

# Theoretical study of the origin of x-ray atomic background anomalies by a full-potential multiple scattering approach

Kazuki Yoshikawa<sup>1,2,\*</sup> Fabio Iesari<sup>3,†</sup> Yoshiaki Tamura<sup>1</sup> Naoki Nakatani<sup>4</sup> Fukiko Ota,<sup>1</sup>  
Andrea Di Cicco<sup>2</sup> and Keisuke Hatada<sup>1</sup>

<sup>1</sup>Department of Physics, University of Toyama, 3190 Gofuku, Toyama 930-8555, Japan

<sup>2</sup>Physics Division, School of Science and Technology, University of Camerino, 62032 Camerino, Italy

<sup>3</sup>Aichi Synchrotron Radiation Center, Seto, Aichi 489-0965, Japan

<sup>4</sup>Department of Chemistry, Tokyo Metropolitan University, Hachioji, Tokyo 192-0397, Japan



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Previous extended x-ray absorption fine structure (EXAFS) studies have shown evidence of anomalous contributions in the atomic background function whose origin was debated in the literature. The present study presents advanced multiple scattering calculations aimed to put to a test the existence and origin of the so-called atomic XAFS (AXAFS) contribution, discussed in details in some previous works. We show with specific examples that the muffin-tin approximation normally used in EXAFS calculations is inappropriate to study this phenomenon as spurious oscillations in the atomic background are related to the potential truncation at the border of the muffin-tin spheres. We thus employed a more sophisticated approach beyond the muffin-tin approximation based on the full-potential multiple scattering theory and self-consistent charge densities. The comparison of EXAFS calculations with previous experimental results allowed us to exclude the presence of the AXAFS as due to modulations of the charge density as previously suggested. This study confirms the importance of a proper account of the atomic background in EXAFS data analysis, which may contain effects beyond the single-electron approximation but are found not affected by AXAFS. We conclude that the contribution of AXAFS in EXAFS experiments, if existing at all, is negligible and should not be considered in EXAFS data analysis.

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## I. INTRODUCTION

The extended x-ray absorption fine structure (EXAFS) [1] technique is a widely used spectroscopy for accurate determinations of the structure of materials in any aggregation state. The signal of interest  $\chi$  is defined as the normalized modulation of the absorption coefficient ( $\alpha$ ) above a specified core electron level:  $\chi = (\alpha - \alpha_{\text{bck}}) / \alpha_{\text{at}}$ . Suitable background  $\alpha_{\text{bck}}$  and atomic absorption  $\alpha_{\text{at}}$  functions are used for this purpose. The  $\chi(k)$  signal is an oscillatory function in the photoelectron wave-vector  $k$  space, related to the average short-range configuration around selected photoabsorbing sites. In most applications, EXAFS data analysis involves subtracting a smooth background, typically represented by a piecewise polynomial function in each subdivided  $k$  region, to extract the EXAFS signal  $\chi(k)$ . Fourier transformations of the EXAFS signals  $\chi(k)$ , although suffering from obvious limitations due to the  $k$  window and noise, show peaks

at positions related to the distances of neighboring atoms. However, due to phase shifts, the positions of these Fourier transform peaks are shifted to distances smaller than the actual interatomic distances. In general, the standard extraction procedure does not guarantee a unique and unbiased  $\chi(k)$  signal, so the Fourier transforms can also reflect possible anomalies in the background function, and several peaks and ripples may not have a direct connection with the structure. In particular, it was pointed out by several authors that well-defined peaks in the Fourier transforms can also appear at distances lower than those of the nearest-neighboring atoms, where there are no possible interatomic distances [2–35]. The occurrence of low-distance Fourier transform peaks was associated with a nonsmooth background function  $\alpha_{\text{bck}}$ , and two different interpretations were discussed in the literature, one based on multielectron excitation channels [2,3] affecting the background shape, and the other related to a possible direct oscillatory contribution called atomic XAFS (AXAFS) [4,5].

The main aim of this work is to shed light on this problem and on the possible existence and origin of the AXAFS contribution that is presently the subject of debate and can possibly affect the interpretation and the quality of the EXAFS data analysis. To clarify the strategy adopted in this work, it is important to summarize what is presently known about the presence of extra-contributions in the EXAFS spectra and x-ray absorption simulation methods.

It is worth noting that many previous works since the 1960s (see, for example, Refs. [36,37]) pointed out that the

\*Contact author: k.yoshikawa0000@gmail.com

†Present address: Keihanna Research Center, KYOCERA Corporation.

x-ray absorption spectra contain widely assessed contributions due to several shake-off and shake-up multielectron channels, excluded by a simple one-electron picture of the photoabsorption process. In fact, modern EXAFS interpretation and data analysis are based on the assumption that the photoabsorption process consists of the excitation of a single electron of a core level (for example  $1s$  for a K edge) promoted to an excited state in the continuum, and other possible multielectron excitation channels, not taken into account explicitly, can be observed in the x-ray absorption background [2,3,6,8,9,38–45] as also confirmed in direct photoemission experiments [46–49]. In particular, the appearance of Fourier transform peaks at short distances in EXAFS data analysis was assigned to the contribution of step-like multielectron excitation channels in the background function (see, for example, Refs. [2,6,7], references therein, and many later works).

In other works, the origin of a short distance additional peak in the Fourier transform was assigned to the AXAFS contribution [4], consisting in the occurrence of photoelectron scattering by the potential barrier created when free atoms are embedded in a condensed phase. It was argued that this scattering can result in a weak oscillatory structure of the atomic absorption [4,5]. Experimental data were compared with *ab initio* calculations within the muffin-tin approximation in several systems [5,10] and an oscillatory fine structure of the atomic absorption  $\chi_e(k)$  similar to EXAFS was introduced (further details in Sec. II B). This finding was discussed and criticized in a later work [7] where the background anomalies were simply assigned to the onset of the shake-up and shake-off channels due to multielectron excitations for which large evidence was already obtained and widely confirmed in successive works [2,3,6,8,9,38–41,43–48]. Moreover, it was also pointed out [7] that muffin-tin potentials used in the derivation of AXAFS [5,10] were a possible source of anomalies due to the discontinuity at muffin-tin borders. After those conflicting interpretations and findings, some other works reported the existence of background anomalies assigned to AXAFS. Some interesting publications [12,14,15] reported evidence of such anomalies in soft x-ray absorption data at surfaces. The authors claimed that the effect cannot be confused with multielectron excitations or experimental artifacts in those cases. Other works were devoted to AXAFS [17,18] showing the dependence of the AXAFS intensity on the embedded potential and the existence of both AXAFS and multielectron excitations that could be individually isolated in  $L$ -edge spectra of a Pt foil. Moreover, research on functional materials by AXAFS was primarily conducted by a group of researchers [16–22,24–26,28] discussing the occurrence of AXAFS in different systems. Although the origin of the low-distance Fourier transform peak remains unclear, some recent studies have cautiously suggested that these spurious peaks may arise from an AXAFS contribution [32–35].

Modern EXAFS data analysis is largely based on accurate multiple scattering simulations performed using the muffin-tin approximation for the optical potential [1,50–54]. Multiple scattering theory is currently widely used to obtain reliable results from both photoabsorption and photoemission experiments. While the muffin-tin approximation is certainly a good approximation for the calculation of the EXAFS, a discontinuity in the potential is obtained at the boundary

between atoms, and it cannot treat in detail nonspherical potentials. Nowadays, we can perform reliable multiple scattering calculations beyond the muffin-tin approximation using the so-called full potential multiple scattering theory [55]. Using this approach, the potential and electron charge density in the interstitial regions between the atoms can be taken into account. This method is computationally more accurate than using the muffin-tin approximation, especially in the x-ray absorption near-edge structure (XANES) region (about within 100 eV from the edge) [55–57]. Clearly, a solid and detailed investigation about the existence and relevance of the AXAFS phenomenon, which was claimed to be related to the scattering by charge distributions localized in the interstitial regions, has to be performed using methods going beyond the standard muffin-tin theory.

Here, we investigate the origin of AXAFS features in x-ray absorption spectra from a theoretical point of view using the full potential multiple scattering approach in several model systems. The paper is organised as follows: in Sec. II, the theory for calculating the x-ray absorption cross-section (proportional to the absorption coefficient  $\alpha$ ) and the EXAFS signal, as well as a simple formulation of the so-called AXAFS, is presented; in Sec. III A, we present a detailed investigation of the effect on the atomic absorption of the introduction of muffin-tin potentials; in Sec. III B, AXAFS features are discussed in light of calculations based on full-potential multiple scattering theory; in Sec. III C, we consider the specific example of CO molecules, calculating self-consistent charge densities and their effect on the absorption cross-section claimed to be at the origin of AXAFS in previous works [12–15,17,21,28]; in Sec. III D, we also investigated the possible origin of O K-edge AXAFS of the  $(2 \times 1)\text{O}/\text{Cu}(110)$  system using self-consistent charge densities and full-potential multiple scattering calculations; the last Sec. IV is devoted to the summary and conclusions of this work.

## II. THEORETICAL BACKGROUND

### A. X-ray absorption cross-section and EXAFS signal

In this study, x-ray absorption spectra have been calculated by using a single-channel approximation, so that they are proportional to the square modulus of the electric-dipole matrix element between the core and continuum states. We have employed the multiple scattering theory to calculate the continuum states. The multiple scattering theory uses a multicenter expansion in spherical harmonics together with a numerical solution of the local Schrödinger equation on each atomic site.

The total absorption cross-section can be written in the electric dipole approximation as [54]

$$\sigma_{\text{tot}} = -8\pi\alpha\hbar\omega \times \sum_{m_c} \text{Im} \iint_{\Omega_c} \langle \phi_{L_c}^c(\mathbf{r}) | \boldsymbol{\varepsilon} \cdot \mathbf{r} G \boldsymbol{\varepsilon} \cdot \mathbf{r}' | \phi_{L_c}^c(\mathbf{r}') \rangle d\mathbf{r} d\mathbf{r}', \quad (1)$$

where  $\phi_{L_c}^c(\mathbf{r})$  is a core state of the photo-absorbing atom with angular momentum quantum numbers  $L_c = (l_c, m_c)$ ,  $\boldsymbol{\varepsilon} \cdot \mathbf{r}$  is obtained under the electric dipole approximation. In this

equation, atomic units of length and Rydberg units of energy are used. The quantity  $\alpha$ , the fine-structure constant, is given by  $\alpha = e^2/\hbar c \sim 1/137$ . One of the advantages of multiple scattering theory is that one can write an explicit form of the full Green's function for  $\mathbf{r}$  in cell  $i$  and  $\mathbf{r}'$  in cell  $j$  in terms of the scattering path operator as [58]

$$\begin{aligned} G(\mathbf{r}_i, \mathbf{r}'_j; E) &= \sum_{LL'} \Phi_L^i(\mathbf{r}_i; k) [\tau_{LL'}^{ij} - \delta_{ij} T_{LL'}^i] \Phi_{L'}^j(\mathbf{r}'_j; k) \\ &\quad + \delta_{ij} \sum_{LL'} \Phi_L^i(\mathbf{r}_i; k) T_{LL'}^i \tilde{\Psi}_{L'}^i(\mathbf{r}'_j; k) \quad (2) \\ &= G_{sc}(\mathbf{r}_i, \mathbf{r}'_j; E) + G_{at}(\mathbf{r}_i, \mathbf{r}'_j; E), \quad (3) \end{aligned}$$

where

$$\begin{aligned} G_{sc}(\mathbf{r}_i, \mathbf{r}'_j; E) &= \sum_{LL'} \Phi_L^i(\mathbf{r}_i; k) [\tau_{LL'}^{ij} - \delta_{ij} T_{LL'}^i] \Phi_{L'}^j(\mathbf{r}'_j; k), \quad (4) \\ G_{at}(\mathbf{r}_i, \mathbf{r}'_j; E) &= \delta_{ij} \sum_{LL'} \Phi_L^i(\mathbf{r}_i; k) T_{LL'}^i \tilde{\Psi}_{L'}^i(\mathbf{r}'_j; k), \quad (5) \end{aligned}$$

where  $\Phi_L^i$  is local basis solution,  $T_{LL'}^i$  is the scattering  $T$ -matrix of the nonspherical potential located inside the  $i$ th cell, and  $\tau_{LL'}^{ij} = [(T_c^{-1} + G)^{-1}]_{LL'}^{ij}$  is the inverse of the multiple scattering matrix, known as the full scattering path operator, and gives the total amplitude of propagation from site  $i$  to site  $j$ , starting with angular momentum  $L$  and arriving with angular momentum  $L'$ . The cell  $T$ -matrix is defined as  $[T_c]_{LL'}^{ij} \equiv T_{LL'}^i \delta_{ij}$ . The atomic Green's function  $G_{at}$  is the singular part of the full Green's function,  $\mathbf{r}_<, \mathbf{r}_>$  is the lesser, greater of  $r, r'$ ,  $\tilde{\Psi}_{L'}^i$  is the irregular solution of the Schrödinger equation. The above expressions are valid for general potentials and provide a formal decomposition of the Green's function into a scattering contribution,  $G_{sc}$ , and an absorbing atomic term,  $G_{at}$ . In practice, however, this separation acquires a clear physical meaning only when the cell associated with the absorbing atom has a spherical shape. In our full-potential multiple scattering implementation, achieving a full potential description requires filling the interstitial region, for example, by enlarging the atomic cells and arranging empty cells. As a result, each scattering cell becomes truncated cell with a shape such as a Voronoi polyhedra, rather than spherical ones. Consequently, although  $G_{at}$  remains mathematically well defined as the singular on-site part of the full Green's function, it no longer represents the Green's function of an absorbing atom and thus loses its physical interpretation. In such cases, the separation into "atomic" and "scattering" contributions should be regarded as merely a formal decomposition without unique physical meaning. In contrast, when the absorbing atomic cell is defined as a sphere (irrespective of whether the potential inside it is spherically symmetric),  $G_{at}$  recovers its standard physical meaning as originality atomic Green's function with the central atomic potential. It should be noted that the atomic absorption cross-section is not a directly observable physical quantity but rather a theoretical construct. Nevertheless, for example, an analogous interpretation exists in the Atomic Sphere Approximation (ASA) [59]. In ASA, each site is treated as a space-filling overlapping sphere with a spherically averaged potential that effectively incorporates the influence of neighboring atoms. In this situation,  $G_{at}$  may

be regarded as the Green's function of an effective atomic scatterer defined by the local spherical potential.

In multiple scattering theory, the total absorption cross-section  $\sigma_{tot}$  is conventionally divided into atomic absorption  $\sigma_{at}$  and scattering contribution  $\sigma_{sc}$ ,

$$\sigma_{tot} = \sigma_{at} + \sigma_{sc}. \quad (6)$$

The  $\sigma_{at}$  is proportional to the imaginary part of the atomic Green's function  $G_{at}$ , and in the case of real potentials using the dipole and single-channel approximations, it can be written as follows:

$$\begin{aligned} \sigma_{at} &= -8\pi\alpha\hbar\omega \\ &\times \sum_{m_c} \text{Im} \iint_{\Omega_c} \langle \phi_{L_c}^c(\mathbf{r}) | \boldsymbol{\varepsilon} \cdot \mathbf{r} G_{at} \boldsymbol{\varepsilon} \cdot \mathbf{r}' | \phi_{L_c}^c(\mathbf{r}') \rangle d\mathbf{r} d\mathbf{r}' \\ &= -8\pi\alpha\hbar\omega \sum_{m_c} \sum_{LL'} \text{Im} M_{L_c L} T_{LL'}^i M_{L_c L'}, \quad (7) \end{aligned}$$

defining the atomic absorption matrix element as

$$M_{L_c L} = \int_{\Omega_c} d\mathbf{r} \phi_{L_c}^c(\mathbf{r}) \boldsymbol{\varepsilon} \cdot \mathbf{r} \Phi_L^i(\mathbf{r}; k). \quad (8)$$

To clearly demonstrate the effects of AXAFS, the theoretical formulations should be presented in a concise manner. Therefore, in the analytical expressions used in the following discussion, real potentials and real energies were employed. The same condition was applied for the numerical calculations. Under this condition, the solutions  $\Phi$  and  $\tilde{\Psi}$  are also real. Consequently, the singular atomic term does not contribute to the imaginary part of the Green's function, and Eqs. (7) and (8) remain valid. In contrast, for complex (optical) potentials,  $\Phi$  and  $\tilde{\Psi}$  acquire complex phases, and the above equations no longer apply. When using the muffin-tin approximation, the potential is spherically symmetric, so the  $T$ -matrix is  $T_{LL'}^i = t_l^i \delta_{LL'} = -k^{-1} \sin \delta_l^i e^{i\delta_l^i} \delta_{LL'}$ . Here,  $\delta_l^i$  is the phase shift of the potential, which is real in this case. For excitation from the K-shell,  $l_c = 0$  and  $l = 1$ , so Eq. (7) can be written as

$$\sigma_{at} \sim 4\pi\alpha\hbar\omega |M_{L_0 L_1}|^2 \frac{1}{k} \{1 - \cos(2\delta_1^i)\}. \quad (9)$$

The scattering contribution  $\sigma_{sc}$  from neighboring atoms, limiting ourselves to the single scattering approximation, is as follows:

$$\begin{aligned} \sigma_{sc} &= -8\pi\alpha\hbar\omega \\ &\times \sum_{m_c} \text{Im} \iint_{\Omega_c} \langle \phi_{L_c}^c(\mathbf{r}) | \boldsymbol{\varepsilon} \cdot \mathbf{r} G_{sc} \boldsymbol{\varepsilon} \cdot \mathbf{r}' | \phi_{L_c}^c(\mathbf{r}') \rangle d\mathbf{r} d\mathbf{r}' \\ &= -8\pi\alpha\hbar\omega \sum_{m_c} \text{Im} \iint_{\Omega_c} d\mathbf{r} d\mathbf{r}' \\ &\times \langle \phi_{L_c}^c(\mathbf{r}) | \boldsymbol{\varepsilon} \cdot \mathbf{r} \sum_{LL'} \Phi_L^i(\mathbf{r}_<; k) (\tau_{LL'}^{ii} - T_{LL'}^i) \\ &\times \Phi_{L'}^i(\mathbf{r}_>; k) \boldsymbol{\varepsilon} \cdot \mathbf{r}' | \phi_{L_c}^c(\mathbf{r}') \rangle \\ &= -8\pi\alpha\hbar\omega \text{Im} M_{L_c L} (\tau_{LL'}^{ii} - T_{LL'}^i) M_{L_c L'} \\ &\sim -8\pi\alpha\hbar\omega \end{aligned}$$

$$\begin{aligned}
& \times \text{Im } M_{L_c L} \left( \sum_{LL'L'} \sum_{j \neq i} T_{LL'}^i G_{LL'}^{ij} T_{L'L}^j G_{L'L}^{ji} T_{L'L}^i \right) M_{L_c L'} \\
& \sim 32\pi^2 \alpha \hbar \omega \sum_{m_c} \sum_{LL'} \sum_{j \neq i} \sin \delta_l^j \sin \delta_{l'}^i \text{Im } M_{L_c L} \\
& \times \left[ i^{l-l'} \frac{e^{2ikR_{ij} + i(\delta_l^j + \delta_{l'}^i)}}{k^2 R_{ij}^2} f^j(k, \pi) Y_L(\hat{\mathbf{R}}_{ij}) Y_{L'}(-\hat{\mathbf{R}}_{ij}) \right] M_{L_c L'}. \quad (10)
\end{aligned}$$

Here,  $G_{LL'}^{ij}$  is the photoelectron propagator expressed under the plane wave approximation, and  $f^j(k, \pi)$  is the back scattering amplitude by site  $j$  under the muffin-tin approximation.  $Y_L(\hat{\mathbf{R}}_{ij})$  are the real spherical harmonics:

$$G_{LL'}^{ij} \sim -4\pi i^{l-l'} k Y_L(\hat{\mathbf{R}}_{ij}) Y_{L'}(\hat{\mathbf{R}}_{ij}) \frac{e^{ikR_{ij}}}{kR_{ij}}, \quad (11)$$

$$f^j(k, \pi) = -4\pi \sum_{L_l} Y_{L_l}(\hat{\mathbf{R}}_{ij}) t_{L_l}^j Y_{L_l}(-\hat{\mathbf{R}}_{ij}), \quad (12)$$

In the case of x-ray absorption,  $T^i G^{ii} T^i$  is zero and  $\sum_{j \neq i} T^i G^{ij} T^j G^{ji} T^i$  represents single scattering at site  $j$ . For excitation from the K-shell, Eq. (10) can be written as

$$\begin{aligned}
\sigma_{\text{sc}} \sim & -4\pi \alpha \hbar \omega |M_{L_0 L_1}|^2 \{1 - \cos(2\delta_1^i)\} \\
& \times \sum_{j \neq i} \frac{1}{k^2 R_{ij}^2} \text{Im}[f^j(k, \pi) e^{2i(kR_{ij} + \delta_1^i)}]. \quad (13)
\end{aligned}$$

Therefore the formula for the EXAFS signal, under K-shell one-electron, electric dipole, muffin-tin, plane wave, high energy approximations, considering only one-photon and single-channel absorption, is given as follows and is widely used in EXAFS analysis:

$$\chi = \frac{\sigma_{\text{sc}}}{\sigma_{\text{at}}} \sim - \sum_{j \neq i} \frac{|f^j(k, \pi)|}{k R_{ij}^2} \sin(2kR_{ij} + 2\delta_1^i + \Phi^j), \quad (14)$$

where  $\Phi$  is the phase of the backscattering amplitude  $f^j(k, \pi) = |f^j(k, \pi)|e^{i\Phi^j}$ .

### B. Original AXAFS derivation

This section presents the AXAFS formula as derived in [5], where the authors noted that the atomic absorption coefficient  $\mu_0$  is not a completely smooth function, but can also have structure  $\chi_e$  due to scattering from the periphery of the absorbing atom itself, giving

$$\mu_0 = \mu_a (1 + \chi_e), \quad (15)$$

where  $\mu_a$  represents the free and smooth atomic background. The difference between the free and embedded atomic potentials is taken as the perturbation  $\delta v$ , and based on first-order perturbation theory, they wrote the AXAFS formula as follows:

$$\chi_e(k) \sim -\text{Im} \frac{1}{k} \int_0^\infty dr [R_a^+(kr)]^2 \delta v(r), \quad (16)$$

where  $R_a^+(kr)$  is the outgoing part of the radial Schrödinger equation. They model the perturbation as

$\delta v = v_{\text{mt}} / \{1 + \exp(\zeta(R_{\text{mt}} - r))\}$ , which leads to the following equation:

$$\chi_e(k) = -\frac{1}{k R_{\text{mt}}^2} |f_e| \sin(2kR_{\text{mt}} + 2\delta_l^a + \Phi_e). \quad (17)$$

Where  $R_{\text{mt}}$  is the muffin-tin radius of the absorbing atom,  $v_{\text{mt}}$  is the final state potential of the absorbing site at distances larger than the muffin-tin radius,  $\zeta$  characterizes the decay of the atomic potential tails near  $R_{\text{mt}}$ ,  $\delta_l^a$  is the central atom phase shift, and  $f_e = |f_e| \exp(i\Phi_e)$  is an effective curved-wave scattering amplitude of the interstitial charge density. This formula is similar to that used in conventional EXAFS analysis Eq. (14), but instead of the interatomic distance, we find the muffin-tin radius  $R_{\text{mt}}$ .

## III. RESULTS AND DISCUSSION

### A. AXAFS and potential discontinuity in the muffin-tin approximation

In the present study, we first investigated the effect of potential truncation caused by using the muffin-tin approximation for calculating the x-ray absorption spectrum. Specifically, the potential was modeled as a sum of 3d spherical-well and Coulomb potentials,

$$U(r) = \begin{cases} -\frac{Z}{r} - U_0 & (U_0 > 0) \quad r < a \\ -\frac{Z}{r} & r \geq a, \end{cases}$$

and we analytically studied effects of discontinuities appearing at  $r = a$ , corresponding to the muffin-tin radius, on EXAFS signals. Here,  $Z$  is the atomic number, and  $U_0$  is the depth of the potential well. The phase shift in the situation where a short-range potential is added to the Coulomb field is expressed by  $\delta_l = \sigma_l + \tilde{\delta}_l$ , where  $\sigma_l$  is the Coulomb phase shift and  $\tilde{\delta}_l$  is the additional phase shift due to the extra potential.  $\tilde{\delta}_l$  is conceptually different from that obtained from the additional potential alone [60]. However, in this study,  $\tilde{\delta}_l$  is approximated to the phase shift of a pure 3d spherical-well potential  $\delta_l^s$  to show analytically the effect of the potential discontinuity produced at the muffin-tin radius. It is a good approximation in the high-energy region, as shown in Appendix A. In this paper, we call this analytical model the “potential step model”. A schematic illustration of the potential used in this model is shown in Fig. 1.

The muffin-tin potentials used in numerical calculations approximates the region inside the atomic cell to have a spherically symmetric potential and the region outside to have a constant potential. In comparison, the present potential model has a Coulomb tail rather than a constant value in the region outside the atomic cell. However, we just want to investigate the effect on the absorption cross-section of a discontinuous potential used for numerical calculations, so we ignore the cut of the Coulomb tail in this model. In the high-energy region, the phase shift in this model can be approximately written as follows:

$$\delta_l \sim \delta_l^{\text{Coul}} + \delta_l^{\text{step}} \quad (18)$$

$$\begin{aligned}
& \sim \arg \left\{ \Gamma \left( l + 1 - i \frac{1}{kaZ} \right) \right\} \\
& - \left( ka - \frac{l\pi}{2} \right) + \arctan \left\{ \frac{k}{\kappa} \tan \left( \kappa a - \frac{l\pi}{2} \right) \right\}, \quad (19)
\end{aligned}$$

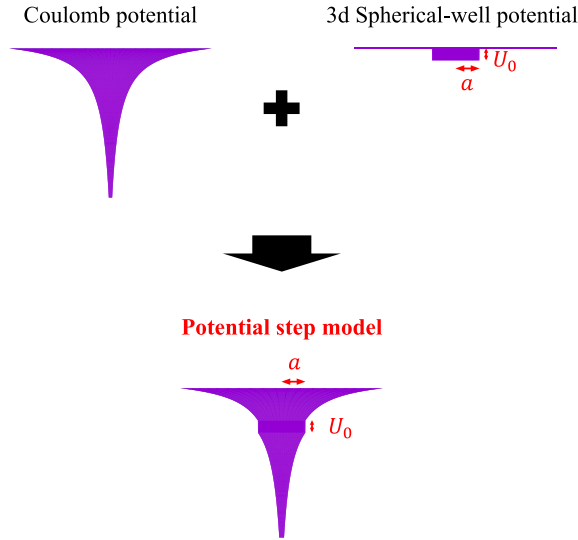


FIG. 1. Sketch of the potential step model, the potential was modeled as a sum of 3d spherical-well and Coulomb potentials.  $U_0$  is the discontinuity in the potential at  $r = a$ , corresponding to muffin-tin radius.

where

$$\delta_l^{\text{Coul}} \sim \arg \left\{ \Gamma \left( l + 1 - i \frac{1}{ka_Z} \right) \right\} \quad (20)$$

$$\delta_l^{\text{step}} \sim - \left( ka - \frac{l\pi}{2} \right) + \arctan \left\{ \frac{k}{\kappa} \tan \left( \kappa a - \frac{l\pi}{2} \right) \right\}. \quad (21)$$

In these equations,  $\Gamma$  is Euler's gamma function,  $a_Z = a_0/Z$  is the Bohr radius of an atom with atomic number  $Z$  ( $a_0 \sim 0.5292$  Å is the Bohr radius of hydrogen). Here,  $\kappa$  is the momentum given by  $\kappa = \sqrt{k^2 + U_0}$ . Under those definitions for the phase shift, we calculated the atomic cross-section  $\sigma_{\text{at}}$ :

$$\begin{aligned} \sigma_{\text{at}} \sim & 4\pi\alpha\hbar\omega |M_{L_0L_1}|^2 \frac{1}{k} \left[ 1 - \cos \left( \frac{U_0^i a^i}{k} + 2\delta_1^{\text{Coul}} \right) \right. \\ & \left. + \frac{U_0^i}{2k^2} \{ \cos(2ka^i - 2\delta_1^{\text{Coul}}) - \cos(2ka^i + 2\delta_1^{\text{Coul}}) \} \right]. \end{aligned} \quad (22)$$

The calculations used an approximation that neglects the order of  $1/k^5$ . When  $Z$  is small, the atomic absorption cross-section can be simply described by approximating the phase shift of the Coulomb potential as follows [61]:

$$\begin{aligned} \delta_l^{\text{Coul}} &= \arg \left\{ \Gamma \left( l + 1 - i \frac{1}{ka_Z} \right) \right\} \\ &= - \frac{\gamma}{ka_Z} + \sum_{n=0}^{\infty} \left[ \frac{1}{n+1} \frac{1}{ka_Z} - \arctan \left( \frac{1}{n+1} \frac{1}{ka_Z} \right) \right] \\ &\quad + \sum_{m=1}^l \arctan \left( \frac{1}{mka_Z} \right) \\ &\sim \frac{1}{2} \arctan \left( \frac{1}{ka_Z} \right) + \frac{1}{ka_Z} \left( \ln \sqrt{1 + \left( \frac{1}{ka_Z} \right)^2} - 1 \right) \\ &\quad + \sum_{m=1}^l \arctan \left( \frac{1}{mka_Z} \right), \end{aligned} \quad (23)$$

where  $\gamma \sim 0.5772$  is Euler's constant. Substituting Eq. (23) into Eq. (22), we obtained the atomic absorption cross-section as a simple formula as follows:

$$\begin{aligned} \sigma_{\text{at}} \sim & 2\pi\alpha\hbar\omega |M_{L_0L_1}|^2 \frac{1}{k^3} \left( \frac{1}{a_Z^i} + U_0^i a^i \right)^2 \\ & \times \left[ 1 + \frac{2U_0^i}{ka_Z^i \left( \frac{1}{a_Z^i} + U_0^i a^i \right)^2} \sin(2ka^i) \right]. \end{aligned} \quad (24)$$

As in the equation for the conventional EXAFS signal, the atomic absorption cross-section  $\sigma_{\text{at}}$  is divided into a smooth function  $\sigma_0$  and an oscillatory term  $\chi_{\text{at}}$ ,

$$\sigma_{\text{at}} = \sigma_0 (1 + \chi_{\text{at}}). \quad (25)$$

The oscillatory term  $\chi_{\text{at}}$  can thus be written as

$$\chi_{\text{at}} \sim \frac{2U_0^i}{ka_Z^i \left( \frac{1}{a_Z^i} + U_0^i a^i \right)^2} \sin(2ka^i). \quad (26)$$

In the AXAFS equation (17) derived in previous works, the oscillations are supposed to be due to an embedded atom potential, whereas in Eq. (26), they are due to potential discontinuities at the muffin-tin radius. Moreover, the  $\mu_a$  defined previously is the absorption of free atoms, whereas the  $\sigma_0$  defined in this study is the atomic cross-section for the Coulomb potential, neither of which has discontinuities. Therefore we assume that the atomic absorption cross-section is a smooth function and this will be shown to be the case for more realistic calculations shown in the next sections. Figure 2(a) shows the oscillation of the atomic absorption cross-section  $k^2 \chi_{\text{at}}$  obtained by multiple scattering calculations using the muffin-tin approximation with the FPMS program [55] (black line) and the analytical formula Eq. (26) of the potential step model (red line) for O K-edge of NO, CH<sub>3</sub>OH, and (2 × 1)O/Cu(110). The muffin-tin radius of the absorbing O atom is  $a=0.6$  Å, and potential discontinuities are 0.25, 0.26, and 0.28 Å<sup>-2</sup>, respectively. In all three cases, oscillations have almost the same period and depend on the position of the potential steps created using the muffin-tin approximation. It can be seen that in this case, the analytical formula in Eq. (26) is sufficient to account for the oscillatory structure.

Next, we derived the expression for the absorption cross-section due to scattering with the surrounding atoms  $\sigma_{\text{sc}}$  using the potential step model. The backscattering amplitude  $f(\pi, k)$  in this potential model can be approximately divided into the Coulomb scattering amplitude  $f^{\text{Coul}}(\pi, k)$  and the scattering amplitude  $f^{\text{step}}(\pi, k)$  arising from the additional 3d spherical-well potential [60]:

$$\begin{aligned} f(\pi, k) &= f^{\text{Coul}}(\pi, k) + f^{\text{step}}(\pi, k) \\ &= \frac{1}{2k^2 a_Z} e^{2i\delta_0^{\text{Coul}}} + \frac{3}{2ik} \sum_l e^{2i\delta_l^{\text{Coul}}} (e^{2i\delta_l^{\text{step}}} - 1) P_l(-1), \end{aligned} \quad (27)$$

$$(28)$$

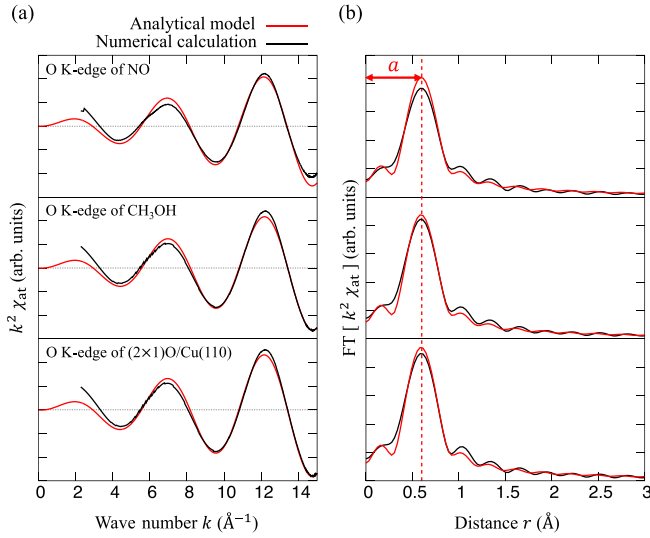


FIG. 2. (a) Oscillation of the atomic absorption cross-section  $k^2 \chi_{\text{at}}$  obtained by multiple scattering calculations using the muffin-tin approximation with the FPMS program (black line) compared with the application of the analytical expression Eq. (26) within the potential step model (red line) for O K-edge of NO, CH<sub>3</sub>OH, (2 × 1)O/Cu(110) (top to bottom). (b) Fourier transform (FT) of the oscillations of atomic absorption cross-section obtained by multiple scattering calculations using the muffin-tin approximation with the FPMS program (black line), and Fourier transform of the oscillations obtained from the analytical expression within the potential step model (red line). The red dashed line is the position of the muffin-tin radius of O atom  $a = 0.6 \text{ \AA}$ .

where

$$f^{\text{Coul}}(\pi, k) = \frac{1}{2k^2 a_Z} e^{2i\sigma_0}, \quad (29)$$

$$f^{\text{step}}(\pi, k) = \frac{3}{2ik} \sum_l e^{2i\sigma_l} (e^{2i\delta_l^{\text{step}}} - 1) P_l(-1), \quad (30)$$

where  $P_l$  is a Legendre polynomial. By substituting the scattering amplitude Eq. (28) and the phase shift Eq. (18) into Eq. (13), we obtain an approximate expression for  $\sigma_{\text{sc}}$  under the Potential step model:

$$\begin{aligned} \sigma_{\text{sc}} &\sim \pi \alpha \hbar \omega |M_{L_0 L_1}|^2 \left( \frac{1}{a_Z^i} + U_0^i a^i \right)^2 \\ &\times \sum_{j (\neq i)} \frac{1}{k^6 R_{ij}^2} \left\{ \frac{1}{a_Z^j} + U_0^j a^j (-1)^{l_{\text{max}}} (l_{\text{max}} + 1) \right\} \\ &\times \sin(2kR_{ij}). \end{aligned} \quad (31)$$

Here we use an approximation that ignores  $k^{-7}$  terms and beyond. The  $\sigma_{\text{sc}}$  calculated by the muffin-tin approximation also contains oscillations proportional to  $\sin(2ka)$ , but the amplitudes are so small that the contribution is negligible; the detailed discussion are provided in the Supplemental Material [62]. To simplify the description of the oscillation structure of the absorption cross-section, the analytical equations assume a small atomic number, but in fact, the oscillation is slightly shifted from  $\sin(2kR)$  due to the Coulomb phase shift. Therefore  $\sigma_{\text{tot}}$  obtained by multiple scattering calculations using the

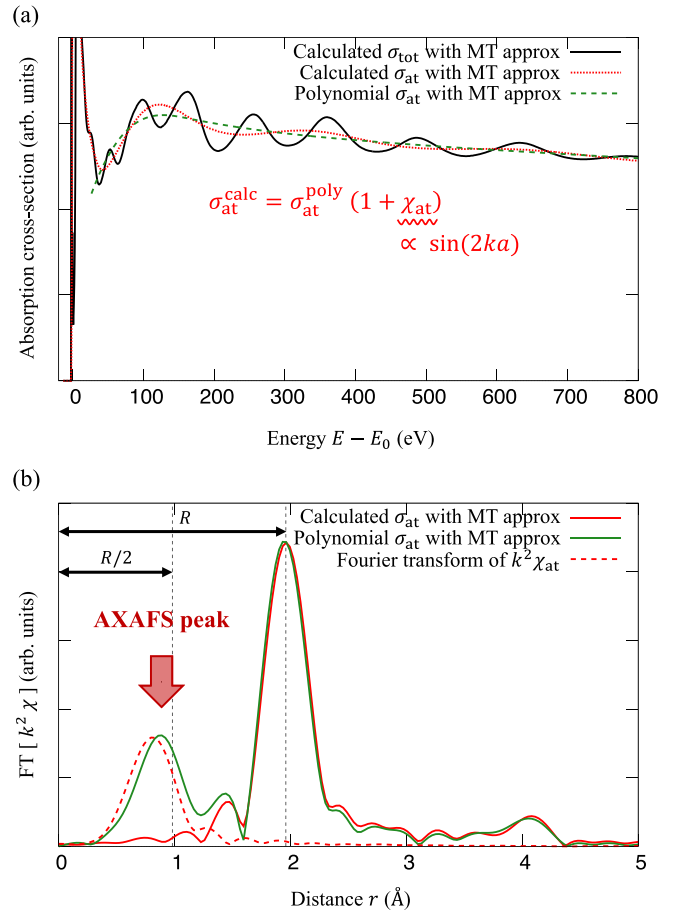


FIG. 3. (a) Total Ge K-edge absorption cross-section calculated in the muffin-tin (MT) approximation of the GeBr<sub>4</sub> molecule (solid black line), which shows two main oscillatory components [ $\sin(2kR)$  and  $\sin(2ka)$ ]. The red line (short dashed) is the atomic absorption cross-section in the muffin-tin approximation shows an oscillation caused by the discontinuous potential at the muffin-tin border. The green line (long dashed) is a smooth atomic background generated by a polynomial function adapted to the total absorption cross-section. (b) Fourier transform (FT) of the EXAFS signal extracted using a calculated atomic background from the total absorption cross-section calculated with the muffin-tin approximation as in Eq. (32) (solid red line). Fourier transform of the EXAFS signal extracted using a smooth polynomial background for the atomic background and the total absorption cross-section calculated with the muffin-tin approximation as in Eq. (33) (solid green line). Fourier transform of  $k^2 \chi_{\text{at}}$ , which is due to the potential muffin-tin approximation (dashed red line). The AXAFS peak at about  $R/2$  is due to the use of the muffin-tin approximation (see text). Hanning windows functions are used for the Fourier transform, and we set  $k_{\text{min}} = 3.5 \text{ \AA}^{-1}$ ,  $k_{\text{max}} = 14.5 \text{ \AA}^{-1}$ , and  $\Delta k = 2.0 \text{ \AA}^{-1}$ .

muffin-tin approximation includes oscillations of  $\sigma_{\text{at}}$ , i.e.,  $\chi_{\text{at}}$ , approximately proportional to  $\sin(2ka)$  due to the potential discontinuity at the muffin-tin radius of the absorbing atom and oscillations of  $\sigma_{\text{sc}}$ , i.e.,  $\chi_{\text{sc}}$ , approximately proportional to  $\sin(2kR)$  due to photoelectron scattering by neighboring atoms.

Figure 3 shows numerical calculations obtained within the muffin-tin approximation using FPMS program. The real part

of the energy-dependent Hedin-Lundqvist potential [63,64] was used as the optical potential. In Fig. 3(a), the solid black line is the total Ge K-edge absorption cross-section for the GeBr<sub>4</sub> molecule, the short dashed red line is the atomic absorption cross-section, and the long dashed green line is the smooth atomic background represented by a polynomial function fitting to the total absorption cross-section.

As can be seen from Eq. (24), the atomic absorption cross-section calculated in the muffin-tin approximation has an oscillatory structure ( $\chi_{\text{at}}$ ). Usually, when calculations are performed within the muffin-tin approximation, the EXAFS signal  $\chi$  is extracted from the total absorption cross-sections using the calculated atomic absorption cross-section as an atomic background. In this case, the  $\sigma_{\text{at}}$  contribution is canceled, so the EXAFS signal  $\chi$  shows only the oscillations  $\chi_{\text{sc}}$  due to the photoelectron scattering by neighboring atoms:

$$\chi^{\text{calc bg}} = \frac{\sigma_{\text{tot}}^{\text{calc}} - \sigma_{\text{at}}^{\text{calc}}}{\sigma_{\text{at}}^{\text{calc}}} = \chi_{\text{sc}}. \quad (32)$$

This can be easily verified looking at the red curve of Fig. 3(b) where a definite Fourier transform peak appears only near the interatomic distance, while the AXAFS peak is absent. On the other hand, if the atomic background is represented by smooth curves, such as those represented by polynomial functions, as in the EXAFS analysis of experimental data, the EXAFS signal  $\chi$  shows two main oscillatory components, one due to photoelectron scattering by neighboring atoms  $\chi_{\text{sc}}$  and the other due to the muffin-tin discontinuity  $\chi_{\text{at}}$ :

$$\begin{aligned} \chi^{\text{poly bg}} &= \frac{\sigma_{\text{tot}}^{\text{calc}} - \sigma_{\text{at}}^{\text{poly}}}{\sigma_{\text{at}}^{\text{poly}}} \\ &= \frac{\sigma_{\text{sc}}^{\text{calc}}}{\sigma_{\text{at}}^{\text{poly}}} + \frac{\sigma_{\text{at}}^{\text{calc}} - \sigma_{\text{at}}^{\text{poly}}}{\sigma_{\text{at}}^{\text{poly}}} \sim \chi_{\text{sc}} + \chi_{\text{at}}. \end{aligned} \quad (33)$$

Therefore, as shown by the green line in Fig. 3(b), the AXAFS peak appears at about the position of the muffin-tin radius of the absorbing atom. This AXAFS peak is due to the oscillation of the muffin-tin atomic absorption cross-section, as can be seen from the fact that this peak almost coincides with the dashed red line. The slight differences in Fourier transform peak positions between the Fourier transform of oscillation of  $\sigma_{\text{at}}$  and  $\sigma_{\text{tot}}$  at around  $R/2$  is due to a ripple structure effect of the Fourier transform of  $\chi_{\text{sc}}$ . The height of the AXAFS peak depends on the height of the discontinuous potential step caused by potential truncation,  $U_0$ , as shown in Eq. (26). In other words, according to this equation, the AXAFS peak does not appear when there is no discontinuity in the potential around the absorbing atom, i.e., when analyzing spectra calculated with the full potential approach or measured EXAFS.

As can be seen in Fig. 4(a), the oscillation structures related to the potential discontinuity at the border of muffin-tin sphere of the absorbing atom can be found in the atomic absorption cross-section of different molecular and crystalline systems. Figure 4(b) shows oscillations extracted from total and atomic absorption cross-sections using a smooth polynomial background. The amplitude of AXAFS oscillation is relatively small compared to the EXAFS peak in systems with many neighboring atoms, such as a material with the FCC structure,

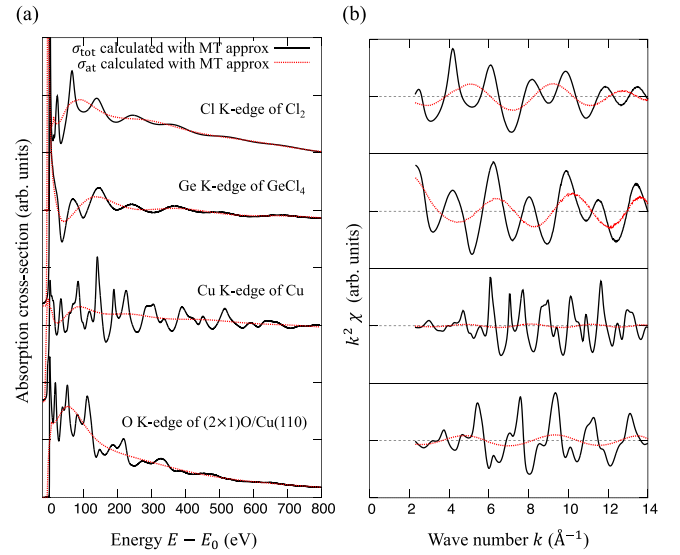


FIG. 4. (a) The total absorption cross-section (solid black line) and atomic absorption cross-section (dashed red line) calculated with the muffin-tin (MT) approximation for Cl K-edge of Cl<sub>2</sub> molecule, Ge K-edge of GeCl<sub>4</sub> molecule, Cu K-edge of Cu foil, and O K-edge of (2 × 1)O/Cu(110). (b) Oscillations of the total absorption cross-section (solid black line) and atomic absorption cross-section (dashed red line) calculated with the muffin-tin approximation for Cl K-edge of Cl<sub>2</sub> molecule, Ge K-edge of GeCl<sub>4</sub> molecule, Cu K-edge of Cu foil, and O K-edge of (2 × 1)O/Cu(110).

while the amplitude of AXAFS oscillation is relatively large for systems with few neighboring atoms, such as diatomic molecules.

Here, we mention the AXAFS contributions reported in the muffin-tin numerical calculations of the previous studies. In light of present calculations, the reason for the oscillatory structure in the atomic absorption coefficient in Fig. 2 of Ref. [5], Fig. 2 of Ref. [10], Fig. 1 of Ref. [11], Fig. 2 of Ref. [12], Fig. 1 of Ref. [13], and Fig. 6 of Ref. [14] can be assigned to the use of the muffin-tin approximation in the numerical calculations. In addition, for the same reasons, the AXAFS peak appears in the Fourier transform of the oscillation of the calculated atomic absorption coefficient in Figs. 2 and 4 of Ref. [12], Fig. 2 of Ref. [13], Fig. 7 of Ref. [14], and Fig. 13 of Ref. [15]. Therefore our results show that the verification of AXAFS by muffin-tin calculations of  $\sigma_{\text{at}}$  is certainly an inappropriate method, as this approximation generates oscillations at the AXAFS distance of interest.

## B. Numerical calculation with full-potential multiple scattering

In order to remove the problem of the discontinuity of the potential at the border of the muffin-tin spheres, we have performed full-potential multiple scattering calculations. In this approach [55], to treat the potential outside an atomic cell, a number of empty cells (35 in this case) are placed around the considered atomic cell. In this way, the potential can be made continuous, with no discontinuity at the atomic radius, differently from the simple muffin-tin approximation. Similarly to muffin-tin calculations, we used the energy-dependent real part of the Hedin-Lundqvist potential as the optical

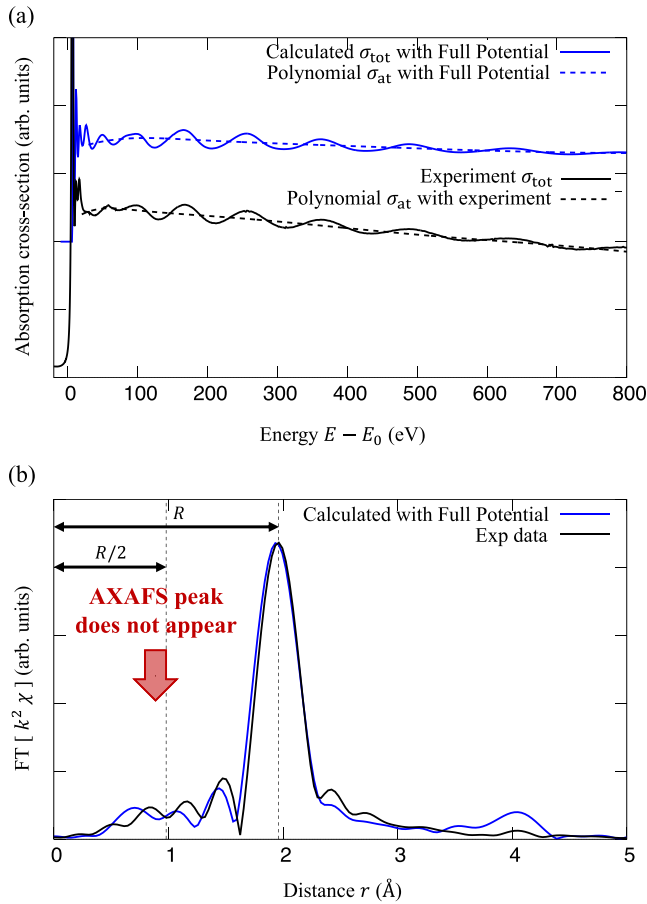


FIG. 5. (a) Total calculated Ge K-edge absorption cross-section (full potential) of the  $\text{GeBr}_4$  molecule (solid blue line), and smooth polynomial atomic background (dashed blue line). Experimentally Ge K-edge measured spectrum of a  $\text{GeBr}_4$  molecule (solid black line) and the smooth polynomial atomic background (dashed black line). (b) Comparison of Fourier transform (FT) spectra of the EXAFS signals obtained by calculated (blue line) and experimental (black line) data shown in (a). Hanning window functions are used for Fourier transforms, set to  $k_{\min} = 3.5 \text{ \AA}^{-1}$ ,  $k_{\max} = 14.5 \text{ \AA}^{-1}$ , and  $\Delta k = 2.0 \text{ \AA}^{-1}$ .

potential. Within the full-potential multiple scattering approach, an atomic absorption cross-section can in principle be constructed and calculated; however, its definition is not unique and depends on the chosen cell partitioning. As a result, it cannot be interpreted as a physically meaningful atomic background. A detailed discussion of this point is provided in Supplemental Material [62]. Therefore the EXAFS signal, either calculated by the full potential approach or measured experimentally, is obtained using  $\sigma_{\text{at}}$  as a realistic smooth function represented by a polynomial curve that contains no extra oscillations.

Figure 5 shows full-potential multiple scattering numerical calculations using the FPMS program compared with experimental data. In Fig. 5(a), the solid blue line is the total Ge K-edge absorption cross-section calculated by the FPMS program of the  $\text{GeBr}_4$  molecule, while the dashed blue line is the smooth atomic background generated by a polynomial function adapted to the total absorption cross-section. The

solid black line is the Ge K-edge experimental spectrum of the  $\text{GeBr}_4$  molecule, while the dashed black line is the smooth atomic background generated by a polynomial function adapted to the experimentally measured spectrum [65].

Looking at Fig. 5(a), we can notice a close similarity between FPMS calculations and experimental data in the EXAFS region. This similarity can be appreciated considering the comparison between the Fourier Transforms of calculated and experimental spectra shown in Fig. 5(b). We can see that, differently from the case of muffin-tin calculations shown in Fig. 3, no significant AXAFS peaks appear using the same smooth atomic background ( $\sigma_{\text{at}}$ ) when calculations are performed using Full Potentials because there are no discontinuities in the potential. From these results, we conclude that the AXAFS peak is produced only when using muffin-tin calculations, and appears only when the atomic absorption cross-section caused by the muffin-tin potential discontinuity.

### C. Charge density modulation on AXAFS using CO molecule

To investigate the possible effect of interatomic charge density modulations on AXAFS, we prepared molecular potentials and electron charge densities for multiple scattering calculations using two different methods. In the first method, which we call “non-SCF” (nonself-consistent), the molecular potential and electron charge density were constructed by simply superimposing the free atomic densities. This approximation is usually good enough for EXAFS calculations, where is normally used. The free atom calculations were performed using the Desclaux code [66], which employs a multiconfiguration relativistic Dirac-Fock theory, and the excited states were calculated with a fully relaxed core hole. The second method, which we call “SCF”, utilizes a self-consistent electron charge density calculated by MOLCAS 8.2 [67] for the excited state of the final state, employing a Hermite Gaussian basis function set [68]. The (Coulomb) static part of the scattering potential was calculated under the McMurchie-Davidson scheme [68] with a Boys function [69]. Since the SCF method accounts for potential changes due to the formation of intermolecular covalent bonds, if AXAFS was influenced by charge density modulations, differences should appear between non-SCF and SCF calculations as an example for CO molecules, where localized bonding states in the interatomic region exist.

Figure 6 shows the total electron charge densities calculated for (a) non-SCF, (b) SCF, and (c) the difference (SCF – non-SCF) of CO molecule for excited states with a core hole in C  $1s$  orbital, and (d) non-SCF, (e) SCF, and (f) the difference (SCF – non-SCF) of CO molecule for excited states with a core hole in O  $1s$  orbital. These comparisons show the change of charge distributions varying with electronic configuration.

In Fig. 7, we show the (a)  $z$ -polarized C K-edge x-ray absorption (XANES), (b) EXAFS signal, (c) Fourier transform of the EXAFS signal for C K-edge of CO molecule oriented along the  $z$  axis, (d)  $z$ -polarized O K-edge XANES, (e) EXAFS signal, and (f) Fourier transform of the EXAFS signal for O K-edge of CO molecule oriented along the  $z$ -axis, calculated using the Full Potential and both non-SCF (blue

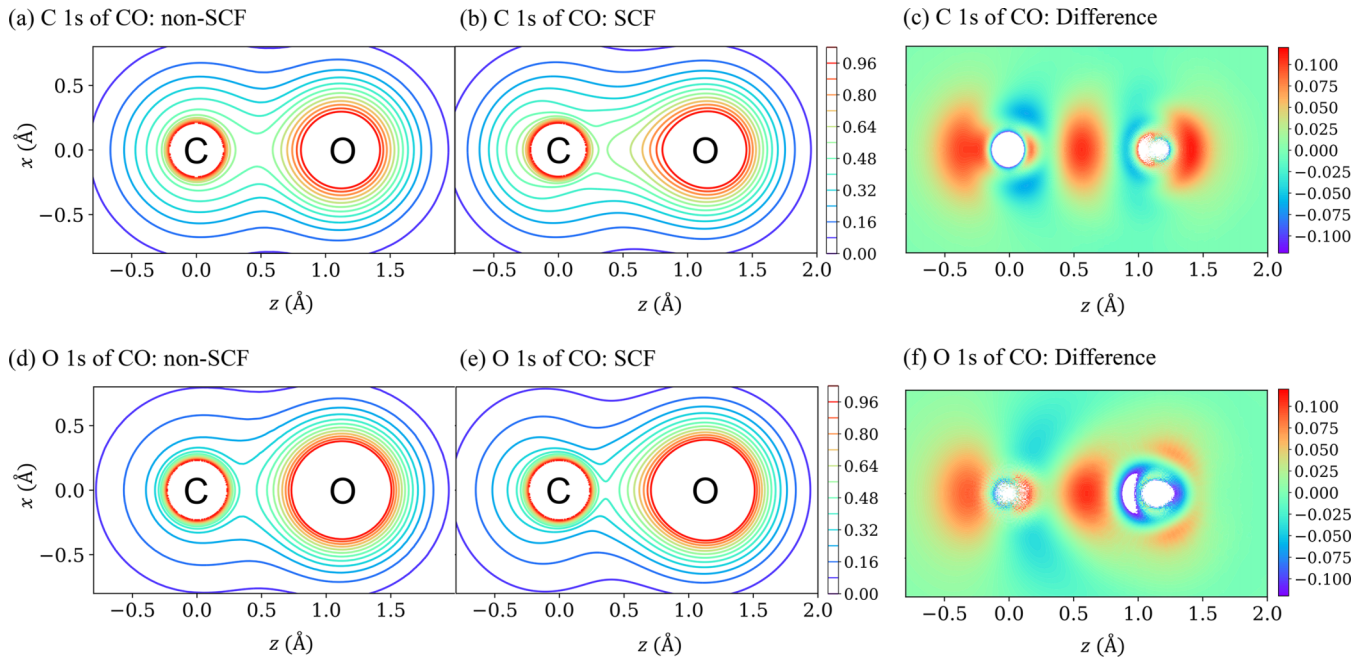


FIG. 6. The electron charge densities calculated with the Full Potential for (a) non-SCF, (b) SCF, and (c) the difference (SCF–non-SCF) of CO molecule for excited states with a core hole in C 1s orbital. The electron charge densities calculated with the Full Potential for (d) non-SCF, (e) SCF, and (f) the difference (SCF–non-SCF) of CO molecule for excited states with a core hole in O 1s orbital.

line) and SCF (orange line) charge densities. There is almost no difference between SCF and non-SCF calculations, suggesting that Fourier transform peaks are not affected by charge

density modulations. The change in potential between atoms due to the formation of covalent bonds makes a difference in the low photoelectron energy region, such as XANES,

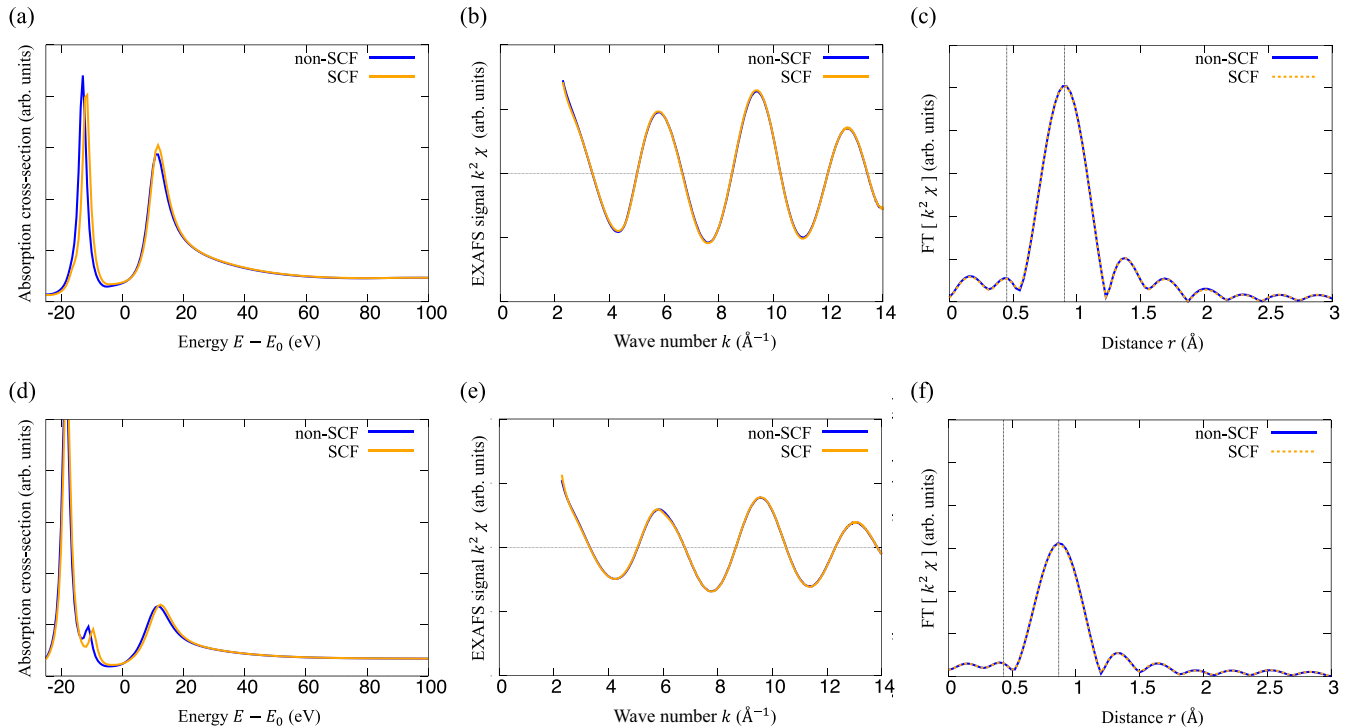


FIG. 7. (a)  $z$ -polarized XANES, (b) EXAFS signal, and (c) Fourier transform (FT) of the EXAFS signal for C K-edge of CO molecule oriented along the  $z$  axis, (d)  $z$ -polarized XANES, (e) EXAFS signal, and (f) Fourier transform of the EXAFS signal for O K-edge of CO molecule oriented along the  $z$ -axis, calculated with the Full Potential for non-SCF (blue line), and the SCF (orange line). A smooth polynomial background is used for the atomic background. Hanning window function is used for the Fourier transform, and we set  $k_{\min} = 3.0 \text{ \AA}^{-1}$ ,  $k_{\max} = 13.5 \text{ \AA}^{-1}$ , and  $\Delta k = 0.5 \text{ \AA}^{-1}$ .

but this effect is negligible in the high photoelectron energy region, such as EXAFS. Additionally, as seen from Fig. 6, the charge densities of about  $R/2$  from the absorbing atom between atoms are almost the same in the case of the C atom being the absorbing atom, and in the case of the O atom being the absorbing atom. No AXAFS Fourier transform peak can be found in both SCF and non-SCF calculations as shown in Figs. 7(c) and 7(f).

We further investigated the effect of scattering by interatomic charge densities on AXAFS using calculations of the polarization-averaged molecular-frame photoelectron angular distributions (PA-MFPADs) in CO molecules. PA-MFPADs have been known to be more sensitive to potential shape than XANES at high energies [70], and have the advantage that they are less dependent on the accuracy of the smooth background and less sensitive to extra oscillations created analytically. Nevertheless, we confirmed that the effect of charge density modulation at high energies is negligible, even in PA-MFPADs.

#### D. Verification the AXAFS of O K-edge of $(2 \times 1)\text{O}/\text{Cu}(110)$

In a previous study [14] a specific AXAFS signal was reported to be present in O K-edge spectra of the  $(2 \times 1)\text{O}/\text{Cu}(110)$  surface system. To put to a test this observation, we have applied O K-edge full-potential multiple scattering calculations for that system. For a detailed investigation of the anisotropy of the AXAFS such as Wende *et al.* performed in their experiments, we compared the Fourier transforms of the polarized EXAFS signals with E-vectors along the O-Cu rows on the surface and perpendicular to the O-Cu rows. When the E-vector is parallel to the O-Cu row, the EXAFS signal is significantly affected by photoelectron interference with the nearest Cu atom on the O-Cu row, and when the E-vector is perpendicular to the O-Cu row, the EXAFS signal is significantly affected by photoelectron interference with the second nearest Cu atom in the second layer. Wende *et al.* claimed that the dependence of the AXAFS peak position on the bond being probed is a strong indication that this feature does indeed stem from the scattering at interstitial charges between the absorbing and the backscattering atoms.

However, as shown in Fig. 8, the Fourier transform of the spectra obtained from the full-potential multiple scattering calculations showed no significant AXAFS peaks (solid blue line), contrary to the previous study (dashed black line). In this study, the atomic background was modeled using a smooth polynomial spline fitted to the calculated absorption cross-section. Specifically, three spline knots were placed at  $E - E_0 = 20.0$  eV above the edge (to minimize XANES contributions), at 20% and 50% of the maximum energy, and finally slightly above the maximum energy ( $E_{\text{max}} - E_0 + 3.0$  eV). A third-order polynomial was used for the fitting. This parameter set was optimized for the O K-edge of the  $(2 \times 1)\text{O}/\text{Cu}(110)$  system. For systems with different energy ranges, the spline intervals and polynomial order should be adjusted accordingly. The analytical code used to generate the polynomial background and perform the Fourier transform, along with examples for other systems, is provided in Supplemental Material [62]. We note that the present calculations are based on one-electron excitation theory and therefore do not

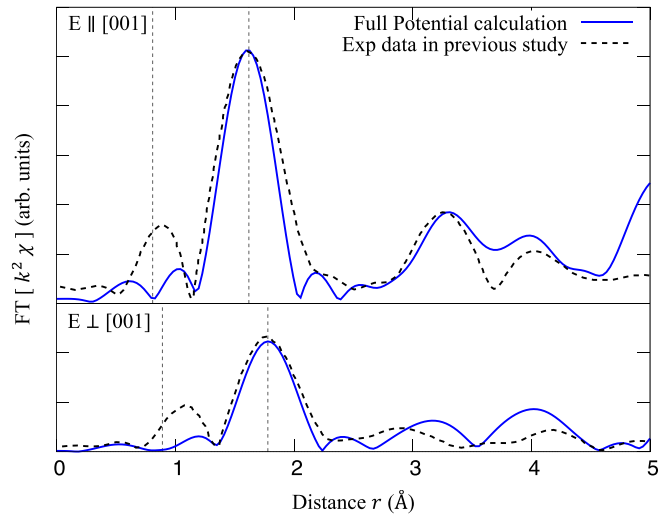


FIG. 8. Fourier transforms (FTs) of calculated O K-edge EXAFS signals (Full Potential) of the  $(2 \times 1)\text{O}/\text{Cu}(110)$  system obtained using a smooth atomic background (solid blue line). FTs were calculated using Hanning windows ( $k_{\text{min}} = 5.0 \text{ \AA}^{-1}$ ,  $k_{\text{max}} = 13.0 \text{ \AA}^{-1}$ , and  $\Delta k = 3.0 \text{ \AA}^{-1}$ ). Results are compared with a previous experimental work [14] (dashed black line).

include multielectron effects. In experimental spectra, steplike structures may appear due to such effects, for which a simple polynomial spline may not provide an adequate background model. In those cases, programs that explicitly treat multielectron excitations, such as GnXAS [53], are recommended.

The potential and charge density were calculated also self-consistently to investigate the effect of photoelectron scattering between neighboring atoms of this system on AXAFS. The self-consistent charge densities and Hartree potentials were calculated using the Vienna *ab initio* simulation package (VASP) [71,72] within the framework of density functional theory (DFT) [73,74], and reconstructed those for multiple scattering calculations with the interface package ES2MS [75]. The exchange-correlation interactions were treated using the local density approximation (LDA) [76].

Figure 9 shows the electron charge densities calculated with the Full Potential for (a) non-SCF, (b) SCF, and (c) the difference (SCF–non-SCF) of the surface of  $(2 \times 1)\text{O}/\text{Cu}(110)$  system for excited states with a core hole in O K-edge. These comparisons show the change of charge distributions for different electron configurations.

The calculated O K-edge  $E \parallel [001]$  EXAFS signals (Full Potential) of the  $(2 \times 1)\text{O}/\text{Cu}(110)$  system is shown in Fig. 10 for the (a) non-SCF (blue line) and SCF (orange line) cases. The EXAFS signals in the low energy (wave-vector) region show slight differences between the non-SCF and SCF calculations but they both agree quite well with the experimental data (calculations do not take into account thermal disorder). However, as shown by the Fourier transforms reported in Fig. 10(b), there is almost no difference between the non-SCF and SCF calculations, similar to the case of the calculations for C and O K-edge of CO molecule reported in the preceding section. Therefore, we conclude that AXAFS is not related to charge density modulation in this system as well.

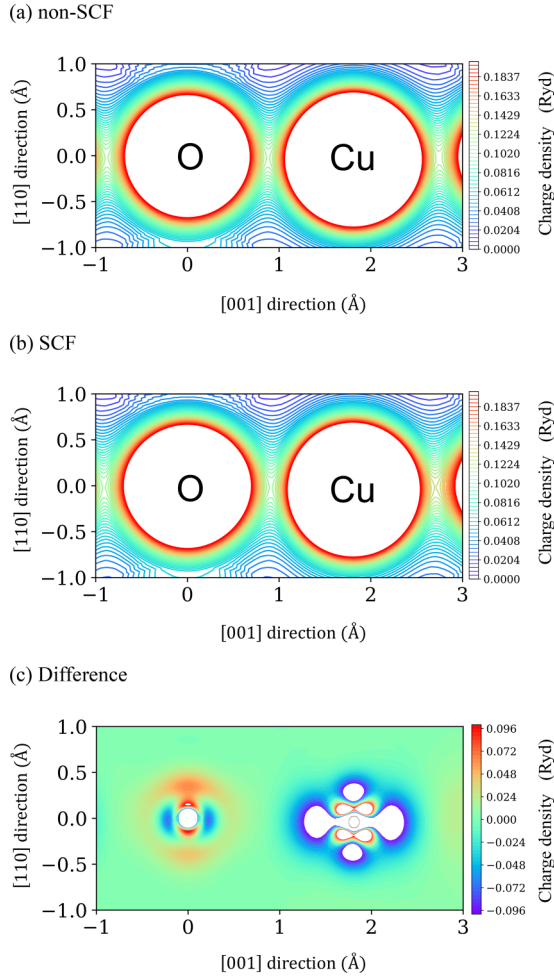


FIG. 9. Maps of the total electron charge densities (a) non-SCF, (b) SCF, and (c) the difference (SCF–non-SCF) of the  $(2 \times 1)\text{O}/\text{Cu}(110)$  surface system for excited states with a  $1s$  oxygen core hole.

However, as the results of the previous study discussed the AXAFS features in specific  $k$  ranges for EXAFS analysis, we have also performed different Fourier Transform calculations varying the Fourier transform  $k_{\min}$ ,  $k_{\max}$  range. In Fig. 11, we report the Fourier transforms calculated for  $k_{\min}$  fixed at  $5.0 \text{ \AA}^{-1}$  and varying  $k_{\max}$  from  $10.0$  to  $13.0 \text{ \AA}^{-1}$ . These Fourier transforms are normalized by the height of the peak at the distance of the nearest neighbor atoms. Although the effect of interstitial charge density modulation on the absorption cross-section should be more visible at lower wave-vector values, AXAFS is found to be absent in any Fourier transform range of choice in calculated signals. The Fourier transform ripple structure increases as the range of the Fourier transform window narrows, and ripple intensity is much larger than any possible  $R/2$  signal (see Sec. I of Supplemental Material [62] for details). Therefore we can confirm that the interatomic charge density modulation is not responsible for any possible AXAFS feature that is not found in the present calculations.

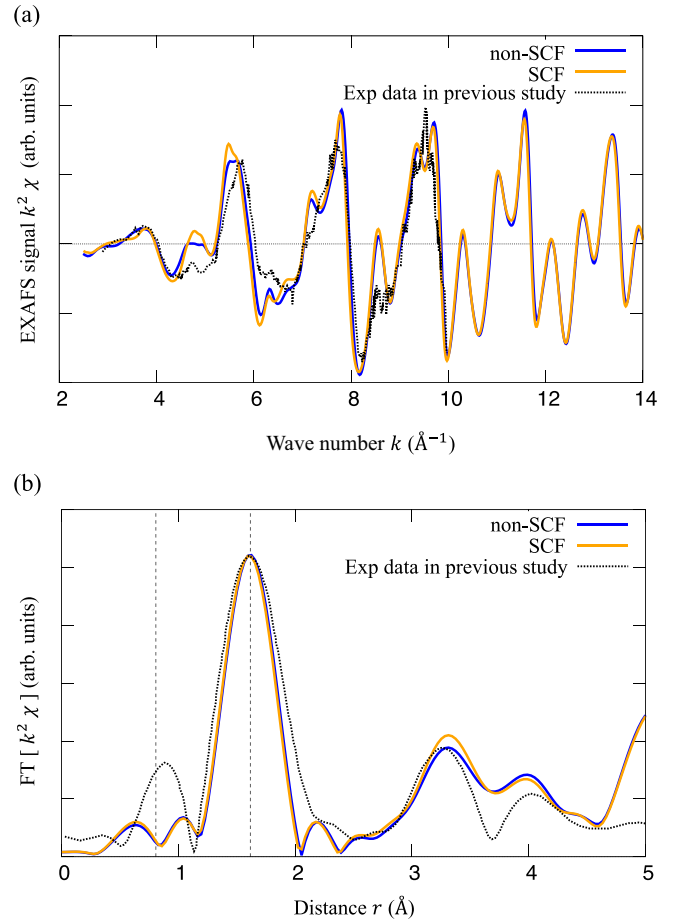


FIG. 10. (a) EXAFS signal extracted a smooth atomic background from the total absorption cross-section for O K-edge of  $(2 \times 1)\text{O}/\text{Cu}(110)$  system in the case of  $E \parallel [001]$  calculated with the Full Potential for the non-SCF (blue line) and the SCF (orange line). (b) Fourier transform (FT) of the EXAFS signal calculated using Hanning windows ( $k_{\min} = 5.0 \text{ \AA}^{-1}$ ,  $k_{\max} = 13.0 \text{ \AA}^{-1}$ , and  $\Delta k = 3.0 \text{ \AA}^{-1}$ ). Previous experimental work [14] are shown for comparison (dashed black line).

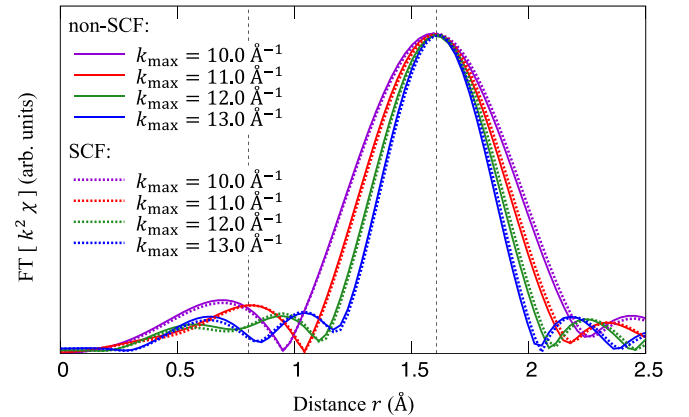


FIG. 11. Fourier transforms with different  $k$  limits of the calculated EXAFS signal (Full potential) of the  $(2 \times 1)\text{O}/\text{Cu}(110)$  system in the case of  $E \parallel [001]$  for the non-SCF (solid line) and the SCF (dotted line) cases. Fourier transforms (FTs) were calculated Hanning windows set to  $k_{\min} = 5.0 \text{ \AA}^{-1}$ ,  $k_{\max} = 10.0$  (purple line),  $11.0$  (red line),  $12.0$  (green line),  $13.0$  (blue line)  $\text{\AA}^{-1}$ , and  $\Delta k = 3.0 \text{ \AA}^{-1}$ .

In order to understand the origin of the AXAFS features reported in the previous study [14] we have carried out an EXAFS analysis by Wavelet transform [77–79] on both calculated (full potential, SCF) and experimental O K-edge ( $E \parallel [001]$ ) signals of the  $(2 \times 1)\text{O}/\text{Cu}(110)$  system. The Wavelet transform can resolve the wave-vector dependence of the EXAFS signals and is, therefore, better suited to distinguish between heavier (Cu) and lighter (O) backscattering atoms, even if they are at the same distance from the absorbing atom. Atoms with smaller atomic numbers have weaker scattering amplitudes decaying at high  $k$  values and thus appear as components at short  $k$  values in the Wavelet transform. Therefore particular attention should be paid to the intensity distribution around  $0.89 \text{ \AA}$ , where the AXAFS-related Fourier peak was previously reported. In the Wavelet representation, this enables us to determine which  $k$ -range (*i.e.*, which energy components of the EXAFS signal) is responsible for the apparent short-distance feature. For EXAFS analysis, the MorletE code [80] with a complex Morlet wavelet was used for the Wavelet transformation. To align the analytical conditions of the experimental and calculated data, the wave-vector range was set from  $3.5$  to  $10.0 \text{ \AA}^{-1}$ .

In Fig. 12, we report the calculated [panel (a)] and experimental [panel (b)] EXAFS signals related to a previous work [14] (O K-edge,  $(2 \times 1)\text{O}/\text{Cu}(110)$  system) as black curves. Those signals are superimposed on the results of the Morlet Wavelet transforms, shown as contour plots with different colors (intensity scale depicted on the right of Fig. 12). Here, Fig. 12(a) provides a theoretical reference in which the EXAFS signal is obtained without contributions from multi-electron excitation effects and is not affected by experimental noise, while Fig. 12(b) represents the experimentally derived EXAFS signal. In the experimental data, an intensity enhancement is observed at a distance of about  $0.89 \text{ \AA}$ , corresponding to the AXAFS peak previously reported in the Fourier transform analysis, whereas no corresponding feature is found in the theoretical result.

However, looking carefully at Fig. 12, one can see that the high intensity enhancement at about  $0.89 \text{ \AA}$  is mainly concentrated at high  $k$  values in the region  $6\text{--}10 \text{ \AA}^{-1}$ . This is not compatible with the scattering due to an embedded potential or interstitial charge density, which would show larger amplitudes at low wave-vector values like those of light atoms (few electrons involved in rather extended distributions). Therefore, we can safely conclude that the oscillation producing a Fourier transform peak at about  $0.89 \text{ \AA}$  does not originate from modulations of the charge density. A reason for the appearance of the Fourier transform AXAFS peak in the experimental data of Ref. [14] is more likely due to a specific background choice and shape producing spurious Fourier transform peaks at low distances. This may be another example of the fact that standard data analysis procedures do not produce a unique and unbiased EXAFS signal as mentioned in the introduction. In many cases, to avoid biased background choices, it is preferable to perform the EXAFS data analysis on the raw absorption data as it is carried out by EXAFS data analysis programs like GnXAS [53]. We can also conclude that when Fourier transform peaks appear at distances shorter than the nearest neighbors one, like in the so-called AXAFS

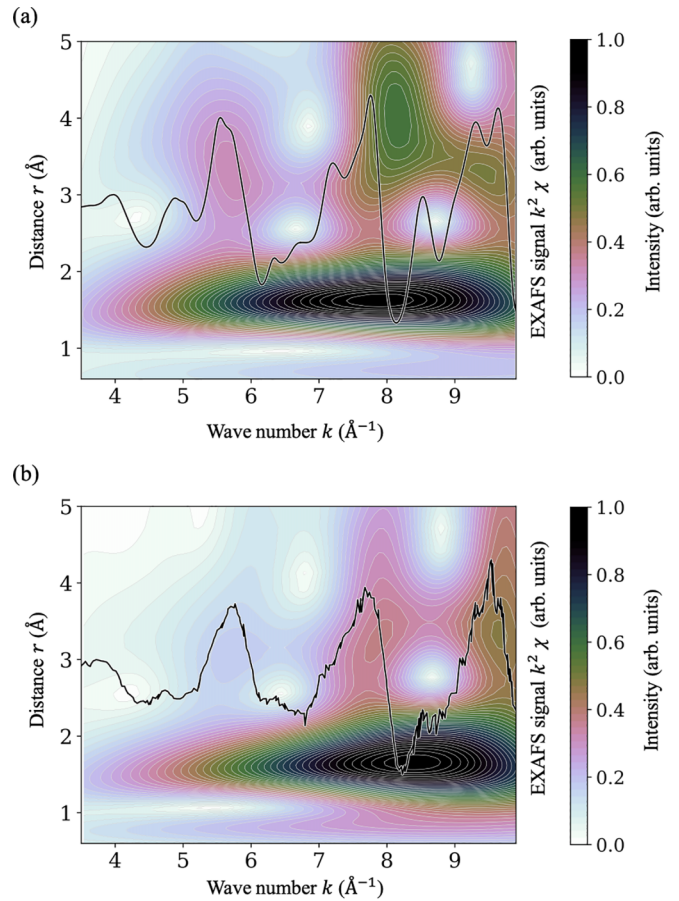


FIG. 12. The calculated and experimental O K-edge EXAFS signals of the  $(2 \times 1)\text{O}/\text{Cu}(110)$  system with  $E \parallel [001]$  are shown on a double scale, one related to the original  $k^2\chi(k)$  signals (black lines, scale on the right), the second related to the Morlet wavelet transforms (contour plots,  $r$  scale on the left and intensity color diagram on the right). More specifically: (a) theoretical result based on the EXAFS signal extracted from the total absorption cross-section calculated with the Full Potential using a charge density calculated self-consistently, after subtraction of a smooth atomic background, and (b) experimental result based on the previous work [14]. The contour plots represent the normalized intensity of the Morlet wavelet transform as a function of the photoelectron wave number  $k$  and the radial distance  $r$ . The color scale represents the wavelet transform intensity, with darker colors indicating higher intensity.

phenomenon, it would be useful to investigate their origin using the Wavelet transform.

#### IV. CONCLUSIONS

In this study, we have discussed the possible existence and origin of the so-called Atomic XAFS (AXAFS) contribution in the x-ray absorption background used to extract structural information by EXAFS in light of advanced multiple scattering calculations.

As a first step, we investigated the presence of an oscillatory contribution in the background using the muffin-tin approximation. In this case, it was found that the atomic absorption cross-section  $\sigma_{\text{at}}$  shows an oscillatory structure which is simply related to the potential truncation introduced

at the border of the muffin-tin sphere. Therefore, the Fourier transform of the oscillation of  $\sigma_{\text{at}}$  shows a peak at a distance corresponding to the radius of the muffin-tin sphere of the absorbing atom  $r = a$ , *i.e.*, at about  $R/2$ . However, this oscillatory structure is removed from the calculated EXAFS spectrum obtained using  $\sigma_{\text{at}}$  as a background and normalization factor. We thus verified that the muffin-tin approximation can not be used as a test for studying the AXAFS signal, due to the spurious oscillations introduced by the potential truncations as also previously suggested.

The possible occurrence of AXAFS was thus investigated using full-potential multiple scattering calculations beyond the simple muffin-tin approximation. The effects of the interatomic charge density modulation claimed to be responsible of the AXAFS phenomenon were put to a test for C and O K-edge of CO molecules and O K-edge of the  $(2 \times 1)\text{O}/\text{Cu}(110)$  system using self-consistent charge density distributions obtained by the MOLCAS and VASP, respectively. However, differently from previous studies, the presence of a relevant interstitial charge density modulation on AXAFS was not confirmed. Therefore, no significant AXAFS peak appeared in our numerical calculations, and the contribution of charge density modulation to the AXAFS was found to be negligible.

Furthermore, to discuss the origin of the AXAFS contribution found in a previous study, an EXAFS analysis by Wavelet transform was performed on the experimental EXAFS signal for O K-edge of the  $(2 \times 1)\text{O}/\text{Cu}(110)$  system ( $E \parallel [001]$ ). We found that the oscillatory signal contributing to the Fourier transform peak at the position of about  $R/2$  is due to the high-energy side of the EXAFS spectrum and can originate only from signals incompatible with small charge modulations. So we infer that the oscillation of the background is not due to AXAFS but to the particular choice made by the authors for EXAFS analysis, such as atomic background and normalization defining the EXAFS signal.

The main conclusion of this work is thus that the existence of AXAFS is not confirmed and can be considered just a speculation. The appearance of Fourier transform peaks at low distances as a consequence of low-frequency oscillations of the atomic background discussed in some previous works has rather to be regarded as an effect of the standard procedure of the extraction of the experimental EXAFS signal, which does not provide a unique and unbiased  $\chi(k)$  signal. On the other hand, there are many consisting evidences of the real effect due to the opening of multielectron channels in the x-ray absorption spectra that are known to produce anomalies in the background function used for EXAFS analysis and can be often confused with AXAFS.

### ACKNOWLEDGMENTS

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### DATA AVAILABILITY

All numerical data supporting the figures in this paper are available in the Zenodo repository (see the reference to the Zenodo dataset) [81]. The dataset includes the numerical data corresponding to the figures in the manuscript and the code used for the Fourier transform analysis. Detailed descriptions of the data files, calculation conditions, and analysis procedures are provided in the Supplemental Material [62] and the accompanying README file.

### APPENDIX: APPROXIMATION ABOUT THE PHASE SHIFT IN POTENTIAL STEP MODEL

In this study, we use the potential step model introduced in Sec. III A, where the total phase shift is approximated as the sum of the Coulomb phase shift and the phase shift due to a 3d spherical-well potential:  $\delta_l \sim \delta_l^{\text{Coul}} + \delta_l^{\text{step}}$ . However, when a short-range potential  $V(r)$  is added to the Coulomb potential  $V_c(r)$ , the resulting phase shift is not simply additive. Instead, it takes the form,  $\delta_l = \delta_l^{\text{Coul}} + \tilde{\delta}_l$ , where  $\tilde{\delta}_l$  differs from  $\delta_l^{\text{step}}$  [60]. This Appendix examines the validity of the above approximation.

First, consider the case of a 3d spherical-well potential without the Coulomb field:

$$U(r) = \begin{cases} -U_0 & (U_0 > 0) \quad r < a \\ 0 & r \geq a \end{cases} \quad (\text{A1})$$

The radial wave function for  $r < a$  is

$$R_l(r) = C_l j_l(\kappa r) \quad (\text{A2})$$

where  $j_l$  is the spherical Bessel function,  $C_l$  is the function independent on  $r$ , and  $\kappa = \sqrt{2m(E + U_0)/\hbar^2}$ . For  $r > a$ , where there is no interaction, the radial wave function is given by

$$R_l(r) = j_l(\kappa r) - \tan \delta_l^{\text{step}} n_l(\kappa r), \quad (\text{A3})$$

where  $n_l$  is the spherical Neumann function and  $\delta_l^{\text{step}}$  is the phase shift of the Square well potential. From the boundary conditions at  $r = a$ , the phase shift can be obtained as follows:

$$\tan \delta_l^{\text{step}} = \frac{k j_l(\kappa a) j_l'(ka) - \kappa j_l'(\kappa a) j_l(ka)}{k j_l(\kappa a) n_l'(ka) - \kappa j_l'(\kappa a) n_l(ka)}. \quad (\text{A4})$$

Here,  $j_l'(x) = d(j_l(x))/dx|_{x=ka}$ . In the high-energy limit ( $ka \gg 1$ ), using the asymptotic forms of the spherical Bessel function and spherical Neumann function,

$$\begin{aligned} j_l(x) &\xrightarrow{x \rightarrow \infty} \frac{1}{x} \sin\left(x - \frac{l\pi}{2}\right), \\ n_l(x) &\xrightarrow{x \rightarrow \infty} -\frac{1}{x} \cos\left(x - \frac{l\pi}{2}\right), \end{aligned}$$

the approximate formula for phase shift is obtained as follows:

$$\tan \delta_l^{\text{step}} \sim \tan \left[ -ka + \frac{l\pi}{2} + \arctan \left\{ \frac{k}{\kappa} \tan \left( \kappa a - \frac{l\pi}{2} \right) \right\} \right], \quad (\text{A5})$$

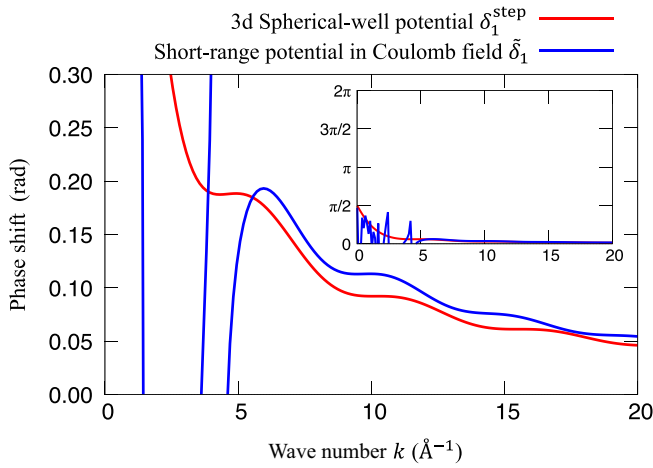


FIG. 13. Phase shift of the 3d spherical-well potential  $\delta_1^{\text{step}}$  (red solid line) and the additional phase shift when a 3d spherical-well potential is added as a short-range potential to the Coulomb field  $\tilde{\delta}_1$  (blue dotted line). The inset shows the phase shifts plotted over the extended range  $0 \leq \delta \leq 2\pi$ .

$$\delta_l^{\text{step}} \sim -ka + \frac{l\pi}{2} + \arctan \left\{ \frac{k}{\kappa} \tan \left( \kappa a - \frac{l\pi}{2} \right) \right\}. \quad (\text{A6})$$

Now consider the case where the same 3d spherical-well potential is added to the Coulomb field as a short-range potential:

$$U(r) = \begin{cases} -\frac{Z}{r} - U_0 & (U_0 > 0) \quad r < a \\ -\frac{Z}{r} & r \geq a \end{cases}. \quad (\text{A7})$$

The radial wave-function solution for  $r < a$  is

$$R_l(r) = C_l F_l(\kappa r), \quad (\text{A8})$$

and for  $r > a$ , it is given by

$$R_l(r) = F_l(\kappa r) - \tan \tilde{\delta}_l G_l(\kappa r), \quad (\text{A9})$$

where  $F_l$  and  $G_l$  are the regular and irregular Coulomb wave functions. From the boundary conditions at  $r = a$ , the additional phase shift can be obtained as follows:

$$\tan \tilde{\delta}_l = \frac{k F_l(\kappa a) F_l'(ka) - \kappa F_l'(\kappa a) F_l(ka)}{k F_l(\kappa a) G_l'(ka) - \kappa F_l'(\kappa a) G_l(ka)}, \quad (\text{A10})$$

$$\tilde{\delta}_l = \arctan \left\{ \frac{k F_l(\kappa a) F_l'(ka) - \kappa F_l'(\kappa a) F_l(ka)}{k F_l(\kappa a) G_l'(ka) - \kappa F_l'(\kappa a) G_l(ka)} \right\}. \quad (\text{A11})$$

In the high-energy limit,  $F_l(x)$  and  $G_l(x)$  behave asymptotically as

$$F_l(x) \xrightarrow{x \rightarrow \infty} \sin \left\{ x - \frac{l\pi}{2} - \eta \ln(2x) + \delta_l^{\text{Coul}} \right\}, \quad (\text{A12})$$

$$G_l(x) \xrightarrow{x \rightarrow \infty} -\cos \left\{ x - \frac{l\pi}{2} - \eta \ln(2x) + \delta_l^{\text{Coul}} \right\}, \quad (\text{A13})$$

where  $\sigma_l$  is the Coulomb phase shift. Substituting these forms into the above expression (A11) yields  $\tilde{\delta}_l$  as the correction to the Coulomb phase shift due to the presence of the short-range potential.

As shown in Fig. 13, the two phase shifts  $\delta_1^s$  (red solid line) and  $\tilde{\delta}_1$  (blue solid line) exhibit noticeable differences in the low-energy region, primarily due to the breakdown of the asymptotic approximation for the Coulomb wave functions. The inset shows the phase shifts displayed over an extended range  $0 \leq \delta \leq 2\pi$ . However, in the high-energy region relevant to EXAFS, the difference in their slopes is approximately  $0.0012 \text{ rad } \text{\AA}$ , which is negligible. This validates the approximation  $\delta_l = \delta_l^{\text{Coul}} + \tilde{\delta}_l \sim \delta_l^{\text{Coul}} + \delta_l^{\text{step}}$ , employed in the potential step model, confirming its accuracy in the EXAFS-relevant energy region.

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