

Probability density of wave function of excited photoelectron: understanding XANES features

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Interpretation of XANES spectra suffers from a poor intuitive understanding of the relation between spectral features and structural elements of a material. An attempt to alleviate this shortcoming is made by exploring a spatial distribution of probability density of wave functions of photoelectrons excited during the photoabsorption process. One has to add incoherently squares of wave functions which describe participating photoelectron diffraction (PED) processes, weighted by normalized PED cross sections. As an example, we investigate probability density of wave functions relevant to Ag L_1 and L_3 XANES of Ag₂O.

1. Introduction

There are two challenges in the theory of x-ray absorption near-edge structure (XANES) spectroscopy: How to calculate XANES most accurately and how to interpret it in physically plausible terms. For the latter task, it would help to have a means to connect specific spectral and structural features one with another.

Various procedures were applied in the past, such as inspecting the effect of adding or removing certain atoms in the test cluster (Šipr *et al.*, 1999), investigating the dependence of the height of the pre-peak on the geometry of the nearest neighborhood (Farges *et al.*, 1997), calculating XANES by summing over many scattering paths (Zabinsky *et al.*, 1995) or employing “direct inversion” technique for obtaining atomic positions from experimental XANES (Migal, 1999). In this paper, we explore the potential of evaluating the density of the photoelectron wave function. Such a procedure can be — from a certain viewpoint — considered as an answer to the naive question “where the electron really is”.

2. The wave function problem

An immediate evaluation of the probability density $P(\mathbf{r})$ via the notorious *ansatz*

$$P(\mathbf{r}) = |\psi_{\text{phe}}(\mathbf{r})|^2 \quad (1)$$

is prevented by the fact that it is not clear what ought to be taken for the photoelectron wave function $\psi_{\text{phe}}(\mathbf{r})$. The XANES intensity is proportional to the probability w of absorption of a photon by a core electron. It can be expressed, within a first-order perturbation theory, as

$$w = \frac{2\pi}{\hbar} \int d\nu |\langle \phi_c | H_I | \psi_\nu \rangle|^2 \delta(E_c + \hbar\nu - E_\nu) \quad (2)$$

where H_I is the interaction hamiltonian perturbing the initial core state $|\phi_c\rangle$ of the electron and the sum/integration over ν spans any complete set of final electron wave functions $|\psi_\nu\rangle$. Applying standard techniques, Eq. (2) can be transformed into expression involving sums over Bloch states (Müller & Wilkins, 1984), molecular cluster basis functions (Dill & Dehmer, 1974), photoelectron

diffraction states (Lee, 1976) or, in the case of Green function formalism, disposing of the final state wave functions altogether (Vvedensky, 1992). The choice of the set of wave functions in Eq. (2) does not affect the outcome.

It follows from Eq. (2), that the total absorption rate is a resultant of many *incoherent* processes. Hence there is *no single wave function* like $|\psi_{\text{phe}}\rangle$ which could have been inserted into Eq. (1). Rather, the quantity of interest should be a weighted sum of probability densities of those wave functions which describe states participating in the absorption process,

$$P(\mathbf{r}) = \sum_f w_f |\psi_f(\mathbf{r})|^2 \quad (3)$$

The weights w_f are the probabilities that a core electron $|\phi_c\rangle$ is ejected into the state $|\psi_f\rangle$,

$$w_f \sim |\langle \phi_c | H_I | \psi_f \rangle|^2 \quad (4)$$

and ought to be normalized so that their sum yields w . Unlike in the case of Eq. (2), the outcome of Eqs. (3)–(4) *does depend* on the choice of the set of wave functions $|\psi_f\rangle$ (complete on the energy surface determined by the delta function in Eq. (2)). It is only matter of physical intuition, not formal mathematical procedures, to establish which set of states $|\psi_f\rangle$ is relevant to the physical process in question.

For transitions to bound states of molecules, the states $|\psi_f\rangle$ are just asymptotically decaying bound states $|\psi_b\rangle$, normalizable so that $\int d\mathbf{r} |\psi_b(\mathbf{r})|^2 = 1$. The choice of $|\psi_f\rangle$ is not so straightforward for transitions to the continuous part of the spectrum. Let us contemplate a finite cluster of atoms. As a result of absorption of a photon, a core electron is torn off an atom and must finally turn into a plane wave with a well-defined momentum direction $\hat{\mathbf{k}}$. Hence, elementary incoherent processes involved in (3) must be photoelectron diffraction (PED) events. Indeed, x-ray absorption is nothing else but angularly averaged PED (Lee, 1976). The final states $|\psi_f\rangle$ are therefore time-inversed scattering states, $|\psi_{\mathbf{k}}^{(-)}\rangle$, which are in turn solutions of the Lippman-Schwinger equation (Bethel & Salpeter, 1957; Lee, 1976; Natoli *et al.*, 1986)

$$\psi_{\mathbf{k}}^{(-)}(\mathbf{r}) = \exp(i\mathbf{k}\mathbf{r}) + \int d\mathbf{r}' G_0^{(-)}(\mathbf{r}, \mathbf{r}') V(\mathbf{r}') \psi_{\mathbf{k}}^{(-)}(\mathbf{r}') \quad (5)$$

where $G_0^{(-)}(\mathbf{r}, \mathbf{r}')$ is the advanced free electron Green function and $V(\mathbf{r}')$ describes the potential of the cluster. These states are normalizable to the delta function $\delta(\mathbf{k})$. Therefore, by evaluating (3)–(4), one gets only a relative probability, which cannot be properly normalized. However, by fixing the normalization of $|\psi_{\mathbf{k}}^{(-)}\rangle$ via (5), i.e., by “pegging” it to the free-electron wave function $\exp(i\mathbf{k}\mathbf{r})$, one keeps a universal definition of $P(\mathbf{r})$, making thus possible to compare $P(\mathbf{r})$ calculated in various circumstances. Note that by taking $|\psi_{\mathbf{k}}^{(-)}\rangle$ from (5), the density $P(\mathbf{r})$ is made dimensionless.

The wave function $|\psi_{\mathbf{k}}^{(-)}\rangle$ can be viewed as that wave function, from which a plane wave evolves within a sufficiently long time. It represents the state into which the core electron “jumps” as a result of the electromagnetic perturbation H_I . Thus, the quantity $P(\mathbf{r})$ ought to be interpreted as the probability, that the electron ejected from a core level can be found at position \mathbf{r} , “just after” having absorbed an x-ray photon. By evaluating $P(\mathbf{r})$, one provides the most sensible answer to the provocative question from the end of the Introduction. We bear in mind, at the same time, that

this Lippman-Schwinger-like description cannot fully substitute a proper time-dependent treatment.

3. Evaluating probability density $P(\mathbf{r})$

By inserting $|\psi_{\mathbf{k}}^{(-)}\rangle$ into (3)–(4), we get

$$P(\mathbf{r}) = \int d\hat{\mathbf{k}} \frac{1}{4\pi} \frac{\sigma_{\text{PED}}(\hat{\mathbf{k}})}{\sigma_{\text{XAS}}} |\psi_{\mathbf{k}}^{(-)}(\mathbf{r})|^2, \quad (6)$$

where

$$\sigma_{\text{PED}}(\hat{\mathbf{k}}) \sim |\langle \phi_c | H_I | \psi_{\mathbf{k}}^{(-)} \rangle|^2 \quad (7)$$

is the PED cross-section and its angular average

$$\sigma_{\text{XAS}} = \frac{1}{4\pi} \int d\hat{\mathbf{k}} \sigma_{\text{PED}}(\hat{\mathbf{k}}) \quad (8)$$

is the x-ray absorption cross-section. For muffin-tin potentials, the wave function $\psi_{\mathbf{k}}^{(-)}(\mathbf{r})$ can be expanded within each sphere in terms of solutions of single-site Schrödinger equation (Natoli *et al.*, 1986). Evaluation of $P(\mathbf{r})$ within any muffin-tin sphere is therefore straightforward.

Actual calculations reveal that the probability density $P(\mathbf{r})$ defined by (6) is dominated by its density of states (DOS) constituent,

$$P_{\text{DOS}}(\mathbf{r}) = \int d\hat{\mathbf{k}} \frac{1}{4\pi} |\psi_{\mathbf{k}}^{(-)}(\mathbf{r})|^2 \quad (9)$$

(indeed, $P_{\text{DOS}}(\mathbf{r})$ is just the local DOS, $n(\mathbf{r}, E) \equiv -(2/\pi) \text{Im}G(\mathbf{r}, \mathbf{r}; E)$, multiplied by $2\pi^2/k$). Typically, P does not differ from P_{DOS} by more than 10%. Specific XANES-related effects are thus obscured in $P(\mathbf{r})$ by generic DOS effects. Therefore, we introduce the *difference probability density* $\delta P(\mathbf{r}) \equiv P(\mathbf{r}) - P_{\text{DOS}}(\mathbf{r})$,

$$\delta P(\mathbf{r}) = \int d\hat{\mathbf{k}} \frac{1}{4\pi} \left(\frac{\sigma_{\text{PED}}(\hat{\mathbf{k}})}{\sigma_{\text{XAS}}} - 1 \right) |\psi_{\mathbf{k}}^{(-)}(\mathbf{r})|^2. \quad (10)$$

In this way, effects not directly connected with XANES are filtered out.

4. Results

As an illustrative example, we present here probability densities relevant to Ag L_1 and L_3 XANES of Ag_2O , calculated within the real-space multiple-scattering formalism for a cluster of 57 atoms, using for both edges identical muffin-tin potential without core hole.

The wave function $\psi_{\mathbf{k}}^{(-)}(\mathbf{r})$ inside a muffin-tin sphere can be readily found using molecular-oriented formalism of Dill & Dehmer (1974). The coefficients of the expansion of $\psi_{\mathbf{k}}^{(-)}(\mathbf{r})$ in terms of single-site wave functions are determined by a version of the notorious multiple scattering equation. Necessary formulas can be found, e.g., in Natoli *et al.* (1986) — in particular Eqs. (2.1), (2.13), (2.14), (2.18), (2.20), (2.25), and (2.28) of that paper. Technical details are left out for a separate publication (Šipr, 2001).

In order not to be overburdened with too many data, we calculate the “average probability density” $\delta P^{(j)}$ for an atom at $\mathbf{R}^{(j)}$, defined as the average of $\delta P(\mathbf{r})$ over a normalization sphere around $\mathbf{R}^{(j)}$. The quantity $\delta P^{(j)}$ is thus a measure of how the probability, that a photoelectron can be found in the vicinity of the j -th atom, is affected by the XANES process.

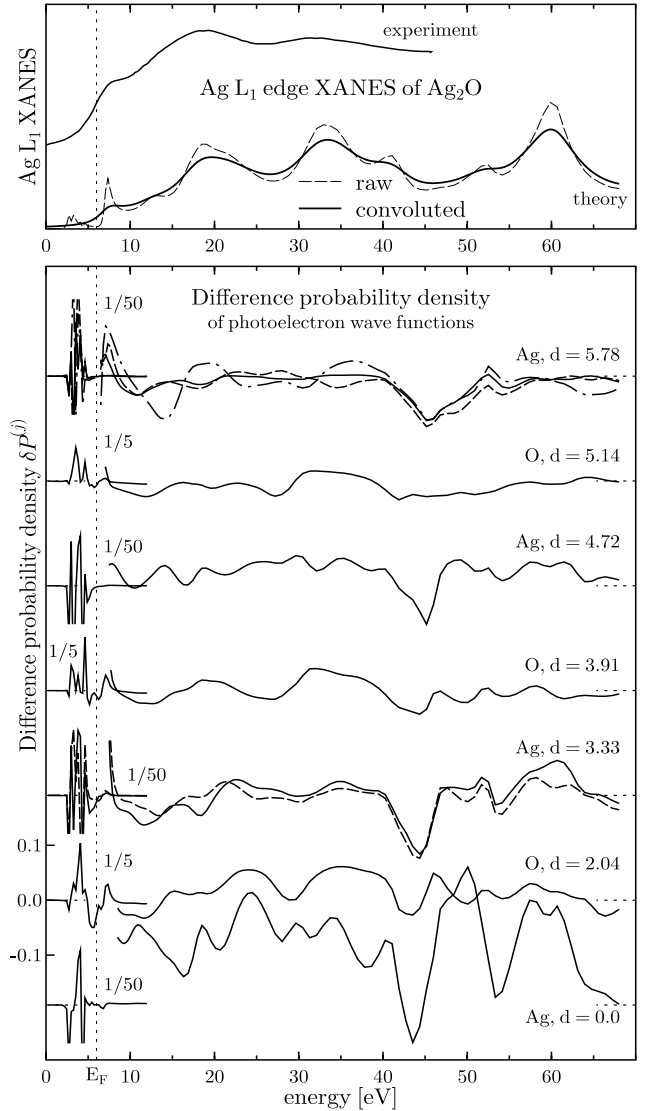


Figure 1

Difference probability density and XANES spectrum at Ag L_1 edge of Ag_2O . Each graph in the lower block corresponds to a coordination sphere identified by chemical type and distance from the center. Two different probability density curves for the 2-nd and three curves for the 6-th coordination sphere are distinguished by their line types. The vertical scale is shown for the second block from the bottom only. Zeros for each block are marked by thin dashed line at the right margin. For $E < 12$ eV, probability density curves are vertically scaled down by 50 or 5, as labeled. Calculated XANES is displayed both in its raw form and partially smeared by a lorentzian convolution.

The outcome of this procedure is displayed in Figs. 1–2. Each sub-graph corresponds to one coordination sphere, labeled by its distance (Table 1). The XANES curves are included for comparison (Czyżyk *et al.*, 1989; Šipr *et al.*, 1999). The Fermi level E_F was put at 6 eV as indicated, so only states above it contribute to XANES. All probability density curves were vertically scaled down close to the edge, as hinted by the labeling.

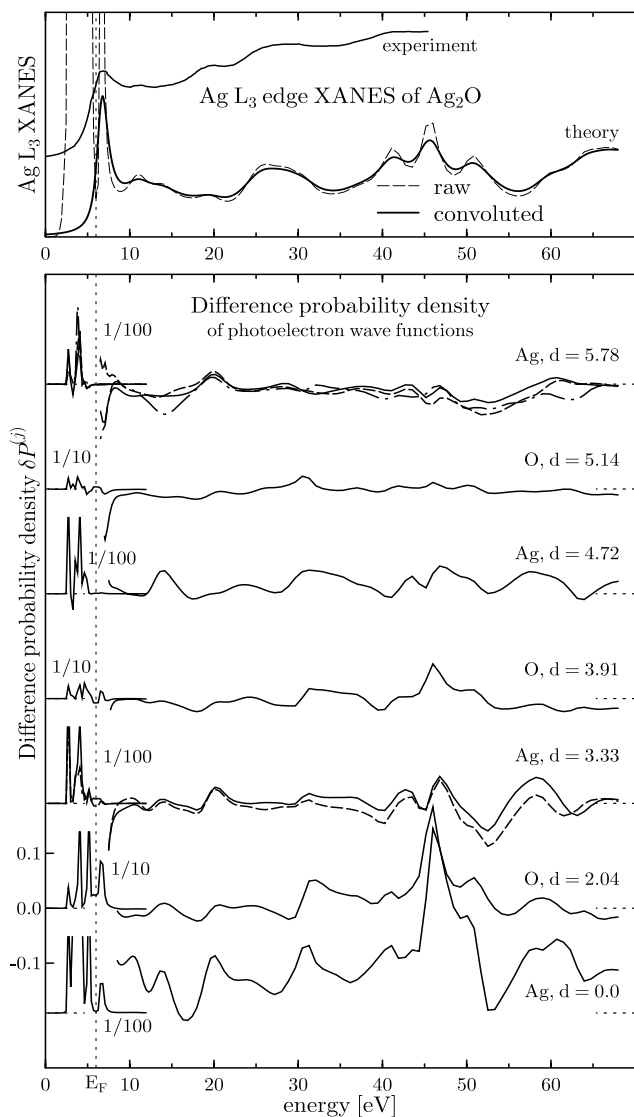


Figure 2
Difference probability density and XANES spectrum at Ag L_3 edge of Ag_2O . All curves have similar meaning as in Fig. 1, only the vertical scaling in the $E < 12$ eV region is now by factors of 100 and 10.

Typically, probability density curves for different atoms belonging to the same coordination sphere are identical. This is probably due to the fact that the spectra are unpolarized. Only for the 2-nd and 6-th coordination spheres, two and three distinct classes emerge, respectively — as marked in the plots.

5. Discussion

It is evident from Figs. 1–2, that the fine structure of difference probability density curves $\delta P^{(j)}(E)$ does *not* copy corresponding XANES curves. This can be interpreted as demonstration that XANES is not generated by mere “presence” of the photoelectron but rather by interference of many multiple-scattering paths. Plausibly, probability densities differ for L_1 and L_3 edges, as photoelectron wave function must depend on the initial core state.

Table 1

Coordination spheres around a central Ag atom in Ag_2O .

sphere no.	0	1	2	3	4	5	6
type	Ag	O	Ag	O	Ag	O	Ag
coord. no.	1	2	12	6	6	6	24
distance [Å]	0.00	2.04	3.33	3.91	4.72	5.14	5.78

One can assess the degree of localization of a particular XANES resonance by observing the dependence of its possible counterparts in the difference probability densities on the distance of respective atoms from the center. E.g., the L_1 first peak at ~ 7 –8 eV is a delocalized one, as the probability density peak at that energy is nearly as high for the 4-th coordination sphere as for the second one (Fig. 1, scale-down curves). On the other hand, the L_3 white line at 7 eV is highly localized, as its probability density counterparts essentially die out beyond the 2-nd sphere.

The dependence of the probability density on the distance provides a complementary, rather than duplicative, information with regard to the effect of cluster size on the XANES spectrum. Namely, the fact that wave function probability is high at a point A and low at another point B does not necessarily mean that region around B is not important: In a standard particle-in-a-box case, the probability density is low close to the walls of the box and yet these walls *are* important. Hence, to get a complete view, one should investigate both probability density of the photoelectron and effects of removing specific atoms from the cluster. Such a procedure might be helpful especially in the case of polarized spectra.

6. Conclusions

It is possible to assess the probability density of photoelectrons participating in a XANES process. The quantity in question is a sum of squares of wave functions describing PED processes, weighted by normalized PED cross sections. The fine structure of such a probability density, taken as a function of photoelectron energy, does not copy the corresponding XANES, which can be seen as a consequence of the interference nature of x-ray absorption fine structure. The spatial dependence of this probability density provides information complementary to XANES cluster size effect analysis.

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