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A UNIFYING SCHEME OF INTERPRETATION OF X-RAY ABSORPTION SPECTRA BASED ON THE MULTIPLE SCATTERING THEORY

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A UNIFYING SCHEME OF INTERPRETATION OF X-RAY ABSORPTION SPECTRA BASED ON THE MULTIPLE SCATTERING THEORY

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ABSTRACT

The various schemes for calculating inner shells X-ray absorption spectra are reviewed and shown to be mutually equivalent. The unifying framework is provided by the multiple scattering (MS) theory. In particular the formulation based on the Green's function approach allows one under certain conditions to write the absorption coefficient as a sum of an infinite number of terms which have a direct physical meaning. The conditions under which this expansion is possible is discussed and as a consequence a unifying scheme of interpretation of X-ray absorption spectra is proposed. Finally an approximate formula for the rapid evaluation of the n-th order term of the expansion is given.

INTRODUCTION

Starting from the general expression for the X-ray absorption cross-section of a cluster of atoms

$$\sigma(E) = 4\pi^2 E \alpha \sum_f | (\psi_f | \vec{p}.\vec{D} | \psi_{in}) |^2 \delta(E - E_f + E_{in}) \quad (\alpha = e^2/\hbar c = \frac{1}{137}) \qquad (1)$$

where E is the photon energy, $\vec{p}$ its polarization versor and $\vec{D}$ is the dipole transition operator (atomic units are used throughout), there are basically three different approaches for evaluating this quantity :

1 - the scattering approach where one calculates the time-reversed scattering wave function ψ_ε^- for the photoelectron in the final state with energy $\varepsilon = E - I_o$, where I_o is the ionization energy, suitably defined for the system under study ([1, 2]).

2 - The Green's function approach, whereby $\sigma(E) \sim E\ \mathrm{Im}\ (\psi_{in} | \vec{p}.\vec{D}\ G^- \vec{p}.\vec{D} | \psi_{in})$ so that the problem reduces to the solution of the equation $(\varepsilon - H)\ G^- = I$, where I is the unit operator, H the hamiltonian of the system and G^- is the related Green's function, with incoming wave boundary conditions [3].

3 - The band structure approach for periodic systems, where the scattering states are replaces by Bloch states so that the sum over the final photoelectron states becomes an integral over the appropriate Brillouin zone [4].

We shall show in the following that in the framework of the multiple scattering (MS) theory all three approaches are numerically equivalent. Only their language is different, according to the different points of view taken to describe the photoabsorption process.

It will turn out however that the expression for the absorption cross section obtained by the Green's function approach is the most suitable for tackling structural problems. In particular we shall show that, under certain conditions, the inner shell X-ray absorption spectroscopy provides a straightforward, direct means for obtaining structural information about higher order correlation functions in the systems under study. In this sense geometrical information concerning bonding angles and positional correlations around the absorbing atom can come within experimental reach. The field of application that opens up in this way is extremely reach and it is now time to exploit all the potentiality of the technique.

The scattering approach

In this approach the sum over the continuum of the final states is performed first. The energy conserving delta function selects one particular final state ψ_ε^- normalized to one state per Rydberg :

$$\sigma(\varepsilon) = 4\pi^2\ (\varepsilon + I_o)\ \alpha\ |(\psi_\varepsilon^- | \vec{p}.\vec{D} | \psi_{in})|^2$$

where $\psi^- = (\psi^+)^*$ (neglecting spin), in order to impose the physical boundary conditions for the photoabsorption process [1] and ψ_{in} is an inner shell core state.

It is useful to treat both the atomic case and the cluster case :

a) Atomic case

Assuming the atomic potential to be of the muffin-tin type, the angular momentum L=(l,m) is conserved in the scattering process. In the external region,

where $V(r) = 0$, the solution of the Schrødinger equation is .

$$\psi_L^+(r,\varepsilon) = J_L(\vec{r}) + i\, t_l H_L^+(\vec{r})$$

where

$$J_L(\vec{r}) = j_l(kr)Y_L(\hat{r}), \quad H_L^+(\vec{r}) = h_l^+(kr)Y_L(\hat{r}), \quad N_L(\vec{r}) = n_l(kr)Y_L(\hat{r})$$

$k = \sqrt{\varepsilon}$ and $j_l(x)$, $n_l(x)$, $h_l^+ = j_l(x) + in_l(x)$ are the usual Bessel, Neumann and Hankel functions. J_L represents the incoming wave, H_L^+ the scattered wave. This solution is to be matched smoothly to the solution $C_l R_L(\vec{r}) = C_l R_l(r) Y_L(\vec{r})$ of the Schrodinger equation inside the muffin-tin sphere of radius ρ, which is regular at the origin.

One finds, defining $W[f,g] = fg' - gf'$, where $f' = \frac{d}{dr} f$

$$t_l = e^{i\delta_l} \sin\delta_l = \frac{W[j_l, R_l]}{W[h_l^+, R_l]}\Bigg|_{r=\rho} = C_l$$

$$R_l^{(')}(\rho) = j_l^{(')}(k\rho)\cot g\delta_l - n_l^{(')}(k\rho)$$

so that

$$\sigma_{sc}(\varepsilon) = 4\pi^2 \alpha (\varepsilon + I_o) \left| (R_L | \vec{p}.\vec{D} | \psi_{in}) \right|^2 |t_l|^2 \frac{k}{\pi} \qquad (2)$$

where we have explicitly factorized the density of the final states k/π coming from the normalization to one state per Rydberg. For simplicity we assume that the dipole operator $\vec{D}$ selects only one final state, as for K-edge absorption. The generalization only adds complication to the formulas.

b - Cluster case

We assume again that the potential is of the muffin-tin type. In this case L is not conserved, so that now one can describe asymptotically the physical situation as an incoming $\underline{L}$ partial wave $J_{\underline{L}}(\vec{r}_o)$, referred to the center of the cluster where the absorbing atom is located, plus a set of outgoing waves having all L values, emanating from each site j located at $\vec{R}_j$ with amplitude $B_L^j(\underline{L})$

$$\psi_{\underline{L}}^+(\vec{r},\varepsilon) = J_{\underline{L}}(\vec{r}_o) + i \sum_{jL} B_L^j(\underline{L})\, H_L^+(\vec{r}_j) \qquad (\vec{r}_j = \vec{r} - \vec{R}_j)$$

Inside the muffin-tin sphere j, in analogy with the atomic case, the solution which matches smoothly with the external solution is given by $\sum_L B_L^j(\underline{L})\, R_L^j(\vec{r}_j)$. Since the initial state is confined at site o and assuming again K-shell photoabsorption, we find

$$\sigma_{sc}(\varepsilon) = 4\pi^2 \alpha (\varepsilon + I_o) \left| (R_L^o(\vec{r}) | \vec{p}.\vec{D} | \psi_{in}^o) \right|^2 \sum_{\underline{L}} |B_L^o(\underline{L})|^2 \frac{k}{\pi} \qquad (3)$$

As in the atomic case, $R_L^j(\vec{r})$ is the solution of the Schrødinger equation inside sphere j that matches smoothly to $J_L(\vec{r}_j)\cot g\ \delta_l^j - N_L(\vec{r}_j)$ at the muffin-tin radius ρ_j and δ_l^j is the l wave phase shift of the potential inside sphere j. However since now the angular momentum is not conserved and we are calculating total cross sections, we have to add up incoherently all amplitudes $B_L^j(\underline{L})$ squared relating to different $\underline{L}$ incoming waves [2].

The scattering amplitudes $B_J^j(\underline{L})$ satisfy the following equations

$$B_L^i(\underline{L}) - t_l^i \sum_{j\neq i} G_{LL'}^{ij}\ B_{L'}^j(\underline{L}) = t_l^i\ J_{L\underline{L}}^{io} \tag{4}$$

where t_l^i is the t-matrix of the atom located at site i, $G_{LL'}^{ij}$ is the amplitude of propagation of a spherical wave of angular momentum L emanating from site i for arriving at site j with angular momentum L' and $J_{L\underline{L}}^{io}$ is the amplitude of the incoming wave $J_{\underline{L}}(\vec{r}_o)$ when referred to site i. With the help of the reexpansion theorem [5] one finds

$$\begin{Bmatrix} G_{LL'}^{ij} \\ J_{LL'}^{ij} \end{Bmatrix} = 4\pi i \sum_{L''} i^{l''+l-l'}\ C_{L\ L''}^{L'} \begin{Bmatrix} h_{l''}^{+}(kR_{ij}) \\ ij_{l''}(kR_{ij}) \end{Bmatrix} Y_{L''}(\hat{R}_{ij}) \tag{5}$$

where $C_{L\ L''}^{L'} = \int d\Omega\ Y_L(\Omega) Y_{L'}^*(\Omega) Y_{L''}(\Omega)$ are the Gaunt coefficients and $\vec{R}_{ij} = \vec{R}_i - \vec{R}_j$. It is useful for the future to define $G_{LL'}^{ii} = 0$.

Eq. (4) has a simple physical meaning. It tells that the total L wave scattered amplitude at site i is the sum of the scattered wave due to the incident $J_{\underline{L}}(\vec{r}_o)$ wave plus the waves that have been scattered by all other sites j, travel from here to site i with amplitude $G_{LL'}^{ij}$ and finally get scattered at site i with amplitude t_l^i.

By introducing the matrices

$$T_a = (T_a)_{LL'}^{ij} = \delta_{ij}\ \delta_{LL'}\ t_l^i \qquad\qquad G = G_{LL'}^{ij}$$

and the vectors $\vec{B}(\underline{L}) = B_L^i(\underline{L})$, $\vec{J}(\underline{L}) = J_{L\underline{L}}^{io}$ we can write Eq. (4) as

$$(I - T_a G)\ \vec{B}(\underline{L}) = T_a\ \vec{J}(\underline{L})$$

The scattering approach is useful in discussing shape resonances. In this case it happens that only one scattering amplitude $B_L^o(\underline{L}_r)$ for a particular $\underline{L}_r$ becomes big at a certain energy, all the other amplitudes with $\underline{L} \neq \underline{L}_r$ being negligible. This means that the $\underline{L}_r$ wave incoming from infinity (in a time reversed picture) can easily

overcome the centrifugal barrier, penetrate the cluster potential and attain a sizable amplitude $B_L^o(\underline{L}_r)R_L^o(\vec{r}_o)$ at the atomic core of the photoabsorber. An example is the $\underline{l}_r = 3$ resonance in diatomic molecules (N_2, O_2) [6].

The Green's function approach

In this approach one transforms Eq. (1) as :

$$\sigma(\varepsilon) = \sigma_{GF}(\varepsilon) = \frac{1}{\pi} \lim_{\eta \to o+} \mathrm{Im} \left(\psi_{in} \middle| \vec{p}.\vec{D} \; \frac{1}{\varepsilon - H - i\eta} \; \vec{p}.\vec{D} \middle| \psi_{in}\right) 4\pi^2 (\varepsilon + I_o)\alpha$$

$$= -4\pi (\varepsilon + I_o)\alpha \, \mathrm{Im} \int d^3r \, d^3r' \, \psi_{in}(\vec{r}) \, \vec{p}.\vec{D}(r) \, G^+(\vec{r},\vec{r}') \, \vec{p}.\vec{D}(\vec{r}') \, \psi_{in}(\vec{r}') \qquad (6)$$

where $(\varepsilon - H)\, G^+ = I$ or in the coordinate representation

$$(\nabla^2 + \varepsilon - V(\vec{r}))\, G^+(\vec{r}, \vec{r}') = \delta(\vec{r}, \vec{r}')$$

where $V(\vec{r}) = \sum_j V_j(\vec{r})$ is the collection of the muffin-tin potentials. Since $\psi_{in}(\vec{r})$ is a core state localized at site o. Eq. (5) shows that we need calculate the Green's function only for r and r' inside the muffin-tin sphere located at o.

a) Atomic case

The solution for G^+ in this case is [3] :

$$G^+(\vec{r}, \vec{r}') = -k \sum_L R_L(\vec{r})\, t_1\, R_L(\vec{r}') - k \sum_L R_L(\vec{r})\, S_L(\vec{r}') \qquad (7)$$

where, as before, at the muffin-tin radius ρ

$R_L(\vec{r}) \sim J_L(\vec{r})\cot g\delta_1 - N_L(\vec{r})$ (regular at the origin)

$S_L(\vec{r}) \sim J_L(\vec{r})$ (singular at the origin)

smoothly in $\vec{r}$.

Insertion of Eq. (7) into Eq. (6) gives

$$\sigma_{GF}(\varepsilon) = 4\pi (\varepsilon + I_o)\alpha \, \mathrm{Im}\, k \left\{\left[\left(R_L \middle| \vec{p}.\vec{D} \middle| \psi_{in}\right)\right]^2 t_1 - \left(\psi_{in} \middle| \vec{p}.\vec{D} \middle| R_L\right)\left(S_L \middle| \vec{p}.\vec{D} \middle| \psi_{in}\right)\right\}$$

When the potential is real, R_L and S_L are real so that

$$\sigma_{GF}(\varepsilon) = 4\pi(\varepsilon + I_o)\alpha\, k\, [(R_L|\vec{p}.\vec{D}|\psi_{in})]^2\, \mathrm{Im}\, t_1 \qquad (8)$$

Due to the optical theorem

$$|t_1|^2 = \mathrm{Im}\, t_1$$

Eq. (8) reduces to Eq. (2)

b) Cluster case

Again we quote the result of ref [3]

$$G^+(\vec{r}, \vec{r}') = -k \sum_{LL'} R_L^o(\vec{r}_o)\, \tau_{LL'}^{oo}\, R_{L'}^o(\vec{r}'_o) - \sum_L R_L^o(\vec{r}_o) S_L^o(\vec{r}'_o)$$

where now

$$\tau_{LL'}^{oo} = [(I - T_a G)^{-1} T_a]_{LL'}^{oo} = [(T_a^{-1} - G)^{-1}]_{LL'}^{oo}$$

With this solution

$$\sigma_{GF}(\varepsilon) = 4\pi(\varepsilon + I_o)\alpha\, \mathrm{Im}\, k\, \{[(R_L^o|\vec{p}.\vec{D}|\psi_{in}^o]^2\, \tau_{LL}^{oo} - (\psi_{in}^o|\vec{p}.\vec{D}|R_L^o)(S_L^o|\vec{p}.\vec{D}|\psi_{in}^o)\} \qquad (9a)$$

where the superscript o in ψ_{in}^o reminds that the core initial state is located at site o.

Again for real potential

$$\sigma_{GF}(\varepsilon) = 4\pi(\varepsilon + I_o)\alpha\, k\, [(R_L^o|\vec{p}.\vec{D}|\psi_{in}^o)]^2\, \mathrm{Im}\, [(I - T_a G)^{-1} T_a]_{LL}^{oo} \qquad (9)$$

Using Eq. (4) it is possible to prove the generalization of the optical theorem valid for the atomic case [7] :

$$\sum_{\underline{L}} |B_L^o(\underline{L})|^2 = \mathrm{Im}\, [(I - T_a G)^{-1} T_a]_{LL}^{oo}$$

which allows us to recover Eq. (3).

We shall see that Eq. (9) is very useful for analysing the photoabsorption cross section in terms of multiple scattering events.

Band structure approach

In an infinite regular lattice (for simplicity we assume all sites to be equivalent), the KKR method [8] writes the Bloch function as :

$$\psi^{n}_{\vec{q}}(\vec{r}) = \sum_{L} \alpha^{n}_{L}(\vec{q})\ R_{L}(\vec{r}) \tag{10}$$

with the same definition of $R_L(\vec{r})$ as above, n labelling the band indices.

The coefficients $\alpha_L(\vec{q})$ satisfy the homogeneous equations

$$\sum_{L'} (t_l^{-1}\ \delta_{LL'} - G_{LL'}(\vec{q}))\ \alpha_{L'}(\vec{q}) = 0 \tag{11}$$

where $t_l = e^{i\delta_l} \sin \delta_l$ is the usual l wave atomic t-matrix, common to all sites,

and

$$G_{LL'}(\vec{q}) = \frac{1}{N} \sum_{i,j} e^{i\vec{q}.(\vec{R}_i - \vec{R}_j)}\ G^{ij}_{LL'} = \sum_{j \neq o} e^{i\vec{q}.(\vec{R}_o - \vec{R}_j)}\ G^{oj}_{LL'}$$

since now the second sum is independent of the initial site o.

A non trivial solution of Eq. (11) demands that

$$\mathrm{Det}\ ||\ t^{-1}\ (\epsilon) - G\ (\vec{q};\epsilon)\ || = 0$$

which determines the band dispersion $\epsilon = \epsilon_n(\vec{q})$. Correspondingly Eq. (11) provides $\alpha^n_L(\vec{q})$. Using the expression (10) for the final states wavefunctions. Eq. (1) gives

$$\sigma_{BS}(\epsilon) = 4\pi^2\ k\ (\epsilon + I_o)\alpha\ |\ (R_L|\ \vec{p}.\vec{D}\ |\ \psi^{o}_{in})|^2 \sum_{n} \frac{v}{(2\pi)^3} \int_{BZ} d^3q\ \delta(\epsilon - \epsilon_n(\vec{q}))|\ \alpha^n_L(\vec{q})|^2$$

where v is the volume of the unit primitive cell.

It is now a matter of labour to show that :

$$\pi \sum_{n} \frac{v}{(2\pi)^3} \int_{BZ} d^3q\ \delta\ (\epsilon - \epsilon_n(\vec{q}))|\ \alpha^n_L(\vec{q})|^2 = \mathrm{Im}\ \frac{v}{(2\pi)^3} \int_{BZ} d^3q\ (t^{-1} - G(\vec{q}))^{-1}_{LL}$$

$$= \mathrm{Im}\ [(T_a^{-1} - G)^{-1}]^{oo}_{LL} = \mathrm{Im}\ \tau^{oo}_{LL}$$

where now site o is any site in the lattice. This last relation establishes the sought equivalence of the band approach to the other methods.

The multiple scattering series

For simplicity we have assumed up to now absorption from K-shell core states. For unpolarized absorption the generalization to an initial core state of l angular momentum is straightforward (9). For the atomic absorption we find :

$$\alpha_{at}(\varepsilon) = (l+1)\,\alpha_{at}^{l+1}(\varepsilon) + l\,\alpha_{at}^{l-1}(\varepsilon)$$

where

$$\alpha_{at}^{l\pm1}(\varepsilon) = n_{ab}\,4\pi^2\,(\varepsilon + I_o)\,\alpha\,\sin^2\delta_l \int_o^\infty r^3\,R_{l\pm1}(r)\,\psi_{in}^{l}(r)\,dr$$

having introduced the absorption coefficient $\alpha(\varepsilon) = n_{ab}\sigma(\varepsilon)$ and the density n_{ab} of the photoabsorber in the medium.

For a cluster, remembering Eq. (9), we have :

$$\alpha_c(\varepsilon) = (l+1)\,\alpha_o^{l+1}(\varepsilon)\,\chi^{l+1}(\varepsilon) + l\,\alpha_o^{l-1}(\varepsilon)\,\chi^{l-1}(\varepsilon) \qquad (12)$$

where now $\alpha_o^l(\varepsilon)$ indicates the atomic absorption coefficient of the photoabsorber and

$$\chi^l(\varepsilon) = \frac{1}{2l+1}\,\frac{1}{\sin^2\delta_l^o}\,\sum_m \mathrm{Im}\,[(I - T_a G)^{-1} T_a]_{lm\ lm}^{o\ \ o} \qquad (13)$$

is a structure factor carrying the information about the environment. Notice that, if G=0 (absence of environment), then $\chi^l(\varepsilon) = 1$.

The factorization between atomic absorption and structure factor is possible only if the potential is real. For a complex potential the more general expression Eq. (9a) should be used, since now $R_L(\vec{r})$ and $S_L(\vec{r})$ are complex. The physical interpretation of the theory becomes more involved in this case. In the following we shall only discuss the real case.

As it is, Eq. (13) is not very useful for getting some physical insight into the photoabsorption process. However if one can perform the matrix inversion by series

$$(I - T_a G)^{-1} = \sum_{n=0}^{\infty} (T_a G)^n \qquad (14)$$

then the physical meaning of the process becomes transparent. In this case

$$\chi^l(\varepsilon) = \sum_{n=0}^{\infty} \chi_n^l(\varepsilon) = 1 + \sum_{n=2}^{\infty} \chi_n^l(\varepsilon) \qquad (15)$$

with

$$\chi_n^l(\varepsilon) = \frac{1}{2l+1}\,\frac{1}{\mathrm{Sin}^2\delta_l^o}\,\sum_m \mathrm{Im}\,[(T_a G)^n T_a]_{lm\ lm}^{o\ \ o} \qquad (16)$$

and $\chi_0^l(\varepsilon) = 1$, $\chi_1^L(\varepsilon) = 0$, since G is off-diagonal in the site indices. Clearly

$\chi_n^l(\varepsilon)$ represents the partial contribution of order n to the photoabsorption coefficient of the cluster under study, coming from all processes where the photoelectron emanating from the absorbing site o is scattered n-1 times by the surrounding atoms before escaping to free space after returning to site o. In other words only closed paths beginning from and ending to the photoabsorbing site are possible. This last condition is due to the fact that one is calculating total cross sections and that the initial state is localized at site o. It is this peculiarity that entails the site specificity of the X-ray absorption spectroscopy and makes it a unique tool for studying structural problems and for probing higher order correlation functions in condensed materials. In photoelectron diffraction where this condition is not operating, the interpretation of the experimental data becomes more complicated.

The development in Eq. (15) is nothing else that the familiar MS expansion with spherical wave propagators. For example, using Eq. (16) and Eq. (5), one finds

$$\chi_2^l(\varepsilon) = \frac{1}{2l+1} \sum_{j'\neq o} \sum_{ml'm'} \mathrm{Im}\left(e^{2i\delta_l^o}\, G^o_{lm\, l'm'}\, t^{j'}_{l'}\, G^{j'\, o}_{l'm'\, lm}\right)$$

$$= (-1)^l \,\mathrm{Im}\left\{e^{2i\delta_l^o} \sum_{j\neq o} \sum_{l'} t^j_{l'}\, (2l'+1)\, (-1)^{l'} \sum_{l''} (2l''+1) \begin{pmatrix} l & l' & l'' \\ 0 & 0 & 0 \end{pmatrix}^2 \underline{h}^{+2}_{l''}(kR_{jo})\right\}$$

$$\chi_3^l(\varepsilon) = \frac{1}{2l+1} \sum_m \sum_{j'\neq o} \sum_{j''\neq j'} \sum_{l''m''} \sum_{l'm'} \mathrm{Im}\left\{e^{2i\delta_l^o}\, G^o_{lm\, l'm'}\, t^{j'}_{l'}\, G^{j'\, j''}_{l'm'\, l''m''}\, t^{j''}_{l''}\, G^{j''\, o}_{l''m''\, lm}\right\}$$

$$= 4\pi^2\, \mathrm{Im}\left\{ e^{2i\delta_l^o} \sum_{i\neq o} \sum_{j\neq i} \sum_{l'l''} (2l'+1)\, t^i_{l'}\, (2l''+1)\, t^j_{l''}\, (-1)^{l+l'+l''} \right.$$

$$\sum_{\underline{l}\,\underline{l}'\underline{l}''} \begin{pmatrix} l & l' & \underline{l} \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} l' & l'' & \underline{l} \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} l'' & l & \underline{l} \\ 0 & 0 & 0 \end{pmatrix} \begin{Bmatrix} \underline{l} & \underline{l}'' & \underline{l}' \\ l & l' & l'' \end{Bmatrix} [(2\underline{l}+1)\,(2\underline{l}'+1)\,(2\underline{l}''+1)/4\pi]^{1/2}$$

$$\left. \sum_{\underline{m}\,\underline{m}'\underline{m}''} \begin{pmatrix} \underline{l} & \underline{l}'' & \underline{l}' \\ \underline{m} & \underline{m}'' & \underline{m}' \end{pmatrix} \underline{h}^+_{\underline{l}'}(kR_{oi})\, Y_{\underline{l}'\underline{m}'}(\hat{R}_{oi})\, \underline{h}^+_{\underline{l}''}(kR_{ij})\, Y_{\underline{l}''\underline{m}''}(\hat{R}_{ij})\, \underline{h}^+_{\underline{l}}(kR_{jo})\, Y_{\underline{l}\,\underline{m}}(\hat{R}_{jo}) \right\}$$

where we have introduced 3-j and 6-j symbols as defined in the literature [10] and the "reduced" Hankel function $\underline{h}^+_l(\rho)$:

$$\underline{h}^+_l(\rho) = i^{l+1}\, h^+_l(\rho) = \frac{e^{i\rho}}{\rho} \sum_{k=0}^{l} \frac{(l+k)!}{(l-k)!}\, \frac{1}{k!}\, \left(\frac{i}{2\rho}\right)^k \qquad (17)$$

It is possible to write down more cumbersome expressions for the higher order terms $\chi_n^l(\varepsilon)$ (n>3) using the (3n-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 matrix $(I-T_a G)$ and can perform the matrix inversion either

exactly or via the series expansion Eq. (14). For application to data analysis we wish to remark that the functional expression of the quantities $\chi_n^l(\varepsilon)$ is quite simple, despite the complexity of their definition. In fact a little reflection shows that :

$$\chi_n^l(\varepsilon) = \sum_{p_n} A_n^l(k, R_{ij}^{p_n}) \sin(k R_{p_n}^{tot} + 2\delta_l^o + \phi_n^l(k, R_{ij}^{p_n})) \tag{18}$$

where the sum is over all possible paths p_n of order n defined above and $R_{p_n}^{tot}$ is the corresponding path length. This form follows from the fact that each $G_{LL'}^{ij}$ carries a factor $e^{ikR_{ij}}$ independent of L, L', contained in the Hankel function (see Eq. (5)) that can be factorized. By defining a new matrix

$$\underline{G}_{LL'}^{ij} = e^{-ikR_{ij}} G_{LL'}^{ij}$$

and putting

$$A_n^l(k, R_{ij}^{p_n}) \exp\{i\phi_n^l(k, R_{ij}^{p_n})\} = \frac{1}{2l+1} \left\{ \sum_m \sum_{j_1 \neq o} \sum_{j_2 \neq j_1} \cdots \sum_{j_{n-1}} \sum_{L_1 \cdots L_{n-1}} \right.$$

$$\left. \underline{G}_{L\,L_1}^{o\,j_1}\, t_{l_1}^{j_1}\, \underline{G}_{L_1 L_2}^{j_1 j_2}\, t_{l_2}^{j_2} \cdots \underline{G}_{L_{n-1}\,L}^{j_{n-1}\,o} \right\} \tag{19}$$

where the indices j_k run over the particular path p_n, we arrive at the expression (18), with $R_{p_n}^{tot} = \sum_{i=0}^{n-1} R_{j_i j_{i+1}}$. 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.

It is obviously of practical importance to find approximate expressions for the SW propagators $G_{LL'}^{ij}$ that would allow a rapid computation of the amplitude and phase functions defined in Eq. (19). We have found that the simple approximation

$$G_{LL'}^{ij} = 4\pi\, Y_L(\hat{R}_{ij})\, Y_{L'}^{*}(\hat{R}_{ij})\, \frac{e^{i\rho_{ij}}}{\rho_{ij}}\, f_{ll'}(\rho_{ij}) \qquad (\rho_{ij} = k R_{ij})$$

$$f_{ll'}(\rho) = \left[1 + \frac{\alpha_{ll'}}{2\rho^2}\right]^{1/2} e^{i\alpha_{ll'}/(2\rho)} \qquad (\alpha_{ll'} = l(l+1) + l'(l'+1)) \tag{20}$$

generally reproduces quite well the exact EXAFS $\chi_2^l(\varepsilon)$ term (single scattering) both in amplitude and phase, but fails to reproduce (sometimes by a factor of two) the amplitude of the exact $\chi_3^l(\varepsilon)$ term (double scattering). Figs. 1 and 2 illustrate this comparison in the case of MnO_4 tetrahedral cluster. The usual PW approximation is obtained by putting $f_{ll'}(\rho) = 1$, but it can be shown to be never good, not even at the highest energies. The reason is that the phase correction goes like $\alpha_{ll'}/(2\rho) \sim l_{max} \gg 1$, since $\rho = kR \sim l_{max}$ by the well known semiclassical argument of the impact parameter. See Ref. [11] for more details on this aspect. Clearly more work needs to be done for a more accurate approximation.

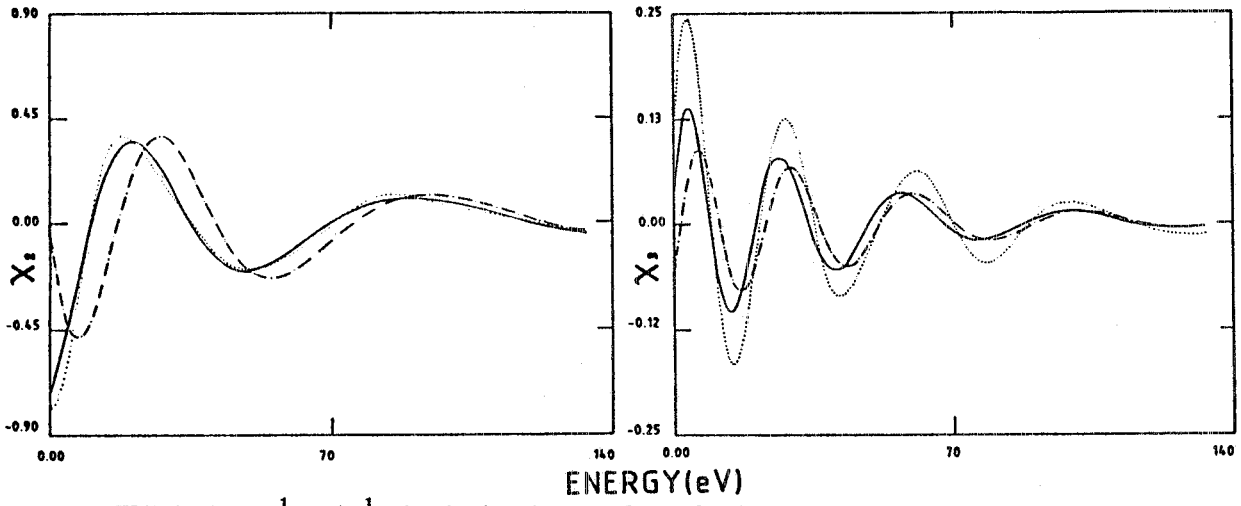

FIG. 1 - Exact χ^1_2 and χ^1_3 signals (dotted curves) for MnO_4 cluster, compared with S.W. approximation (Eq. 20) (full lines) and P.W. approximation (dot-dashed lines).

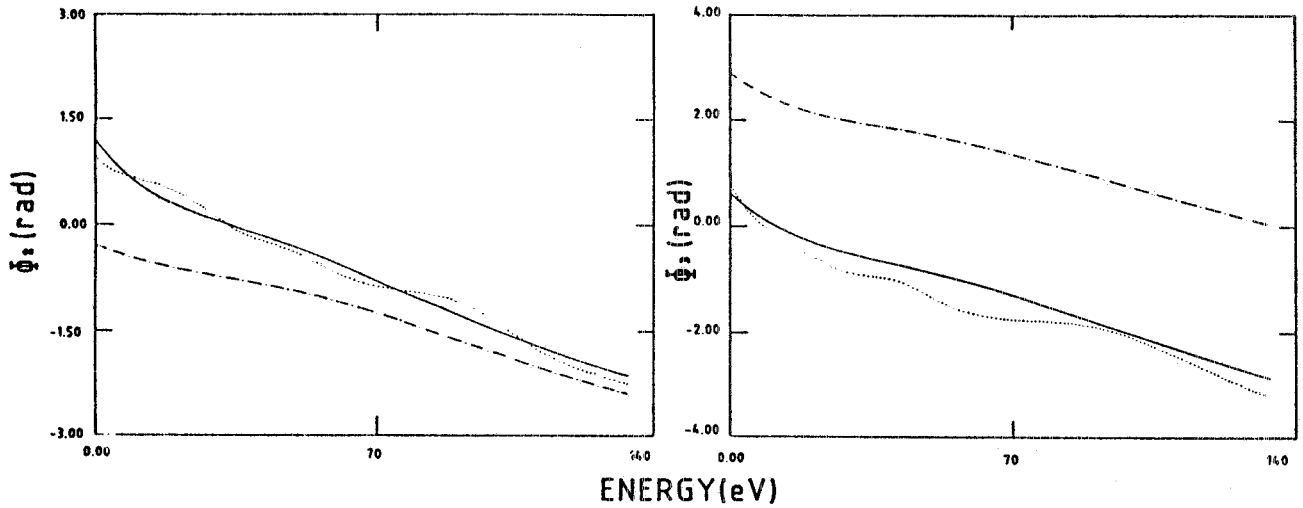

FIG. 2 - Same as Fig. 1 for ϕ_2^1 and ϕ_3^1 phase functions.

The importance of being able to detect the $\chi_n^1(\varepsilon)$ signals in experimental data comes from the fact that they provide information about the n-th order correlation functions $g_n(\vec{R}_{1o}\ldots \vec{R}_{n-1o})$. In fact what is actually measured is the quantity $\langle\chi^1(\varepsilon)\rangle$, where the brackets indicate the configurational average with respect to the distribution of the positions $\vec{R}_i$ around the reference center $\vec{R}_o$ (photoabsorber). In other words

$$\langle\chi^1(\varepsilon)\rangle = 1 + \sum_{n=2}^{\infty} \int \prod_{m=1}^{n-1} d^3R_{mo}\, g_n(\vec{R}_{1o}\ldots\vec{R}_{n-1o})\, \chi_n^1(\varepsilon, \vec{R}_1\ldots \vec{R}_{n-1o}) \qquad (21)$$

That one can actually detect terms other than $\langle\chi_2^1(\varepsilon)\rangle$ in X-ray absorption spectra, has been proved possible in some particular cases [12]. The real challenge is to deconvolute Eq. (21) to obtain the functions g_n. Future effort should be put into this kind of analysis.

The question of convergence of the MS series : discussion and conclusions

The interpretation of the X-ray absorption spectra in terms of MS pathways of the photoelectron in the final state is meaningfull only if there is numerical equivalence between the two sides of Eq. (14). This implies that the expansion on the r.h.s. must converge to the l.h.s. relative to some convergence criterium. From matrix theory one knows that absolute convergence (relative to a suitably defined matrix norm) is ensured if $\rho(T_a G) < 1$.

This criterium is extremely useful since absolute convergence entails the property that terms of order n in the series higher than a certain n_o (which can be very low in favorable cases) do not contribute appreciably to the sum. Now $\rho(T_a G)$ is a continuous function of the photoelectron wave number $k = \sqrt{\varepsilon}$, which goes to zero as k goes to infinity (since $|t_1^i| \to 0$ in this case) and tends to infinity as k approaches zero (since $G^{ij}_{LL'}$ is singular at k=0, due to the presence of the Hankel function in the definition of Eq. (5)). As a consequence it must cross at least once the value $\rho=1$. Moreover the nearer to 1 is its value, the slower is the convergence of the series.

The implication of the above considerations are immediate. At extremly high energies, where $|t_1^i| \sim 0$, we have only atomic absorption ($\chi_n^1 \sim 0$, $n \geq 2$). At high energies, where still $|t_1^i| \ll 1$, also $\rho(T_a G) \ll 1$ so that only the $\chi_2^1(\varepsilon)$ term contributes to give structural information. This is the single scattering (EXAFS) regime, that probes only the pair correlation function. At lower energies, where $\rho(T_a G)$ is still less than one and of the order of, say, one half, higher order terms $\chi_n^1(\varepsilon)$ begin to contribute to the absorption coefficient, typically $n = 3,4$. This is an intermediate MS (IMS) region that can even span as much as 100 + 150 eV and provides information about g_3 and g_4. At still lower energies several things may happen depending on the behavior of the phase shifts δ_1^i and the photoelectron damping and their interplay. The spectral radius $\rho(T_a G)$ may continue to rise, as the energy approaches the edge from above, so as to reach one or stay very near to it (normal situation). In such a case very many paths contribute to the shape of the absorption coefficient or an infinite number of them, depending on whether $\rho(T_a G)$ is less or greater than one. 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. It might be adequate to call it full multiple scattering (FMS) region. One has only a global information in this case. However a rather unexpected situation may also occur. $\rho(T_a G)$ may stay near one at some intermediate energies and then decrease 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 $\chi_2^1(\varepsilon)$ alone is capable of reproducing the experimental spectrum and the exact band calculation [13]. However deviations begin to show up in the energy range 50 + 200 eV [11]. This behavior is due to the peculiarity of the relevant atomic phase shifts that are small at low energy and cross $\pi/2$ ($|t_1| \sim 1$) at ~ 130 eV. Around this energy MS contributions show up in the absorption coefficient.

Summarizing we can say that at least in principle any X-ray absorption spectrum contains all three regions mentioned above. Their order with increasing energy and their energy extent are obviously system dependent. The only feature common to all systems is that in the limit of high energy the IMS structure should continuously merge into the SS region and finally reduce to a pure atomic absorption.

The experimental situation presents additional complicating factors some of which however have a simplifying effect on the shape of the absorption spectrum, with a corresponding loss of informational content. It is clear that the finite core hole lifetime, the limited experimental resolution, the damping of the photoelectron in the final state (extrinsic losses), the thermal and configurational disorder, when present, all conjure up to reduce the size of $\rho(T_a G)$ at such a point that sometimes only the SS term survives as the dominant signal. There are already indications that in some crystalline materials (Si, Al) lifetime effects alone are sufficient to make the series convergent in the whole energy range except perhaps 10-15 eV near the edge [14]. The use of the Fourier transform technique in following the organization of crystalline order with annealing temperature in amorphous thin films of Ge grown on a substrate finds its rationale in this kind of considerations [15]. On the other hand shake-up and shake-off processes of intrinsic origin tend to add features to the spectrum that modify the expected one electron shape. In this case the analysis in terms of MS paths should be done after the removal of these extra features. We have found an example of this situation in analysing the MnO_4 cluster [12].

In any case a careful theoretical assessment of all these effects is highly desirable and work is in progress. In particular the a priori garantee that the MS series is convergent gives confidence that one can parametrize the experimental data by a series of functions of the type shown in Eq. (18) with a well defined expression for A_n^l and ϕ_n^l. This point is essential if one wish to address the problem of the determination of the $g_n(\vec{R}_{ij})$'s for n>2. Otherwise alternative ways for analysing photoabsorption data must be devised.

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