Photoexcitation processes in atoms

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Photoelectric absorption is characterized by a smooth power-law decrease of the cross section with photon energy. Absorption edges reveal rich structure, which continues into the high-energy side. The quasiperiodic signal, superposed onto the smooth basis, due to scattering of the photoelectron on the neighbours of the target atom provides the basis for the structural (XAFS) analysis of the material. Irregular tiny resonances and edges that appear over the same general range as XAFS are recognized as intra-atomic effects: multielectron excitations (MEE) owing to correlated motion in the electronic cloud. The systematic study of MEE began on noble gases and metallic vapours, both of which are gases of free atoms. With some extremely strong MEE, mostly coexcitations of the sub-valence $d$ and $f$ electrons, the structural XAFS analysis may be compromised; hence, there is a need to independently determine the MEE signal, the atomic absorption background (AAB) for the analyzed element, and remove it prior to analysis. In view of the scarcity of elements which can practically be prepared in a free-atom gas state, several approaches to approximate the AAB have been developed: analysis of disordered compounds, where the weak and simple XAFS signal can be modelled and removed, and correlation analysis of the absorption spectra of several independent samples, where the AAB is extracted in an iterative procedure.

In the process of inner-shell photoelectric absorption, an atomic electron is promoted into an orbital, bound or unbound, modified by the field of neighbouring atoms. Only far above the energy threshold, i.e. the X-ray absorption edge, can the orbital be approximated by an outgoing Coulomb wave, where a smooth power-law dependence of the cross section on the photon energy is observed. Closer to the edge, the density of the continuum energy states is modulated by the atomic neighbourhood, and the cross section is modulated accordingly. The process can be approximated by a finite series of photoelectron scattering events (EXAFS). In the immediate vicinity of the absorption edge, the slow photoelectron is caught in a complex potential of neighbours and the scattering description becomes inadequate (XANES). In any case, the quantum yield of the process shows a loss of the order of 10% as many photons are absorbed in competing processes that do not produce a photoelectron with the same well defined energy. The yield, which to a good approximation is only dependent on the target atomic number, is routinely denoted as the amplitude-reduction factor $S^2_0$ in XAFS analysis.

The fingerprints of the competing processes have been observed during the development of XAS techniques, most directly on noble gases, which are ensembles of free atoms without neighbours (Wuilleumier & Krause, 1974), but it was in the study of Deslattes et al. (1983) on the Ar $K$ edge that a
complete picture of the processes was presented. The sharp features were recognized as the fingerprints of multielectron photoexcitations (MEE), an effect in which more than one electron orbital is changed in the quantum state of the atom.

A flurry of reports on MEE followed, most of them from standard absorption measurements on thin metal foils and most of them erroneous (see references in Kodre et al., 1992). The tiny steps in the cross section that were identified as $K + L, L + L, \ldots$ thresholds were mostly vestiges of EXAFS oscillations and sometimes also monochromator glitches. The true progress remained with noble gases: soon, systematic surveys of MEE, including some double-core excitations, at the absorption edges within the normal X-ray range were reported (Esteva et al., 1983; Schaphorst et al., 1993; Deutsch & Kizler, 1992; Arčon et al., 1995).

Together with this, metallic vapours, which are the only other monatomic gases, came into focus, using high-temperature absorption cells developed earlier in studies of ‘chemical’ shifts of core levels (Materlik et al., 1983; Keski-Rahkonen et al., 1984; Arp et al., 1993). The study of MEE progressed in the order of metal volatility: mercury (Filipponi et al., 1993), alkali metals (Padežnik Gomišek et al., 2001, 2003; Kodre et al., 2002, 2010), zinc (Mihelić et al., 2002) and cadmium (Kodre et al., 2006; Padežnik Gomišek, Kodre, Arčon & Bratina, 2011).

The study of MEE spectra in adjacent element pairs (Ar–K, Kr–Rb and Xe–Cs) provided good clues for the identification of individual excitation processes (Fig. 1).

Although a basic explanation of the individual MEE processes had been given in the report by Deslattes, the MEE profiles soon turned out to be richer than the mere superposition of resonant multiple excitations, shake-up processes in the form of tiny absorption edges, and changes of slope at shake-off thresholds (Fig. 2). There have been several successful attempts at the theoretical reconstruction of specific features, but a general approach to MEE is still in development, while ever more complex atomic models are being used. The simple self-consistent description of the atom has proved to be insufficient to describe the details: MEE depend strongly on correlations in the electronic envelope (Amusia, 1990). This also means that the subshell classification (for example $K + L$) or the orbital assignation (for example $1s^2p^3$) is merely a useful but tentative notation and not a definite description. This subject is also treated in Kodre et al. (2021).

The amplitude of some larger MEE features was found to be comparable to the amplitude of EXAFS oscillations, especially in cases of weak structural signal, and it became clear that MEE might affect EXAFS analysis, leading to increased error in the deduced structural parameters (Chaboy et al., 1994). A need arose to measure the MEE signal alone and its interference with the XAFS signal on real samples. Furthermore, the MEE signal or, as it became termed, the atomic absorption background (AAB) should be measured for as many elements as possible so that it can be removed from the absorption data before EXAFS analysis. This idea was based on two assumptions: (i) that the structural signal is

![Figure 1](image1.png)

Figure 1
The absorption spectrum of Rb vapour in the vicinity of the $K$ edge (15 206.9 eV). Inset: above-edge spectra of Rb and Kr on a relative energy scale normalized to unit $K$-edge jump. Thresholds of two-electron excitation groups are indicated (Kodre et al., 2002).

![Figure 2](image2.png)

Figure 2
The relative contribution to Rb and Kr $K$-shell absorption of $1s2d$ and $1s3p$ MEE groups, together with model components: resonance (red), shake-up (blue), shake-off (green) and their sum (magenta) (Kodre et al., 2002). The residual (below) indicates the presence of three-electron and perhaps even four-electron excitations. The energies of Dirac–Fock multiplets are shown.
simply superposed onto the atomic absorption and (ii) that the AAB is transferable, i.e. independent of the chemical or physical state of the element.

The first assumption was tested on some metals for which the vapour-absorption spectrum was available (Fig. 3). However, it soon became clear that for nonvolatile metals the experimental difficulties in preparing a viable vapour sample outweighed the advantage of determining the exact AAB.

Several experimental approaches to approximate the AAB avoiding the use of vapour have been devised. One straightforward idea is to measure absorption in metals above the melting point, at which the intensity of the EXAFS signal is drastically reduced owing to the disorder in the liquid phase. In an ingenious device to confine tiny droplets of metals in a low-absorption powder matrix, a temperature as high as 2800 K was achieved in a measurement on molybdenum carbide; rhodium, palladium, silver, indium and tin were also measured (Filipponi & Di Cicco, 1995). Another idea, which was implemented on bromine, involved the use of a compound in which the Br atom was virtually free, surrounded by a layer of hydrogen-rich ligands which removed stronger scatterers beyond 3 Å (D’Angelo & Pavel, 2001). In strongly disordered media the structural signal is weak and simple, so that the AAB can be recovered by the subtraction of a single harmonic component. Alloys of alkali metals are sufficiently disordered within broad intervals of mixing ratios, so that the EXAFS signal falls off close above the edge (Arčon et al., 2005; Fig. 4). Chemical forms that are more generally applicable for this purpose are found in solutions (D’Angelo et al., 2004) and gels (Padežnik Gomišek et al., 2006).

In X-ray absorption spectra of molecular gases the structural signal is also rather small and is easily modelled for the geometrical simplicity of the atomic neighbourhood. Gaseous hydrides were soon recognized as a useful approximation for free atoms in view of the low scattering power of the H atom (Bodeur et al., 1989). Prešeren et al. (2001) studied hydrides of the series of elements from Ge to Br, extracted the AAB and showed that the fine structure of the AAB features is modified by the symmetry group of the molecule. Molecular-gas data provided a test of assumption (ii): the transferability of AAB. It was shown in K-edge absorption spectra of gaseous arsenic hydride and the vapours of the element and its oxide (Fig. 5) that the AAB is largely the same in the three samples, with the exclusion of the immediate vicinity of the edge involving the fingerprints of coexcitations of valence electrons (Kodre et al., 2001).

An approximate AAB for any element that is adequate for use in EXAFS analysis can be prepared by extension of the idea of the numerical subtraction of a weak and simple structural signal (Li et al., 1992; Bridges et al., 1995). This
approach has been demonstrated on a collection of absorption data for the 4p elements (Padezni? Gomi?ek et al., 1999). Absorption spectra of an element in two or more chemical compounds are separated into the structural signal and the atomic background in an iterative alternating sequence: the AAB from a previous step involving one of the samples is subtracted from the spectrum of the next sample, and the remainder is analyzed using an EXAFS code. The reconstructed EXAFS signal is subtracted from the measured data to obtain the next iteration of the AAB. The procedure was shown to converge rather rapidly, typically in three cycles. A series of AABs for the elements from Ga to Br was prepared with this method, using the absorption spectra of elements, oxides, salts and disordered sulfides (Fig. 6).

In the practice of EXAFS analysis, some elements, or rather ranges of elements, are known for their strong MEE features, which interfere with analysis. The most salient case is the strong resonance in L\textsubscript{2}-edge EXAFS of barium and the subsequent lanthanide elements (Fig. 7), which is recognized as a fingerprint of 2p4d excitation (Solera et al., 1995). The exceptionally large MEE interferes with EXAFS analysis even in well ordered samples with a strong structural signal. The problem is aggravated by the small k-range of the useful L\textsubscript{3} EXAFS signal and the fact that both alternatives (switching to the K edge or the L\textsubscript{2} edge) are less practical. The remedial use of an independently determined atomic background or a model thereof has been demonstrated in studies of cerium oxide (Padezni? Gomi?ek et al., 2004) and barium hexaferrite (Padezni? Gomi?ek, Kodre, Ar?con, de Panfilis et al., 2011). In the same way, the strong 2p4f resonances interfere with the structural signal in actinide elements (Hennig, 2007).

It is evident that the atomic absorption background is a useful and sometimes essential tool in the interpretation of EXAFS spectra and should be eliminated from the structural signal at the beginning of the analysis. Using the general approach described above, AABs of all elements could be collected and installed in EXAFS analysis software (Chaboy et al., 1994). An alternative idea, which has already been realized to some extent, is a simple analytic ansatz for the strongest MEE features that can be included in the best-fit procedure for EXAFS parameters (Burattini et al., 1993).

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![Figure 6](image6.png)

*Figure 6*

The contribution of the 1s3p and 1s3d MEE groups in elements from Ga to Kr. The energies of the lowermost resonances in each group are indicated by arrows (Padezni? Gomi?ek et al., 1999). Except for directly measured Kr absorption, the AABs are extracted by iteration from the absorption spectra of elements, sulfides, oxides and salts. Spectra are normalized to unit K-edge jump, average slope is removed.

![Figure 7](image7.png)

*Figure 7*

The k\textsuperscript{2}-weighted L\textsubscript{1}-edge and L\textsubscript{3}-edge EXAFS signals of Ba\textsuperscript{2+} ions in aqueous solution normalized to the respective edge jump (Padezni? Gomi?ek, Kodre, Ar?con, de Panfilis et al., 2011). Note the opposite phases of the s and p wave signals which ensure almost total cancellation in the summed signal over a wide interval of 2.7–6.3 Å\textsuperscript{-1} between the XANES residuals on the low-k side and noise on the high-k side, displaying the nonstructural 4d resonance at ~5.5 Å\textsuperscript{-1}.


