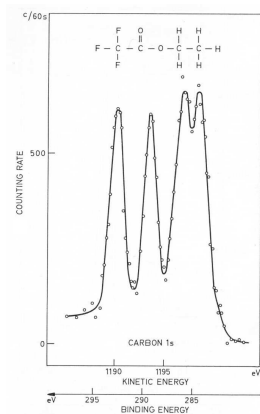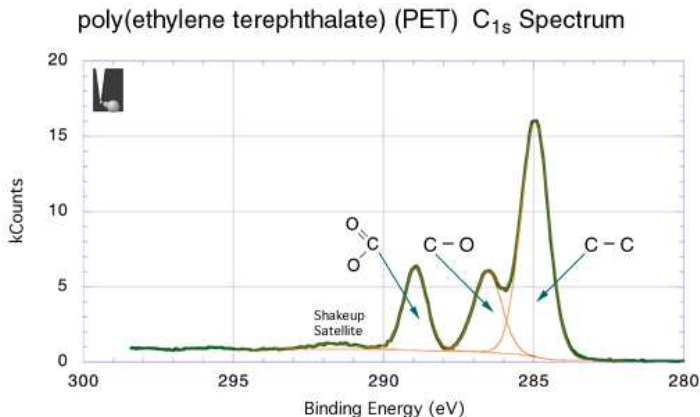
Intuition: what to expect

Generally: Binding energies depend on the charge on atom.

Rule of thumb: Reducing the charge leads to increase of the binding energy (because the nuclear charge is less screened).

Core level shifts are related to charge transfer between constituting atoms:

- number of neighbours,
- electronegativity,
- oxidation state.

Side-step: Hydrogen issues

- Neither XPS nor AES can identify H or He.

- Their $1s$ "core" levels are interpenetrated by valence levels of other elements so they cannot be distinguished from them.

    - Besides, photoionization cross-section of hydrogen is by orders of magnitude smaller than photoionization cross-section of other atoms.
      However, this is *not* the main problem.

- Caution: hydrogen matters !
    - Example: easy magnetization axis of a clean Ni thin film on Cu(001) will be out-of-plane for a clean Ni surface and in-plane for Ni surfaces covered by hydrogen [JMMM **272-276**, 1194 (2004)].

Outline

Calculating the core level shifts

Binding energy:

$$E_B = E_f^{(N-1)} - E_i^{(N)}$$

Factorizing the many-body wave functions $\Psi_i^{(N)}$:

$$\Psi_i^{(N)} = A \phi_i \Psi_{i,R}^{(N-1)} \ ,$$

A stands for antisymmetrization (to guarantee the Pauli exclusion p[rinciple], R means "remaining electrons".

Final state wave function: $\Psi_{f,R}^{(N-1)}$.

Different ways of calculating the energies $E_i^{(N)}$ and, especially, $E_f^{(N-1)}$ could be classified according to how the wave-functions of the remaining $(N-1)$ electrons are treated.

What really matters. . .

Good news:
For ESCA, we need just to know the differences between binding
energies E_B of core electrons for different compounds.

Solids vers. molecules

For finite systems such as molecules, it is possible to calculate $E_i^{(N)}$ and $E_f^{(N-1)}$ truly exactly and *ab initio* (albeit sometimes by brute force at high cost).

For systems connected to an electron reservoir (solids, surfaces, adsorbates), this cannot be done straightforwardly.
Such a system would be too big to handle by quantum-chemistry methods.

For solids, the only practical way to calculate core levels binding energies is to associate binding energies to differences between energy levels.

Caveat: This goes against the internal spirit of the DFT!

Tricks can be introduced to make this approximation (or, better said, *ansatz*) more accurate.

Total energies and Kohn-Sham energies (1)

DFT: Kohn-Sham orbitals ϕ_i and Kohn-Sham energies ϵ_i
(relying on exchange-correlation potential which we do not know in its
exact form).

Strictly speaking, ϕ_i and ϵ_i are just auxiliary quantities with no
physical meaning.
They have been introduced just to represent the electron density as
$\sum_i |\phi_i|^2$.

Efforts to relate binding energies to differences in Kohn-Sham
energies ϵ_i are thus principally flawed.

Nevertheless, we usually rely just on them. . .

Total energies and Kohn-Sham energies (2)

Some exactness can be introduced into the business.

Janak theorem: The first ionization energy ("the binding energy of the HOMO") is just the highest Kohn-Sham energy:

$$E_B^{(\text{ionize})} = |\epsilon_{\text{HOMO}}| \quad .$$

For Hartree-Fock theory, analogous Koopmans theorem is valid.

This approach is often used for calculating binding energies of core states. That means using the "HOMO" formula for "non-HOMO" states.

Usually, it is tacitly assumed that one can treat the Kohn-Sham energies ϵ_i as real energies.

Going beyond this approximation would require heavy machinery.

Frozen orbital approximation

A.k.a. **initial state approximation.**
This is the most simple way to proceed.

Assume the system does not notice the hole: $\Psi_{i,R}^{(N-1)} = \Psi_{f,R}^{(N-1)}$.

The relaxation of the "passive" electrons to the core hole is neglected.

Then the binding energy is just the negative orbital energy of the excited core orbital:
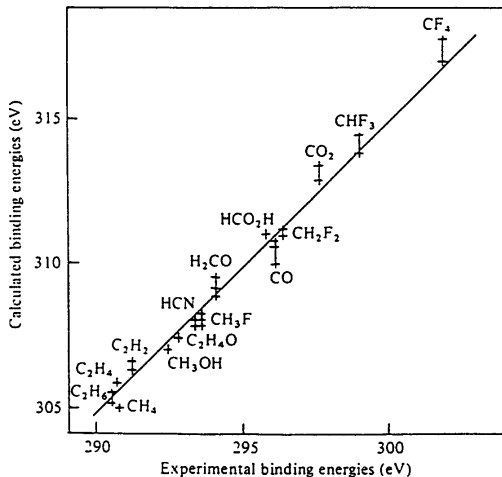
$$E_B = -\epsilon_i .$$

(recall Janak, Koopmans).

This is not a very good approximation to E_B itself.

However, we are interested only in the differences between E_B when changing the local environment.

Initial state approximation and experiment

Big differences in absolute numbers.

Differences between binding energies for different systems reproduced quite well.

Can we do better?

Fig. 3.13 Comparison of experimental XPS C 1s binding energies with those calculated via Koopman's theorem for C in a range of molecules. Although experimental and theoretical values differ by 15 eV (associated with relaxation effects) the systematic comparison is excellent as indicated by the straight line of unity gradient (after Shirley, 1973).

Simon J. Garrett

Core hole affects the rest of the system
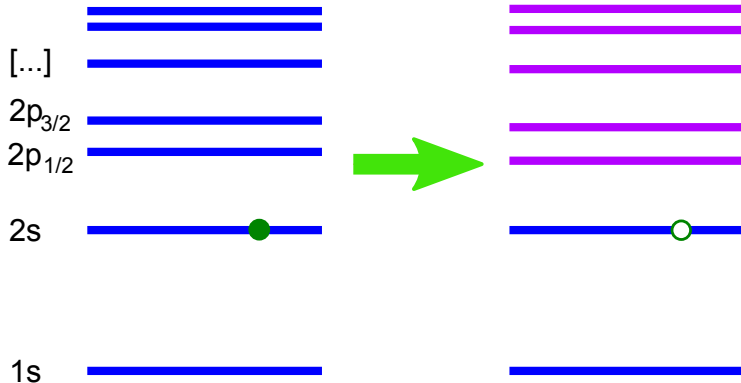
The rest of the system reacts to the presence of the core hole, energy levels changes.

How to account for the core hole?

Initial state approximation does not always work:

The system notices the hole: $\quad \Psi_{i,R}^{(N-1)} \neq \Psi_{f,R}^{(N-1)}$.

Dealing with the core hole in solids is difficult.

We have to apply tricks (approximations).

Final state approximation

Electron levels are calculated in the presence of the core hole.

Assuming a static situation ("final state" only).

Other electrons will screen the hole, so its effect will not be *so* big.

The screening is modeled by adding an extra electron to the valence band ("complete screening picture").

The total number of electron thus remains: one electron less in the core, one electron more in the valence band. This is computationally appealing.

Even in most favourable circumstances this is still an approximation, because we rely on differences in Kohn-Sham energies.

Equivalent core approximation

Technical simplification of the final state approximation.

Equivalent core approximation a.k.a. $Z+1$ approximation:

Ionization of the core level is approximated by an addition of a proton to the nucleus.

Justification: The spatial extension of the core electron is small w.r.t. valence electrons.

Technically appealing: Core hole is taken into account and yet electronic structure has to be calculated for the ground states (of the $Z + 1$-th element).

Examples

Differences in the C $1s$ ionization potential between the CH_4 molecule calculated using equivalent core approximation:

Molecule	δI (calc.) [eV]	δI (exper.) [eV]
C_2H_6	-0.32	-0.10
benzene	-1.08	-0.40
CH_3OH	2.09	1.90
CH_2O	2.98	3.30
CH_3F	3.33	2.80

Chem. Phys. Lett. **33**, 298 (1975)

Note: The technical accuracy of the computational method also matters.

(Slater) transition state approximation

Another way of accounting for the core hole.

Used in connection with DFT and, specifically, LDA.

Assuming that the LDA one-electron energy ϵ_i is a linear function of the occupancy of the i-th orbital, the binding energy of the associated electron is

$$E(n_i = 1) - E(n_i = 0) = \int_0^1 \mathrm{d}n_i \left(\frac{\partial E}{\partial n_i}\right) \approx \epsilon_i(n_i = 0.5) \ .$$

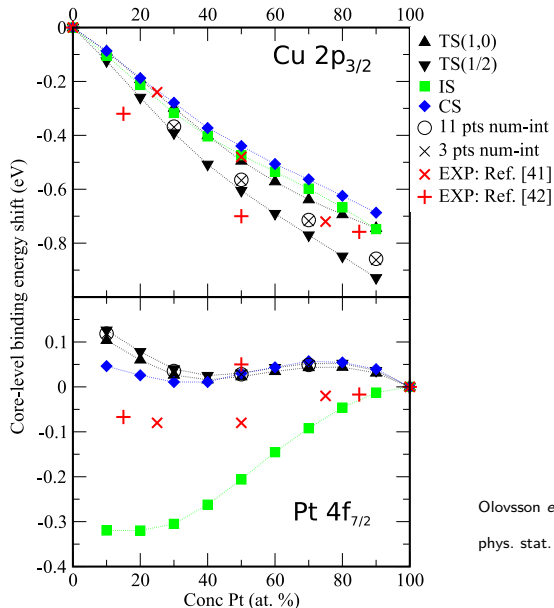This approximation is used also in theories which go beyond the LDA (such as LDA+U etc.).

Technicalities

Treating an atom with a core hole or with $Z+1$ charge or with a half of a core hole is equivalent to solving electronic structure of an impurity.

Supercells.

Green functions.

Example: core levels in CuPt alloy

Variation of the binding energy with composition of $Cu_{1-x}Pt_x$ alloy.

Transition state approximation (TS),

initial state approximation (IS),

final state approximation (CS).

Outline

Core level lifetime (1)

Empty core level does not stay so forever — it is filled by another electron.

[...]

$2p_{3/2}$

$2p_{1/2}$

2s

1s
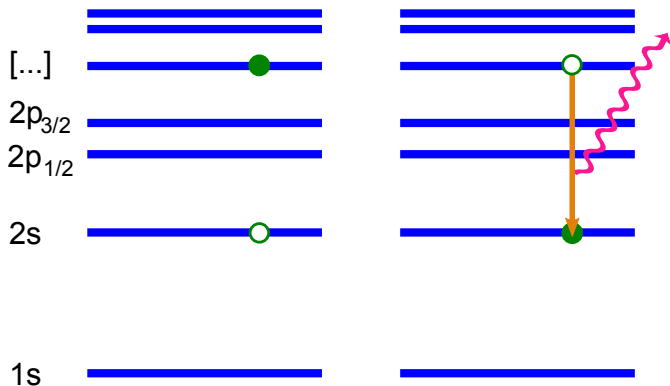
Core level lifetime (2)

- Formally:

  - Ideally sharp core levels are eigenstates of an unperturbed Hamiltonian H_0, which neglects the electromagnetic interaction H_I.

  - Electromagnetic interaction H_I is a small perturbation to the original "coulombic only" Hamiltonian H_0, it makes the core levels non-stationary.

- Perturbation theory $\Rightarrow$ core level decay is exponential with time.

Core level width

- Energy released during a decay of an eigenstate of the unperturbed (=approximative) Hamiltonian H_0 is dispersed according to a Lorenzian.
  - Intuitively: finite lifetime Δt invokes finite energy width ΔE according to the time-energy uncertainty principle,
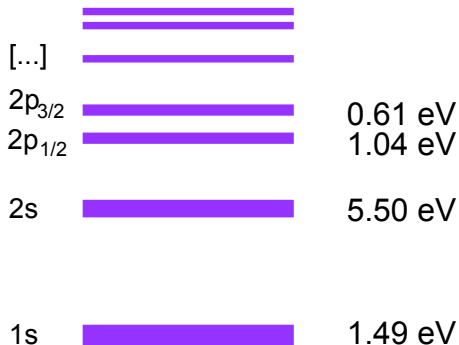
$$\Delta t \cdot \Delta E \, > \, \hbar \ .$$

- Energy associated with transitions between various states of an atom (molecule, solid) is not just a discrete quantity, there is a finite spread around some middle value.
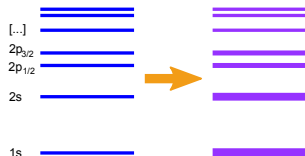
All core level widths are not the same

- Rule of thumb: Deep core levels have larger width than shallow levels.

- Example: Core level width of copper.

Final state lifetime

- ▶ Final state has a finite lifetime as well !

- ▶ Excited electron: its lifetime is limited due to inelastic scattering (plasmon losses, valence electrons excitations etc.).

- ▶ If there is a core hole in the final state (Auger), it has a finite lifetime, too.

- ▶ Width of a spectral line is determined by the sum of initial state width and final state width.

Practical aspects

- Energy resolution is limited by the spectral line width.

- Chemical resolution possible only if the linewidth is sufficiently small.
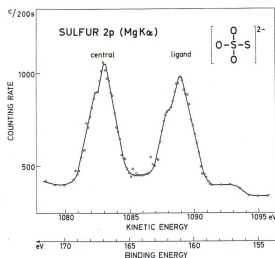
Surface sensitivity (1)

Possible sources of surface sensitivity:

1. Finite penetration depth of the exciting probe.
   For a transition to occur, energy has to be brought to the system. In XPS, excitation is via incoming x-rays. In AES, excitation is via incoming electrons.

2. Finite escape depth of the ejected electron.
   Both XPS and AES produce excited electrons that have to escape from the sample before they can be detected.

Surface sensitivity (2)
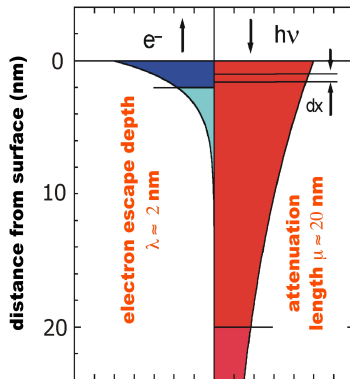
Mean-free path of electrons is much less than of x-ray photons
$\rightarrow$ escape depth of the excited electron is the crucial factor.

Differences between XPS and AES

	XPS	AES
exciting beam	x-rays	electrons
analyzed beam	electrons	electrons
area of analysis	10 μm	10 nm
surface selectivity	1–5 nm	1–5 nm
studying chemical bonding	via shifts, straightforwad	via shifts and shapes, requires analysis

Strengths and weaknesses of XPS and AES

- ▶ XPS has sharper lines $\Rightarrow$ it can be used in chemical analysis (ESCA).

- ▶ AES is excited by electron beam which can be focused $\Rightarrow$ can yield information width good lateral resolution.