

IUCr Dictionary entries

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Dictionary entry 1

X-ray Absorption Spectroscopy (XAS)

Definition

X-ray Absorption Spectroscopy (XAS) is a technique for measuring the linear absorption coefficient $\mu(E)$ of a substance as a function of the incident photon energy E in the X-ray regime. This technique is element and orbital-specific and determines the local atomic and electronic structure of matter. XAS conventionally includes techniques of XAFS (q.v.), which in turn includes both XANES and EXAFS (q.v.). An XAS spectrum may also be obtained using fluorescence, electron yield and scattering processes indirectly (i.e. without directly measuring the absorption of X-rays).

See also (cross link)

X-ray Absorption Fine Structure (XAFS)

EXAFS - Extended X-ray Absorption Fine Structure

Dictionary entry 2

X-ray Absorption Fine Structure (XAFS)

Definition

X-ray Absorption Fine Structure (XAFS) is the modulation of the **absorption coefficient** (q.v.) at and above an Absorption Edge (q.v.) of an element due to its chemical state and structure of its immediate surroundings. XAFS is commonly divided into the 'near edge' region (XANES or NEXAFS) which extends to ~50 eV above the absorption edge (q.v.) and the 'extended' region (EXAFS) that displays oscillations in the absorption coefficient extending from ~50 eV above the absorption edge.

The distinction in usage for XANES (X-ray Absorption Near Edge Spectroscopy) and NEXAFS (Near-edge X-ray Absorption Fine Structure) is historical. Generally, XANES is used for hard X-ray edges (~1 keV and above), while NEXAFS is used for soft X-ray edges. Spectral features that occur before the rise of the main absorption edge are referred to as 'pre-edge' features, associated with transitions to bound states.

The Extended X-ray Absorption Fine Structure (EXAFS) (q.v.) region contains modulation of the absorption coefficient that can be interpreted in terms of photo-electron scattering.

In relation to the (linear) absorption coefficient, the XAFS is defined as

$$\chi(E) = \frac{[\mu(E) - \mu_0(E)]}{\mu_0(E)}$$

Where $\mu(E)$ is the linear absorption coefficient measured or calculated and $\mu_0(E)$ a smooth background as calculated in the absence of scattering or fit (e.g., a spline fit) etc.

The XAFS is often practically defined as

$$\chi(E) = \frac{[\mu(E) - \mu_0(E)]}{\Delta\mu(E)}$$

where $\mu(E)$ is either measured or calculated and $\Delta\mu(E)$ is either the jump in absorption at the edge or a reference background that simulates the edge and a smooth atomic-like background.

See also (cross link)

Absorption edge

Absorption coefficient

Extended X-ray Absorption Fine Structure

Dictionary entry 3

Absorption edge

Definition

An absorption edge is the energy at which there is a sharp rise (discontinuity) in the (linear) absorption coefficient of X-rays by an element, which occurs when the energy of the photon corresponds to the energy of a shell of the atom (K , L_I , L_{II} , L_{III} , etc. corresponding to the creation of electron holes in the 1s, 2s, 2p_{1/2}, 2p_{3/2} etc. atomic subshells).

Associated with this transition is the **absorption threshold (q.v.)** characterized by the corresponding energy E_0 .

See also (cross link)

Fermi level

Absorption threshold

[http://reference.iucr.org/dictionary/Absorption edge](http://reference.iucr.org/dictionary/Absorption%20edge)

Dictionary entry 4

Absorption coefficient

Definition

The X-ray mass absorption coefficient, $\left[\frac{\mu}{\rho}\right](E)$ or $\left[\frac{\mu}{\rho}\right]_{pe}(E)$ follows the Beer-Lambert law for a parallel beam of photons of energy E in which the transmitted photon intensity $I(t)$ is related to the incoming photon intensity I_0 such that $I(t) = I_0 e^{-\left[\frac{\mu}{\rho}\right]_{pe} \rho t}$ where t is the thickness of a uniform sample and the density ρ is usually given in (g/cm^3). The mass absorption coefficient is labeled as such because the absorption exponent is linear in the mass per unit area ρt , otherwise known as the integrated column density through a sample. Use of μ for this term is not recommended because it is highly ambiguous and dimensionally inconsistent. The subscript *pe* emphasizes that this is the **photo-electric mass absorption coefficient** rather than the **mass attenuation coefficient** (q.v.), which of course does not obey the Beer-Lambert law. Note also that it is rare for SI units to be used in texts on absorption spectroscopy.

The X-ray linear absorption coefficient, $\mu(E)$, or $\mu_{pe}(E)$ follows $I(t) = I_0 e^{-\mu t}$, with units of length^{-1} (conventionally cm^{-1}). μ is the product of density ρ (g/cm^3) and the mass absorption coefficient $\left[\frac{\mu}{\rho} \right]$ (cm^2/g).

It is sometimes convenient to describe the decrease in the beam intensity in terms of the absorption length: the thickness of the material in question at which the beam intensity has fallen to $(1/e)$ of the incident beam intensity: that is when $\mu t = 1$, or when 63% of the flux is absorbed. In soft X-ray spectroscopy one absorption length can be some tens of nm while typical values in hard X-ray spectroscopy are microns or millimetres.

μ depends on energy, E , of the incoming photon and the elemental composition of the sample. The XAFS technique measures the variations in $\mu(E)$.

Historical Note:

Early references are P. Bouguer, *Essai d'Optique sur la Graduation de la Lumiere* (Paris, Jombert, 1729); J. H. Lambert, *Photometria sive Mensura et Gradibus Luminus, Colorum et Umbrae* (Augsburg, 1760); A. Beer, *Bestimmung der Absorption des rothen Lichts in farbigen Flüssigkeiten*, *Annalen der Physik*. 86 (1852) pp78-87.

Note that all these preceded the discovery of X-rays, and were based on visible optics. From 'A History of Light and Colour Measurement' (S. F. Johnston, IoP 2001) p18: 'The logarithm of the quantity of light received is inversely [meaning multiplied by -1] proportional to the thickness (Bouguer's Law) and to the chemical composition (Beer's Law) of an absorbing material, and the quantity of light to the cosine of the angle of incidence of the illuminated sample (Lambert's Law)'.

See also (cross link)

linear attenuation coefficient

mass attenuation coefficient

Dictionary entry 5

Mass attenuation coefficient

Definition

The **mass attenuation coefficient** in cm^2/g can be written as a sum of separated photo-electric mass absorption coefficients $[\mu/\rho]_{\text{PE}}$ and coherent $[\sigma/\rho]_{\text{coh}}$ and incoherent $[\sigma/\rho]_{\text{incoh}}$ scattering contributions:

$$[\mu/\rho]_{\text{TOT}} = [\mu/\rho]_{\text{PE}} + [\sigma/\rho]_{\text{coh}} + [\sigma/\rho]_{\text{incoh}} \text{ or equivalently}$$

$$[\mu/\rho]_{\text{TOT}} = [\mu/\rho]_{\text{PE}} + [\mu/\rho]_{\text{coh}} + [\mu/\rho]_{\text{incoh}}.$$

It is recommended that $[\mu/\rho]_{\text{TOT}}$ be used to distinguish this from the mass absorption coefficient $[\mu/\rho]_{\text{PE}}$ (q.v.) as they are both commonly presented as $[\mu/\rho]$.

The last two contributions are angle-dependent. Note that while absorptive processes are linear (q.v. Absorption Coefficient), coherent scattering (and incoherent scattering) are not linear and hence the attenuation coefficient does not obey the Beer-Lambert Law.

The mass attenuation coefficient is conventionally given by the symbol $[\mu/\rho] = \sigma/(uA)$, where σ is the cross-section in barns/atom ($1 \text{ barn} = 10^{-24} \text{ cm}^2$), u is the atomic mass unit, and A is the relative atomic mass of the target element (i.e. in amu; the mass relative to 12 for carbon 12).

Where a material is composed of separate layers, the total *absorption* is given by the sum

$$\ln\left(\frac{I}{I_0}\right)\bigg|_{pe} = -\sum_i \left[\frac{\mu}{\rho} \right]_{pe,i} [\rho t]_i$$

Sometimes mass fractions are used as an approximation for a mixture, assuming that each atomic scatterer is independent.

See also (cross link)

Linear Attenuation Coefficient

Absorption Coefficient

Cross-section

Dictionary entry 6

Linear attenuation coefficient

Definition

The linear attenuation coefficient $\mu(E)$, or preferably $\mu_{TOT}(E)$ in cm^{-1} , is a measure of the photon beam attenuation by a material due to absorption and scattering processes and hence differs from the absorption coefficient, which is a measure of beam attenuation due to absorption processes only.

$\mu_{TOT}(E)$ is given by $\mu_{TOT} = \left[\frac{\mu}{\rho} \right]_{TOT} \rho$ where ρ is the density of the material in g/cm^3 .

History

Coefficients for converting between these units are given by many authors (Cohen, E. R., Taylor, B. N., (1987) Rev. Mod. Phys. 59 1121-1148; D. C. Creagh and W. J. McAuley, (1992) International Tables for Crystallography, ed. AJC Wilson Kluwer Academic, Boston; Chantler C.T. (1995) J. Phys. Chem. Ref. Data 24, 71-643.

See also (cross link)

Absorption coefficient

Mass attenuation coefficient

Dictionary entry 7

Cross-section

Definition

Cross-section is a measure of the probability of interaction between the incident photons with the material via photoabsorption or scattering processes. It is the effective area that will yield a transition process for a perpendicularly incident flux of one particle per unit area. The total interaction **cross-section** σ_{tot} is usually represented as a sum over the individual photon interaction cross-sections (per atom):

$$\sigma_{tot} = \sigma_{coh} + \sigma_{incoh} + \tau_{PE} + \kappa_n + \kappa_e + \sigma_{p.n.} \text{ [following standard tabulations] or}$$

$$\sigma_{tot} = \sigma_{coh} + \sigma_{incoh} + \sigma_{PE} + \sigma_n + \sigma_e + \sigma_{p.n.} \text{ [following IUCr international tables}$$

nomenclature].

The components are, in order, the coherent scattering cross-section, the incoherent scattering cross-section, the photoelectric absorption cross-section, the nuclear (coherent) pair-production cross-section, the nuclear incoherent (or triplet) cross-section and the photonuclear cross-section. These cross-sections are conventionally given in barns/atom (1 barn = 10^{-28} m² = 100 fm²). For most crystallographic applications the energy range of interest is 3 keV < E < 200 keV where the photoelectric, coherent and incoherent cross-sections are dominant. The three corresponding nuclear cross-sections are minor in this energy regime but become dominant from 1 MeV - 10 MeV, and it may be noted that some of the cross-sections can be in phase and hence amplitudes can add rather than cross-sections.

The atomic form factor can be represented as the sum of the angle-dependent component, and the anomalous real and imaginary energy-dependent components (the latter two are also referred to as the dispersive or resonant contributions):

$$f = f_0(\theta) + f'(E) + if''(E)$$

The imaginary component of the atomic form factor $\text{Im}(f) = f''$ (in electrons per atom) = f_2 (used by Henke et al.) is directly related to the atomic photoabsorption cross-section given as σ_{PE} or μ_{PE} in different references:

$$\text{Im}(f) = f''(E) = f_2(E) = \frac{E\sigma_{PE}(E)}{2hcr_e}$$

where r_e is the Bohr electron radius and other symbols have their usual meanings (C. T. Chantler, J. Phys. Chem. Ref. Data. 29(4) (2000) 597-1056). The Kramers-Kronig relation expresses causality and determines the real component of the (atomic) form factor in terms of the imaginary component:

$$f'(E, Z) = f'(\infty, Z) - P \int_0^{\infty} \frac{\mathcal{E}' f''(\mathcal{E}')}{(\hbar\omega)^2 - (\mathcal{E}')^2} d\mathcal{E}'$$

where $E = \hbar\omega$ is the photon energy, \mathcal{E}' is the energy above the electron binding energy of the intermediate (bound or continuum) state, and P represents the Cauchy principal value. Fundamental constants and conversion factors are given (for example) in (Chantler C.T. (1995) J. Phys. Chem. Ref. Data 24, 71-643)

In measurements as in XAFS, the flux is often measured before $I(0)$ and after $I(t)$ the sample of thickness t (in cm). The Beer-Lambert law suggests

$$\left[\frac{\mu}{\rho} \right] = \frac{-\ln(I(t)/I(0))}{\rho t}$$

In practice fluxes must be corrected for background signal, normalisation and scattering, following

$$\left[\frac{\mu}{\rho} \right] = \frac{-\ln \left[\frac{\left((I(t)_d - D_d) / (I(0)_u - D_u) \right)_s}{\left((I(t)_d - D_d) / (I(0)_u - D_u) \right)_b} \right]}{\rho t}$$

where the subscript *s* refers to the intensity measured with a sample in the path of the beam and the subscript *b* refers to the intensity measured without a sample in the path of the beam (correcting, for example, for air attenuation and window effects). The subscript *u* refers to the upstream detector or monitor, while the subscript *d* refers to the downstream detector. *D* refers to the dark current or the electronic noise for either the upstream or downstream detectors. This formula does not explicitly correct for the scattering components, and is valid for the absorption cross-section [e.g. Phys. Rev. A 64 062506 (2001); Phys. Rev. A 71, 032702 (2005)].

To derive the mass absorption coefficient (or equivalent linear coefficients) including back-scattering and correcting for harmonics, further corrections are sometimes important. For central X-ray energies, the photoelectric absorption is often dominant and hence this can be a useful approximation. However, many measurements of XAFS use fluorescence, and the normalization is further complicated by self-absorption, and in particular there is no clean *I(t)* measurement.

See also (cross link)

Atomic scattering factor

Absorption coefficient

Mass Attenuation Coefficient

Linear Attenuation Coefficient

Dictionary entry 8

Extended X-ray Absorption Fine Structure (EXAFS)

Definition

Extended X-ray Absorption Fine Structure (EXAFS) is the portion of **XAFS** (cross link) spectra well above an **Absorption Edge** (cross link) - typically starting ~ 50 eV above the absorption edge. EXAFS can be interpreted as due to scattering of the photo-electron ejected from the absorbing atom by the photo-electric effect. The photo-electron will scatter from surrounding atoms and a portion of it will return coherently to the absorbing atom still in its excited state (before the hole in the core electron level has been refilled). The amplitude of the scattered photo-electron at the absorbing atom will modify the probability of creating a photo-electron, and so the probability of X-ray absorption.

EXAFS can be modelled with the EXAFS Equation:

$$\chi(k) = \sum_j \frac{N_j S_0^2}{kR_j^2} F_j(k) e^{-2R_j/\lambda_j(k)} e^{-2k^2\sigma_j^2} \sin[2kR_j + \Phi_j(k)]$$
$$k = \frac{2\pi}{\lambda} = \sqrt{\frac{2m_e(E - E_0)}{\hbar^2}}$$

where k is the photoelectron wavenumber, E is the X-ray energy, E_0 is the energy of the **Absorption Edge** (q.v.), and m_e is the electron mass. Note that k is really the ‘photoelectron momentum index’ and differs from the physical momentum (See Rehr, Albers cited in History below). The normalised value of $\chi(k)$ is dimensionless, because the (standard) expression above has F in units of $1/k$ (i.e. length). Other definitions for F being dimensionless (as a form factor or scattering amplitude) have $(kR)^2$ in the denominator to maintain consistency of units.

The sum in the EXAFS Equation is most simply over *shells* of atoms of a particular type j and similar distances from the origin of the initial photoelectron. Then N_j is the coordination number, R_j the interatomic distance, and σ_j^2 represents the mean-square disorder in the distance for the j^{th} shell. F_j is the photoelectron (back-)scattering amplitude and $\Phi_j(k)$ is the corresponding (back-)scattering phase for the j^{th} atomic shell. S_0^2 is an amplitude reduction factor accounting for relaxation of the absorbing atom due to the presence of the empty core level and **Multi-Electron Excitations** (cross link). $\lambda_j(k)$ is the photoelectron inelastic mean free path, which has a strong dependence upon k , and has values in the range of 1 to 100 Å over the XAFS regime.

The crude approximation of $\Phi_j(k) \approx -2a_0k$ (a_0 is the Bohr radius) works for many systems and causes peaks for a particular shell in the Fourier transform of $\chi(k)$ to be shifted $\sim 0.5 \text{ \AA}$ below the actual interatomic distance. Both $F_j(k)$ and $\Phi_j(k)$ depend upon the atomic number Z of the scattering atom, and have non-linear dependence on k .

The $e^{-2k^2\sigma_j^2}$ term is often referred to as the EXAFS isotropic or effective Debye-Waller Factor, including thermal vibration and static disorder. The sum over shells and use of σ_j^2 in the standard EXAFS equation can be generalized to an integral over the partial pair distribution function $g(R)$ in which one atom is always the absorbing atom.

The sum in the EXAFS Equation can be generalized to be over photo-electron *scattering paths* instead of *shells of atoms*. This formalism allows the inclusion of multiple scattering paths for the photo-electron, which can give important contributions in many systems. The interpretation of many components of the EXAFS Equation are then slightly modified, so that R_j is then half the path length, and $F_j(k)$ and $\Phi_j(k)$ become the (multiple) scattering amplitude and phase-shift for the entire path.

The EXAFS Equation allows the numerical determination of the local structural parameters N_j and R_j , and σ_j^2 knowing the scattering amplitude $F_j(k)$ and $\Phi_j(k)$ for a small number (typically 1 to 10) of shells or paths. It breaks down at low k (the XANES region) as the $1/k$ term increases, $\lambda_j(k)$ increases, the disorder terms do not strongly dampen the EXAFS, and the EXAFS picture of single particle scattering is no longer a good approximation.

History

The history is reviewed in Lytle, F. W., 1999, J. Synchrotron Radiat. 6, 123 and Stumm von Bordwehr, R., 1989, Ann. Phys. (Paris) 14, 377. EXAFS Scattering Theory: Sayers, Stern, Lytle, Phys. Rev. Lett. 27 (1971) 1204 developed a quantitative parametrization of the central EXAFS region from the Kronig short-range order theory. Their EXAFS equation has become standard for much current work; an extensive review Rehr, Albers, Rev. Mod. Phys. 72 (2000) 621-654 covers significant developments of the scattering perspective, especially in terms of theoretical calculations for EXAFS used in quantitative analysis and the inclusion of spherical outgoing photoelectron waves.

See also (cross link)

X-ray Absorption Fine Structure (XAFS)

Absorption Edge

Multi-electronic Excitation

Dictionary entry 9

Multi-electron excitations

Definition

The assignment of a spectral feature as multi-electron excitation depends on the level of theory, *i.e.* how the electronic states are described. A general definition can be stated as follows: If there exists no one-electron operator that gives a matrix element unequal to zero between the reference state and an excited state, the latter must be multi-electron in nature. The reference state is in most cases the ground state of the system. Some spectral features in XAFS are commonly denoted multi-electron spectral features and referred to as 'shake-up', 'shake-down' and 'shake-off' excitations. The amplitude reduction factor S_0^2 in the EXAFS equation is included to consider multi-electron excitations.

Dictionary entries 10 and 11

Fermi level and Fermi Energy

The **Fermi level** is also known as the **Fermi Energy**. Two definitions are proposed the first one is concentrating on a general formal definition while the second one is focussing on theoretical convergence for use by XAS users and programs.

- 1) In an independent particle approach to the description of a fermion system (*i.e.* particles obeying Pauli's exclusion principle), the Fermi level is the energy value lying between the highest occupied level and the lowest unoccupied level, usually defined as their average. If the energy level spectrum is a continuum (or almost a continuum) the three levels coincide. In a many-body approach, the Fermi level is the energy necessary for adding or subtracting a particle from the system. This definition encompasses the non interacting case.

Like all energy states, the Fermi level is measured from the vacuum level. In XAS spectra the Fermi level is below or at the first allowed transition, depending on the system and the absorption edge.

- 2) In X-ray absorption spectroscopy (XAS), the **Fermi energy** dictates possible pre-edge features and explains the possibility or impossibility of open scattering channels adding to the near-edge structure. When theoretical formalisms compute the reference Fermi energy, crucial for the XANES region, the convergence of the complete quantum mechanical system is an absolute requirement, whether atomic, cluster, or periodic boundary conditions are used. The lack of convergence for theoretical

formalisms can at this time lead to systematic errors in the determination of the Fermi energy and corresponding pre-edge structure of order 1- 10 eV in the X-ray regime and should be considered carefully as this affects the interpretation of XAFS and XANES.

Dictionary entry 12

Absorption threshold

Definitions

In the literature there is much confusion, even in modern papers, concerning the definition of the absorption threshold. The absorption threshold should indicate the first allowed transition in an absorption spectrum. Many definitions are used in common parlance. Practically, they yield very different values in common analysis. We present and comment upon the most commonly used:

1. The energy at which the open continuum channel for photo-electric absorption becomes available, producing a continuum photo-electron. This has an exact value from theory, subject to convergence issues (q.v. **Fermi energy**).
2. An (higher) energy at which a secondary (two-step) photoionization channel becomes energetically possible (see shake-up, shake-off) ; in general this is more challenging to compute theoretically, and is less easily separable in conventional XAS experimental data, but can be investigated incisively in RIXS, XFS and related spectroscopies (q.v.).
3. Experimentally, the **absorption threshold** is sometimes defined as the inflection point in the first derivative of the experimental edge spectrum (the point of maximum slope on the rising edge for a particular sub-shell); this is a convenient marker for experimentalists but – a. it is source (beam-line) and band-width dependent; b. it is affected by pre-edge structure and the **Fermi level** (cross link) due to potential contributions from bound-bound channels ; c. the experimental edge may contain two or more such inflection points, and the determination depends upon instrumental resolution.
4. Experimentally, the **absorption threshold** is sometimes defined as the point exactly 50% of the jump ratio from the background absorption (from other shells, including scattering) to the peak absorption coefficient of the XANES spectrum, defined either by the clear maximum or by the smooth line representing the background to be subtracted in the determination of $\chi(k)$ (q.v. XAFS); this is a problematic measure, since it depends upon beam-line dependent effects (3 above), and a wide variety of different predictions of the ‘true background level’ μ_0 above the edge (q.v. XAFS).

5. Computationally, an **absorption threshold** is defined for XAFS fitting (and occasionally XANES fitting) as E_0 which is considered either as an arbitrary fitting coefficient or the starting point of the k transform, which in turn generates the Fourier transform for the XAFS structure $\chi(k)$; as the latter, it should be defined as per 1 above; as the former, this will often yield a function of r and errors in E_0 of order 10 eV or more which can result in bond length errors of order 0.02 Å or more.

Both computationally and experimentally, the energy axis is often not defined except in a relative sense, so that inconsistencies between the implementations of these definitions are at this point relatively common.

See also (cross link)

Fermi level/Fermi energy

Dictionary entry 13

Selection rules

Definition

Selection rules refer to the conditions under which the quantum mechanical transition matrix elements for a process are different from zero (and hence the process is allowed), due to constraints derived from the symmetry properties of the states involved and those of the transition operator. Since the set of symmetries for a quantum system form a group, one can classify the transformation properties of the states (eigenfunctions) and the transition operator according to the irreducible representations of the group itself. In such a case the Wigner-Eckart theorem dictates the conditions for the process to occur (see any standard text on group theory).

In the most common example for transition theory, if we classify the system states (eigenfunctions) according to the full rotation group and expand the transition operator in multipoles as

$$\mathbf{p}e^{i\mathbf{k}\cdot\mathbf{r}} = \sum_l f_l(r) \mathbf{Y}_l(\hat{\mathbf{r}})$$

then the angular part of the matrix element will be proportional to

$\langle J_f | Y_l | J_i \rangle$ where $J=L+S$ ($j=l+s$) in a Russell-Saunders coupling scheme. Therefore, from addition of angular momenta and the fact that the transition operator does not affect the spin, we derive

$$|J_f - J_i| \leq l \leq J_f + J_i$$

$$|L_f - L_i| \leq l \leq L_f + L_i$$

$$\Delta S = 0; \Delta M_s = 0; \Delta M_j = m_l$$

which provide a set of selection rules in this case. $J_f=0$ to $J_i=0$ transitions are forbidden by the above rule, since the lowest multipole operator (dipole radiation) is a vector ($l=1$; $m_l = \pm 1, 0$). Conditions on symmetries include those relating to parity, orbital angular momentum quantum number, spin quantum number, (multi-)polarity of the photon field causing the transition, polarisation of the photon field causing the transition, etc. For summation of angular momenta, such as for molecular levels; hyperfine structure including nuclear angular momenta; or coupling within Russell-Saunders, $j-j$ or mixed schemes, a vector triangle summation must generally be followed as above, which provides most selection rules. Different polarisations have different selection rules, so an edge or XAFS spectrum using (polarised) synchrotron radiation will have a different shape and structure depending upon whether the incident X-ray field is linear polarised, circularly polarised, partially polarised.

Electric dipole transition is only the dominant lowest order transition coupling, tending to be dominant for low energies or low- Z elements (even in compounds). However, for such elements as transition metals, higher order terms including electric quadrupole radiation and magnetic dipole radiation become stronger and have complementary selection rules for atomic, molecular and condensed matter quantum systems. Higher order radiation is crucial for the interpretation of K_α spectra satellites; for continuum photoionisation amplitudes and XAFS and absorption edges and for pre-edge features.

History

In widespread tabulations of photoeffect for atomic systems (viz Creagh in IUCr tables, FFAST in the USA and XCOM/Hubbell), some authors have clarified the significance in the computations of dipole, higher order or 'all-order' computations.

Dictionary entry 14

Secondary process detection

Definition

It is experimentally often favourable to use methods other than transmission detection to obtain the linear absorption coefficient $\mu(E)_{pe}$ or $\mu(E)$ (q.v.). This requires recording a signal that arises from a process that occurs with a probability that is proportional to μ_{pe} . This can be the direct photoemission channel. The core hole that is created in the photoabsorption process decays with a lifetime τ . The energy that is released in the decay or secondary process can either be carried by an outgoing electron (e.g. Auger) or a photon (fluorescence). Weak processes, such as excitations of phonons, are neglected here. Detection of the outgoing electrons of all kinetic energies is called Total Electron Yield (TEY) and that of all photons of all energies Total Fluorescence Yield (TFY).

If the secondary process detection is realized with an energy or wavelength dispersive instrument it is possible to further discriminate between the decay channels, e.g. only the K_{α} fluorescence lines. The techniques are then referred to as partial yield detection. An instrumental resolution in the secondary process detection that is on the order of the core hole lifetime broadening or even below may enable one to observe resonance phenomena in the decay channel (e.g. resonant inelastic X-ray scattering, resonant Auger spectroscopy).

Detection of the intensity of a secondary process as a function of the incident energy that is tuned across an absorption edge may be proportional to μ_{pe} to sufficient accuracy. This assumption is the pre-requisite for all secondary process detection schemes which aim to measure the absorption cross section. This may be a good approximation when the dominant decay channel is chosen for the secondary process detection, for example, the fluorescence lines in the hard X-ray range when not detected in high-resolution mode (fluorescence-detected absorption spectroscopy).

Electron yield detection is surface sensitive due to the short mean free path of the electrons.

See also (cross link)

Absorption cross section

Dictionary entry 15

X-ray emission spectroscopy (XES)

Definition

Detection of the X-rays that are emitted from the sample with an instrumental energy bandwidth that is on the order of the core hole lifetime broadening. XES can be performed by taking advantage of various modes of core hole creation the most common being photo-excitation but also ion/electron bombardment and radioactive isotopes (K capture decay) have been used. XES following photo-excitation is a second-order optical process that is theoretically treated using the Kramers-Heisenberg equation. XES thus includes high energy resolution X-ray fluorescence spectroscopy (e.g. K_{β} spectroscopy), resonant X-ray emission spectroscopy (RXES) and resonant inelastic X-ray scattering (RIXS).

In the hard X-ray regime instruments based on perfect crystal Bragg optics are used to analyze the emitted X-rays. Common geometries are Rowland or von Hamos. Applications of XES include electronic structure studies (*e.g.* chemical characterization) but also spectral sharpened XAFS (q.v. HERFD) and range-extended EXAFS. The instrumentation for XES provides the possibility to perform X-ray Raman spectroscopy.

See also (cross link)

Inelastic X-Ray scattering

Dictionary entry 16

Inelastic X-ray scattering (IXS)

Definition

A scattered photon may transfer some of its energy to the sample. The transferred energy can excite the atomic lattice (phonons), single electrons or an ensemble of electrons (collective excitations). IXS considers the energy and the momentum of an incoming and a scattered (emitted) photon. The difference is the energy and momentum transfer, respectively. An **IXS** process can occur after non-resonant or resonant X-ray excitation.

X-ray Raman scattering (XRS) is non-resonant inelastic scattering of X-rays from core electrons. It is analogous to Raman scattering, which is a largely-used tool in optical spectroscopy, with the difference being that the wavelengths of the exciting photons fall in the X-ray regime and the corresponding excitations are from deep core electrons. The

process is in principle analogous to **X-ray absorption**, but the energy transfer plays the role of the X-ray photon energy in X-ray absorption. XRS can be used to measure absorption edges of low Z elements using hard X-rays.

The cross section of non-resonant inelastic X-ray scattering is

$$\frac{d^2\sigma}{d\Omega dE} = \left(\frac{d\sigma}{d\Omega} \right)_{Th} \times S(q, E)$$

with $(d\sigma/d\Omega)_{Th}$ being the Thomson cross section, which signifies that the scattering is that of electromagnetic waves from electrons. The physics of the system under study is buried in the dynamic structure factor $S(q,E)$, which is a function of momentum transfer q and energy transfer E . The dynamic structure factor contains all non-resonant electronic excitations, including not only the core-electron excitations observed in XRS but also e.g. plasmons (the collective fluctuations of valence electrons) and Compton scattering. At small momentum transfer $\mathbf{q} = \mathbf{k} - \mathbf{k}'$ the XRS signal is proportional to the **X-ray absorption** (cross link) cross section. A large momentum transfer allows access to transition matrix elements of higher order, e.g. quadrupole transitions.

Resonant Inelastic X-ray scattering (RIXS) or Resonant X-ray Emission Spectroscopy (RXES) is frequently used to study the electronic structure. It requires the incident energy to be close to an absorption edge. It is possible to distinguish between two cases of resonant scattering:

1) A fluorescence line can be measured after resonant excitation. This is referred to as resonant X-ray emission spectroscopy (RXES) or direct RIXS. In a one-electron picture one could refer to this process as a spectator decay: The photo-excited electron remains in a bound, previously unfilled orbital and an electron from a filled orbital decays to fill the core hole.

2) The photo-excited electron decays to fill the core hole (participator decay). The modification of the Coulomb potential due to photo-excitation and decay may give rise to an excited final state, *i.e.* the system does not return to its ground state. The final state excitation can be a local (e.g. *dd*-excitation), including the ligand (charge transfer excitation) or higher coordination spheres and/or the long-range order of the system (plasmons, magnons, orbitons). The technique is often referred to as (indirect) resonant inelastic X-ray scattering (RIXS).

The general usage in the literature does not strictly distinguish between the two cases.

RIXS/RXES is a second-order process that is theoretically described (A. Kotani and S. Shin, Rev. Mod. Phys. (2001) 73, 203-246) by the Kramers-Heisenberg equation:

$$F(\Omega, \omega) = \sum_f \left| \sum_n \frac{\langle f | T_2^\dagger | n \rangle \langle n | T_1 | g \rangle}{E_g - E_n + \Omega - i \frac{\Gamma_n}{2}} \right|^2 * \frac{\frac{\Gamma_f}{2\pi}}{(E_g - E_f + \Omega - \omega)^2 + \frac{\Gamma_f^2}{4}}$$

With the ground (g), intermediate (n) and final (f) state electron wavefunctions, their energies E_g , E_n and E_f , the lifetime broadenings Γ_n and Γ_f (full width at half maximum) as well as the transition operators T_1 and T_2 for absorption and emission of an X-ray photon, respectively. The difference between incident and emitted X-ray energy is the energy transfer $\Omega - \omega$. The Kramers-Heisenberg equation is often simplified by neglecting interference effects, multi-electron excitations and/or the angular dependence.

RIXS allows spectra to be recorded broadened only by Γ_f and not Γ_n . In most cases it holds that $\Gamma_n > \Gamma_f$ and RIXS thus enables the observation of spectral features with sharper line width than for an absorption spectrum. The method requires that the instrumental energy band width is sufficiently small.

See also (cross link)

X-ray absorption

High Energy Resolution Fluorescence Detection (HERFD)

Dictionary entry 17

X-ray Excited Optical Luminescence (XEOL)

Definition

X-ray excited optical luminescence is an X-ray photon in/optical photon out technique. It concerns the conversion of the X-ray energy absorbed by the system to optical photons

often involving multi-step cascade processes. XEOL is often used together with XANES/NEXAFS to provide site specificity which in turn can help reveal the electronic structure and optical properties of the system of interest.

XEOL can be studied in the time domain if a pulsed X-ray source is used. It is possible to use the time structure of a synchrotron radiation source to study the decay dynamics of a system via various optical de-excitation pathways. This technique is called **Time-Resolved X-ray Excited Optical Luminescence**.

See also (cross link)

XANES/NEXAFS

Secondary Process Detection

Dictionary entry 18

High Energy Resolution Fluorescence Detection (HERFD)

Definition

The **High Energy Resolution Fluorescence Detection (HERFD)** requires measurement of the fluorescence lines with an instrumental energy bandwidth on the order or below the core hole lifetime broadening of the absorption edge (q.v. XES). A HERFD-XAS experiment measures the intensity of the fluorescence line as a function of the incident energy (**fluorescence-detected XAS, secondary process detection**) and may yield spectral features with line broadenings that are smaller than the lifetime broadening of the core hole excited state of absorption. HERFD has to be understood within the framework of **resonant X-ray emission spectroscopy (RXES)**. A HERFD-XAS spectrum may present a good approximation to the **absorption cross section** with reduced lifetime broadening. This is, however, not necessarily the case and has to be carefully verified.

See also (cross link)

Inelastic X-ray scattering (IXS)

Secondary Process Detection