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Systematic approach to the calculation of the polarization-dependent (and polarization-averaged) general term of the curved-wave multiple-scattering series in the x-ray-absorption cross section

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By exploiting in a systematic manner the transformation properties of the general term of the curved-wave multiple-scattering series under rotations, we derive a recursion formula that allows us to compute in a fast and efficient way the building blocks of such terms. This method is applicable both to the polarization-averaged, as well as the polarization-dependent, quantities. One can therefore exploit in data analysis, when possible, the additional simplification brought about by the selective power of the polarization, especially at low energies 20–150 eV, where the effect of the curvature of the photoelectron wave becomes sizable.

I. INTRODUCTION

Since the work of Lee and Pendry[1] in 1975, the importance of the multiple-scattering (MS) contributions to the x-ray absorption coefficient has been stressed in various occasions, especially in relation to collinear configurations of atoms where, because of the focusing effect, the corresponding MS contributions dominate over the single-scattering signal. However, in practice, their effects have been usually considered more as a nuisance in the data analysis than as a real piece of structural information to be carefully exploited. The argument was that, except in the collinear case, their effects are negligible in a first approximation, so that one could get away with the single-scattering approximation.

It was not until two or three years ago that it became possible to refine the EXAFS (extended x-ray-absorption fine structure) analysis and to show that noncollinear MS contributions, although small in comparison with the single-scattering signal, can nonetheless be extracted from the experimental spectrum and used to obtain information about bond angles around the photoabsorber. This was done for the permanganate ion MnO_4^- in solution,[2] for the ferrocene and nickelocene molecules,[3] and for the silicon crystal.[4] In all these cases, the type of analysis was inspired by the underlying assumption, supported by the theory,[5] that the contributions of the final l channel to the absorption spectrum can be written as $[\kappa=(\hbar\omega-E_0)^{1/2}]$

$$\alpha_l(\omega)=\alpha_l^0(\omega)\left[1+\sum_{n>1}\chi_l^n(\kappa)\right],$$

where $\alpha_l^0(\omega)$ is the atomic absorption and

$$\chi_l^n(\kappa)=\sum_i A_l^n(\kappa,p_i)\sin[\kappa R(p_i)+\varphi_l^n(\kappa,p_i)]$$

represents the partial contribution of order n to the absorption coefficient coming from all processes where the photoelectron emanating from the absorbing site 0 is scattered $n-1$ times by the surrounding atoms along path p_i of length $R(p_i)$ before returning to site 0. Its oscillatory character signifies the self-interference process of the photoelectron wave in the final state. Under broad assumptions discussed in Ref. 5, the series converges uniformly starting at 20–30 eV above the absorption edge and sometimes at lower energy. This fact strongly suggests a type of analysis based on modelling the two strongest signals present in the spectrum under study [i.e., the atomic absorption $\alpha_l^0(\omega)$ and the single-scattering oscillation $\chi_l^2(\kappa)$] either by theoretical considerations or by a fitting procedure and subtracting them from the experimental spectrum. The residual signal so obtained contains both structural information related to MS paths and higher-order correlation functions, and dynamical information connected to electronic correlation effects (when present). The latter should be further isolated and subtracted if structural analysis is done. Due to the convergence of the MS series and especially for light atomic scatterers one expects these MS contributions to be sizeable at relatively low energy 20–150 eV where the distortion introduced in the propagation amplitude of the photoelectron by the curvature of the waves is substantial and cannot be neglected.[6]

For a careful analysis, it is therefore of the utmost importance to have an exact, fast and efficient way of calculating the general term of the MS series in the spherical wave representation. The purpose of this paper is to provide such a development. Furthermore, the following treatment constitutes a useful compendium of the MS theory of x-ray absorption spectra.

The calculation hinges on the systematic exploitation of the transformation properties of the general term of the MS series under rotations, which will allow us to derive a recurrence formula for the building blocks of such terms. This method can be applied both to polarization-averaged as well as to polarization-dependent quantities. The expressions obtained for the latter are not much more complicated than their averaged counterparts.

II. PRELIMINARIES

In all of the following, we make use of the basic reference concerning angular momentum: Ref. 7. According to the multiple-scattering formalism, the x-ray absorption cross section for an atomic system in the muffin-tin approximation is, in SI units,[8,9]

$$\sigma(\hat{\varepsilon})=-4\pi\alpha\hbar\omega\kappa^2\sum_{m_0}\sum_{L,L''} M_L M_{L''}\,\mathrm{Im}\langle\kappa L|\tau^{00}|\kappa L''\rangle \times(2m/\hbar^2)\ ,$$

where α is the fine structure constant, $\hbar\omega$ is the energy of the x-ray photon, κ is the photoelectron wave number, L is the compound index $L\equiv(l,m)$, and l_0 and m_0 are the azimuthal and magnetic quantum numbers of the core electrons in the initial state, respectively. Furthermore we have defined the atomic dipole matrix element:

$$M_L\equiv\int d^3r\,R_l(r)Y_l^m(\hat{\mathbf{r}})\boldsymbol{\varepsilon}\cdot\mathbf{r}R_{l_0}^c(r)Y_{l_0}^{m_0}(\hat{\mathbf{r}})\ ,$$

where $R_{l_0}^c(r)Y_{l_0}^{m_0}(\hat{\mathbf{r}})$ is the wave function of the core electron (before absorption) and $R_l(r)Y_l^m(\hat{\mathbf{r}})$ is the photoelectron wave function inside the muffin-tin sphere. It is defined so that the radial part $R_l(r)$ matches smoothly to $j_l(\kappa r)\cot(\delta_l^0)-n_l(\kappa r)$ at the muffin-tin radius of the photo absorbing atom (δ_l^0 is the lth phase shift of the photoabsorbing atom, the index 0 refers to the absorbing site). The sum over m_0 is the sum over the initial states while the sum over L and L'' is the sum over all the possible final states of the photoelectron.

In the above formula, we have used real spherical harmonics $Y_l^m(\hat{\mathbf{r}})$ which are defined in terms of the usual complex spherical harmonics $\mathcal{Y}_l^m(\hat{\mathbf{r}})$ by the unitary transformation:[10]

$$Y_l^m(\hat{\mathbf{r}}_i)=\sum_{m'}A_{mm'}^l\mathcal{Y}_l^{m'}(\hat{\mathbf{r}}_i)\ ,$$

where the nonzero elements of $A_{mm'}^l$ are (for $m>0$)

$$A_{mm}^l=(-1)^m/\sqrt{2},\quad A_{m\,-m}^l=1/\sqrt{2},$$

$$A_{-mm}^l=-i(-1)^m/\sqrt{2},\quad A_{-m\,-m}^l=i/\sqrt{2},\quad A_{00}^l=1\ .$$

The matrix element $\langle\kappa L|\tau^{00}|\kappa L''\rangle$ of the scattering path operator τ^{00} is defined by the matrix equation

$$\langle\kappa L|\tau^{00}|\kappa L''\rangle\equiv\tau_{LL''}^{00}=\{(1-\kappa T_aH)^{-1}T_a\}_{LL''}^{00}\ .$$

In this equation $\{T_a\}_{LL'}^{ij}=(-1/\kappa)t_l^i\delta_{ij}\delta_{LL'}$ is a diagonal matrix describing the scattering process of the photoelectron spherical wave with angular momentum l by the atom located at site i through the atomic dimensionless t-matrix element $t_l^i=\sin(\delta_l^i)\exp(i\delta_l^i)$, δ_l^i being the associated phase shift (muffin-tin potentials are assumed). The structural information about the cluster is represented by the matrix

$$\{H\}_{lm,l'm'}^{ij}\equiv-4\pi i\sum_{\lambda,\mu}i^{l+\lambda-l'}\tilde{C}_{lm,\lambda\mu}^{l'm'}h_\lambda^+(\kappa R_{ij})Y_\lambda^\mu(\hat{\mathbf{R}}_{ij})\ ,$$

where $\tilde{C}_{lm,\lambda\mu}^{l'm'}$ is a kind of Gaunt coefficient for real spherical harmonics defined by

$$\tilde{C}_{lm,\lambda\mu}^{l'm'}\equiv\int d\Omega\,Y_{l'}^{m'}(\hat{\mathbf{r}})Y_\lambda^\mu(\hat{\mathbf{r}})Y_l^m(\hat{\mathbf{r}})\ ,$$

and h_λ^+ is the Hankel function given by[11]

$$h_l^+(\rho)\equiv i^{-(l+1)}\frac{e^{i\rho}}{\rho}\sum_{k=0}^{l}\frac{(l+k)!}{k!(l-k)!}\left[\frac{i}{2\rho}\right]^k\ .$$

The vector $\mathbf{R}_{ij}\equiv\mathbf{R}_i-\mathbf{R}_j$ is the vector joining the two atoms in the cluster located at sites i and j, R_{ij} being its modulus and $\hat{\mathbf{R}}_{ij}$ the associated unit vector. The dimension of the matrices used in the above formulas is $N(l_m+1)^2$, where N is the number of sites and l_m the maximum azimuthal quantum number used in the calculation.

We shall also use complex spherical harmonics. Then the corresponding scattering path operator is defined by the same equation with H replaced by $\mathcal{H}$. This latter matrix is expressed by

$$\{\mathcal{H}\}_{lm,l'm'}^{ij}\equiv-4\pi i\sum_{\lambda,\mu}i^{l+\lambda-l'}C_{lm,\lambda\mu}^{l'm'}h_\lambda^+(\kappa R_{ij})\mathcal{Y}_\lambda^\mu(\hat{\mathbf{R}}_{ij})\ ,$$

where $C_{lm,\lambda\mu}^{l'm'}$ are now the standard Gaunt coefficients defined by

$$C_{lm,\lambda\mu}^{l'm'}\equiv\int d\Omega[\mathcal{Y}_{l'}^{m'}(\hat{\mathbf{r}})]^*\mathcal{Y}_\lambda^\mu(\hat{\mathbf{r}})\mathcal{Y}_l^m(\hat{\mathbf{r}})$$
$$=[(2l+1)(2\lambda+1)/4\pi(2l'+1)]^{1/2}\times(l0\lambda0|l'0)(lm\lambda\mu|l'm')\ ,$$

where $(lm\lambda\mu|l'm')$ are Clebsch-Gordan coefficients. We remind the reader that $(l0\lambda0|l'0)$ is zero if $l+\lambda+l'$ is odd. We shall rewrite the $\mathcal{H}$ matrix as

$$\mathcal{H}_{lm,l'm'}^{ij}=\sum_a O_{ll'}^a(\kappa R_{ij})\sum_\alpha(-1)^{l-m}(l-ml'm'|a\alpha)\mathcal{Y}_a^\alpha(\hat{\mathbf{R}}_{ij}),$$

$$O_{ll'}^a(\kappa R_{ij})\equiv i^{l'-l-a-1}h_a^+(\kappa R_{ij})[4\pi(2l+1)]^{1/2}(l0a0|l'0)\ .$$

The equivalence of this definition with the previous one is a direct consequence of the symmetry relations

$$(lma\alpha|l'm')=(-1)^{l'-a-m}[(2l'+1)/(2a+1)]^{1/2}\times(l-ml'm'|a\alpha)$$

(Ref. 7, 3.180). We shall show that the $\underline{\mathcal{H}}$ matrix is related to the $\underline{H}$ matrix by the same unitary transformation as that between real and complex spherical harmonics.

In his derivation of the curved-wave extended x-ray-absorption fine structure (EXAFS) formula, Schaich[8] has shown that the polarization-averaged absorption cross section could be written

$$\sigma = 2\times 4\pi\alpha\hbar\omega\kappa(2m/\hbar^2)\tfrac{1}{3}[l_0 M^2_{l_0,l_0-1}\chi_{l_0-1} + (l_0+1)M^2_{l_0,l_0+1}\chi_{l_0+1}] ,$$

where χ_l is defined by

$$\chi_l \equiv \{-\kappa/[(2l+1)\sin^2(\delta_l^0)]\}\sum_m \mathrm{Im}\langle \kappa l m|\tau^{00}|\kappa l m\rangle$$

and $M_{l_0 l} \equiv \sin(\delta_l^0)\int dr\, r^2 R_l(r) r R^c_{l_0}(r)$ is the radial integral. The prefactor 2 comes from the sum over the spin states of the initial orbitals.

If $\kappa T_a \mathcal{H}$ is "small enough," or more precisely if the maximum modulus of the eigenvalues of $\kappa T_a \mathcal{H}$ is less than 1, then τ can be expanded into

$$\tau = \sum_n (\kappa T_a \mathcal{H})^n T_a .$$

Thus we can define $\chi_l = \sum_n \chi_l^n$ with

$$\chi_l^n \equiv \{-\kappa/[(2l+1)\sin^2(\delta_l^0)]\}\sum_m \mathrm{Im}\{(\kappa T_a\mathcal{H})^n T_a\}^{00}_{lm,lm}$$

or

$$\chi_l^n = [(-1)^n/(2l+1)]\mathrm{Im}\left[\exp(2i\delta_l^0)\sum_{mi,}\sum_{l',m'j,}\sum_{l'',m''}\cdots\sum_{k,\lambda,\mu}(\mathcal{H}^{0i}_{lm,l'm'}t^i_{l'}\mathcal{H}^{ij}_{l'm',l''m''}t^j_{l''}\cdots t^k_\lambda \mathcal{H}^{k0}_{\lambda\mu,lm})\right] .$$

A similar expansion will be carried out for the polarization-dependent multiple-scattering series. For the time being, we concentrate on the invariance properties of the sum that is on the right-hand side of the above equation.

III. INVARIANCE AND COUPLING OF THE MULTIPLE-SCATTERING TERMS

In this section we study the symmetries and the coupling procedures of the terms of the multiple-scattering series. First we show how one can go from complex to real spherical harmonic representations, then we find the symmetries of the multiple-scattering terms, finally we describe a general coupling procedure that will enable us to obtain painlessly the first terms of the multiple-scattering series of the polarized and nonpolarized x-ray absorption cross sections.

A. From complex to real representations

Since the theory of angular momentum has been devised to deal with complex spherical harmonics, the theoretical approach of the coupling of the scattering terms is easier in that representation. However, the real spherical harmonics are much more practical from a computational point of view. In this section we investigate the transition from one representation to the other. Moreover, this easy calculation will illustrate clearly the general method that will be used in the following sections.

During the preliminaries, we have shown that the calculation of the nth order scattering term of the nonpolarized absorption cross section involves quantities with the following form:

$$X = \sum_m \sum_{m',m''}\cdots\sum_\mu(\mathcal{H}^{0i}_{lm,l'm'}t^i_{l'}\mathcal{H}^{ij}_{l'm',l''m''} \times t^j_{l''}\cdots t^k_\lambda\mathcal{H}^{k0}_{\lambda\mu,lm}) .$$

Note that X has a number of implicit arguments $(l,l',l'',\ldots,\lambda;i,j,\ldots,k)$ that we drop for notational convenience.

The first thing we shall note is that X is invariant with respect to any transformation changing $\mathcal{H}^{ij}_{l'm',l''m''}$ into $\mathcal{H}^{i'j'}_{l'\mu',l''\mu''}$ with

$$\mathcal{H}^{i'j'}_{l'\mu',l''\mu''} = \sum_{m',m''} U^{l'}_{\mu'm'}\mathcal{H}^{ij}_{l'm',l''m''}(\underline{U}^{l''\dagger})_{m''\mu''} ,$$

where $U^{l'}_{\mu'm'}$ are unitary matrices. To show this, we shall write symbolically

$$X = \mathrm{tr}(\underline{\mathcal{H}}_{ll'}t^i_{l'}\underline{\mathcal{H}}_{l'l''}t^j_{l''}\cdots t^k_\lambda\underline{\mathcal{H}}_{\lambda l}) ,$$

where

$$\mathrm{tr}[\underline{A}] \equiv \sum_m A_{mm} .$$

The transformed quantity obtained by applying the previous unitary transformation is, assuming $t^{i'}_{l'} = t^i_{l'}$

$$X' = \mathrm{tr}(\underline{U}^l\underline{\mathcal{H}}_{ll'}\underline{U}^{l'\dagger}t^i_{l'}\underline{U}^{l'}\underline{\mathcal{H}}_{l'l''}\underline{U}^{l''\dagger}t^j_{l''}\cdots t^k_\lambda\underline{U}^\lambda\underline{\mathcal{H}}_{\lambda l}\underline{U}^{l\dagger}) .$$

Since the $\underline{U}^l$ matrices are unitary, we obtain

$$X' = \mathrm{tr}(\underline{U}^l\underline{\mathcal{H}}_{ll'}t^i_{l'}\underline{\mathcal{H}}_{l'l''}t^j_{l''}\cdots t^k_\lambda\underline{\mathcal{H}}_{\lambda l}\underline{U}^{l\dagger}) .$$

Using now the cyclic property of the trace,

$$X' = \mathrm{tr}(\underline{\mathcal{H}}_{ll'}t^i_{l'}\underline{\mathcal{H}}_{l'l''}t^j_{l''}\cdots t^k_\lambda\underline{\mathcal{H}}_{\lambda l}\underline{U}^{l\dagger}\underline{U}^l) = X .$$

To conclude, we have proved that the terms which have the form of X are invariant with respect to any transformation that can be expressed as a matrix product over the index m, where the transformation matrices are unitary.

Now, we show that the transition from complex to real spherical harmonics can be represented by a multiplication of the $\underline{\mathcal{H}}$ matrices by a unitary matrix. To do that we start from the two forms of the expansion formula of the free-space Green function:[12]

$$G_0^+(\mathbf{r}_i-\mathbf{r}_j+\mathbf{R}_{ij};\kappa)$$
$$=\kappa\sum_{l,l'}\sum_{m,m'} j_l(\kappa r_i)\mathcal{Y}_l^m(\hat{\mathbf{r}}_i)\mathcal{H}^{ij}_{lm,l'm'}j_{l'}(\kappa r_j)[\mathcal{Y}_{l'}^{m'}(\hat{\mathbf{r}}_j)]^* ,$$

$$G_0^+(\mathbf{r}_i-\mathbf{r}_j+\mathbf{R}_{ij};\kappa)=\kappa\sum_{l,l'}\sum_{m,m'} j_l(\kappa r_i)Y_l^m(\hat{\mathbf{r}}_i)$$
$$\times H^{ij}_{lm,l'm'}j_{l'}(\kappa r_j)Y_{l'}^{m'}(\hat{\mathbf{r}}_j) .$$

The orthogonality of the spherical Bessel functions leads to

$$\sum_{m,m'}\mathcal{Y}_l^m(\hat{\mathbf{r}}_i)\mathcal{H}^{ij}_{lm,l'm'}[\mathcal{Y}_{l'}^{m'}(\hat{\mathbf{r}}_j)]^*$$
$$=\sum_{m,m'}Y_l^m(\hat{\mathbf{r}}_i)H^{ij}_{lm,l'm'}Y_{l'}^{m'}(\hat{\mathbf{r}}_j) .$$

One can obtain the real spherical harmonics from the complex ones by the unitary transformation:

$$Y_l^m(\hat{\mathbf{r}}_i)=\sum_{m'}A^l_{mm'}\mathcal{Y}_l^{m'}(\hat{\mathbf{r}}_i) .$$

The orthogonality of the spherical harmonics yields

$$H^{ij}_{lm,l'm'}=\sum_{\mu\mu'}(A^l_{m\mu})^*\mathcal{H}^{ij}_{l\mu,l'\mu'}A^{l'}_{m'\mu'} .$$

Since the transpose of a unitary matrix is also unitary, the transformation of the $\underline{\mathcal{H}}$ matrices has the right form and the terms X are equal in real and complex representations.

The same reasoning shows that the terms of the form

$$X=\sum_{m,m''}\sum_{m'}\cdots\sum_{\mu}\{\mathcal{Y}_l^m(\hat{\mathbf{r}}_0)\mathcal{H}^{0i}_{lm,l'm'}$$
$$\times t^i_{l'}\cdots t^k_\lambda\mathcal{H}^{k0}_{\lambda\mu,l''m''}[\mathcal{Y}_{l''}^{m''}(\hat{\mathbf{r}}_0)]^*\}$$

are also invariant with respect to the transformation from the complex to the real representations. This result will be useful for the investigation of the polarized multiple-scattering terms.

B. The symmetries of the multiple-scattering terms

Take a rotation $\underline{U}(\alpha,\beta,\gamma)$ which leaves invariant the photoabsorbing atom and that transforms each interatomic vector $\mathbf{R}_{ij}$ of a specific scattering path into $\mathbf{R}_{i'j'}$. Then the transformations of the spherical harmonics by the rotation matrices (Ref. 7, p. 93)

$$\mathcal{Y}_l^m(\underline{U}\hat{\mathbf{r}}_i)=\sum_{m'}D^l_{m'm}(\underline{U}^{-1})\mathcal{Y}_l^{m'}(\hat{\mathbf{r}}_i)$$

and the rotational invariance of the free-space Green function leads as before to the unitary transformation:

$$\mathcal{H}^{i'j'}_{lm,l'm'}=\sum_{\mu,\mu'}[D^l_{\mu m}(\underline{U}^{-1})]^*\mathcal{H}^{ij}_{l\mu,l'\mu'}D^{l'}_{\mu'm'}(\underline{U}^{-1}) .$$

If an inversion is combined with the rotation, one simply adds a factor $(-1)^{l+l'}$ to the above result. This shows that the rotations and the inversions of a complete path $0,i,j,\ldots,k,0$ leave invariant the multiple-scattering term. Accordingly, it is possible to simplify the computation of the multiple-scattering contributions by noting that all paths that can be transformed into each other by a rotation and/or an inversion are equal. By way of example, for the first shell of neighbors in an octahedral environment, one computes χ_l^2 with one path instead of six, χ_l^3 with two paths instead of 30. Note that this rotational invariance is true for each particular set of atomic sites $0,i,j,\ldots,k,0$ and azimuthal quantum numbers $l,l',l'',\ldots,\lambda,l$.

C. The coupling of multiple-scattering terms

In this section, we shall derive some formulas that will enable us to calculate the multiple-scattering terms. This procedure will be used to get, in a straightforward way the double, triple, quadruple, and quintuple scattering terms.

Firstly, we define the quantities

$$X^{n+1}(l,m;l'',m'')$$
$$=\sum_{l_1,\ldots,l_n}\sum_{m_1,\ldots,m_n}(\mathcal{H}^{ij_1}_{lm,l_1m_1}t^{j_1}_{l_1}\mathcal{H}^{j_1j_2}_{l_1m_1,l_2m_2}$$
$$\times t^{j_2}_{l_2}\cdots t^{j_n}_{l_n}\mathcal{H}^{j_nj}_{l_nm_n,l''m''})$$

which are sums over azimuthal quantum numbers of the X introduced in the previous section. It will be proved that these quantities can be put into the form

$$X^{n+1}(l,m;l'',m'') ,$$
$$=\sum_{\alpha,\alpha}\Xi^{n+1}(l,l'';a,\alpha)(-1)^{l-m}(l\ -m\ l''\ m''|a\alpha) ,$$

where the arguments $i,j_1,\ldots,j_n,j$ of $\Xi^{n+1}(l,l'';a,\alpha)$ are implicit (for notational convenience) and $\Xi^{n+1}(l,l'';a,\alpha)$ is an (a,α)-spherical tensor. We arrived at this expansion during a study of the influence of rotations on the $\underline{\mathcal{H}}$ matrices. It appeared that all the quantities that can be so expanded transform under rotation as a single $\underline{\mathcal{H}}$ matrix or a product of them. To demonstrate that, conversely, all products of $\underline{\mathcal{H}}$ matrices have this form, we argue by induction, assuming the validity of the above relation for X^n. Then

$$X^{n+1}(l,m;l'',m'')=\sum_{l'm'}X^n(l,m;l',m')t^{j_n}_{l'}\mathcal{H}^{j_nj}_{l'm',l''m''}$$
$$=\sum_{l',a,\alpha}\sum_{b,\beta}\Xi^n(l,l';a,\alpha)t^{j_n}_{l'}O^b_{l'l''}(\kappa R_{j_nj})\mathcal{Y}_b^\beta(\hat{\mathbf{R}}_{j_nj})$$
$$\times\sum_{m'}(-1)^{l-m}(l\ -m\ l'\ m'|a\alpha)(-1)^{l'-m'}(l'\ -m'\ l''\ m''|b\beta) .$$

The last sum can be transformed by using the symmetries of the Clebsch-Gordan coefficients (Ref. 7, 3.180):

$$\sum_{m'}(-1)^{l-m}(l\,-m\;l'\,m'|a\alpha)(-1)^{l'-m'}(l'\,-m'\;l''\,m''|b\beta)$$
$$=(-1)^{l+l''-a-b}[(2a+1)(2b+1)/(2l''+1)(2l'+1)]^{1/2}\sum_{m'}(lma\alpha|l'm')(l'm'b\beta|l''m'')\;.$$

From Ref. 7, 3.269, we find that the sum equals

$$\sum_{m'}(lma\alpha|l'm')(l'm'b\beta|l''m'')=\sum_{c,\gamma}[(2l'+1)(2c+1)]^{1/2}W(l,a,l'',b;l',c)(a\alpha b\beta|c\gamma)(lmc\gamma|l''m'')\;,$$

where $W(l,a,l'',b;l',c)$ is a Racah coefficient (Ref. 7, 3.240) related to the Wigner 6-j symbol (Ref. 7, 3.312) by

$$W(l,a,l'',b;l',c)\equiv(-1)^{l+a+l''+b}\begin{Bmatrix} l & a & l' \\ b & l'' & c \end{Bmatrix}\;.$$

Using again the symmetries of the Clebsch-Gordan coefficients we obtain

$$\sum_{m'}(-1)^{l-m}(l\,-m\;l'\,m'|a\alpha)(-1)^{l'-m'}(l'\,-m'\;l''\,m''|b\beta)$$
$$=(-1)^{a+b}[(2a+1)(2b+1)]^{1/2}\sum_{c}(-1)^{c}W(l,a,l'',b;l',c)\sum_{\gamma}(a\alpha b\beta|c\gamma)(-1)^{l-m}(l\,-m\;l''\,m''|c\gamma),$$

so that finally

$$X^{n+1}(l,m;l'',m'')=\sum_{l'}\sum_{a,b,c}t_{l'}^{j_n}O_{l'l''}^{b}(\kappa R_{j_nj})(-1)^{a+b}[(2a+1)(2b+1)]^{1/2}(-1)^{c}W(l,a,l'',b;l',c)$$
$$\times\sum_{\alpha,\beta,\gamma}\Xi^{n}(l,l';a,\alpha)\mathcal{Y}_{b}^{\beta}(\hat{\mathbf{R}}_{j_nj})(a\alpha b\beta|c\gamma)\times(-1)^{l-m}(l\,-m\;l''\,m''|c\gamma)\;.$$

The resulting expression has exactly the expected form; thus we have proved that the relation is true for $n+1$ if it is true for n. We have also obtained the recursion relation:

$$\Xi^{n+1}(l,l'';c,\gamma)=\sum_{l',a}\sum_{\alpha,b,\beta}\Xi^{n}(l,l';a,\alpha)t_{l'}^{j_n}O_{l'l''}^{b}(\kappa R_{j_nj})\mathcal{Y}_{b}^{\beta}(\hat{\mathbf{R}}_{j_nj})$$
$$\times(-1)^{a+b}[(2a+1)(2b+1)]^{1/2}(-1)^{c}W(l,a,l'',b;l',c)(a\alpha b\beta|c\gamma)\;.$$

Moreover, according to Ref. 7, 3.249,

$$\sum_{\alpha,\beta}\Xi^{n}(l,l';a,\alpha)\mathcal{Y}_{b}^{\beta}(\hat{\mathbf{R}}_{j_nj})(a\alpha b\beta|c\gamma)$$

is a (c,γ)-spherical tensor. Therefore, since the other terms do not depend on α, β, and γ, $\Xi^{n+1}(l,l'';c,\gamma)$ is also a (c,γ)-spherical tensor. The proof is now completed by noting that, according to the definition of the $\underline{\mathcal{H}}$ matrix, the property is true for $n=1$.

The above result can be generalized to

$$\Xi^{n}(l,l'';c,\gamma)=\sum_{l',a}\sum_{\alpha,b,\beta}\Xi^{m}(l,l';a,\alpha)t_{l'}^{j_m}\,\Xi^{n-m}(l',l'';b,\beta)(-1)^{a+b}[(2a+1)(2b+1)]^{1/2}(-1)^{c}W(l,a,l'',b;l',c)(a\alpha b\beta|c\gamma)\;.$$

The physical interpretation of this relation is very simple. We consider a scattering path that starts from the atom i and reaches the atom j after $n-1$ scatterings on the sites $j_1,\ldots,j_m,\ldots,j_{n-1}$. This path can also be considered as a scattering from i to j_m followed by a scattering from j_m to j. Mathematically, it is a direct consequence of the associativity of tensor coupling (Ref. 7, 3.275).

From the above relation, we deduce that if we expand $\langle\kappa L|\tau^{00}|\kappa L''\rangle$ in terms of n-scattering contributions,

$$\langle\kappa L|\tau^{00}|\kappa L''\rangle=\langle\kappa L|\tau^{0}|\kappa L''\rangle$$
$$+\langle\kappa L|\tau^{1}|\kappa L''\rangle+\langle\kappa L|\tau^{2}|\kappa L''\rangle+\cdots\;,$$

all the terms have the form

$$\langle\kappa L|\tau^{n}|\kappa L''\rangle=\sum_{c,\gamma}\tau^{n}(l,l'';c,\gamma)(-1)^{l-m}(l-m\;l''\,m''|c\gamma)$$

with

$$\tau^{0}(l,l'';c,\gamma)=(-1/\kappa)t_{l}^{0}(2l+1)^{1/2}\delta_{c0}\delta_{\gamma0}\delta_{ll''}\;,$$
$$\tau^{1}(l,l'';c,\gamma)=0\;,$$
$$\ldots\;.$$

Therefore, by resumming the series we obtain

$$\langle\kappa L|\tau^{00}|\kappa L''\rangle=\sum_{c,\gamma}\tau(l,l'';c,\gamma)$$
$$\times(-1)^{l-m}(l\,-m\;l''\,m''|c\gamma)\;.$$

This expression will be useful for the calculation of the polarization-dependent multiple-scattering terms.

The calculation of the nonpolarized multiple-scattering terms requires the evaluation of

$$\sum_{m} \langle \kappa l m | \tau^{n+1} | \kappa l m \rangle = \sum_{m} \sum_{c,\gamma} \tau^{n+1}(l,l;c,\gamma)(-1)^{l-m}(l\; -m\; l\; m|c\gamma) \;.$$

To carry out the last sum we note that (Ref. 7, 3.234)

$$(l\mu l m|00) = (-1)^{l-m}\delta_{\mu,-m}/(2l+1)^{1/2}$$

so that

$$\sum_{m}(-1)^{l-m}(l\; -m\; l\; m|c\gamma) = (2l+1)^{1/2}\sum_{m,\mu}(l\mu l m|c\gamma)(l\mu l m|00) \;.$$

According to the orthogonality relation for the Clebsch-Gordan coefficients (Ref. 7, 3.175), one obtains

$$\sum_{m}(-1)^{l-m}(l\; -m\; l\; m|c\gamma) = (2l+1)^{1/2}\delta_{c0}\delta_{\gamma 0}$$

so that

$$\sum_{m}\sum_{c,\gamma}\tau^{n+1}(l,l;c,\gamma)(-1)^{l-m}(l\; -m\; l\; m|c\gamma) = (2l+1)^{1/2}\tau^{n+1}(l,l;0,0)$$

and

$$\begin{aligned}(2l+1)^{1/2}\Xi^{n+1}(l,l;0,0) &= \sum_{l',a}\sum_{\alpha,b,\beta}\Xi^{n}(l,l';a,\alpha)t_{l'}^{j_n}O_{l'l}^{b}(\kappa R_{j_n j})\mathcal{Y}_{b}^{\beta}(\hat{\mathbf{R}}_{j_n j})(-1)^{a+b} \\ &\qquad\times[(2a+1)(2b+1)(2l+1)]^{1/2}W(l,a,l,b;l',0)(a\alpha b\beta|00) \\ &= \sum_{l',a,\alpha}\Xi^{n}(l,l';a,\alpha)t_{l'}^{j_n}O_{l'l}^{a}(\kappa R_{j_n j})\mathcal{Y}_{a}^{-\alpha}(\hat{\mathbf{R}}_{j_n j})(-1)^{l-l'-\alpha}\end{aligned}$$

since $W(l,a,l,b;l',0)=\delta_{a,b}(-1)^{a+l-l'}/[(2a+1)(2l+1)]^{1/2}$ (Ref. 7, 3.258). More generally

$$(2l+1)^{1/2}\Xi^{n}(l,l;0,0) = \sum_{l',a,\alpha}\Xi^{m}(l,l';a,\alpha)t_{l'}^{j_m}\,\Xi^{n-m}(l',l;a,-\alpha)(-1)^{l-l'-\alpha} \;.$$

Now we have all the relations required for a fast calculation of the multiple-scattering terms. Note that all the above formulas would also be true if we had *not* summed over the azimuthal quantum numbers in the definition of Ξ^n.

IV. NONPOLARIZED MULTIPLE-SCATTERING TERMS

The calculation of the multiple-scattering terms is now obvious. First we shall consider two special cases of $\Xi^n(a,\alpha)$:

$$\Xi^{1}(l,l'';a,\alpha;i,j) = O_{ll''}^{a}(\kappa R_{ij})\mathcal{Y}_{a}^{\alpha}(\hat{\mathbf{R}}_{ij})$$

and

$$\begin{aligned}\Xi^{2}(l,l'';c,\gamma;i,j_1,j) &= \sum_{a,b,l'}O_{ll'}^{a}(\kappa R_{ij_1})O_{l'l''}^{b}(\kappa R_{j_1 j})t_{l'}^{j_1}(-1)^{a+b}[(2a+1)(2b+1)]^{1/2}(-1)^{c}W(l,a,l'',b;l',c) \\ &\qquad\times\sum_{\alpha,\beta}(a\alpha b\beta|c\gamma)\mathcal{Y}_{a}^{\alpha}(\hat{\mathbf{R}}_{ij_1})\mathcal{Y}_{b}^{\beta}(\hat{\mathbf{R}}_{j_1 j}) \;.\end{aligned}$$

These two quantities will play the role of building blocks of the multiple-scattering terms. Computer experiments have shown that the high-order multiple-scattering terms could be economically evaluated by first computing Ξ^1 and Ξ^2 for all the values of the indices. Moreover, in experimental spectra, the multiple-scattering terms that contribute the most correspond to a linear arrangement of the atoms, because of the so-called focusing effect. For these configurations, one has the further simplification of taking the z axis along the direction $\hat{\mathbf{R}}_{ij}$:

$$\Xi^{1}(l,l'';a,\alpha;i,j) = O_{ll''}^{a}(\kappa R_{ij})[(2a+1)/4\pi]^{1/2}\delta_{\alpha 0} \;,$$

$$\Xi^{2}(l,l'';c,\gamma;i,j_1,j) = \sum_{a,b,l'}O_{ll'}^{a}(\kappa R_{ij_1})O_{l'l''}^{b}(\kappa R_{j_1 j})t_{l'}^{j_1}[(2a+1)(2b+1)/4\pi]W(l,a,l'',b;l',c)(a0b0|c0)\delta_{\gamma 0}$$

if j_1 is between i and j.

Each term of the sum defining the last quantity must be multiplied by $(-1)^a$ if i is between j_1 and j, and by $(-1)^b$ if j is between j_1 and i or if $j=i$.

The amount of memory required for the storage of Ξ^1 and Ξ^2 can be further decreased by noting the following symmetries:

$$\begin{aligned}\Xi^{1}(l,l'';a,\alpha;i,j) &= \Xi^{1}(l'',l;a,\alpha;i,j) \\ &= (-1)^{a}\Xi^{1}(l,l'';a,\alpha;j,i) \;,\end{aligned}$$

$$\Xi^{2}(l,l'';c,\gamma;i,j_1,j) = (-1)^{c}\Xi^{2}(l'';l,c,\gamma;j,j_1,i) \;.$$

One observes that $\Xi^{2}(l,l'';c,\gamma;i',j_1',j') = \Xi^{2}(l,l'';c,\gamma;i,j_1,j)$ if i',j_1',j' can be obtained from i,j_1,j by a translation (conserving the atomic species in site j_1). Because of the tensorial nature of Ξ^2 one has also the rotational relation:

$$\Xi^2(l,l'',c,\gamma';i',j_1',j')=\sum_{\gamma} D^{c}_{\gamma\gamma'}(\underline{U}^{-1})\Xi^2(l,l'';c,\gamma;i,j_1,j)$$

where i',j_i',j' is the result of the transformation of i,j_1,j by the rotation $\underline{U}$ and $D^{c}_{\gamma\gamma'}(\underline{U}^{-1})$ the corresponding rotation matrix. If the rotation is followed by an inversion, just multiply the above equation by $(-1)^{l+l''}$. All the above relations concerning translations, rotations, or inversions are also valid for any Ξ^n, as long as the atomic species of the sites $j_1,\ldots,j_{n-1}$ are conserved by the symmetry operation.

The dimensions of $\Xi^2(l,l'';c,\gamma;i,j_1,j)$ considered as a linear vector with respect to the indices l'', c, and γ, are given by the formula

$$\sum_{l''=0}^{l_m}\sum_{c=|l''-l|}^{l''+l}(2c+1)=(2l+1)(l_m+1)^2\ ,$$

where l_m is the maximum value allowed in the l expansion. In practice, since l and l'' are either free or saturated with $t^{j}_{l(l'')}$, l_m is the maximum l value scattered by any muffin-tin potential of radius R_{MT}, i.e., $l_m\simeq\kappa R_{\mathrm{MT}}$. Using this relation, one can also derive the position of the element $l'';c,\gamma$ when $\Xi^2(l,l'';c,\gamma;i,j_1,j)$ is stored as a linear vector. This is given by the relation

$$\gamma+(2l+1)(l'')^2+\sum_{\lambda=|l''-l|}^{c-1}(2\lambda+1)+c+1$$
$$=2ll''(l''+1)+c(c+1)+1-l^2+\gamma\ .$$

The modifications needed when l itself is not fixed are straightforward.

According to the recursion relations developed in the previous section, we obtain immediately the term required for the calculation of the double-scattering term:

$$(2l+1)^{1/2}\Xi^3(0,0)$$
$$=\sum_{l'a\alpha}\Xi^2(l,l';a,\alpha;0,j_1,j_2)$$
$$\times t^{j_2}_{l'}\Xi^1(l',l,a-\alpha;j_2 0)(-1)^{l-l'-\alpha}\ .$$

Since

$$\chi^n_l=(-1)^n(2l+1)^{-1/2}\mathrm{Im}\left[\exp(2i\delta^0_l)\sum_{[n-1]}\Xi^n(l,l;0,0)\right]\ ,$$

where $[n-1]$ means a sum over all the paths starting from 0, visiting $n-1$ sites and coming back to 0, we find

$$\chi^3_l=[(-1)/(2l+1)]\mathrm{Im}\left[\exp(2i\delta^0_l)\sum_{j_1,j_2}\sum_{l',a,\alpha}\Xi^2(l,l';a,\alpha;0,j_1,j_2)t^{j_2}_{l'}\Xi^1(l',l;a,-\alpha;j_2,0)(-1)^{l-l'-\alpha}\right]\ .$$

Once expanded, we find the same expression as in Refs. 13 and 3:

$$\chi^3_l=(4\pi)^{3/2}\mathrm{Im}\left[\exp(2i\delta^0_l)\sum_{i,j}\sum_{l',l''}(-1)^{l'}(2l'+1)(2l''+1)t^{i}_{l'}t^{j}_{l''}\right.$$
$$\times\sum_{a,b,c}(-1)^{a+b-c-1}(l0l'0|a0)(l'0l''0|b0)(l''0l0|c0)$$
$$\times W(l,a,l'',b;l',c),h^{+}_a(\kappa R_{0i})h^{+}_b(\kappa R_{ij})h^{+}_c(\kappa R_{j0})$$
$$\left.\times(2c+1)^{-1/2}\sum_{\alpha,\beta,\gamma}(-1)^{c-\gamma}(a\alpha b\beta|c\gamma)\mathcal{Y}^{\alpha}_{a}(\hat{\mathbf{R}}_{0i})\mathcal{Y}^{\beta}_{b}(\hat{\mathbf{R}}_{ij})\mathcal{Y}^{-\gamma}_{c}(\hat{\mathbf{R}}_{j0})\right]\ .$$

The term

$$(2c+1)^{-1/2}\sum_{\alpha,\beta,\gamma}(-1)^{c-\gamma}(a\alpha b\beta|c\gamma)\mathcal{Y}^{\alpha}_{a}(\hat{\mathbf{R}}_{0i})\mathcal{Y}^{\beta}_{b}(\hat{\mathbf{R}}_{ij})\mathcal{Y}^{-\gamma}_{c}(\hat{\mathbf{R}}_{j0})$$

is a rotational invariant that plays an important role in the theory of angular correlations in particle physics and may be viewed as a basic structure for determining the Wigner coefficients (Ref. 7, 3.335). Since the vectors $\mathbf{R}_{0i}$, $\mathbf{R}_{ij}$, and $\mathbf{R}_{j0}$ are coplanar, one can use an expression for the last term (Ref. 7, 6.160), which might decrease the computing time:

$$(2c+1)^{-1/2}\sum_{\alpha,\beta,\gamma}(-1)^{c-\gamma}(a\alpha b\beta|c\gamma)\mathcal{Y}^{\alpha}_{a}(\hat{\mathbf{R}}_{0i})\mathcal{Y}^{\beta}_{b}(\hat{\mathbf{R}}_{ij})\mathcal{Y}^{-\gamma}_{c}(\hat{\mathbf{R}}_{j0})$$
$$=[(2a+1)(2b+1)(2c+1)]^{1/2}(4\pi)^{-3/2}$$
$$\times\sum_{k,l}\{(2c+1)!/[(2c-2k)!(2k)!]\}^{1/2}y^{c-k}z^{k}(-1)^{l}((c-k)0a0|l0)(k0b0|l0)W(c-k,c,l,b;k,a)P_l(\hat{\mathbf{R}}_{0i}\cdot\hat{\mathbf{R}}_{ij})\ ,$$

where $y=-R_{0i}/R_{0j}$ and $z=-R_{ij}/R_{0j}$.

The coupling formula yields immediately the triple-scattering term as well:

$$\chi^4_l=[1/(2l+1)]\mathrm{Im}\left[\exp(2i\delta^0_l)\sum_{j_1,j_2,j_3}\sum_{l',a,\alpha}\Xi^2(l,l';a,\alpha;0,j_1,j_2)t^{j_2}_{l'}\Xi^2(l',l;a,-\alpha;j_2,j_3,0)(-1)^{l-l'-\alpha}\right]\ .$$

Once expanded, this expression is identical to the formula of Refs. 13 and 3. We would like to stress that, from a computational point of view, our formula is very efficient since the Ξ^2 can be calculated once and for all for each energy, and then combined to give χ_l^4. We thus avoid the repeated computation of spherical harmonics, Clebsch-Gordan, and Racah coefficients.

Concerning the triple-scattering term χ_l^4, we add a comment that could have some practical value when the bond-angle dependence of χ_l^4 is noticeable. Generally the bond lengths are relatively well known from the analysis of the χ_l^2 term and/or the comparison with model compounds, so that the remaining questions concern the bond angles. In the investigation of nearly linear atomic arrangements in molecules, it has often been observed that the triple-scattering term χ_l^4 is greater than the double-scattering term χ_2^3 because of the focusing effect. Now consider the path $0,i,j,i,0$. Take as a starting point 0, i, and j aligned and use the rotational invariance of the multiple-scattering terms to take the z axis along the bonds. If we decompose the path into $0,i$ plus i,j,i, plus $i,0$, the first two paths couple to

$$\Xi^3(l,l'';c,\gamma;0,i,j,i)=\sum_{l';a,b}\Xi^1(l,l';a,0;0,i)t_{l'}^{i}\Xi^2(l',l'';b,0;i,j,i)$$
$$\times(-1)^{a+b}[(2a+1)(2b+1)]^{1/2}(-1)^{c}W(l,a,l'',b;l',c)(a0b0|c0)\delta_{\gamma 0}\ .$$

To obtain the term χ_l^4 we must couple this Ξ^3 to the Ξ^1 representing the last bond $i,0$. This yields

$$(2l+1)^{1/2}\Xi^4(l,l;0,0;0,i,j,i,0)=\sum_{l',l''}\sum_{a,b}\Xi^1(l,l';a,0;0,i)t_{l'}^{i}\Xi^2(l',l'';b,0;i,j,i)$$
$$\times(-1)^{l-l''}[(2a+1)(2b+1)]^{1/2}W(l,a,l'';b;l';c)(a0b0|c0)t_{l''}^{i}\Xi^1(l'',l;c,0;i,0)\ .$$

Now, if we sum over all the indices except b, we obtain a set of $\chi_l^4(b)$ terms. The advantage of this procedure is that, because of the tensorial character of Ξ^2, the χ_l^4 corresponding to any bond angle θ (with $\theta=0$ for aligned bonds) is obtained by the simple computation:

$$\chi_l^4(\theta)=\sum_b D_{00}^{b}(\pi,\theta,\pi)\chi_l^4(b)=\sum_b P_b(\cos\theta)\chi_l^4(b)\ ,$$

where $P_b(\cos\theta)$ are Legendre polynomials. This enables one to fit precisely the bond angle to the experimental χ_l^4. This procedure can obviously be generalized to higher-order terms of the multiple-scattering series, in which one rotates each bond independently. In that case, one must perform the sum before taking the imaginary part if the rotation matrices are not real. It should be emphasized that the length of each subpath must be kept constant, so that the arguments of the Hankel functions do not change. Consequently, this procedure cannot be used for a χ_l^3.

After this digression, we consider now the quadruple and quintuple scattering terms. They are obtained with the coupling formula:

$$\chi_l^5=[(-1)/(2l+1)]\mathrm{Im}\left\{\exp(2i\delta_l^0)\sum_{j_1,j_2}\sum_{j_3,j_4}\sum_{l',l''}\sum_{a,\alpha,b,\beta,c,\gamma}\Xi^2(l,l';a,\alpha;0,j_1,j_2)t_{l'}^{j_2}\Xi^2(l',l'';b,\beta;j_2,j_3,j_4)\right.$$
$$\times t_{l''}^{j_4}\Xi^1(l'',l;c,-\gamma;j_4,0)(-1)^{a+b}[(2a+1)(2b+1)]^{1/2}$$
$$\left.\times(-1)^{c}W(l,a,l'',b;l',c)(a\alpha b\beta|c\gamma)(-1)^{l-l''-\gamma}\right\}\ ,$$

$$\chi_l^6=[1/(2l+1)]\mathrm{Im}\left\{\exp(2i\delta_l^0)\sum_{j_1,j_2,j_3}\sum_{j_4,j_5}\sum_{l',l''}\sum_{a,\alpha,b\beta,c,\gamma}\Xi^2(l,l';a,\alpha;0,j_1,j_2)t_{l'}^{j_2}\Xi^2(l',l'';b,\beta;j_2,j_3,j_4)\right.$$
$$\times t_{l''}^{j_4}(-1)^{a+b}[(2a+1)(2b+1)]^{1/2}\Xi^2(l'',l;c,-\gamma;j_4,j_5,0)$$
$$\left.\times(-1)^{c}W(l,a;l'',b;l',c)(a\alpha b\beta|c\gamma)(-1)^{l-l''-\gamma}\right\}\ ,$$

The advantages of this formulation from the computational point of view are self-evident.

V. POLARIZED MULTIPLE-SCATTERING TERMS

Up to now, we have considered only the case of a nonpolarized electromagnetic wave or of a nonoriented sample. With the tools developed above, we can consider the case of a linearly polarized beam interacting with an oriented sample. We shall expand the polarization-dependent absorption cross section in multiple-scattering contributions. We calculate the first orders with standard methods, then we use the block form of the multiple-scattering formulas developed in Sec. III C to obtain the influence of polarization on the higher-order scattering terms.

A. General treatment

To obtain the polarization-dependent absorption cross-section we must start from the basic formula:

$$\sigma(\hat{\varepsilon})=-4\pi\alpha\hbar\omega\kappa^2\sum_{m_0}\sum_{L,L''}M_L M_{L''}\,\mathrm{Im}\langle\kappa L|\tau^{00}|\kappa L''\rangle(2m/\hbar^2)\ .$$

The discussion of the transition from real to complex spherical harmonics enables us to write the corresponding formula for complex harmonics:

$$\sigma(\hat{\varepsilon})=-4\pi\alpha\hbar\omega\kappa^2\mathrm{Im}\left[\sum_{m_0}\sum_{L,L''}M_L M^*_{L''}\langle\kappa L|\tau^{00}|\kappa L''\rangle\right](2m/\hbar^2)\ .$$

Using $\boldsymbol{\varepsilon}\cdot\mathbf{r}=(4\pi/3)r\sum_\mu[\mathcal{Y}_1^\mu(\hat{\varepsilon})]^*\mathcal{Y}_1^\mu(\hat{\mathbf{r}})$ we obtain

$$\sigma(\hat{\varepsilon})=4\pi\alpha\hbar\omega\kappa\tfrac{1}{3}(2m/\hbar^2)(2l_0+1)\sum_{l,l''}M_{l_0l}M_{l_0l''}(l_0010|l0)(l_0010|l''0)\chi_{ll''}(\hat{\varepsilon})\ ,$$

where we have defined

$$\chi_{ll''}(\hat{\varepsilon})\equiv[-\kappa/(\sin\delta_l^0\sin\delta_{l''}^0)]\mathrm{Im}\left[\sum_{m_0}\sum_{m,m''}\sum_{\mu,\mu'}C^{l_0m_0}_{lm,1\mu}[\mathcal{Y}_1^\mu(\hat{\varepsilon})]^*\langle\kappa lm|\tau^{00}|\kappa l''m''\rangle C^{l_0m_0}_{l''m'',1\mu'}\mathcal{Y}_1^{\mu'}(\hat{\varepsilon})\right]\Big/N_{ll''}$$

and

$$N_{ll''}\equiv3(2l_0+1)(l_0010|l0)(l_0010|l''0)/(4\pi)^2$$

is a normalization factor. The fact that $N_{ll''}$ may be zero has no consequence since the dipole selection rules ensure that $l=l_0\pm1$ and $l''=l_0\pm1$ ($l=l''=1$ for a K edge). Thus the absorption cross section is zero when $N_{ll''}$ is zero.

Now we can use the representation of $\langle\kappa lm|\tau^{00}|\kappa l''m''\rangle$ developed in Sec. III,

$$\langle\kappa lm|\tau^{00}|\kappa l''m''\rangle=\sum_{c,\gamma}\tau(l,l'';c,\gamma)(-1)^{l-m}(l\ -m\ l''\ m''|c\gamma)\ ,$$

to simplify this expression. Following Ref. 7, 3.437, we define the reduced matrix element,

$$\langle a\|b\|c\rangle\equiv\{(2b+1)(2c+1)/[4\pi(2a+1)]\}^{1/2}(b0c0|a0)\ ,$$

so that

$$C^{l_0m_0}_{lm,1\mu}=\langle l_0\|l\|1\rangle(lm\,1\mu|l_0m_0)\ .$$

This gives us the following expression:

$$\chi_{ll''}(\hat{\varepsilon})=-[\kappa/(\sin\delta_l^0\sin\delta_{l''}^0)]\langle l_0\|l\|1\rangle\langle l_0\|l''\|1\rangle$$
$$\times\mathrm{Im}\left[\sum_{c,\gamma}\tau(l,l'';c,\gamma)\sum_{\mu,\mu'}\sum_{m_0}\sum_{m,m''}(-1)^{l-m}(l\ -m\ l''\ m''|c\gamma)(lm\,1\mu|l_0m_0)\right.$$
$$\left.\times(l''m''1\mu'|l_0m_0)[\mathcal{Y}_1^\mu(\hat{\varepsilon})]^*\mathcal{Y}_1^{\mu'}(\hat{\varepsilon})\right]\Big/N_{ll''}\ .$$

To evaluate the sum over m, m'', and m_0 we first use the symmetries of the Clebsch-Gordan coefficients:

$$(-1)^{l-m}(l\ -m\ l''\ m''|c\gamma)(lm\,1\mu|l_0m_0)(l''m''1\mu'|l_0m_0)$$
$$=(-1)^{1-\mu'}(2l_0+1)[3(2l+1)]^{-1/2}(l_0\ -m_0\ l''\ m''|1\ -\mu')(l\ -m\ l''\ m''|c\gamma)(1\,\mu\,l_0\ -m_0|l\ -m)$$

then we carry out the sum with Ref. 7, 3.267, which gives us

$$\sum_{\mu,\mu'}\sum_{m_0}\sum_{m,m''}(-1)^{l-m}(l\ -m\ l''\ m''|c\gamma)(lm\,1\mu|l_0m_0)(l''m''1\mu'|l_0m_0)[\mathcal{Y}_1^\mu(\hat{\varepsilon})]^*\mathcal{Y}_1^{\mu'}(\hat{\varepsilon})$$
$$=(2l_0+1)W(1,l_0,c,l'';l,1)\sum_{\mu,\mu'}(-1)^{1-\mu'}(1\,\mu\,1-\mu'|c\gamma)[\mathcal{Y}_1^\mu(\hat{\varepsilon})]^*\mathcal{Y}_1^{\mu'}(\hat{\varepsilon})\ .$$

The third step is to use the tensor coupling of spherical harmonics (Ref. 7, 3.439)

$$\sum_{\mu,\mu'}(-1)^{1-\mu'}(1\,\mu\,1\ -\mu'|c\gamma)[\mathcal{Y}_1^\mu(\hat{\varepsilon})]^*\mathcal{Y}_1^{\mu'}(\hat{\varepsilon})=(-1)\langle c\|1\|1\rangle[\mathcal{Y}_c^\gamma(\hat{\varepsilon})]^*\ .$$

All this yields finally the reduced expression:

$$\chi_{ll''}(\hat{\varepsilon})=[4\pi\kappa/(\sin\delta_l^0\sin\delta_{l''}^0)]\sum_{c,\gamma}W(1,l_0,c,l'';l,1)\langle c\|1\|1\rangle \mathrm{Im}\{\tau(l,l'';c,\gamma)[\mathcal{Y}_c^\gamma(\hat{\varepsilon})]^*\}\ .$$

This formula exhibits the general structure of the polarization-dependent absorption cross section. Because of the coefficient $\langle c\|1\|1\rangle$, c must be 0 or 2. The term $c=0$ gives the polarization-averaged absorption cross section $\chi_l\delta_{ll''}$ while the term $c=2$ contains the dependence on polarization.

We know that under suitable conditions, $\tau(l,l'';c,\gamma)$ can be expanded in a series of multiple-scattering contributions:

$$\tau(l,l'';c,\gamma)=\tau^0(l,l'';c,\gamma)+\tau^1(l,l'';c,\gamma)+\cdots+\tau^n(l,l'';c,\gamma)+\cdots$$

with

$$\tau^0(l,l'';c,\gamma)=(-1/\kappa)t_l^0(2l+1)^{1/2}\delta_{c0}\delta_{\gamma 0}\delta_{ll''},\quad \tau^1(l,l'';c,\gamma)=0\ ,$$

and

$$\tau^n(l,l'';c,\gamma)=(-1)^{n+1}(1/\kappa)t_l^0t_{l''}^0\sum_{[n-1]}\Xi^n(l,l'';c,\gamma)\ ,$$

where $[n-1]$ means a sum over all the paths starting from 0, visiting $n-1$ sites and coming back to 0. A direct evaluation gives the first two terms $\chi_{ll''}^0(\hat{\varepsilon})=\delta_{ll''}$ and $\chi_{ll''}^1(\hat{\varepsilon})=0$. The other terms are given by

$$\chi_{ll''}^n(\hat{\varepsilon})=(-1)^{n+1}4\pi\sum_{c,\gamma}\sum_{[n-1]}W(1,l_0,c,l'';l,1)\langle c\|1\|1\rangle \mathrm{Im}\{\exp(i\delta_l^0+i\delta_{l''}^0)\Xi^n(l,l'';c,\gamma)[\mathcal{Y}_c^\gamma(\hat{\varepsilon})]^*\}\ .$$

This concludes our study of the general terms of the polarization-dependent absorption cross section.

B. The polarization-dependent curved-wave EXAFS

For the EXAFS term, we need to evaluate

$$\Xi^2(l,l'';c,\gamma;0,j,0)=\sum_{abl'}O_{ll'}^a(\kappa R_{0j})O_{l'l''}^b(\kappa R_{0j})t_{l'}^j(-1)^{a+b}[(2a+1)(2b+1)]^{1/2}$$
$$\times(-1)^cW(l,a,l'',b;l',c)\sum_{\alpha,\beta}(a\alpha b\beta|c\gamma)\mathcal{Y}_a^\alpha(\hat{\mathbf{R}}_{0j})\mathcal{Y}_b^\beta(\hat{\mathbf{R}}_{j0})\ .$$

The last sum can be calculated with the spherical harmonic coupling formula:

$$\sum_{\alpha,\beta}(a\alpha b\beta|c\gamma)\mathcal{Y}_a^\alpha(\hat{\mathbf{R}}_{0j})\mathcal{Y}_b^\beta(-\hat{\mathbf{R}}_{0j})=(-1)^b\langle c\|a\|b\rangle\mathcal{Y}_c^\gamma(\hat{\mathbf{R}}_{0j})\ .$$

Finally, we use the addition theorem

$$\sum_\gamma[\mathcal{Y}_c^\gamma(\hat{\varepsilon})]^*\mathcal{Y}_c^\gamma(\hat{\mathbf{R}}_{0j})=(2c+1)P_c(\hat{\varepsilon}\cdot\hat{\mathbf{R}}_{0j})/4\pi$$

to obtain

$$\chi_{ll''}^2(\hat{\varepsilon})=\mathrm{Im}\Bigg[\exp(i\delta_l^0+i\delta_{l''}^0)\sum_{j,l'}t_{l'}^j\sum_{a,b}O_{ll'}^a(\kappa R_{0j})O_{l'l''}^b(\kappa R_{0j})(-1)^{a+1}[(2a+1)(2b+1)]^{1/2}$$
$$\times\sum_c(-1)^cW(l,a,l'',b;l',c)\langle c\|a\|b\rangle\langle c\|1\|1\rangle W(1,l_0,c,l'';l,1)(2c+1)P_c(\hat{\varepsilon}\cdot\hat{\mathbf{R}}_{0j})\Bigg]$$

which is our final expression for the polarization-dependent EXAFS of a general edge.

From this expression, we can confirm our previous results. For $c=0$, the Legendre polynomial is $P_0(\hat{\varepsilon}\cdot\hat{\mathbf{R}}_{0j})=1$ and the corresponding term is independent of polarization. For $c=2$, $P_2(\hat{\varepsilon}\cdot\hat{\mathbf{R}}_{0j})=[3(\hat{\varepsilon}\cdot\hat{\mathbf{R}}_{0j})^2-1]/2$, and it is this term which is responsible for the polarization effects. Since the polynomial $P_2(\hat{\varepsilon}\cdot\hat{\mathbf{R}}_{0j})$ averages to zero, the second term disappears when the sample is not oriented, and the first term should give back the χ_l^2 (EXAFS) term averaged over all polarization directions. It can be checked that the term $c=0$ is indeed the curved-wave EXAFS formula:[8,14]

$$\delta_{ll''}\chi_l^2=-\mathrm{Im}\left[\exp(2i\delta_l^0)\sum_{j,l'}(2l'+1)t_{l'}^j\sum_a(l0l'0|a0)^2[h_a^+(\kappa R_{0j})]^2\right]\delta_{ll''}\ .$$

The above formula for $\chi_{ll''}^2(\hat{\varepsilon})$ is valid for any edge. If we specialize to the experimentally common case of a K edge, it becomes much simpler. For a K (or L_{I}) edge $l_0=0$ and we have the identity $W(1,0,c,l'';l,1)=\delta_{ll''}(-1)^{1+l-c}[3(2l+1)]^{-1/2}$, therefore,

$$\chi^2_{ll''}(\hat{\varepsilon})=\tfrac{1}{3}\delta_{ll''}\delta_{l,1}\mathrm{Im}\left[\exp(2i\delta_1^0)\sum_{j,l'}t_{l'}^{j}\sum_{a,b}O^{a}_{1l'}(\kappa R_{0j})O^{b}_{l'1}(\kappa R_{0j})(-1)^{a+1}\right.$$
$$\left.\times[(2a+1)(2b+1)]^{1/2}\sum_{c}W(1,a,1,b;l',c)\langle c\|a\|b\rangle\langle c\|1\|1\rangle(2c+1)P_c(\hat{\varepsilon}\cdot\hat{\mathbf{R}}_{0j})\right].$$

Since there exist simple analytical formulas for the Racah coefficients $W(1,a,1,b;l',c)$ and the relevant Clebsch-Gordan coefficients, one can make a direct evaluation of these terms to simplify the expression for $\chi^2_{ll''}(\hat{\varepsilon})$. This yields

$$\chi^2_{ll''}(\hat{\varepsilon})=-\delta_{ll''}\delta_{l,1}\mathrm{Im}\left[\exp(2i\delta_1^0)\sum_{j,l'}t_{l'}^{j}(\{(l'+1)[h^+_{l'+1}(\kappa R_{0j})]^2+l'[h^+_{l'-1}(\kappa R_{0j})]^2\}\right.$$
$$+\{(l'+1)(l'+2)[h^+_{l'+1}(\kappa R_{0j})]^2+l'(l'-1)[h^+_{l'-1}(\kappa R_{0j})]^2$$
$$\left.-6l'(l'+1)h^+_{l'+1}(\kappa R_{0j})h^+_{l'-1}(\kappa R_{0j})\}P_2(\hat{\varepsilon}\cdot\hat{\mathbf{R}}_{0j})/(2l'+1))\right],$$

which can also be put into the form

$$\chi^2_{ll''}(\hat{\varepsilon})=-3\delta_{ll''}\delta_{l,1}\mathrm{Im}\left[\exp(2i\delta_1^0)\sum_{j,l'}t_{l'}^{j}\{[(l'+1)h^+_{l'+1}(\kappa R_{0j})-l'h^+_{l'-1}(\kappa R_{0j})]^2\cos^2(\theta_j)/(2l'+1)\right.$$
$$\left.+[h^+_{l'+1}(\kappa R_{0j})+h^+_{l'-1}(\kappa R_{0j})]^2\sin^2(\theta_j)l'(l'+1)/(4l'+2)\}\right],$$

where θ_j is the angle between the polarization vector and $\mathbf{R}_{0j}$. Note that in the plane-wave approximation the sine term disappears.

For an $L_{\mathrm{II,III}}$ edge, the algebra is a little more involved, but still manageable, and we obtain

$$\chi^2_{ll''}(\hat{\varepsilon})=\mathrm{Im}\left[\exp(i\delta_l^0+i\delta_{l''}^0)\sum_{j,l'}t_{l'}^{j}(\{A[h^+_{l'+2}(\kappa R_{0j})]^2+B[h^+_{l'}(\kappa R_{0j})]^2+C[h^+_{l'-2}(\kappa R_{0j})]^2\}\right.$$
$$+\{D[h^+_{l'+2}(\kappa R_{0j})]^2+E[h^+_{l'}(\kappa R_{0j})]^2+F[h^+_{l'-2}(\kappa R_{0j})]^2$$
$$\left.+Gh^+_{l'-2}(\kappa R_{0j})h^+_{l'}(\kappa R_{0j})+Hh^+_{l'}(\kappa R_{0j})h^+_{l'+2}(\kappa R_{0j})\}P_2(\hat{\varepsilon}\cdot\hat{\mathbf{R}}_{0j}))\right],$$

with, for $l=l''=2$,

$$A=-\frac{3(l'+1)(l'+2)}{2(2l'+3)},\quad B=-\frac{l'(l'+1)(2l'+1)}{(2l'-1)(2l'+3)},\quad C=-\frac{3(l'-1)l'}{2(2l'-1)},$$
$$D=-\frac{3(l'+1)(l'+2)(l'+3)}{2(2l'+3)^2},\quad E=\frac{l'(l'+1)(2l'-3)(2l'+1)(2l'+5)}{2(2l'-1)^2(2l'+3)^2},$$
$$F=-\frac{3(l'-2)(l'-1)l'}{2(2l'-1)^2},\quad G=\frac{3(l'-1)l'(l'+1)}{(2l'-1)^2},\quad H=\frac{3l'(l'+1)(l'+2)}{(2l'+3)^2},$$

for $l=0$ and $l''=2$ or $l=2$ and $l''=0$, $A=B=C=D=F=0$,

$$E=-\frac{\sqrt{2}l'(l'+1)(2l'+1)}{(2l'-1)(2l'+3)},\quad G=\frac{3(l'-1)l'}{\sqrt{2}(2l'-1)},\quad H=\frac{3(l'+1)(l'+2)}{\sqrt{2}(2l'+3)},$$

and for $l=l''=0$, $A=C=D=E=F=G=H=0$, $B=-(2l'+1)$.

Note that for the accurate analysis of an L edge, the atomic ratio M_{10}/M_{12} should be calculated. For atomic numbers greater than 20, Teo and Lee[15] find $M_{10}/M_{12}\approx 0.2$, approximately independent of the photoelectron energy.

If all the spin orbitals of the initial states have the same radial wave functions, it is possible to take the spin states into account. If j is the total (spin plus orbital) angular momentum of the initial states, the calculation performed by Müller and Wilkins[16] shows that this simply adds a factor $(2j+1)/(2l_0+1)$ to $\chi^2_{ll''}(\hat{\varepsilon})$. This remark is also valid for the higher-order scattering terms.

C. The polarization-dependent double- and triple-scattering terms

The extension of the polarization-dependent EXAFS to higher-order scattering contributions is straightforward. The recursion formula for Ξ^n gives us

$$\Xi^3(l,l'';c,\gamma)=\sum_{l'}\sum_{a,\alpha,b,\beta}\Xi^2(l,l';a,\alpha;0,j_1,j_2)t_{l'}^{j_2}\,\Xi^1(l',l'';b,\beta;j_2,0)$$
$$\times(-1)^{a+b}[(2a+1)(2b+1)]^{1/2}(-1)^{c}W(l,a,l'',b;l',c)(a\alpha b\beta|c\gamma).$$

Therefore we obtain

$$\begin{aligned}\chi^{3}_{ll''}(\hat{\varepsilon})=4\pi(2l_0+1)\sum_{c,\gamma}W(1,l_0,c,l'';l,1)\langle c\|1\|1\rangle\\ \times\operatorname{Im}\Bigg[\exp(i\delta^{0}_{l}+i\delta^{0}_{l''})\sum_{l'}\sum_{a,\alpha,b,\beta}\sum_{j_1j_2}\Xi^{2}(l,l';a,\alpha;0,j_1,j_2)t_{l'}^{j_2}\,\Xi^{1}(l',l'';b,\beta;j_2,0)\\ \times(-1)^{a+b}[(2a+1)(2b+1)]^{1/2}\\ \times(-1)^{c}W(l,a,l'',b;l',c)(a\alpha b\beta|c\gamma)[\mathcal{Y}^{\gamma}_{c}(\hat{\varepsilon})]^{*}\Bigg]\,.\end{aligned}$$

In the same way

$$\begin{aligned}\chi^{4}_{ll''}(\hat{\varepsilon})=-4\pi(2l_0+1)\sum_{c,\gamma}W(1,l_0,c,l'';l,1)\langle c\|1\|1\rangle\\ \times\operatorname{Im}\Bigg[\exp(i\delta^{0}_{l}+i\delta^{0}_{l''})\\ \times\sum_{l'}\sum_{a,\alpha,b,\beta}\sum_{j_1,j_2,j_3}\Xi^{2}(l,l',a,\alpha;0,j_1,j_2)t_{l'}^{j_2}\,\Xi^{2}(l',l'';b,\beta;j_2,j_3,0)\\ \times(-1)^{a+b}[(2a+1)(2b+1)]^{1/2}\\ \times(-1)^{c}W(l,a;l'',b;l',c)(a\alpha b\beta|c\gamma)[\mathcal{Y}^{\gamma}_{c}(\hat{\varepsilon})]^{*}\Bigg]\,.\end{aligned}$$

These expressions look formidable, but they are not so difficult to compute. For a general edge, there exist analytical forms for the Clebsch-Gordan coefficients $(a\alpha b\beta|2\gamma)$ and Racah coefficients $W(l,a;l'',b;l',2)$ (Ref. 7, pp. 637 and 649). For a K edge, $l''=l=1$, and the analytical expressions for $W(l,a;l'',b;l',c)$ are simpler.

VI. CONCLUSION

The curved-wave formalism has proved to give significantly different results from the plane-wave formalism in a number of cases. Generally, the plane-wave analysis gives an incorrect phase shift even at high energies.[6] Moreover, the analysis of experimental spectra with curved-wave multiple-scattering terms has yielded unambiguous results concerning the bond lengths and angles of some molecular systems.[2,3] Therefore, it appears that a thorough treatment of the multiple-scattering contributions both for oriented and unoriented samples has become necessary.

The present work, which is a formal development of ideas suggested in Ref. 3, intends to provide such a treatment. By using the powerful tools of angular momentum coupling we have presented a homogeneous formalism that enabled us to obtain painlessly the first terms of the multiple-scattering series, up to the quintuple scattering for unoriented samples, and up to the triple scattering for oriented samples and polarized light. Besides, our formulation opens the way to an easy calculation of the further terms, if they prove necessary.

For a preliminary application of the curved-wave polarized EXAFS formula presented above to a physical situation, we refer the reader to Ref. 17.

Note added in proof. After the completion of this work, we became aware of the fact that the polarization-dependent curved-wave EXAFS formula for a K edge was given in Refs. 18 and 19. A small-atom approximation of the multiple-scattering contributions to the curved-wave x-ray-absorption cross section can be found in Ref. 20.

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