Polarized curved-wave extended x-ray-absorption fine structure: Theory and application

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(Received 18 August 1988)

We derive, for the first time, an exact polarized extended x-ray-absorption fine-structure formula valid for all edges which takes into account the curved-wave nature of the electron propagators. We show that the deviations from the usual plane-wave limit are not negligible and we discuss the physical implications concerning the determination of the Debye-Waller factors and coordination numbers. We apply our approach to recent surface extended x-ray-absorption fine-structure experiments by Bader *et al.* [Phys. Rev. Lett. **57**, 3273 (1986)] on the O(2×1)/Cu(110) system.

Multiple-scattering (MS) theory[1] has been, and is being, widely used for analyzing x-ray-absorption data in order to extract local structural information.[2] In this scheme the plane-wave approximation (PWA) in the calculation of the single- and multiple-scattering signals has been an essential ingredient both for its simplicity in the applications and for its greater appeal to physical intuition. Recently this approximation has been questioned as being strictly invalid in the whole energy range of the absorption spectra and shown to lead to substantial errors, compared with the exact spherical-wave (SW) results,[3,4] especially in the low-energy range of the spectra. Awareness of this fact has led researchers in the field to use, in their analysis, the exact SW formulas, at least for the single-scattering polarization averaged signal [extended x-ray-absorption fine structure (EXAFS)], which is not more complicated and time consuming to compute than the corresponding PW approximation. Nevertheless, in the analysis of surface extended x-ray-absorption fine structure (SEXAFS) spectra[5,6] the PWA of the EXAFS formula is normally used even though in this latter case the extent of the k range is usually more limited than for bulk spectra. The aim of this paper is to provide a polarized-dependent EXAFS expression valid for all edges and to discuss the physical and practical implications concerning the determination of Debye-Waller factors and coordination numbers.

In the MS scheme the expression for the absorption coefficient from a deep core level of angular momentum l_i can be written as ($L=\{l,m\}$) (Refs. 1 and 3)

$$\alpha_c(\omega)=n_c\omega\frac{4\pi^2}{137}\sum_{m_i,L,L',\sigma}(\phi_{l_i}Y_{L_i}|\mathbf{r}\cdot\boldsymbol{\varepsilon}|R_l^0Y_L\sigma)\,\mathrm{Im}\tau_{LL'}^{00}\times(R_{l'}^0Y_{L'}\sigma|\mathbf{r}\cdot\boldsymbol{\varepsilon}|\phi_{l_i}Y_{L_i})\ . \quad (1)$$

Here $\boldsymbol{\varepsilon}$ is the photon polarization vector, R_l is the properly normalized, continuum atomic radial wave function, and τ is the scattering-path (SP) operator given by[1,7,8]

$$\mathrm{Im}\tau_{LL'}^{00}=\mathrm{Im}\{(\sin\delta_l^0\sin\delta_{l'}^0)^{-1}[(T_a^{-1}-G)^{-1}]_{LL'}^{00}\}$$
$$=1+\mathrm{Im}\left[e^{i(\delta_l^0+\delta_{l'}^0)}\sum_{n=1}^{\infty}[G(T_aG)^n]_{LL'}^{00}\right], \quad (2)$$

with the usual definition of the diagonal matrix T_a in terms of the atomic phase shifts δ_l^i (0 refers to the photoabsorbing site) and of the spherical-wave propagator $G_{LL'}$. In order to calculate the EXAFS contribution given by the $n=1$ term, we take advantage of the cylindrical symmetry of the problem taking the z axis along the bond direction R and use the following exact relation for the SW propagator $G_{LL'}$,[4] omitting for simplicity the site indices

$$G_{LL'}=4\pi Y_{l0}^*(\hat{\mathbf{R}})Y_{l'0}(\hat{\mathbf{R}})\frac{e^{i\rho}}{\rho}g_{ll'}^{(|m|)}(\rho)\delta_{mm'}\ ,$$

where $\rho=kR$ and the quantities $g_{ll'}^{(|m|)}$ can be derived either exactly or in an approximate way in terms of the leading factors of the modulus and phase asymptotic expansion of the Hankel functions. Both expressions will be given.

Therefore, for one scatterer at distance R from the absorber, writing the scalar product $\boldsymbol{\varepsilon}\cdot\mathbf{r}$ using the addition theorem for spherical harmonics, inserting the $n=1$ term of Eq. (2) in Eq. (1), and performing the intermediate angular momentum and spin sums, one obtains

$$\alpha_2 = 2n_c \frac{4\pi^2}{137}\omega \,\mathrm{Im}\left[\sum_{l,l'} I_{l_i l} I_{l_i l'} (-1)^{l'} (2l_i+1)(2l+1)(2l'+1) \begin{pmatrix} l_i & 1 & l \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} l' & 1 & l_i \\ 0 & 0 & 0 \end{pmatrix} \right.$$
$$\times \frac{e^{i(2\rho+\delta_l+\delta_{l'})}}{\rho^2} \sum_{m_\gamma, m, m_i} \begin{pmatrix} l_i & 1 & l \\ -m_i & -m_\gamma & m \end{pmatrix} \begin{pmatrix} l' & 1 & l \\ -m & m_\gamma & m \end{pmatrix} \frac{(1-m_\gamma)!}{(1+m_\gamma)!} [P_1^{m_\gamma}(\cos\theta)]^2$$
$$\left. \times \sum_\lambda (-1)^\lambda (2\lambda+1) t_\lambda g_{l\lambda}^{|m|}(\rho) g_{l'\lambda}^{|m|}(\rho) \right] ,$$

where θ is the angle between polarization vector $\boldsymbol{\varepsilon}$ and the bond direction, $m_\gamma = 0, \pm 1$ is the photon azimutal quantum number, and we have introduced the usual 3-j symbols, the Legendre polynomial $P_1^m(x)$, the atomic t_l matrix element, and the dipole radial integrals $I_{ll'}$. This formula coincides with the one given in Ref. 8 where a general derivation of the polarization-dependent expressions valid for all MS orders is presented. For K or L_1 edge ($l_i = 0$, $m_i = 0$, $l = l'$) it reduces to the expression already derived by Barton and Shirley in Ref. 9. Putting $A_0 = 8n_c\pi^2\omega/137$ we find

$$\alpha_2 = -A_0 |I_{01}|^2 \,\mathrm{Im}\left[\frac{e^{2i(\delta_1^0+\rho)}}{\rho^2} \sum_l (-1)^l (2l+1) t_1 \{\cos^2\theta\,[g_{1l}^{(0)}(\rho)]^2 + \sin^2\theta\,[g_{1l}^{(1)}(\rho)]^2\} \right] , \tag{3}$$

where

$$g_{1l}^{(0)}(\rho) = \frac{(l+1)C_{l+1}(\rho) + lC_{l-1}(\rho)}{2l+1} ,$$

$$g_{1l}^{(1)}(\rho) \left[\frac{l(l+1)}{2}\right]^{1/2} \frac{C_{l+1}(\rho) - C_{l-1}(\rho)}{2l+1} .$$

The quantities C_l can be written in terms of Hankel functions as

$$C_l(\rho) = i^{(l+1)} \rho e^{-i\rho} h_l^+(\rho)$$
$$\approx \left[1 + \frac{l(l+1)}{2\rho^2}\right]^{1/2} e^{il(l+1)/2\rho} .$$

The last expression is the SW approximation.[1,4] Note that when $\rho \to \infty$ the quantities $g_{1l}^{(0)} \to 1$ and $g_{1l}^{(1)} \to 0$ recovering the usual PW limit. Moreover, by averaging over the field polarizations we obtain the nonpolarized result.[4] The importance of Eq. (3) lies in the presence of a new term proportional to $\sin^2\theta$. This fact has two main implications: firstly, the phase and amplitude functions in EXAFS signal are now angle dependent and secondly there are contributions from atoms with bonds perpendicular to the electric field. To assess the importance of this new term we plot the quantity $\mathcal{R}_g$ versus kR in Fig. 1, where $\mathcal{R}_g$ is the modulus of the ratio between the square of the functions $g_{1l}^{(l)}$ and $g_{1l}^{(0)}$ calculated for various l values ranging from $l = 1$ to 6 (this ratio is 0 for $l = 0$). This quantity does not depend on the physical system and gives the strength of the $\sin^2\theta$ term versus the $\cos^2\theta$ term. It is substantially different from zero for a wide range of values of the product kR and becomes negligible only for values of order 18–20 (for high l's). Therefore we expect deviations from the PW behavior in a large energy range of the absorption spectrum. It is interesting to note that as the interatomic distance R decreases, the range of k values for which this effect becomes appreciable increases. Further intuition concerning the origin of the $\sin^2\theta$ term can be obtained by noting that if the radius of the atomic scattering potential collapses to a point then only s-wave scattering ($L = 0$) is possible, and the $\sin^2\theta$ term disappears. Consequently, the $\sin^2\theta$ term is associated with high L components whose magnitude at a given energy, related to t_l, reflects the size of the scattering. We should thus expect that the corrections will depend upon the atomic number Z of the scatterer. Also, at low photoelectron energies where only a few phase shifts dominate the scattering we anticipate oscillations in the magnitude of the $\sin^2\theta$ contribution.

A classical analogue of the effect of the $\sin^2\theta$ term which dominates at $\theta = \pi/2$ can be envisaged. We consider a dipole radiation (analogue of the absorbing atom under K-shell excitation) with a scattering subject (analogue of the scattering atom) positioned at a node in the radiation pattern. As the angle subtended by the object at the dipole increases the object itself is capable of intercepting and scattering progressively large amounts of the

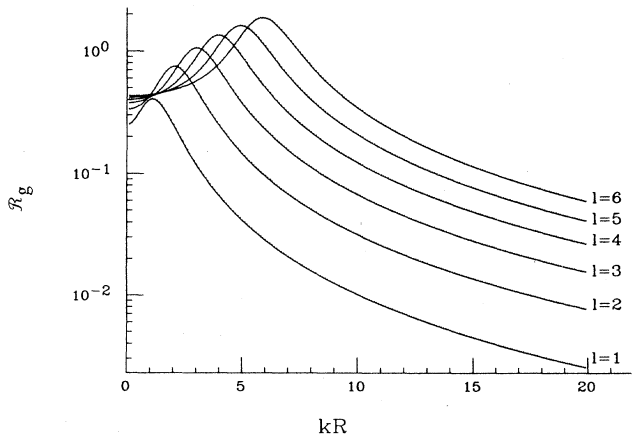

FIG. 1. $\mathcal{R}_g$ vs kR and for various l values. $\mathcal{R}_g \equiv |(g_{1l}^{(1)})^2/(g_{1l}^{(0)})^2|$.

radiation from the dipole. The angle subtended is a function of distance of the scattering object from the emitter, of energy via the change of the back-scattering cross section, and of size of the scattering object.

The physical effects of these SW corrections become clearer in Fig. 2, where the amplitude ratio A_2/A_1 of two EXAFS signals, calculated using Eq. (3), for two different angles θ is depicted. In the same figure the PW limit is also shown as a dashed line. This calculation refers to the O K-edge absorption of an ideal cluster composed of an oxygen atom and a Cu scatterer ($Z=29$) located at a distance of 1.82 Å. A_1 is for $\theta_1=0°$ while A_2 is for $\theta_2=50°$. The deviation from the plane-wave behavior is clear and important in a wide range of k values and only for $k \geq 8$ Å^{-1} the difference between the PW and SW regime becomes negligible. The important point is that contrary to the PW case the ratio A_2/A_1 now depends strongly on the energy. From this discussion it follows that the SW corrections to the "standard" EXAFS formula should be included in the analysis in order to determine correctly the coordination numbers and the Debye-Waller factors. Moreover, these corrections are important for the selection of different structural models by amplitude comparisons. It has recently been shown that the usual exponential form of the Debye-Waller factor in the EXAFS formula valid for a Gaussian pair correlation function can also be adopted when curved-wave electron propagators are used[10] since the phase and amplitude corrections due to this type of propagators are in fact negligible. Consequently, we are now able to propose the following expression for the polarized curved-wave EXAFS signal (written for simplicity just for the K and L_1 edges):

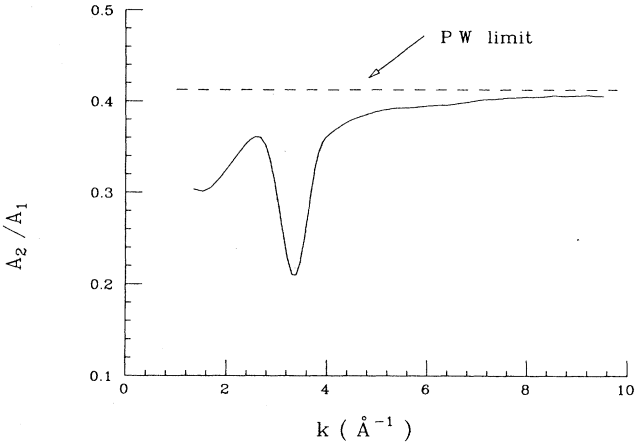

FIG. 2. Amplitude EXAFS ratio vs k referred to the theoretical experiment described in the text. The solid line is calculated by Eq. (3).

$$\alpha_2 = -A_0 |I_{01}|^2 \operatorname{Im} \sum_i \sum_{j=1}^{N_i} \left\{ \frac{e^{2i(\delta_1^0+\rho_i)}}{\rho_i^2} e^{-2R_i/\lambda_{ij}} \times \sum_l (-1)^l (2l+1) t_l^i \{ \cos^2\theta_{ij} [g_{1l}^{(0)}(kR_i)]^2 + \sin^2\theta_{ij} [g_{1l}^{(1)}(kR_i)]^2 \} e^{-2k^2\sigma_{ij}^2} \right\}, \quad (4)$$

where N_i is the number of atoms in the ith shell, θ_{ij} is the angle between ε and the bond axis $\mathbf{R}_i$, and σ_{ij} is the usual mean-square relative displacement. We have also included the exponential decay factor due to the inelastic losses and possible anisotropies in Debye-Waller and mean-free-path factors.[11–13] The SW approximation for the $g_{1l}^{(m)}$'s can be safely used.

As an application we have simulated recent SEXAFS signals for chemisorbed oxygen on Cu(110). We refer to the paper of Bader *et al.* for notations and experimental details.[11] In this paper the authors employ the conventional procedure based on the amplitude ratio comparison to study different structural surface models and to derive Debye-Waller and mean-free-path factors. In particular, using the Fourier and black-Fourier procedure, they find the behavior of the EXAFS amplitude ratio as a function of k^2 for various azimuthal and polar angles. In the following we concentrate our attention on the case $A_2(45°)/A_1(90°)$. Due to the fact that the experimental amplitude ratios cannot be fitted by any surface reconstruction model they predict an anisotropy in the mean-free-path factors. Our objection is that the experimental values are compared with theoretical predictions made by the PW limit of the theory. For example, for this case

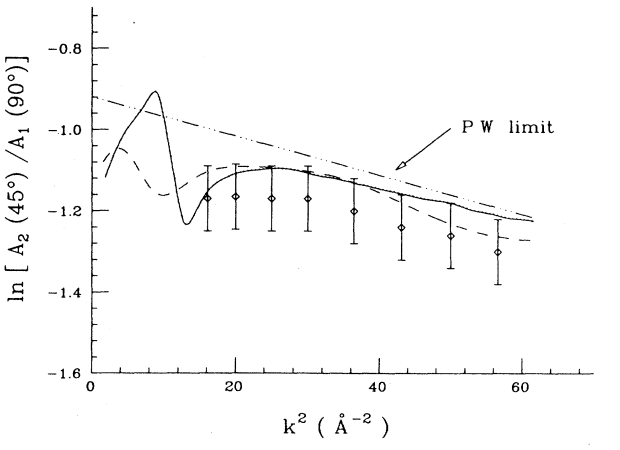

FIG. 3. Comparison between experimental value of logarithm of SEXAFS amplitude ratios as a function of k^2 (points with error bars) with various theoretical calculations. The solid line is calculated using Eq. (4) of the text, the dashed line is derived using the Fourier–back-Fourier treatment of the SW theoretical calculation as described in the text, while the dot-dashed line is the PW limit of the theory.

the experimental value is 0.31 at $k=4$ Å^{-1} while the theoretical value, calculated using the missing-row model and the plane-wave theory of EXAFS, is about 0.38 taking $\Delta\sigma^2=2.4\times10^{-3}$ Å^2 for the Debye-Waller anisotropy and $\lambda=5.2$ Å for the mean-free-path values. The situation changes if the SW corrections are included. In Fig. 3 we report the quantity $\ln[A_2(45°)/A_1(90°)]$ as a function of the photoelectron wave number k calculated with the same choice of the Debye-Waller anisotropy and mean-free-path values and using the missing-row reconstruction model for the structure. The continuous line is calculated using Eq. (4). For comparison the PW limit of the theory is also shown as a dot-dashed one. In order to make contact with the procedure used to extract experimental data (reported in Fig. 3 as points with error bars) we have used the conventional Fourier-transform (FT) method to compute theoretical amplitudes $A_2(45°)$ and $A_1(90°)$. More precisely, we have first calculated the FT of the EXAFS theoretical signal for the two cases in a wave-vector range going from 1 to 10 Å^{-1}. Secondly, the back transform of the Fourier peaks has been taken, using a window from 0.9 to 2.75 Å, to give the required amplitudes. Then the logarithm of the amplitude ratio $A_2(45°)/A_1(90°)$ has been computed and plotted as a dashed line in Fig. 3. This method yields results which are in reasonable agreement with the exact calculation given by Eq. (4). Nevertheless this method depends strongly on the choice of the back-Fourier window as we have verified. In any case the agreement between theory and experimental data is now definitely better than when the PW approximation is used. The remaining discrepancies can be assigned either to some anisotropies in the mean-free-path value, which have not been included in our calculation, or to the treatment of the experimental data in terms of Fourier and back-Fourier procedure.

In conclusion we have shown that the SW corrections are important in a relevant energy range of the spectrum (up to 150–200 eV above the edge) and should be included to reproduce quantitatively the experimental results in order to discriminate between different structural models and obtain reliable numbers for the "amplitude factors" as coordination, Debye-Waller and mean-free-path values. We have also reconfirmed the missing-row reconstruction model for the O(2×1)/Cu(110) system in agreement with Bader *et al.*[11] without having to invoke any anisotropy in the mean-free-path values.

We want to thank Dr. L. Incoccia for the critical comments and Dr. E. Pace for computing help.

[1]P. J. Durham, J. B. Pendry, and C. H. Hodges, Comput. Phys. Commun. **25**, 193 (1982); C. R. Natoli and M. Benfatto, in *EXAFS and Near Edge Structure IV,* edited by P. Lagarde, D. Raoux, and J. Petiau, J. Phys. (Paris), Colloq. **47**, C8-11 (1986).

[2]For reviews, see E. A. Stern and S. M. Heald, in *Handbook of Synchrotron Radiation,* edited by E. E. Kock (North-Holland, New York, 1983), Chap. 10.

[3]W. L. Schaich, Phys. Rev. B **29**, 6513 (1984).

[4]J. J. Rehr, R. C. Albers, C. R. Natoli, and E. A. Stern, Phys. Rev. B **34**, 4350 (1986).

[5]P. H. Citrin, P. Eisenberger, and R. C. Hewitt, Phys. Rev. Lett. **41**, 309 (1978).

[6]For a review we refer the reader to J. Stohr, in *Principles, Techniques and Application of EXAFS, SEXAFS and XANES,* edited by D. Koningsberger and R. Prinz (Wiley, New York, 1984).

[7]M. Benfatto, C. R. Natoli, A. Bianconi, J. Garcia, A. Marcelli, M. Fanfoni, and I. Davoli, Phys. Rev. B **34**, 5774 (1986).

[8]C. Brouder, M. F. Ruiz-Lopez, R. F. Pettifer, M. Benfatto, and C. R. Natoli, Phys. Rev. B (to be published).

[9]J. J. Barton and D. A. Shirley, Phys. Rev. B **32**, 1892 (1985).

[10]M. Benfatto, C. R. Natoli, and A. Filipponi (unpublished); C. Brouder (unpublished).

[11]M. Bader, A. Puschmann, C. Ocal, and J. Hoose, Phys. Rev. Lett. **57**, 3273 (1986).

[12]P. Roubin, D. Chandesris, G. Rossi, J. Lecante, M. C. Desjonqueres, and G. Treglia, Phys. Rev. Lett. **56**, 1272 (1986).

[13]F. Sette, C. T. Chen, J. E. Rowe, and P. H. Citrin, Phys. Rev. Lett. **59**, 311 (1987).