Measuring the intrinsic charge transfer gap using K-edge X-ray absorption spectroscopy

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Pre-edge features in X-ray absorption spectroscopy contain key information about the lowest excited states and thus on the most interesting physical properties of the system. In transition metal oxides they are particularly structured but extracting physical parameters by comparison with a calculation is not easy due to several computational challenges. By combining core-hole attraction and correlation effects in first principles approach, we calculate Ni K-edge X-ray absorption spectra in NiO. We obtain a striking, parameter-free agreement with experimental data and show that dipolar pre-edge features above the correlation gap are due to non-local excitations largely unaffected by the core-hole. We show that in charge transfer insulators, this property can be used to measure the correlation gap and probe the intrinsic position of the upper-Hubbard band.

The description of electronic excitations in correlated materials is a challenge since many relevant phenomena, such as magnetism in transition metal (TM) compounds or high Tc superconductivity in doped Mott-insulators are a consequence of strong electron-electron interaction. Recently, core-hole spectroscopy unveiled unexpected electronic excitations in correlated antiferromagnetic insulators [1, 2] as well as in high Tc superconductors [3, 4]. In La$_2$CuO$_4$, Kα resonant inelastic X-ray scattering (RIXS) and theoretical calculations [5] demonstrated that dipolar pre-edge features just above the correlation gap are due to intersite Cu 4p-3d hybridization. Since in correlated insulators the TM empty d-states form the upper Hubbard bands, it is crucial to see (i) if off-site pre-edge excitations occur in other correlated compounds [6], (ii) to what extent their energy depends on the presence of a core-hole in the final state.

The presence of a core-hole substantially complicates the interpretation of X-ray absorption (XAS) spectra. Since core-hole attraction shifts the empty d-states much more than the empty p-states, typically by several eV, it is unclear to what extent the energy of the pre-edge features can provide useful information on the position of the corresponding excitations in the material in the absence of a core-hole. Furthermore, in correlated insulators core-hole attraction and Hubbard repulsion partially compensate each other. Thus the use of fitting parameters to describe these interactions, as is commonly done in the literature [7], does not allow to distinguish between the two effects. A treatment of core-hole attraction and Hubbard repulsion from first principles is needed.

In the case of K-edge XAS spectra, theoretical calculations are difficult since excitations in a large energy window above the Fermi level need to be described. Thus methods dealing successfully with correlation effects in NiO in an energy window close to the Fermi level (such as DMFT [8] or cluster calculations [9]) cannot be used to describe pre-edge and near-edge structures in K-edge XAS spectra. This is relevant since (i) low energy pre-edge features provide relevant information on the local environment of the absorbing atom [3, 6, 11, 12] and (ii) it has been suggested that in correlated oxides “shake-down” excitations occur as near-edge structures [13].

In this work we present a first-principles approach to describe the K-edge XAS spectra in correlated insulators. The method is based on a recently developed DFT+U method and includes core-hole attraction [14]. Differently from other DFT+U schemes [15], the U parameter is obtained by linear-response [16, 17]. Consequently, $U$ is not a fitting parameter but an intrinsic linear response property since it measures the spurious curvature of the energy functional as a function of occupation [16]. We apply the method to the K-edge XAS of NiO, which is the prototype antiferromagnetic correlated insulator and whose ground state and excitations are incorrectly described by standard DFT approaches. We demonstrate that the pre-edge dipolar features above the correlation gap are due to non-local excitations to second-nearest-neighbor Cu atoms reflecting the superexchange interaction. We show that, due to its non-local nature, the dipolar pre-edge feature is unshifted by core-hole attraction and it is, thus, a measure of the upper-Hubbard band in the absence of a core-hole in the final state. Finally we exploit the insensitivity of the pre-edge dipolar features on core-hole attraction to show how to measure the charge transfer gap using K-edge XAS.

We use the NiO experimental crystal structure. The paramagnetic-cell group-space is then Fm3m, Ni occupies the 4a position and O the 4b. The cubic lattice parameter is $a = 4.1788 A$ for NiO [18]. DFT calculations are performed using the Quantum-ESPRESSO code [19]. We use Troullier-Martins [20] pseudopotentials, the spin-polarized generalized gradient approximation (GGA) [21] and the recently developed DFT+U...
and $\epsilon$ and (ii) $B$ is shifted to $A$ and $B$. In the GGA+U calculation the dipolar peak energy and a too large mixing occurs between structures (see insets in Fig. 1) are evidence of pre-edge structures (see insets in Fig. 1) are seen. On the contrary the energy and angular dependence is in excellent agreement with experimental data. The CGA+U calculation also shows that a very small dipolar component is present in peak A, commonly interpreted as purely quadrupolar. Detailed analysis of the angular dependence of the experimental NiO XAS spectra shows that even for the $t_{2g}$ orientation, where no quadrupolar transition occurs because the $t_{2g}$ states are occupied, a small peak is present in agreement with our findings. Thus, in correlated insulators, the use of the DFT+U approximation is mandatory to obtain a correct description of the pre-edge features.

To complete the understanding of the pre-edge features in NiO we resolve the XAS spectrum in its spin dependence and calculate the density of states projected over atomic orbitals using Löwdin projections. Without loss of generality we have considered the absorbing Ni to be spin-up polarized. As can be seen in Fig. 2 the quadrupolar part of peak A is mostly due to intra-site excitations to d-states lowered by core-hole attraction. However, since the hybridization between Ni and O is very strong, core-hole attraction lowers a small portion of the O 2p states generating a small dipolar component in peak A. In a atomic orbital picture, peak A is due to direct dipole transitions from Ni 1s states to O 2p states.

In our calculation the intensity of this excitations is of the order of 1% of the edge jump. In experiments it is somewhat smaller because of the larger linewidth. This estimate is crucial for the quantitative description of this off-site excitation in multiplet calculation.

The spin-resolved dipolar spectrum shows that peak B is mostly due to transition to up spin-polarized states. Since the absorbing atom has 5 up electrons in d-states, the B excitation must have an off-site component. Löwdin projections demonstrate that it is due to transition to on-site Ni empty 4p-states hybridized to empty 3d-states of next-to-nearest neighbours Ni atoms. This off-site excitation is then a fingerprint of the hopping process leading to superexchange in NiO and a direct probe of the upper Hubbard band in NiO.

To understand the role of core-hole effects on the A and B features we have performed calculations with and without a core hole in the final state. We found that peak A is shifted by 4 eV with respect to the edge by core-hole attraction. On the contrary peak B is essentially unshifted. The difference in the behavior of the two peaks is due to the non-local nature of peak B.

We now demonstrate that the non-local nature of the B excitation and its weak dependence on core-hole effects can be used to measure the correlation gap between the $|3d^6L\rangle$ and the $|3d^9L\rangle$ states. We consider hole-doped NiO. In practice this can be achieved through Li doping, as in the case of Li$_x$Ni$_{1-x}$O. A large range of doping can be experimentally obtained with $0 < x < 0.7$. It has been shown that, when NiO is doped with holes, the holes mainly reside on O atoms, due to the charge transfer character of NiO. Thus the top of the NiO va-
lence band has mainly p character. This suggests that in Ni K-edge XAS of Li$_x$Ni$_{1-x}$O, in the low doping regime, an additional dipolar peak should occur in the pre-edge, resulting from the holes entering the top of the valence band. This is confirmed by oxygen K-edge absorption where the top of the valence band is seen even at dopings as low as $x = 0.05$ [26]. At somewhat larger doping, a similar peak due to Oxygen p-holes should also occur in the dipolar part of Ni K-edge XAS. Since no experimental data are available in the literature, we directly simulate Ni K-edge XAS in Li$_x$Ni$_{1-x}$O.

We calculate hole-doping of NiO in two different ways, namely (i) by rigid-band doping of NiO and (ii) adding a compensating charge background and recalculating self-consistently the charge-density and the XAS spectra. The results of the Ni K-edge XAS in Li$_x$Ni$_{1-x}$O in the pre-edge region with and without a core-hole in the final state are shown in Fig. 3. We find that the top of the valence band should be visible in Ni K-edge XAS at dopings of $x \approx 15 - 20\%$. In the calculated spectra, with or without a core-hole in the final state, the energy position of the top of the valence band and of peak B are independent of doping. The agreement between the rigid band picture and the compensating-charge background calculation validates the rigid band picture for $0 < x < 0.2$

In NiO the experimentally measurable gap is due to the excitation between the top of the valence band and the empty d states (see Fig. 3). This band is lower than the empty d states (see Fig. 3). This band is invisible in experiments since its optical matrix elements are extremely weak [28]. Moreover its also invisible in K-edge XAS since it is highly dispersive and has mostly Ni s and O s components. Thus in the absence of core-hole effects, the distance between the top of the valence band and peak B is a measure of the correlation gap, being the dependence of the energy position on doping very weak (see Fig. 3, right panel). When core-hole attraction is considered (see Fig. 3 left panel), we find that, despite the occurrence of a core-hole exciton (peak A), the distance between the top of the valence band and peak B is very weakly affected ($\approx 5\%$). Consequently in lightly hole-doped NiO the distance between the top of the valence band and peak B is a measure of the correlation gap even in the presence of a core-hole in the final state.

In our calculation the charge-transfer gap is 5 eV (peak-to-peak distance). In NiO optical absorption starts at 3.1 eV and reaches its maximum at 4.0 eV [30, 31]. This value is reduced respect to our due to excitonic effects. In photoemission and inverse photoemission [32] the gap (peak-to-peak distance) is roughly 5.5 eV, in fairly good agreement with our value. Thus our proposal allows for an independent estimate of the optical gap in NiO.

The procedure outlined for NiO can be used to measure the charge-transfer gap and the upper Hubbard band in other charge-transfer insulators. In these systems the top of the valence band is due to Oxygen p-states and it is
thus visible in dipolar TM K-edge XAS upon doping. If the doping necessary to detect this feature is low enough not to affect substantially the electronic structure then a rigid-band doping picture applies and the top of the valence band is at the same energy as in the undoped system. Moreover, hole states being dipolar in nature, the effects of core-hole attraction are weak. The top of the valence band of the doped system can then be used as a reference energy for the measurement of the excitations seen in TM K-edge XAS. The second necessary condition is the occurrence of non-local dipolar features \( \text{peak B} \) in the pre-edge region due to transitions to d-states of neighboring TM atoms promoted by hybridization with the TM absorbing atom p-states. If these excitations are visible, we have shown that they represent the upper Hubbard band of the material and the energy difference between this excitation and the top of the valence band in the weakly hole-doped system is a measure of the charge transfer gap. Thus, TM K-edge XAS in weakly hole-doped charge-transfer insulators is unbiased experimental tool to measure the charge-transfer gap.

In this work we have developed a new first-principles parameter-free method to calculate K-edge XAS spectra including core-hole effects in the final state and electronic correlation at the DFT+U level. We have shown that the method provides spectra in excellent agreement with experimental data for NiO, the prototype correlated insulator. We have interpreted all the pre-edge and near-edge features \( \text{peak B} \) in the pre-edge region due to transitions to d-states of neighboring Ni atoms, namely the upper Hubbard band. We have shown that, due to its non-local nature, this excitation is unaffected by the presence of a core-hole in the final state. Starting from this result we have proposed a new way to measure the intrinsic correlation gap in charge-transfer insulators based on TM K-edge XAS. This method is complementary to optical measurements and more straightforward than a combined photoemission-inverse photoemission experiment.

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