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Multiple scattering approach to X-ray absorption spectroscopy

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Abstract In this paper we present the state of the art of the theoretical background needed for analyzing X-ray absorption spectra in the whole energy range. The multiple-scattering (MS) theory is presented in detail with some applications on real systems. We also describe recent progress in performing geometrical fitting of the XANES (X-ray absorption near-edge structure) energy region and beyond using a full multiple-scattering approach.

Keywords X-ray absorption spectroscopy, X-ray absorption near-edge structure, Multiple-scattering theory

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1 Introduction

Electromagnetic radiation has been historically the most widely used tool in the investigation of the properties of the physical state of the matter. The main reason lies in the smallness of the fine structure constant α= 1/137 that governs the coupling of the radiation with matter. This fact makes possible the use of linear response theory as an interpretative scheme of experimental observations and, on the other hand, the perturbation of the system under study is negligible so that one can investigate the physical properties of the unperturbed system. Most of the studies of the electronic excitation dynamics, in the various states of the matter, benefit by this fortunate circumstance.

However, due to the smallness of the coupling constant scattering experiments can only probe the pair correlations function of observable operators that couple to the electromagnetic probe, like the local density $\rho(r)$. This information is usually sufficient to reconstruct the spatial geometry of the atoms in periodic systems; for example, diffraction experiments, but is not enough in materials where no any long-range order is present. There is an exception: the X-ray absorption (XAS) spectroscopy from core levels. In fact it has been realized that, although the primary probe couples weakly with the matter, the secondary probe generated in the photoabsorption process, i.e. the photoelectron, can couple strongly with the atoms of the system and therefore can carry information beyond the pair correlation functions through final state interactions. As consequences photoabsorption and photoemission data, especially from core level, have been extensively used for structural purposes.

The advent of the use of Synchrotron Radiation (SR) has given a tremendous impulse to the areas of research using X-ray. The unique properties of SR source, like tunability, brilliance, intensity and polarization, to cite few, make the X-ray spectroscopies a unique tool for the investigation of geometrical and electronic structure of materials. The high quality of the experimental data makes now possible several studies regarding the electronic excitation dynamics, like screening, polarization and relaxation mechanism, and elucidates the interplay between geometrical and electronic structure in many systems from biological to condensed matter materials. Therefore a theoretical scheme for interpreting such type of data would be highly desirable. This scheme is provided by the multiple-scattering (MS) theory, which form the objects of this article.

2 Multiple scattering theory

The MS theory is essentially a method to calculate, from first principle, the electronic structure of polyatomic molecules and solids. This theoretical technique avoids many of the difficulties of the standard methods of quantum chemistry and band theory, leading to an accurate description of the wave function in molecules and solids of considerable stereo-chemical complexity.[1]

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This method works in the real space without the need of any spatial symmetry and translation invariance. This last point is particularly important in the calculation of the X-ray absorption spectra from core levels because the presence of the core–hole in the final state breaks any translation symmetry. Using this theoretical approach one can calculate both bound and continuum parts of the molecular wave function. At the beginning of ’70, Johnson and co-workers introduced this method for the calculation of bound levels and optical transitions in small cluster of atoms, later several groups have extended this approach to the continuum part.[2,3]

The MS theory uses the so-called “muffin-tin” (MT) approximation for the shape of the potential of the cluster of atoms used in the calculation. This means that the space is partitioned into distinct atomic and interatomic regions. Each atom is enclosed in a sphere of specific radius, the so-called “ muffin-tin ” radius, and an “outer sphere” envelops the whole molecule. Three regions can be identified in this partitioning: atomic regions (spheres centered upon nuclei) normally called region I; extramolecular region (the space beyond the outer sphere radius), region III, and an interstitial region of complicated geometry, region II, in which the molecular potential is approximated by a constant, position independent potential. As a further approximation the potential is spherically averaged within the atomic spheres and outside the outer region. A pictorial view is reported in Fig.1.

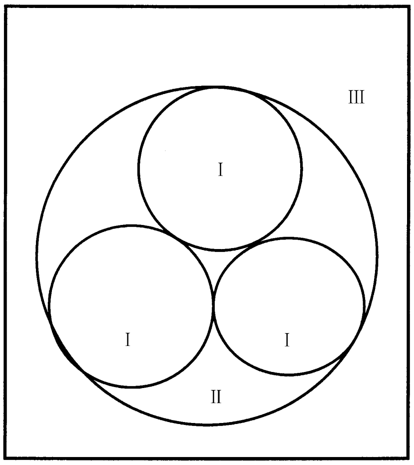

Fig.1 Pictorial view of the cluster of atoms; the different regions are explicitly indicated.

The Coulomb and exchange part of the input potential are calculated on the basis of a total charge density obtained by superimposing the atomic charge densities of the individual atoms constituting the cluster. For the exchange potential V_{ex} it is possible to use either the usual energy independent Slater approximation

$$V_{\mathrm{ex}} = -6\alpha\,[(3/8\pi)\,\rho(x)]^{1/3} \tag{1}$$

where $\rho(x)$ is the charge density and α, the Slater exchange factor, is obtained from Schwartz or the energy dependent Hedin-Lundqvist potential in order to incorporate some of the dynamical effects.

Within each atomic sphere and beyond the outer sphere the Schrödinger equation is solved by numerical integration (we normally use the Numerov procedure), with the usual regularity conditions at the nuclear centers nd the scattering or bound state conditions at infinity. Hence, one function is obtained for each angular momentum L (L indicates both l and m) of each atom, and for each L value of the outer sphere. Each function carries a coefficient, the magnitude of which is characteristic of the whole molecular wave function. These coefficients are determined by imposing continuity of the logarithmic derivatives with the interstitial region wave function, which, because of the MT potential, is a linear combination of Bessel and Neumann functions. The total electronic wave function may be schematically expressed as[3]:

$$\Psi = \sum_{i} \Psi_{\mathrm{I}} + \Psi_{\mathrm{II}} + \Psi_{\mathrm{III}} \tag{2}$$

where each term in the sum is a solution to the potential in the corresponding region. The outer sphere function, which is general to both continuum and bound state problem, is:

$$\Psi_{\mathrm{III}} = \sum_{L,L'} [A_{\mathrm{L}}^{\mathrm{III}}\; f_{\mathrm{l}}^{\mathrm{III}}(kr_0)\,\delta_{\mathrm{LL'}} + B_{\mathrm{LL'}}^{\mathrm{III}}\; g_{\mathrm{l'}}^{\mathrm{III}}(kr_0)]\;\mathrm{Y}_{\mathrm{L'}}(\hat{r}_0) \tag{3}$$

where $f_{\mathrm{l}}^{\mathrm{III}}$ and $g_{\mathrm{l}}^{\mathrm{III}}$ are regular and irregular solution (at the origin) of the Schrödinger equation, respectively. $Y_{\mathrm{L}}(\hat{r}_0)$ are the usual spherical harmonics. Energies k^2 are measured in Rydbergs (1 Ry = 13.60529 eV) and lengths in Bohrs. The vector $\vec{r}_0$ is referred to the center of the whole molecule. The continuity requirements define a set of secular equations, which depends essentially on the type of atoms, the energy and the geometry of the molecule. In the bound state problem the f_l^{III} may be taken to be growing exponential functions, and thus the set $[A_{\mathrm{L}}^{\mathrm{III}}]$ will be zero. This fact produces a set of homogeneous equations that can be solved finding the energies at which the secular determinant is zero. These energies correspond to the eigenstates of the whole cluster.

To calculate the photoabsorption cross section we need to impose different boundary conditions because we use the continuum part of the eigenstates.[4] We suppose, for simplicity, that the potential in the extramolecular region III is constant and equal to the muffin-tin potential; there is not any difference between the regions II and III. This approximation, called the "extended continuum" scheme,[3,5] gives good results in the numerical applications and it has the advantage of calibrating on the same energy scale the bound state features relative to the continuum features without the need to perform ionization energy calculation. In other words we can calculate in a unique energy scale the pre-edge energy region with the rest of the XAS spectrum.

In this case, the functions f_l^{III} and g_l^{III} asymptotically behave like the usual Bessel j_l and Hankel $h_l^{+}=j_l+\mathrm{i}\,n_l$ functions, and the external region part of the total wave function can be calculated imposing the T-matrix normalization. With this choice one can treat on the some footing bound states and continuum resonances. In fact from general scattering theory bound states correspond to poles of the T matrix of the scattering potential at points in the real negative axis, whereas poles near the real positive axis in the fourth quadrant of the complex energy plane give rise to shape resonances with widths defined according to their distance from the real axis. Each partial $\underline{L}$ component of the Ψ_{III} part has now the form:

$$\Psi_{\mathrm{III},\underline{\mathrm{L}}}=j_{\underline{l}}\;Y_{\underline{L}}+\mathrm{i}\sum_{i,L'}B_{L'}^{\mathrm{i}}(\underline{L})\;(j_{l'}+\mathrm{i}\;n_{l'})\;Y_{L'} \tag{4}$$

This function describes a physical situation formed by an incoming partial wave j_l plus a set of outgoing waves having all L' values, emanating from each site i, located at a distance $\vec{R}_{\mathrm{i}}$ from the center, with amplitude $B_{L'}^{\mathrm{i}}(\underline{L})$.

Inside the atomic muffin-tin sphere i, the scattering solution, which matches smoothly with the external wave function, is given by $\sum_{\mathrm{L}} B_{\mathrm{L}}^{\mathrm{i}}(\underline{L})R_{\mathrm{L}}^{\mathrm{i}}(\vec{r}_{\mathrm{i}})$ with $R_{\mathrm{L}}^{\mathrm{i}}(\vec{r}_{\mathrm{i}})=R_{\mathrm{l}}^{\mathrm{i}}(r_{\mathrm{i}})Y_{\mathrm{lm}}(\hat{r}_{\mathrm{i}})$. The scattering amplitudes satisfy the matching equations:

$$B_{\mathrm{L}}^{\mathrm{i}}(\underline{L})-t_{\mathrm{l}}^{\mathrm{i}}\sum_{\mathrm{j}\neq\mathrm{i}}G_{\mathrm{LL'}}^{\mathrm{ij}}B_{\mathrm{L'}}^{\mathrm{j}}(\underline{L})=t_{\mathrm{l}}^{\mathrm{i}}J_{\mathrm{L}\underline{\mathrm{L}}}^{\mathrm{io}} \tag{5}$$

where $t_{\mathrm{l}}^{\mathrm{i}}$ is the t-matrix of the atom located at site *i*, $G_{\mathrm{LL'}}^{\mathrm{ij}}$ is the amplitude of the free propagation between sites *i* and *j* in the spherical wave representation and $J_{\mathrm{L}\underline{\mathrm{L}}}^{\mathrm{io}}$ is the amplitude of the incoming wave referred to site *i*. Equation (5) represent a typical multiple scattering model for several centers with free propagation in the interstitial region. This equation can be written in the compact form:

$$(I-T_{\mathrm{a}}G)\vec{B}(\underline{L})=T_{\mathrm{a}}\vec{J}(\underline{L}) \tag{6}$$

with obvious notation. The matrix T_{a} is a diagonal matrix defined through the atomic t-matrix as $T_{\mathrm{a}}=\delta_{\mathrm{ij}}\delta_{\mathrm{LL'}}t_{\mathrm{l}}^{\mathrm{i}}$.

Since the core wave function is localized in the muffin-tin sphere I_0 of the photoabsorbing atom, assumed located at site 0, we only need that part of the scattering wave function which is centered on I_0, so that, in the one electron approximation, the unpolarized photoabsorbing cross section for photon with energy ω is given by:

$$\sigma(\omega)=2\pi\alpha\,\omega\,(4\pi/3)^2\frac{k}{\pi}\bullet$$

$$\sum_{\underline{L},L,m_\gamma,m_0}\left|B_{\mathrm{L}}^{0}(\underline{L})\right|^2\left|(R_{\mathrm{L}}^{0}(\vec{r}_0)\,|\,r_0Y_{\mathrm{lm}_\gamma}(\hat{r}_0)\,|\,\varphi_{\mathrm{l}_0}(r_0)Y_{\mathrm{L}_0}(\hat{r}_0))\right|^2 \tag{7}$$

where the factor 2 results from the spin degrees of freedom, α = 1/137 is the fine structure constant and $k=\sqrt{E}$, E being the photoelectron kinetic energy defined as $E=\omega-I_0$, where I_0 is the ionization energy of the system. For simplicity we have assumed only dipole transitions because they dominate the continuum part of the XAS spectrum. In the atomic limit the ratio between quadrupole and dipole transitions scales like:

$$\frac{\sigma_{\mathrm{q}}(\omega)}{\sigma_{\mathrm{d}}(\omega)}\approx\frac{\omega^2}{c^2}\frac{1}{Z^2}$$

where Z is the nuclear charge. Typically this ratio is about 1/100 in the X-ray range, for this reason quadrupole transitions are usually neglected in the XAS analysis.

It is convenient, for practical purposes, to go from amplitudes to the imaginary part using the equation[5]:

$$\sum_{\underline{L}}[B^0_{\mathrm{L}}(\underline{L})]^*[B^0_{\mathrm{L'}}(\underline{L})]=\mathrm{Im}[(I-T_{\mathrm{a}}G)^{-1}T_{\mathrm{a}}]^{00}_{\mathrm{LL'}} \quad (8)$$

which represent a generalization of the optical theorem. The quantity $\tau^{00}_{LL'}=[(I-T_aG)^{-1}T_a]^{00}_{LL'}$ is called the scattering path operator and contains all the electronic and geometrical information about the atomic cluster. Moreover, through this operator it is possible to demonstrate the complete equivalence between Green function approach, band structure calculation and MS theory.[4]

3 Applications to XAS spectroscopy

The absorption coefficient μ depends on the energy and on the density of the sample. When the X-ray photon energy increases, the absorption coefficient decreases smoothly up to sharp discontinuities, the absorption edges, generated by photons with energy high enough to excite an electron from core levels. In correspondence of an edge, the absorption coefficient μ is proportional to the density n_{ab} of the photoabsorber in the medium and can be written as $\mu(E) = n_{\mathrm{ab}}\sigma(E)$, where $\sigma(E)$ is the total absorption cross section defined in Eq.(7) that exhibits strong oscillations with energy, the so-called X-ray Absorption Fine Structure (XAFS). A typical spectrum is shown in Fig.2. In this figure we report the normalized absorption spectrum at the Ni *K*-edge of the Ni^{2+} in water solution. The data have been recorded in transmission mode using Mylar cell at beam station 7.1 of the Daresbury Laboratory. The sample has been prepared to obtain a water solution of 5 mM and the pH has been controlled in order to have the hydrated species. The background contribution from previous edges has been fitted with a linear function and subtracted from the raw data.

The E_0 is the binding energy of the system and corresponds to the energy needed to move one electron from the 1*s* state of the Ni to the continuum energy levels. In the following we develop the theoretical formalism [6-8] able to provide a suitable guideline to calculate and interpret such type of experimental data.

Using Eq.(8) the unpolarized absorption cross section can be written as:

$$\sigma(E)=(l+1)\sigma_0^{l+1}(E)\,\chi^{l+1}(E)+l\sigma_0^{l-1}(E)\,\chi^{l-1}(E) \quad (9)$$

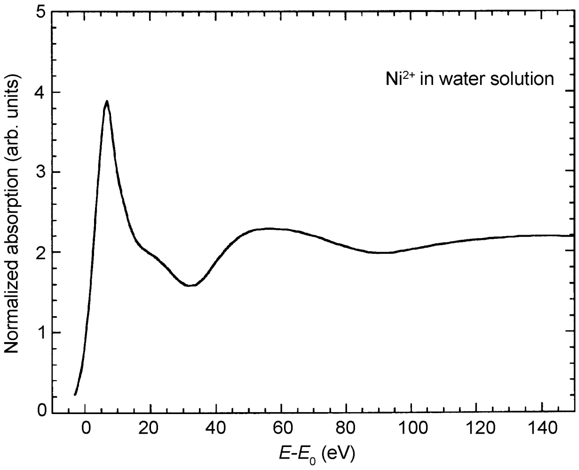

Fig.2 Normalized experimental absorption spectrum of Ni^{2+} in water solution at the Ni *K*-edge.

where $\sigma_0^l(E)$ indicates the atomic cross section of the absorbing atom at a given edge and

$$\chi^l(E)=\frac{1}{(2l+1)\sin^2\delta_l^0}\sum_m \mathrm{Im}[(I-T_aG)^{-1}T_a]^{00}_{lmlm} \quad (10)$$

is a structure factor carrying out all the information about the atomic cluster around the absorber. Notice that in the case of isolated atom, i.e. if $G = 0$, this structure factor is equal to one and the total cross section reduces to the atomic one, which is defined as:

$$\sigma_0^1(E)=\frac{8\pi^2}{3}\alpha k(E+I_0)\sin^2\delta_1^0\int_0^\infty r^3R_1^0(r)\phi_{l_0}(r)\,\mathrm{d}r \quad (11)$$

where δ_l^0 is the *l*-phase shift of the absorbing atom for a muffin-tin type of potential. The atomic cross section is essentially without structures (in a one-electron approximation) and almost independent from the energy. The final angular momentum *l* is defined as $l=l_0\pm1$ according to the dipole selection rules.

The factorization between atomic absorption and structure factor is possible only if the potential is real. For complex potential, i.e. a potential with an absorptive part to account for the inelastic losses, a more general expression should be used and it will be treated at the end of this paragraph.

To enlighten the physical meaning of the photoabsorption process, it is convenient to perform the matrix inversion in Eq.10 by series:

$$(I-T_aG)^{-1}=\sum_{n=0}(T_aG)^n \tag{12}$$

provided that the spectral radius $\rho(T_aG)$ (maximum modulus of the eigenvalues) of the matrix T_aG is less than one. In such a case the structural factor $\chi^l(E)$ becomes:

$$\chi^l(E)=1+\sum_{n=2}\chi^l_n(E) \tag{13}$$

with

$$\chi^l_n(E)=\frac{1}{(2l+1)\sin^2\delta^0_l}\sum_m \mathrm{Im}[(T_aG)^nT_a]^{00}_{lmlm} \tag{14}$$

and $\chi^l_0(E)=1,\ \chi^l_1(E)=0$, since G is off-diagonal in the site indices. Clearly $\chi^l_n(E)$ represents the partial contribution of order *n* to the photoabsorption coefficient of the cluster under study, coming from all process where the photoelectron emanating from the absorbing site 0 is scattered *n*-1 time by the surrounding atoms before escaping to free space after returning to site 0.[8] Due to the localization of the initial core state only closed paths beginning and ending to the absorbing atom are possible. It is this peculiarity that entails the site specificity of the XAS spectroscopy and makes it a unique tool for studying structural problems and for probing higher order correlation functions in condensed matter.[9] The development in Eq.(13) is the MS expansion with spherical wave propagators; the $\chi^l_2(E)$ term is the usual EXAFS signal. It is possible to write down complicated expressions for each higher order term $\chi^l_n(E)\,(n\geq 3)$ using the (3*n*-3)-*j* symbols. However their practical usefulness decreases with increasing order. It is much easier to generate them by using a MS program that already calculates the structural signal $\chi^l(E)$ by performing the matrix inversion either exactly or via the series expansion. It is also possible to derive recursive relations between consecutive $\chi^l_n(E)$ terms.

For practical application to data analysis the functional form of the quantities $\chi^l_n(E)$ is given by the simple expression:

$$\chi^l_n(E)=\sum_{p_n}A^l_n(k,R^{p_n}_{ij})\sin[kR^{tot}_{p_n}+\varphi^l_n(k,R^{p_n}_{ij})] \tag{15}$$

where the sum is over all possible paths p_n of order *n* defined above and $R^{tot}_{p_n}$ is the corresponding path length. This form follows from the fact that each spherical wave propagator *G* carries a factor $e^{ikR_{ij}}$ independent from *L* and *L*', contained in the Hankel functions of the propagators, that can be factorized. It is the form expected on the basis of interference process between the outgoing and backscattered photoelectron wave at the absorbing site. As a consequence, under the assumption that the MS series converges, one can always fit an experimental spectrum with a series of EXAFS like functions.

The interpretation of the XAS spectrum in terms of MS pathways of the photoelectron in the final state is meaningful only if there is numerical equivalence between the two sides of Eq.(12). This implies that the expansion on the r.h.s. must converge to the l.h.s. relative to some convergence criterion. From the matrix theory the absolute convergence (relative to some matrix norm) is ensured if $\rho(T_aG)<1$. This criterion is extremely useful since the absolute convergence entails the property that terms of order n in the series higher than a certain n_0 do not contribute appreciably to the sum. Now $\rho(T_aG)$ is a continuous function of the photoelectron wave number *k*, which goes to zero as *k* goes to infinity (since $t^i_l\to 0$ in this case) and tends to the infinity as *k* goes to zero because *G* is singular at k = 0 due to the presence of the Hankel function in the definition of the propagators. As a consequence it must cross at least once the value ρ = 1; the nearer to 1 is its value the slower is the convergence of the series.

According to the size of the spectral radius $\rho(T_aG)$, one can roughly divide the photoabsorption spectrum into three regions.[5,8] (1) A full multiple-scattering (FMS) region, characterized by $\rho(T_aG)\geq 1$, where an infinite number of path (or a great number of them) contribute to the shape of the spectrum. For low *Z* scattering atoms, this is usually near the edge region, 20-40 eV within the absorption edge. This is the region of the shape resonances where the scattering power of the environment is strong enough that it can scatter the photoelectron many times. Only global information can be extracted from the experimental data such as the point group symmetry and relations of the type k_rR = const. This last equation can be derived from the resonance condition $\mathrm{Det}\,\mathrm{M}(E_{\mathrm{r}})=0$ for a given energy *E*r, where the matrix *M* is determined via the equation:

$$\sum_{\underline{L}}[B_{L}^{0}(\underline{L})]^{*}[B_{L'}^{0}(\underline{L})] = [(M-\mathrm{i}\Delta)^{-1}\Delta(M+\mathrm{i}\Delta)^{-1}]_{LL'}^{00} \tag{16}$$

that is an alternative form of the optical theorem Eq.(8). (2) An intermediate multiple-scattering (IMS) region characterized by $0.5 \leq \rho(T_a G) \leq 0.8$, where only a limited number of paths of low order contribute due to the convergence of the MS series. Typically this is in the energy range 30 eV to 200 eV above the absorption edge. It is also the region where information on bond lengths and angles between bonds are contained, since the photoelectron is sensitive to the relative position of two, three or more atoms at the time via the MS paths. (3) A single scattering (SS) region, characterized by $\rho(T_a G) \leq 0.5$, where only paths of order n = 2 contribute significantly. This is the region where the photoelectron is sensitive only to the pair-correlation function, i.e. the relative positions of the central atom and the backscattering atoms.

It obviously extends in the IMS and FMS region as well. The corresponding signal is usually referred to as EXAFS in the literature and its energy region extend beyond 200 eV. In Fig. 3 the experimental evidence of the existence of the three energy regions[8] discussed above is pointed out. The 50 mM aqueous solutions of $MnCl_2$ and $KMnO_4$ salts form an octahedral and tetrahedral cluster of metal-oxygen ions respectively. Mn ion is octahedrally coordinated by six H_2O molecules forming a stable $[Mn(OH_2)_6]^{2+}$ cluster with a Mn-O distance $d_1 = 0.217$ nm while the tetrahedral (MnO_4)- cluster is known to have a Mn-O distance $d_2 = 0.163$ nm. In Fig.3 the absorption spectra of both compounds are reported. The corresponding energy scale are in the ratio $d_2/d_1 = 0.47$ where d_2 and d_1 are now the Mn-O distances in the two complexes, corrected for the linear term coefficient of the backscattering phase shift according to Eq.(15). The zero of the energy has been set at the first absorption feature, the 1*s*-3*d* transition, in both spectra. In this way the two spectra, after a further rescaling of the amplitude to take into account of the different number of atoms around the absorber, show a superposed behavior in that energy region that contain information only about the pair correlation function, i.e. the SS energy region. Below in energy the two spectra are different indicating that information about higher order correlation functions is contained in the XAS spectra.

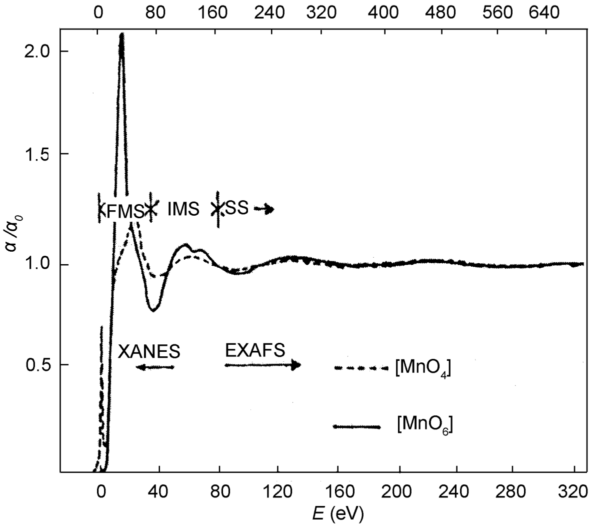

Fig.3 Comparison between normalized Mn *K*-edge XAS spectra of $(MnO_4)^-$ and $[Mn(OH_2)_6]^{2+}$ ions in water solution. The respective energy scales are given in the upper and lower part of the figure respectively. The normalization is to a value of the atomic absorption at very high energy. A partition of the spectra in FMS, IMS and SS regions is sketched.

This is the normal behavior, however a rather unexpected situation may also occur when the spectral radius may stay near one at some intermediate energies and decreases as the energy decreases toward the edge. This situation is encountered in the cupper *K*-edge spectrum, where in the first 50 eV above the edge the EXAFS signal alone is capable of reproducing the XAS experimental data. Deviations begin to show up in the energy range 50 eV to 200 eV due to the peculiarity of the relevant atomic phase shifts $\delta_l^j(E)$ that are small at low energy and cross π/2 at about 130 eV. Around this energy MS contributions show up in the XAS spectrum.

The general picture of an XAS spectrum that emerges from the preceding discussion is one in which oscillating signals with variable amplitudes are superimposed on a background of a more or less smooth atomic absorption. In the region of convergence of the MS series the SS signal is strongest and acts as a carrier wave that supports all of the other MS waves. Summarizing we can say that in principle any XAS spectrum contains all the three regions mentioned above. Their order with increasing energy and their energy extend are obviously system dependent. The only feature common to all system is that in the limit of high energy the IMS region should continuously merge into the SS region and finally reduce to pure atomic absorption. This picture is inspiring all the modern methods of analysis of the experimental XAS data.

In the previous treatment we have neglected the finite lifetime of the photoelectron in the final state that is due essentially to the finite core hole width and to the inelastic excitations suffered by the photoelectron in its way out from the absorbing atom. These inelastic channels drain away amplitude from the elastic channel, which alone gives structural information, and must be included in a realistic calculation to make comparison with experimental data. This situation calls for a many-body treatment of the photoabsorption process.[10,11] Now a formal exact solution of this problem can be found in the language of configuration interaction or channels giving a generalization of the MS theory in terms of multi-channels. This solution is given in Ref. 9. Here we want only to present some arguments, based on that solution, which will enable us to achieve a reasonable guess for a possible complex one-electron potential to be used in an effective one-electron theory. The need of a complex potential implies the concept of mean free path associated to the photoelectron; in other words the photoelectron "sees" only few nanometers around the absorbing atom. Typically at 20-30 eV from the edge the mean free path is of the order of 0.6-0.7 nm, as shown in Fig.4.

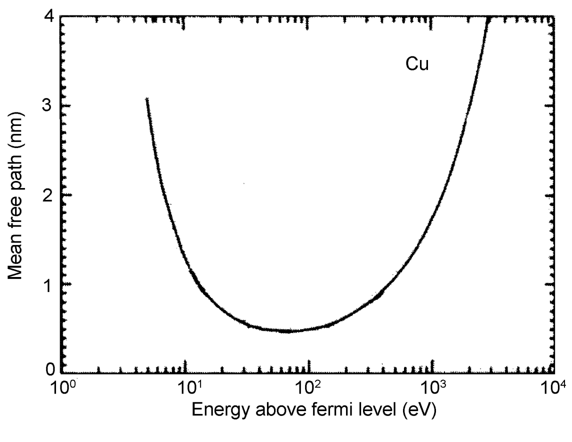

Fig.4 Typical mean free path $\lambda(E)$ behavior in a metal.

According to Ref.9 the photoabsorption cross section can be written as:

$$\sigma(\omega) = -4\pi\alpha\omega \bullet$$

$$\sum_{m_0,\sigma_0} \int d^3r d^3r' \phi_{l_0}(\vec{r}) \vec{\varepsilon} \cdot \vec{r} \,\mathrm{Im}\left\{ \sum_{\alpha,\alpha'} S_\alpha^* S_{\alpha'} G_{\alpha,\alpha'}(\vec{r},\vec{r}';\omega - I_0) \right\} \vec{\varepsilon} \cdot \vec{r}' \phi_{l_0}(\vec{r}') \tag{17}$$

where S_α is the overlap factor $\left\langle \Psi_\alpha^{N-1} \middle| \Psi_G^{N-1} \right\rangle$ giving, in the sudden approximation, the probability amplitude that the excited state Ψ_G^{N-1} of the spectator (N-1) electrons with a core hole relaxes to the state Ψ_α^{N-1}, eigenstate of the (N-1) particles Hamiltonian, leaving in the system an excitation energy ΔE_α. $\mathrm{G}_{\alpha,\alpha'}(\vec{\mathrm{r}},\vec{\mathrm{r}}';\mathrm{E})$ is the interchannel matrix representing the amplitude probability of propagation of the excited photoelectron from point $\vec{r}$ to point $\vec{r}\,'$ while at the same time the excitation energy left into the system changes from ΔE_α to $\Delta E_{\alpha'}$. Due to the completeness of the Ψ_α^{N-1} states and the normalization condition, one has the sum rule $\sum_\alpha |S_\alpha|^2 = 1$. The Green's-functions matrix $G_{\alpha,\alpha'}(\vec{r},\vec{r}';E)$ satisfies a set of coupled equations that contains the complete description of all the possible outcomes of a photoemission process, be it of intrinsic origin, i.e. consequent to the relaxation of the system around the core hole, or of extrinsic origin, i.e. created by the photoelectron on its way out of the system. Although the distinction between intrinsic and extrinsic losses is not in keeping with the general principles of quantum mechanics we keep it as a useful aid for classifying the system excitations according to some convenient scheme. For example, in metals and semiconductors, we might collect all the plasmon-type final channels, whether of intrinsic or extrinsic origin, which give rise to similar interchannel potential. In this way, we can eliminate from the set of Green's-function matrix equations, the submatrix corresponding to these channels by expressing it in terms of the remaining channels. These latter are described by a system analogous to the original one having however a potential submatrix which is now complex and energy dependent due to the elimination of the plasmon channels. The expression of the total cross section Eq.(17) remains the same except that the overlap factors S_α are now energy dependent and the sum is over the remaining channels. In particular we could eliminate all channels in favor of the completely relaxed one (α = 0) that is the channel where the (N-1) particle system remains in its possible lowest state. This latter channel is the only capable of giving structural information and carries most of the weight. This procedure would lead us to a single equation for G_{00} in presence of a complex, energy dependent, non-local optical potential.

Now the construction of such a potential and the consequent solution of the effective equation for G_{00} is out of question. We can however on the basis of physical consideration try to make an ansatz about the nature of this complex potential V_{00}. To do that we must consider some experimental facts: a) in metal one obtains very good agreement with the experimental data using a one-particle approach with an X_α potential and convoluting the calculated spectrum with a Lorentzian broadening function having an energy-dependent width related to the mean-free path of the photoelectron in the system by the relation $\Gamma(E)=\hbar(E/2m)^{1/2}\lambda^{-1}(E)$. In the framework of MS multichannel approach this finding can be rationalized by observing that in a metal the completely relaxed channel togheter with the plasmon excitation channels almost completely exhaust the sum rule; b) double-electron excitations are normally very weak, typically 10^{-2}–10^{-3} times the main relaxed channel. Therefore on optical potential given by $V_{xa}+\mathrm{i}\Gamma(E)$ is able to give a satisfactory picture of the absorption process. One can further argue that, in the spirit of a statistical approximation suggested by the opening of many channel with the same weight, the optical potential in question might be approximated by the self-energy of a uniform interacting electron gas with density given by the local density of the system. This fact points to the Hedin-Lundqvist (HL) potential, with its energy–dependent exchange and its imaginary part that is able to reproduce the observed mean-free path in metal, as being the natural candidate for such effective potential, at least for metals and semiconductors. One can interpret this potential as an effective optical potential that controls the propagation and the damping of the photoelectron everywhere in the system, even in the atomic core region. The complicated many body problem is reduced to an effective one-electron problem where the plasmon excitations exhaust all the possible inelastic excitations of the system. In keeping with this interpretation no $\left|S_0(E)\right|^2$ correction are needed. The application of these ideas to the calculation of the K-edge XAS spectra of many transition metals and semiconductors has yielded results in good agreement with the experimental data. In particular, amplitudes and phases of the MS signals in the IMS and SS regions are very well reproduced. On the other hand, in molecular system the full HL potential introduces in the first 20-30 eV from the edge an over damping of the XAS spectrum.

The Green function obeys an equation, better known as Dyson’s equation, given by:

$$\left[\nabla^2+E-V_c(\vec{r})-\Sigma_{exc}(\vec{r};E)\right]\ G^{+}_{00}(\vec{r},\vec{r}\,';E)=\delta(\vec{r}-\vec{r}\,') \tag{18}$$

where $\Sigma_{exc}(\vec{r};E)$ is the local energy-dependent complex HL exchange and correlation potential, and V_c is the usual Coulomb or Hartree potenial. This equation can be solved for a collection of muffin-tin potentials. Due to the localization of the core state we need the solution of Eq.(18) only for the photoabsorption site 0. This solution is given by:

$$G^{+}_{00}(\vec{r},\vec{r}\,';E)=\\ -k\sum_{L,L'}R^0_L(\vec{r})\,\tau^{00}_{LL'}\,R^0_{L'}(\vec{r}\,')+\sum_{L}R^0_L(\vec{r})S^0_L(\vec{r}\,') \tag{19}$$

where $\tau^{00}_{LL'}$ is the usual scattering path operator defined above and $S^0_L(\vec{r}\,')$ is the irregular part of the solution at the origin that now contributes to the atomic cross section because of the complex potential. Eq.(17) can be now solved to give the total cross section of a cluster of atoms. Essentially the same considerations derived for the case of real potential can be repeated in this case, the only lies in the fact that the atomic cross section does not factorize out from the structural contribution. Therefore the total structural signal in a final angular momentum channel l is defined as:

$$\chi_l(E)=\frac{\sigma_l(E)}{[\sigma_a(E)]_l}-1 \tag{20}$$

and various individual MS signals of order n are given by:

$$\chi^n_l(E)=\frac{\sigma^n_l(E)}{[\sigma_a(E)]_l}$$

(21)

To clarify the effect of using the complex potential we observe that the MS series is formed by two building blocks: the propagator $G^{ij}_{LL'}$ between site *i* and *j* and the *l*-wave atomic *t*-matrix t^i_l of the atom at site *i*. The general term of the MS series is built by several repetition of the product $t^i_l G^{ij}_{LL'}$ that brings out a factor $e^{-2\delta_2} e^{-k_2 R_{ij}}$ when complex potential is used. Here δ_2 and k_2 are the complex part of the atomic phase shift and wave vector respectively. The complex potential results in the existence of a damping factor that reduces the amplitude of the elastic signal. Typical calculations performed with the method presented above are reported in Fig.5. In this figure we report the comparison between the experimental data of the Na *K*-edge in the NaCl system with three different calculations obtained using X-α exchange potential, a Dirac-Hara (DH) energy dependent exchange potential and HL exchange and correlation complex potential. For these calculations we have used a nine shells cluster formed by 123 atoms. Because both DH and X-α potential are real, the corresponding calculations has been convoluted the imaginary part of the HL potential. The theoretical spectra are further convoluted to take into account for the experimental resolution and for the core hole lifetime. The agreement between experimental data and the theoretical calculations is good in the whole energy range both concerning the shape and the energy position of the different features in the spectrum. Moreover it appears clear that the HL potential shows the best agreement with the experiment. This behavior is a general finding for crystalline materials while small problems remain in the first 20-30 eV basically linked to treatment of the inelastic losses in the molecular systems where the HL scheme seems to be inadequate.

In this paper we have presented a brief summary of the work that has been done in the last twenty years by several groups to build a general scheme of interpretation of the XAS spectra. This is the “core” of modern understanding of the X-ray photoabsorption process from core levels. Many other items have not been treated in this paper, for example the problem of the thermal and structural disorder,[12,13] most of them can be found in the references reported at the end of this paper. This theory is able to interpret quantitatively the experimental data essentially in the whole energy range and on this basis different computer codes have been created in the last years and now the XAS spectroscopy is a well-established technique to obtain electronic and structural information from an enormous variety of systems.

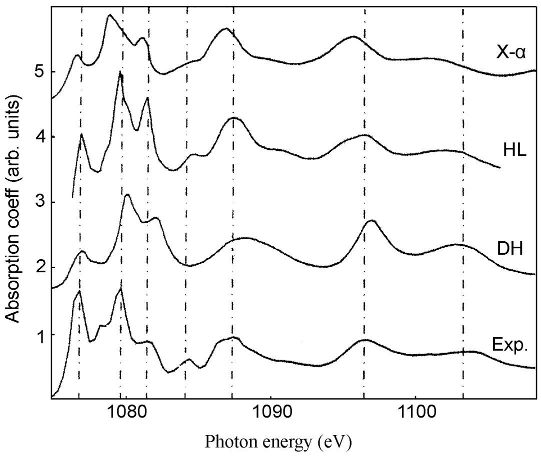

Fig.5 Na *K*-edge in the NaCl system. Comparison between the experimental data (lowermost curve) and three calculations performed with different choices of the exchange and correlation potential.

Recently a new method to perform a quantitative analysis of the low energy range, the so called XANES energy region, i.e. from the edge up to 200 eV, has been proposed in the literature and applied to several systems.[14,15] This method is based on the comparison between experimental data and many theoretical calculations performed by varying selected structural parameters starting from a putative structure, i.e. from a well defined initial geometrical configuration around the absorber. The calculation of XANES spectra related to the hundreds of different geometrical configurations needed to obtain the best fit of the experimental data has been made in the framework of the full MS calculation, i.e. the scattering path operator τ is calculated exactly, and the optimization in the space of parameters is achieved by the minimization of the square residual function in the parameter space. In this way the low energy part of the XAS spectrum is now fully available for a quantitative analysis and we can benefit from the extreme sensitivity to the structural details of the absorbing site (overall symmetry, distances and bond angles) of this energy region. This is important in the study of many systems like extra-dilute systems, trace element analysis, local investigation of materials under extreme conditions and much more in biological systems where the low S/N ratio and the weak scattering power of the light elements limits the *k*-range of the available experimental data and the EXAFS can be barely exploited. The structural information on protein metal sites can be obtained with atomic resolution in any state of the protein sample (crystal, solution), allowing either the comparison with already known X-ray structures at high resolution or to get information on protein that have proven difficult to crystallize. This method is well described in the last two papers reported in the references. Here we want just to emphasize that this new method needs a phenomenological treatment of the inelastic losses to avoid the over damping at low energies of the complex part of the HL potential in the case of covalent molecular systems.

This new method accounts for all the inelastic processes by a convolution with a broadening Lorentzian function having an energy dependent width of the form $\Gamma\ (E) = \Gamma c + \Gamma_{\mathrm{mfp}}(E)$. The constant part Γc includes the core hole lifetime and the experimental resolution, while the energy dependent term represents all the intrinsic and extrinsic inelastic processes. The $\Gamma_{\mathrm{mfp}}(E)$ function is zero below an onset energy *E*s (which in extended systems corresponds to the plasmon excitation energy) and begins to increase from a value *A*s following the universal functional form of the mean free path in solids. Both the onset energy *E*s and the jump *A*s are introduced in the $\Gamma_{\mathrm{mfp}}(E)$ function via an arctangent functional form to avoid discontinuities. Both numbers are derived on the basis of Monte Carlo search at each step of computation. This type of approach is justified on the basis of a multi-channel multiple scattering theory.[11] In the sudden limit, the net absorption is given by a sum over all the possible channels that represent each of the final states allowed in the photo-absorption process. They include the fully relaxed configuration, which gives the main contribution to the spectrum, and all the other possible excited states of the (*N*-1)-electron system. By assuming that the channels coming from the excitation of the *N*-1 electrons are very near in energy, the total absorption is given by a convolution of the one-particle spectrum calculated with the full-relaxed potential with a spectral function representing the weight of the other excited states. Hence the total XAS cross section can be written as[10,11]

$$\mu = \sum_n \mu_n \xrightarrow[\Delta E \to 0]{} \int \mu(\omega-\omega')A(\omega')\,d\omega' \qquad (22)$$

We make the “ansatz” that the spectral function $A(\omega)$ is well approximated by a Lorentzian function with the energy dependent width $\Gamma(E)$ previously defined. Obviously, in the cases when contributions from one or more of these excited states become relevant, they must be considered explicitly in the calculation.

As test cases of the new method, we report in Fig. 6 the analysis of the *K*-edge of Ni^{2+} ion in aqueous solution. This ion is often used as test case due to the well-defined formal valency of the ionic species and the very simple geometry around the absorber. The solid line corresponds to a calculation related to the best-fit structure that is geometry with an octahedral symmetry and an oxygen-metal distance of 0.203 ± 0.003 nm. Hydrogen atoms are included in the calculations. The agreement between the experimental data and the best-fit theoretical curve is good in the whole energy range; small discrepancies remain in the intensity of the resonance at 15 eV essentially due to the muffin-tin approximation for the shape of the potential.

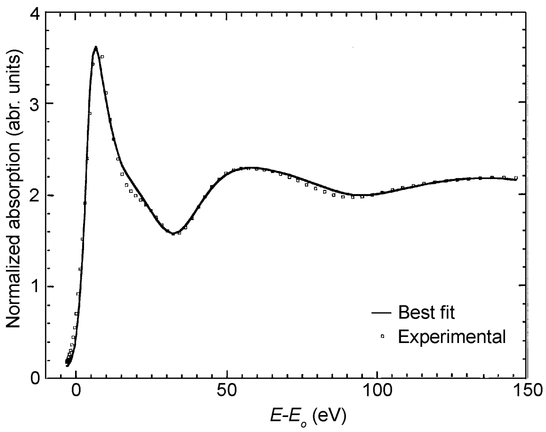

Fig.6 Ni *K*-edge Ni^{2+} in water solution. The solid line corresponds to a best-fit calculation.

4 Conclusions

In this paper we have presented a review of the understanding of the modern interpretation of the XAS spectroscopy coming from the works of several groups in the world. Although very important advances are made in the last two years in the quantitative use of the XANES spectroscopy many other items should be addressed to fully exploit the potentialities of the XAS spectroscopy, most of them are linked to a better treatment of the molecular potential.

We close this paper to emphasize that the multiple scattering theory is a very general approach to calculate physical quantities from “first principle”; to this respect its field of application is not limited to the XAS spectroscopy, many other type of experiments can indeed benefit from this theoretical approach to have a solid background for the physical interpretation. A very important example is reported in Ref.16.

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