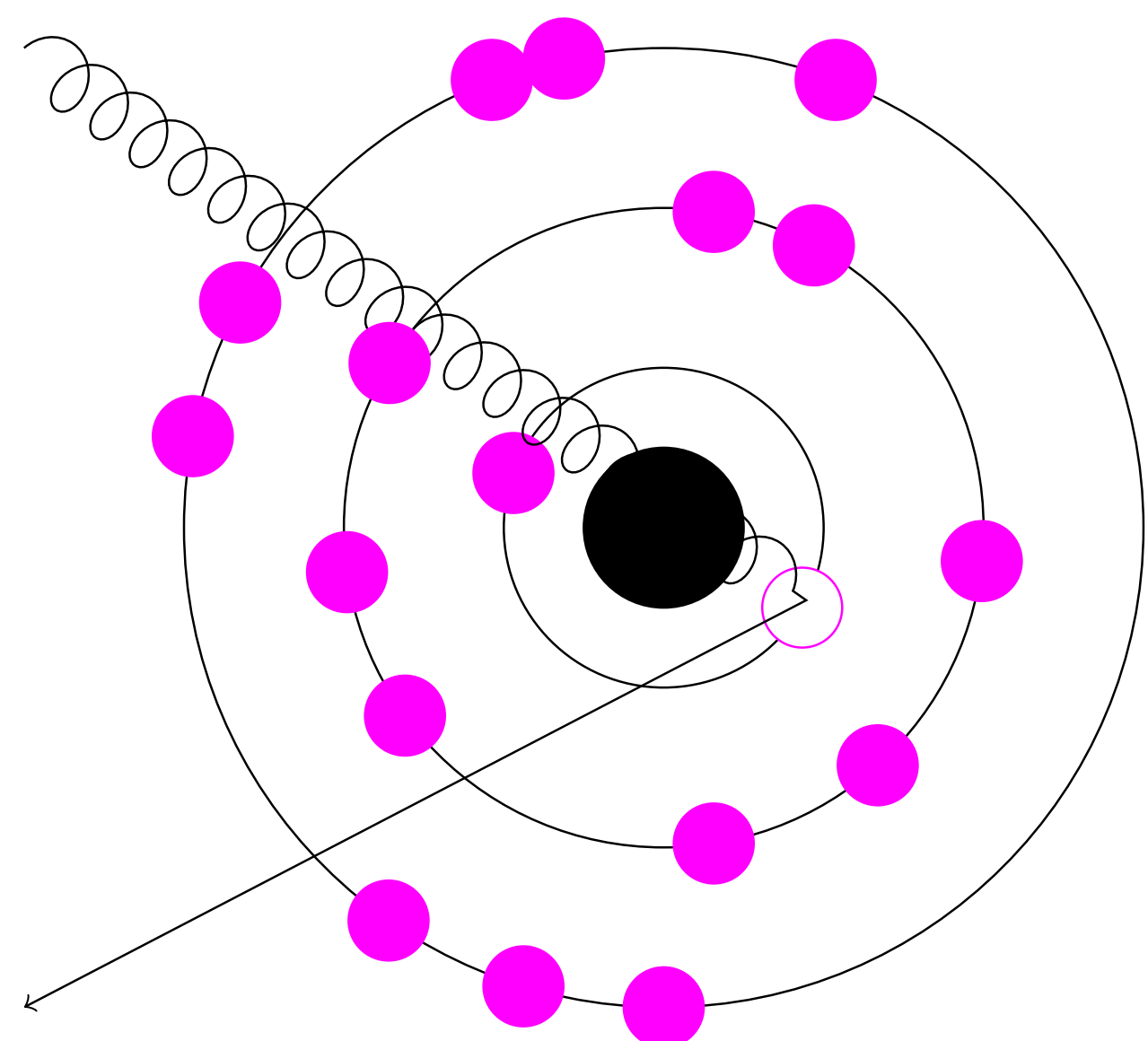


ELECTRON SPECTROSCOPY FOR CHEMICAL ANALYSIS

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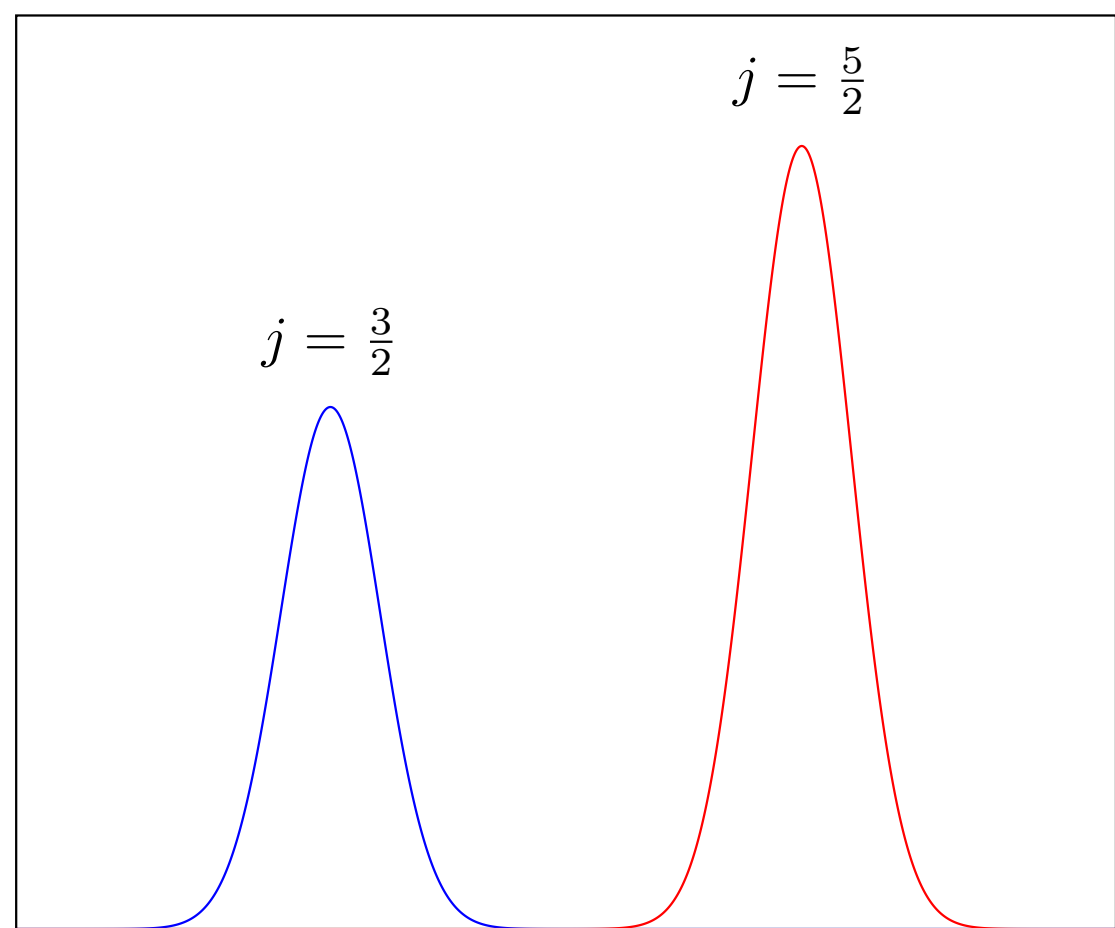
X-ray Photoelectron Spectroscopy (XPS)

XPS principle



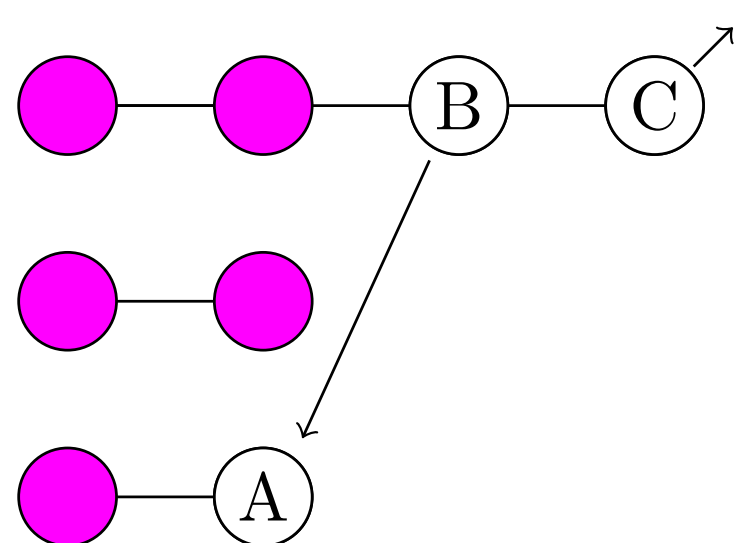
XPS spin orbit coupling

Spin orbit coupling means that the J quantum number is $J = L + S$, and it can be either parallel ($j = l + \frac{1}{2}$, $2j + 1$ fold) or anti-parallel ($j = l - \frac{1}{2}$, $2j + 1$ fold). Thus it only occurs for $l = 1, 2, 3$



Auger Electron Spectroscopy (AES)

Auger electron scheme



Energy

$$E_{\text{kin}} = E_A^Z - E_B^Z - E_C^Z - \Phi$$

But there is a core hole after electron A has left:

$$E_{\text{kin}} = E_A^Z - E_B^{Z+1} - E_C^{Z+1} - \Phi$$

But the atom is not $Z + 1$:

$$E_{\text{kin}} = E_A^Z - \frac{1}{2}(E_B^{Z+1} + E_B^Z) - \frac{1}{2}(E_C^{Z+1} + E_C^Z) - \Phi$$

Nomenclature

The nomenclature is (example) KLL, where the first letter is the initial hole, second letter is the shell of the falling electron, and the third letter is the shell of the emitted electron

EXtended X-ray Absorption Fine Structure (EXAFS)

modes

Possible only with synchrotron radiation!

- EXAFS

There are oscillations in the absorption spectrum. These are due to the transfer from one atom to the next, so the same atom doesn't absorb and emit the electron.

$$\chi(k) = \frac{\sigma(k) - \sigma_0(k)}{\sigma_0(k)}$$

$$\chi(k) = -k^{-1} \sum_i A_i(k) \sin[2kR_i + \phi_i(180^\circ, k)]$$

here the sum is over the shells, the $2kR_i$ term is the actual modulation and the ϕ_i term is the energy dependant phase shift.

$$A_i = \frac{N_i}{R_i^2} |f_i(180^\circ, k)| W(T, K) e^{-\frac{2R_i}{\lambda}}$$

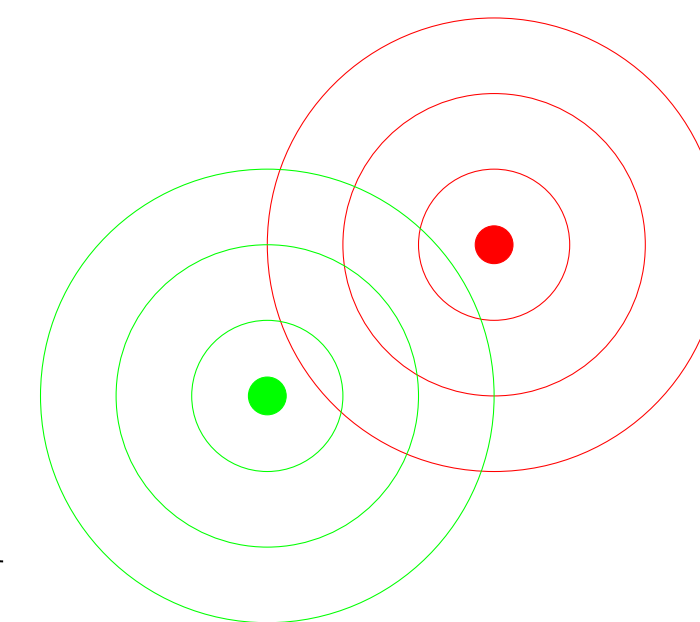
where N_i is the number of atoms in shell i , R_i the radial dependence, making only the first few shells important. f_i the scattering function (atom dependant), W the Debye-Waller factor and the exponential term arises from it being inelastic scattering.

- Surface EXAFS (SEXAFS)

Is the surface version of EXAFS, it gives the bond length but not absorption site. However, by polarizing the different neighbours can be seen one by one. There are however problems: Auger electrons will be generated and EXAFS only raises 3%

- Near-edge EXAFS (NEXAFS)

These are for the oscillations very close to the K-edge of the system. Strong peaks will be seen when enough energy is given to raise the $s1$ electron to the LUMO, LUMO+1, ...



Math

$$E_{\text{kin}} = h\nu - E_{\text{bin}} - \Phi$$

$$E_{\text{bin}} = h\nu - E_{\text{kin}} - \Phi$$

$$I_x = \sigma_x(E) N_x \lambda(E) A D(E) T(E)$$

σ_x is the element specific cross-section, N_x the concentration of the element, λ is the inelastic electron mean free path, A is the sample area, D the detector efficiency and T the analyzer transmission efficiency.

$$\frac{I_A}{I_B} = \frac{\sigma_A(E) N_A \lambda(E) A D(E) T(E)}{\sigma_B(E) N_B \lambda(E) A D(E) T(E)}$$
$$\frac{N_A}{N_B} \approx \frac{I_A}{I_B} \times \frac{\sigma_B \lambda_B}{\sigma_A \lambda_A}$$

using Fermis golden rule, an expression for the differential cross section for photoemission into the element of solid angle $d\Omega$

$$\frac{d\sigma}{d\Omega} \propto \left| \int \psi_f(R) \mathbf{H}' \psi_i(r) dr \right|^2 \partial(E_f - E_i - h\nu).$$

Where \mathbf{H}' is the perturbation hamiltonian, it can be found by replacing the momentum operator \mathbf{p} by $\mathbf{p} - e\mathbf{A}$, \mathbf{A} being the vector potential:

$$\mathbf{H}_0 = -\frac{e}{2m_e} (\mathbf{p} \cdot \mathbf{A} + \mathbf{A} \cdot \mathbf{p}) - e\Phi + \frac{e^2}{2m_e} |\mathbf{A}|^2$$

$|\mathbf{A}|$ is small, so the last term can be ignored, the perturbation is then:

$$\mathbf{H}' = -\frac{e}{2m_e} (\mathbf{p} \cdot \mathbf{A} + \mathbf{A} \cdot \mathbf{p})$$

using $[\mathbf{p}, \mathbf{A}] = -i\hbar \nabla \mathbf{A}$

$$\mathbf{H}' = -\frac{e}{2m_e} (2\mathbf{p} \cdot \mathbf{A} - i\hbar \nabla \mathbf{A})$$

For low energy light, the vector potential is constant, so:

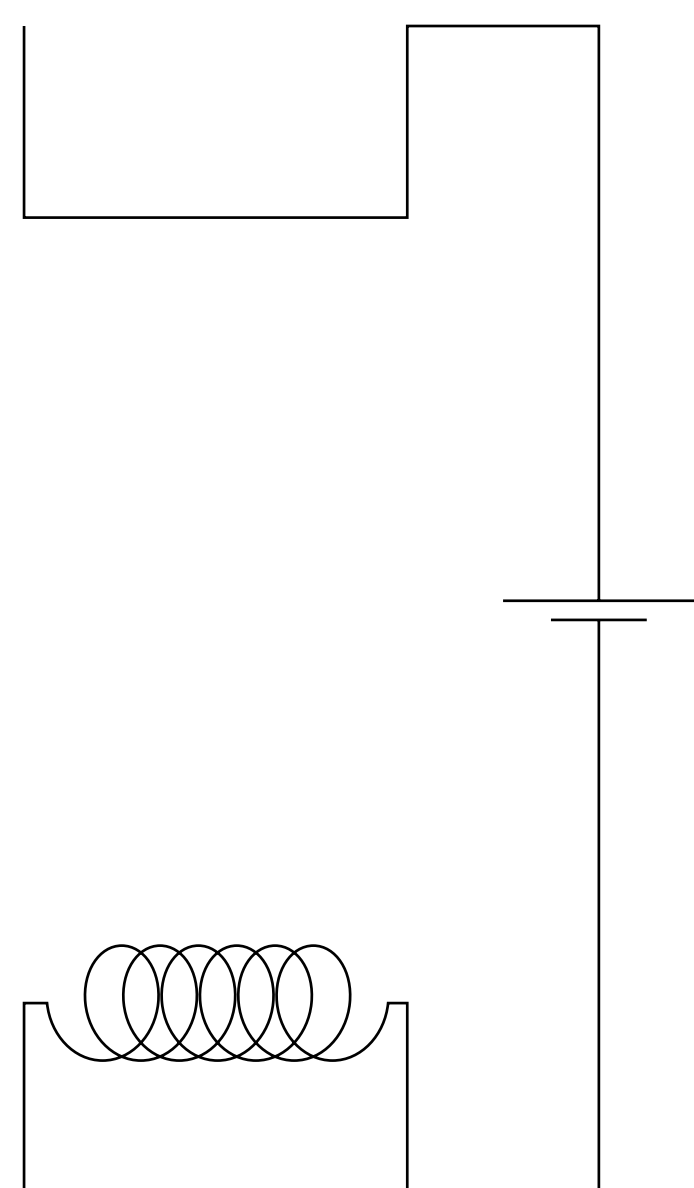
$$\frac{d\sigma}{d\Omega} \propto |\mathbf{A}_0 \int \psi_f(R) \mathbf{p} \psi_i(r) dr|^2 \partial(E_f - E_i - h\nu).$$

Koopmans theorem states that the energy will change due to the relaxation of the surface:

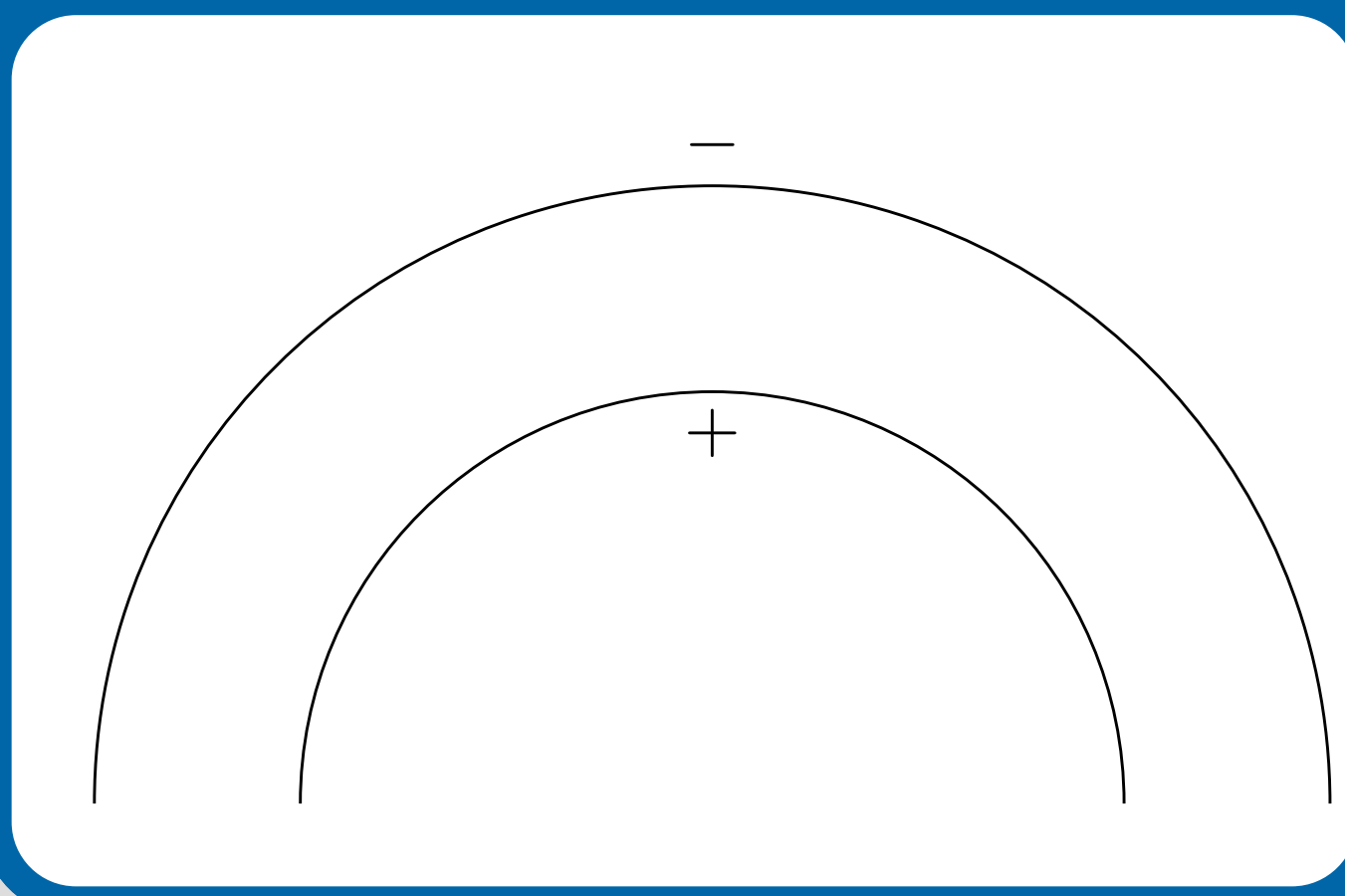
$$E_{\text{kin}} = h\nu - (E_{\text{bin}} - E_r) - \Phi$$

Electron stuff

X-ray generation



Electron mass analyser



Types

$$I(\mathbf{R}) \propto |\psi_0(\mathbf{R} + \sum_j \psi_j s_j \mathbf{R})|^2$$
$$I(k) \propto \left| \cos \Theta_k + \sum_j \frac{\cos \Theta_k}{r_j} |f(\Theta_j, k)| e^{ikr_j(1 - \cos \Theta_j) + \phi(\Theta_j, k)} \right|^2$$

- Angle scan

Here the angle varied, but the x-ray energy is constant, so it can be used with laboratory sources. The diffraction pattern can tell something about the surface structure.

- Energy scan

Here the energy is varied, but angle kept constant, so a synchrotron is needed. It turns out that the spectrum will be modulated due to the difference in energy.

$$\chi(E) = \frac{I(E) - I_0(E)}{I_0(E)}$$

This experiment doesn't need long order to work, and XPS is underlying, so the same structural information is gathered