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# K-edge x-ray absorption spectra in transition-metal oxides beyond the single-particle approximation: Shake-up many-body effects

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Near-edge structures in $K$-edge x-ray absorption spectra (XAS) are widely investigated to understand the electronic and local structure in materials. The precise interpretation of these spectra with the help of calculations is hence of prime importance, especially for the study of correlated materials which have a complicated electronic structure per se. The single-particle approach, for example, has generally limited itself to the dominant dipolar cross section. It has long been known, however, that effects beyond this approach should be taken into account, due to both the inadequacy of such calculations when compared to experiment and the presence of shakeup many-body satellites in core-level photoemission spectra of correlated materials. This effect should manifest itself in XANES spectra, and the question is first how to account for it theoretically and second how to verify it experimentally. By using state-of-the-art first-principles electronic structure calculations and 1$s$ photoemission measurements, we demonstrate that shakeup many-body effects are present in $K$-edge XAS dipolar spectra of NiO, CoO, and CuO at all energy scales. We show that shakeup effects can be included in $K$-edge XAS spectra in a simple way by convoluting the single-particle first-principles calculations including core-hole effects with the 1$s$ photoemission spectra. We thus describe all features appearing in the XAS dipolar cross section of NiO and CoO and obtain a dramatic improvement with respect to the single-particle calculation in CuO. These materials being prototype correlated magnetic oxides, our work points to the presence of shakeup effects in $K$-edge XANES of most correlated transition-metal compounds and shows how to account for them, paving the way to a precise understanding of their electronic structure.

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## I. INTRODUCTION

Low-energy excitations of correlated materials are strongly influenced by electron-electron interaction effects beyond the single-particle approximation. This is particularly evident in core-level x-ray photoemission spectra of transition-metal compounds where the occurrence of many-body satellites is well documented (for a review see Ref. 1). As for x-ray absorption, interpretation of the dipolar $K$-edge x-ray-absorption spectra (XAS) cross section heavily relies on standard single-particle first-principles calculations[2–5] that neglect shakeup excitations. Since dipolar $L_{2,3}$-edge XAS mostly samples $d$ states of the absorbing atom which are more prone to effects of correlation than $p$ states, one normally assumes that shakeup effects are visible mostly in $L_{2,3}$-edge XAS and not in $K$-edge XAS. However, a recent work[6] shows that in NiO the single-particle dipolar $K$-edge spectrum misses some near-edge and far-edge features present in the experimental one.

We concentrate on shakeup many-body excitations arising from a valence electron excitation following the creation of a core hole by the incident x ray.[7] In the past, shakeup effects in core-hole photoemission spectra have been investigated in the framework of quantum-chemical calculations,[8] by using model Hamiltonians[1,9,10] or by computing scalar products of Slater determinants built from nonorthogonal orbitals.[11] The occurrence of these effects in x-ray photoemission spectroscopy (XPS) is well established but they have also been shown to occur at $M_{4,5}$ edges of mixed-valent compounds[12] and at $L_{2,3}$ x-ray-absorption spectra of transition metals and rare-earth compounds[13,14] and were proposed as a possible explanation of the double peak structure in dipolar $K$-edge XAS of high $T_c$ cuprates[15] and copper compounds in general.[16] However, this attribution was questioned in Refs. 2 and 17 and the double peak structure was suggested to have a single-particle origin.

Nailing down the importance of these effects has been difficult due to complications related to many-body calculations but also to the paucity of experimental 1$s$ photoemission spectra. In this work, following earlier suggestions, we demonstrate that shakeup many-body effects can be included in a simple way in $K$-edge XAS spectra by convoluting the single-particle first-principles calculations with experimental $1s$ photoemission spectra, some of which we have newly measured. We show that this procedure explains all features in $K$-edge XAS spectra of NiO and CoO and strongly improves the agreement with experimental data in CuO. Our work points out the relevance of these effects in $K$-edge dipolar XAS of all compounds displaying multiple structures in photoemission spectra.

The structure of the paper is the following. In Sec. II A and II B, following Ref. 18, we briefly sketch the demonstration of the convolution formula relating the many-body XAS cross section to the single-particle one via the photoemission spectrum. We then present experimental details concerning our measured photoemission spectra in Sec. III. The experimental results and the theoretical understanding are presented in Sec. IV.

## II. THEORY

### A. Shakeup theory

Shakeup satellites are many-body peaks present in core-electron spectra. They originate from a valence electron excitation following the creation of a core hole by the incident x ray.[7] Quantum chemical calculations of shakeup satellites have been recently reviewed by Carravetta and Ågren.[8]

An electric dipole transition between two Slater determinants built from the same set of orbitals does not allow for shakeup satellites. Indeed, the orthogonality of orbitals enables only one transition from the core level to the empty one. Therefore, a shakeup can only be obtained by describing the (initial) state with a linear combination of Slater determinants or by using different orbitals for the initial and final determinants.[19] The first approach was extensively used by Sawatzky and collaborators.[9] Here we use dipole transitions between single Slater determinants using nonorthogonal orbitals, the orbitals of the final state being relaxed in the presence of the core hole.

The possibility of describing the electronic state of NiO by a single Slater determinant was strongly advocated by Brandow and Harrison.[20–22] Moreover, relaxed Slater determinants can sometimes describe a state much better than the sum of a small number of unrelaxed Slater determinants.[20]

A single Slater determinant is also the noninteracting ground state of the Kohn-Sham version of density-functional theory (DFT). The corresponding Kohn-Sham orbitals are usually considered to have no physical meaning. This would be a problem for our approach that calculates electric dipole transitions between these orbitals. The success of DFT calculations of XAS seems to indicate that Kohn-Sham orbitals are physically meaningful, and indeed Gidopoulos[23] discovered that the noninteracting Kohn-Sham ground state is the best approximation of the true ground state in a subtle way. To describe his finding, let $h(\mathbf{r}) = -\hbar^2\Delta/2m + v(\mathbf{r})$ be a one-body potential and $H_v = \sum_i h(\mathbf{r}_i)$ be the corresponding noninteracting many-body Hamiltonian. Denote by $|\Psi_v\rangle$ the (Slater determinant) ground state of $H_v$ and by $|\Psi\rangle$ the ground state of the interacting Hamiltonian $H$. By the Rayleigh-Ritz minimum principle we have $\langle\Psi|H_v|\Psi\rangle - \langle\Psi_v|H_v|\Psi_v\rangle > 0$. Gidopoulos proved that the potential $v$ that minimizes this difference is precisely the Kohn-Sham potential. In that sense, the Kohn-Sham determinant and the Kohn-Sham potential provide the best single-particle description of the ground state of an interacting system.

Therefore, it is relevant to describe shakeup processes with nonorthogonal Slater determinants. Other calculations were carried out within this framework by Tyson,[24] who could calculate double-electron excitations in XAS[25] for $\mathrm{LN}_{4,5}$ edges. Similar calculations for x-ray photoemission spectroscopy are more common.[11]

### B. Cross section

The many-body x-ray photoemission cross section can be written as[26]

$$\sigma_{\mathrm{XPS}}(\epsilon_k) = \frac{2\pi}{\hbar}\sum_f |\langle k,\Psi_f(N-1)|M|\Phi_i(N)\rangle|^2 \times\delta(\epsilon_k - \hbar\omega - E_i(N) + E_f(N-1)). \quad (1)$$

$E_i(N)$ is the energy of the $N$ electrons ground state, and $|\Phi_i(N)\rangle$, $E_f(N-1)$, and $|\Psi_f(N-1)\rangle$ are excited energies and states of the $N-1$ electron system with a core hole. The state $|k,\Psi_f(N-1)\rangle$ is obtained from $|\Psi_f(N-1)\rangle$ by creating a photoelectron with momentum $k$ and energy $\epsilon_k$, namely, $|k,\Psi_f(N-1)\rangle = c_k^+|\Psi_f(N-1)\rangle$. Finally $\hbar\omega$ is the energy of the incident x-ray beam. The electric dipole transition operator is denoted by $M$. The transform $I_{\mathrm{XPS}}(t)$ of the XPS cross section is defined as

$$\sigma_{\mathrm{XPS}}(\epsilon) = 2\mathrm{Re}\int_0^{+\infty} dt e^{i\epsilon_+ t} I_{\mathrm{XPS}}(t), \quad (2)$$

where $\epsilon_+ = \epsilon + i\eta$ and Eq. (2) has to be understood as the limit for $\eta \to 0^+$.

The many-body x-ray-absorption cross section in the dipolar approximation can be written as

$$\sigma_{\mathrm{XAS}}(\omega) = \frac{2\pi}{\hbar}\sum_f |\langle\Psi_f(N)|T|\Phi_i(N)\rangle|^2 \times\delta(E_f(N) - E_i(N) - \hbar\omega), \quad (3)$$

where now $\omega$ is the energy of the incident beam and $T$ is written as $T = \sqrt{2\pi\hbar^2\omega\alpha_0}M$ and $\alpha_0$ is the fine structure constant. The $\omega$ dependence of $T$ is negligible for core-level spectra because the energy range of a spectrum ($\Delta\hbar\omega$) is around 50 eV, while the energy of the core level ($\hbar\omega$) is around 10 keV.

Similarly to what was done for the case of XPS and using a similar notation, we can define the transform $I_{\mathrm{XAS}}(t)$ of the XAS cross section as

$$\sigma_{\mathrm{XAS}}(\omega) = 2\mathrm{Re}\int_0^{+\infty} dt e^{i\omega_+ t} I_{\mathrm{XAS}}(t). \quad (4)$$

Under the assumption that *both* $\Phi_i$ *and* $\Psi_f(N-1)$ *are single-determinant states*, Ohtaka and Tanabe[18,27] demonstrated that

$$I_{\mathrm{XAS}}(t) = I_{\mathrm{XPS}}(t)I_0(t), \quad (5)$$

where both $I_{\mathrm{XPS}}(t)$ and $I_0(t)$ [see Eq. (4.43) in Ref. 18] include many-body shakeup processes at all orders. Equation (5) holds for a generic static core-hole potential. A similar relation was found for the case of a contact core-hole potential by Nozières and Dominicis[28] using the linked-cluster theorem.

If shakeup processes are neglected both in $I_{\mathrm{XPS}}(t)$ and $I_0(t)$, Eq. (5) is the single-particle x-ray-absorption spectrum broadened by the core-hole lifetime. To go beyond single-particle theory, shakeup excitations should be included both in $I_{\mathrm{XPS}}(t)$ and $I_0(t)$. However, the inclusion of these effects in $I_0(t)$ is computationally unfeasible as one needs to calculate a Slater determinant for each possible excitation. A realistic first step is to neglect shakeup processes in $I_0(t)$ and to include them in $I_{\mathrm{XPS}}(t)$ by extracting $I_{\mathrm{XPS}}(t)$ from experiments. In the current work we validate against experiments this latter approach.

If shakeup processes are neglected only in the $I_0(t)$ term then $I_0(t)$ reduces to $I^{\mathrm{sp}}_{\mathrm{XAS}}(t)$, namely, the transform of the single-particle XAS cross section calculated in the presence of a static core-hole potential. We include some of the many-body effects in the XAS cross section $\sigma_{\mathrm{XAS}}(\omega)$ by performing the convolution

$$\sigma_{\mathrm{XAS}}(\omega) = \int d\epsilon\, \sigma^{\mathrm{exp.}}_{\mathrm{XPS}}(\epsilon)\sigma^{\mathrm{sp}}_{\mathrm{XAS}}(\omega - \epsilon). \qquad (6)$$

In Eq. (6), $\sigma^{\mathrm{sp}}_{\mathrm{XAS}}(\omega - \epsilon)$ is the single-particle cross section that is calculated in the framework of density-functional theory. The quantity $\sigma^{\mathrm{exp.}}_{\mathrm{XPS}}(\epsilon)$ is the part of the measured XPS cross section that can be attributed to a single Slater determinant. Thus, many-body shakeup processes need to be included in $\sigma^{\mathrm{exp.}}_{\mathrm{XPS}}(\epsilon)$, but excitations arising from coherent superposition of particle-hole states (i.e., plasmons[29,30]) should be excluded as they do not respect the basic assumption of the Ohtaka and Tanabe theory, namely, that both $\Phi_i$ and $\Psi_f(N-1)$ are single-determinant states. In addition, plasmon excitations are included in the self-energy,[31] where they lead to an energy-dependent broadening of the one-particle spectrum. Their inclusion in $\sigma^{\mathrm{exp.}}_{\mathrm{XPS}}(\epsilon)$ would lead to double counting.

### C. Technical details

The single-particle XAS cross section $\sigma^{\mathrm{sp}}_{\mathrm{XAS}}(\omega)$ is calculated in the framework of density-functional theory using the the XSPECTRA code[2] distributed with the Quantum-Espresso[32] distribution. The technical details for the NiO calculation are the same as in Ref. 6. We use norm-conserving pseudopotentials with inclusion of semicore states. The energy cutoffs used in the calculations are 140 and 160 Ryd for CuO and CoO, respectively. In the case of CoO, we neglect the tetragonal structural distortion below the 290-K Néel temperature and adopt magnetic and crystal structures similar to those of NiO. The electron-momentum grids for the Brillouin-zone integration and the choice of the supercell for the XAS calculation are the same as for the NiO case in Ref. 6. The CuO XAS cross section was calculated in the supercell obtained by doubling the antiferromagnetic cell along the shortest direction. The antiferromagnetic cell is obtained from the nonmagnetic one by defining as new lattice vectors $\mathbf{a}' = \mathbf{a} + \mathbf{c}$, $\mathbf{b}' = \mathbf{b}$ and $\mathbf{c}' = \mathbf{a} - \mathbf{c}$ where $\mathbf{a}$, $\mathbf{b}$, and $\mathbf{c}$ are the direct lattice vectors. We then use a $3 \times 3 \times 3$ electron-momentum grid in the supercell to obtain the self-consistent charge density and a $3 \times 3 \times 3$ electron-momentum grid in the supercell to calculate the XAS cross section. The Lorentzian broadening of the peaks in the single-particle equivalent of Eq. (3) is determined by setting the broadening parameter $\eta$ in the Lanczos procedure equal to the core-hole width of the $1s$ level, as done in Ref. 6. The broadening is then kept constant over all the spectrum.

Finally we employ the DFT + U approximation in all cases, with $U = 7.75$ and 11.1 eV for CoO and CuO, respectively. These values of the Hubbard repulsion are calculated from first principles using the method of Ref. 33.

## III. EXPERIMENT

The Ni-$1s$ photoemission spectrum of NiO was measured at the HIKE station of the KMC-1 beamline at BESSY.[34,35] The spectra were recorded with a SCIENTA R4000 photoelectron analyzer placed at 90° from the x-ray beam. The incident x-ray beam (≈8.95 keV) was monochromatized by a pair of Si(422) crystals providing ∼500-meV energy bandwidth. To avoid charging effects, a 25-nm-thick NiO thin film was grown on a Ag substrate in the presence of oxygen, and capped by 3 nm of MgO. The growth of NiO was found fully epitaxial with the NiO(001) direction parallel to Ag(001) as confirmed by the low-energy electron-diffraction patterns. The sample was positioned at a grazing angle of 89.99° from the incident x rays in order to reduce the penetration depth of photons and enhance the photoelectron yield.

The experimental XAS spectra of NiO and CoO were borrowed from Refs. 36 and 37, respectively.

## IV. RESULTS

### A. Nickel oxide

The measured $1s$ photoemission spectrum of NiO is shown in Fig. 1. The fit to the data is consistent with a three peak structure in the 590–610 eV energy region. The results closely resemble the $2p_{3/2}$ Ni photoemission spectrum of NiO[10,38] in this energy region. The additional broad feature centered at ≈575 eV is a plasmon excitation.[39] As discussed above, it should be excluded from the convolution.

In the literature the attribution of the different features in $2p_{3/2}$ Ni XPS is very controversial and was subject to several

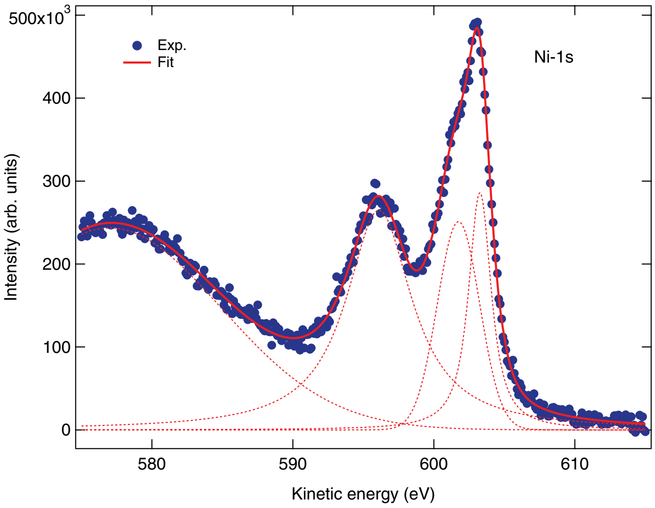

FIG. 1. (Color online) Experimental (circle) and fitted (lines) $1s$ photoemission spectra in NiO.

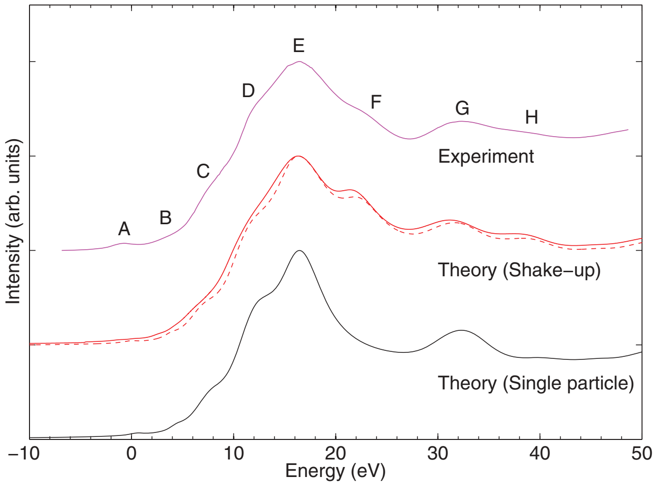

FIG. 2. (Color online) Convolution of experimental XPS (this work) and single-particle XAS calculation in NiO at the Ni $K$ edge. Convolution with two or three components is shown with solid line and dashed line, respectively (middle spectra). Experimental XAS data are from Ref. 36.

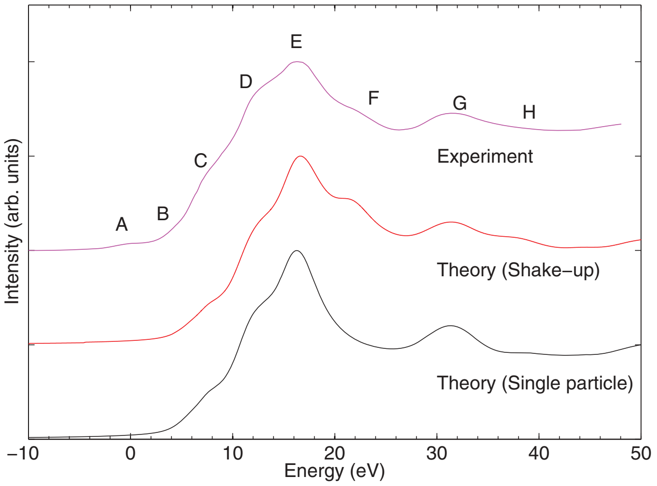

FIG. 3. (Color online) Convolution of experimental XPS data of Refs. 38 and 41 and single-particle XAS calculation in CoO at the Co $K$ edge. Experimental XAS data are from Ref. 37.

interpretations. Van Veenendaal and Sawatzky[9] attributed the main feature at high energy to a $2p^5 3d^9 \underline{L}$ state, where $\underline{L}$ denotes a hole in the ligand state. The satellite of the main peak (shoulder) was attributed to nonlocal screening coming from the nearest-neighbor Ni atoms, while the lower-energy satellite at ≈596 eV was attributed to a $2p^6 3d^{10} \underline{L}$. Recently this was reconsidered in Ref. 10 where the main feature was attributed to a $2p^5 3d^9 \underline{Z}$, where $\underline{Z}$ is a Zhang-Rice k-dispersing bound state.[40] The shoulder of the main peak is attributed to a $2p^5 3d^9 \underline{L}$ state and the lowest-energy feature to a $2p^5 3d^8$ state. Here we show that, regardless of their attribution, the features measured in $1s$ Ni NiO XPS are present also in the dipolar Ni $K$-edge XAS spectrum of NiO.

In Fig. 2 we show the measured and calculated XAS cross sections. The single-particle cross section is generally in good agreement with the dipolar part of the measured spectrum except for the two peaks indicated by the letters $F$ and $H$. Peak F is missing in the single-particle calculation while peak H has a very low intensity and is almost absent. In order to determine if these excitations have a many-body nature, and possibly arise from shakeup processes, we then proceed by using Eq. (6) and obtain new XAS spectra. We first perform the convolution using the complete three peak structure of the XPS spectra, but neglecting the low kinetic-energy part below 590 eV due to plasmon excitation. We find that the convolution of the DFT calculated XAS cross section with the photoemission spectra greatly improves the agreement with experiments. In particular the missing peaks are now present in the spectrum and a better agreement occurs at all energy scales. Peak F is a replica of the single-particle peak E, while the replica of peak G is very close in energy to the peak H, increasing its intensity and improving the agreement with experiments. This result demonstrates that peaks F and H have a many-body origin. We can further test to what extent this interpretation is robust by altering the XPS spectrum before convolution with the theoretical single-particle XAS calculation. We do this for NiO by artificially suppressing the main peak of the XPS spectrum, leaving the shoulder and the satellite. We find that the resulting absorption spectrum (dashed line in Fig. 2) is less in agreement with the experimental spectrum supporting our interpretation.

### B. Cobalt oxide

Co $1s$ photoemission data of CoO are not available in literature. However, $2p_{3/2}$ and $3s$ Co XPS data[38,41] are extremely similar and composed of two main peaks and a small shoulder at low energy visible only in the $3s$ data. We then consider $3s$ photoemission data of Ref. 38 and fit them with a two peak structure and neglect the very small shoulder, invisible in $2p$ photoemission data. The results are shown in Fig. 3.

The situation is very similar to NiO, namely, peak F is missing from the single-particle spectrum and peak H is weak. Convolution with photoemission improves substantially the agreement although the main-edge peak is narrower than the experimental data.

### C. Copper oxide

The copper oxide CuO has a monoclinic crystal structure with symmetry group $C/2c$. The experimental $K$-edge spectrum of Cu in CuO was reported in Refs. 42 and 43. We follow their notation and label the configuration of the crystal with respect to the incident beam by three angles $(\theta,\phi,\psi)$. These angles correspond to the three rotation angles of the goniometer. In particular, when the three angles are zero, then the polarization is parallel to the $\theta$ axis of the goniometer and to the $c$ axis of the crystal. At zero angles, the plate holding the sample is orthogonal to the incident beam and parallel to one of the plaquette chains in the crystal (see Fig. 10 of Ref. 43 for more details).

Given the low symmetry of the crystal, the polarization dependence of CuO $K$-edge XAS spectra is very complicated, as can be seen in Fig. 4. The calculated single-particle spectra are in strong disagreement with experiments. Both the peak positions and the polarization dependence of the intensities

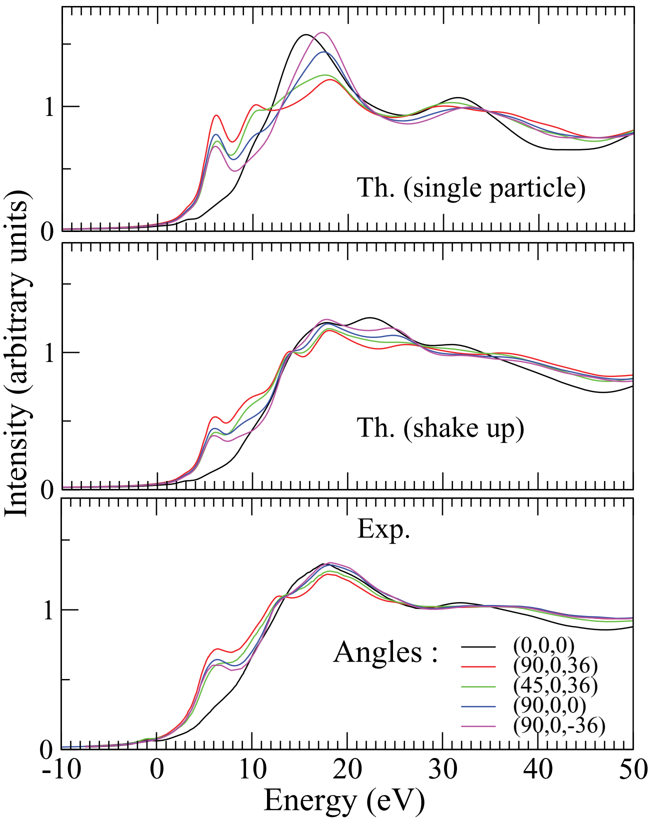

FIG. 4. (Color online) Convolution between measured XPS from Ref. 44 and single-particle XAS calculation at the Cu $K$ edge. Experimental XAS data are from Refs. 42 and 43.

disagree with the measured data. Furthermore, as noted in Ref. 42 and as it is evident in Fig. 4, all the experimental spectra for different angles cross at an "isosbestic" point at 13 eV. No isosbestic point appears in the single-particle calculation and no such point is expected from symmetry arguments, because of the very low symmetry of CuO.

In order to see if the broad disagreement is due to the lack of many-body effects in the XAS cross section, we consider the convolution with Cu $1s$ photoemission spectra.[44] Cu $1s$ photoemission spectra of CuO are composed of two peaks, usually attributed to $3d^9$ and $3d^{10}\underline{L}$. Performing the convolution with the calculated single-particle Cu $K$-edge XAS leads to an impressive improvement. In particular, both the position of the peaks and their angular dependence are now in much better agreement with experiments. Moreover an isosbestic point does occur in the convoluted spectra at 13 eV, again in agreement with experimental data.

However, when comparing with experiments, there is still some disagreement. Notably the peak at 25 eV is too intense with respect to the edge. This is partly due to the use of a constant linewidth equal to the core-hole linewidth. In experiments this is not true as it is well known that the linewidth (i.e., the imaginary part of the electron self-energy) increases from the pre-edge to the far-edge region.[31] Using a linewidth that smoothly increases from the pre-edge to the far edge improves the agreement with experiments but also introduces an additional functional dependence in the calculated spectra. In our work we have chosen not to introduce a variable self-energy in the spectrum and we kept the linewidth constant, so that the results of the convolution are not mixed with a variable linewidth. This means that our spectral features are more resolved and have larger intensities with respect to experiments beyond the edge. Even if this partly explains the disagreement in intensity of the 25-eV peak, we cannot exclude that the difference in intensity is also to some extent due to the neglecting of shakeup effects in $I_0(t)$.

Nevertheless the better agreement between the convoluted spectrum and experimental data demonstrates that the Cu $K$-edge XAS spectrum in CuO exhibits sizable shakeup many-body processes.

## V. CONCLUSIONS

We have demonstrated that shakeup processes occur at the $K$-edge XAS spectra of NiO, CoO, and CuO. As these are prototype correlated transition-metal oxides, we expect these excitations to be present in all XAS data of correlated materials. To be more precise, whenever charge-transfer satellites occur in XPS core-hole spectra, then shakeup satellites should also occur in the corresponding x-ray-absorption edge, at all energy scales.

We have also proposed a practical way to include these effects in single-particle calculations by performing a convolution with the XPS spectrum at the same edge, as suggested by Eq. (6). Despite the fact that Eq. (6) was obtained many years ago,[18,27,28] we are currently unaware of other works that explicitly apply this equation to $K$-edge XAS by using state-of-the-art calculations. Our work that fully includes core-hole attraction and Hubbard U at the DFT $+$ U level demonstrates that this approach is feasible and allows, for the first time, the attribution of all dipolar peaks in NiO and CoO $K$-edge XAS spectra.

In Eq. (6) we neglected the additional many-body terms[18,27] that are present in $I_0(t)$. These terms seem to be negligible in NiO and CoO, but could explain the remaining discrepancy between theory and experiment in CuO. Further work is required to calculate these many-body correction terms.

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[44] See, for example, experimental Cu 1*s* hard x-ray photoemission collected at the Hiroshima Synchrotron radiation center at http://www.hsrc.hiroshima-u.ac.jp/cuprates.htm.