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Intermediate coupling for core-level excited states: Consequences for X-Ray absorption spectroscopy

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ABSTRACT

The origin of the complex NEXAFS features of X-Ray Absorption, XAS, spectra in transition metal complexes is analyzed and interpreted in terms of the angular momentum coupling of the open shell electrons. Especially for excited configurations where a core-electron is promoted to an open valence shell, the angular momentum coupling is intermediate between the two limits of Russell-Saunders, RS, coupling where spin-orbit splitting of the electron shells is neglected and j–j coupling, where this splitting is taken as dominant. The XAS intensities can be understood in terms of two factors: (1) The dipole selection rules that give the allowed excited RS multiplets and (2) the contributions of these allowed multiplets to the wavefunctions of the intermediate coupled levels. It is shown that the origin of the complex XAS spectra is due to the distribution of the RS allowed multiplets over several different intermediate coupled excited levels. The specific case that is analyzed is the $L_{2,3}$ edge XAS of an Fe^{3+} cation, because this cation allows a focus on the angular momentum coupling to the exclusion of other effects; e.g., chemical bonding. Arguments are made that the properties identified for this atomic case are relevant for more complex materials. The analysis is based on the properties of fully relativistic, ab initio, many-body wavefunctions for the initial and final states of the XAS process. The wavefunction properties considered include the composition of the wavefunctions in terms of RS multiplets and the occupations of the spin–orbit split open shells; the latter vividly show whether the coupling is j–j or not.

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1. Introduction

X-Ray Absorption Spectra, XAS, are often taken at edges; i.e., for energies just below and just above ionization limits. In these cases, the spectra have been described as NEXAFS [1], Near Edge X-Ray Absorption Fine Structure, and we follow this usage. Often, the NEXAFS spectra have several features. For example, for the $L_{2,3}$, or 2p, edges of transition metal complexes, the NEXAFS have several peaks, rather than simply one each for the L_2 and L_3 ionization limits; see, for example, the review by de Groot [2]. Furthermore, several distinct final excited states, not always resolved because of broadenings that are due to core-hole lifetime and to limits of experimental time and energy resolution, may contribute to an observed spectral feature [2,3]. On the basis of a restricted complete open shell configuration interaction, COSCI, formalism, theoretical predictions for the $L_{2,3}$ NEXAFS of the isolated $Fe^{3+}(3d^5;{}^6S)$ cation are shown in Fig. 1. Here the intensities to individual final states

within the configuration $2p^5 3d^6$ have been broadened with a Voigt convolution [4] to represent lifetime and resolution broadening. The details of this spectrum, including the basis of the theoretical predictions, will be described later. For the present our concern is to illustrate the complexity of the spectrum. The dark curve in Fig. 1 is the sum of the contributions from all final states while the underlying curves are from the states making the largest contributions to the total. The leading peak, expected, and shown below, to be from $2p_{3/2} \rightarrow 3d$ excitations, the L_3 edge, has a satellite at ∼2 eV higher excitation energy, ΔE, and less intense satellites at higher ΔE of ∼6 to ∼10 eV. In addition, at higher excitation energies, where the $2p_{1/2}$ or L_2 edge is expected, the total spectrum is a doublet rather than a single peak. Furthermore, judging from the large number of underlying contributions, many final excited states, often unresolved, contribute to the total $L_{2,3}$ edge XAS curve. As evidence that the theoretical curve of Fig. 1 for the Fe^{3+} cation includes important physical features for the NEXAFS of ionic complexes, we note that Fig. 1 has significant similarities with the Mn $L_{2,3}$ edge NEXAFS for MnO, where Mn^{2+} is isoelectronic with Fe^{3+} both being $3d^5$. This is shown by the inset in Fig. 1 where we have digitized and plotted the Mn 2p $L_{2,3}$ edge NEXAFS of MnO from Fig. 1(d) in the paper by Bayer
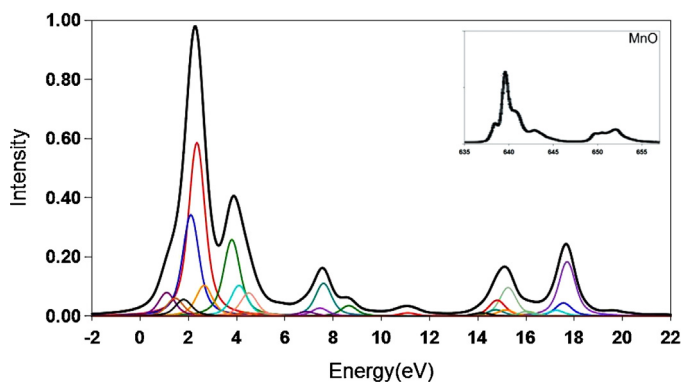
Fig. 1. Theoretical $L_{2,3}$ edge NEXAFS for the Fe^{3+} cation. The full line is the sum of contributions to the NEXAFS from all allowed final states and the underlying lines (in color online) are for individual contributions of final states with large intensities. The zero of energy is taken as the energy of the lowest level of the excited ......$2p^5$......$3d^6$ configuration. The Voigt broadening and other details are described in Section 4 of the text. The inset for the experimental $L_{2,3}$ NEXAFS edge of MnO is plotted from the data in Ref. [5].

et al. [5]. We would expect similarities between these two systems since, in both cases, the initial state of the metal cation is $3d^5$. Indeed there are similarities between our theory for the $L_{2,3}$ edge of Fe^{3+} and the measured $L_{2,3}$ edge XAS of MnO that we will discuss later in the paper after we have analyzed the origin of the Fe^{3+} features in our theoretical spectra. However, our main objective in the present paper is to develop an explanation and understanding of the physical origin of the complex features and contributions to the Fe $L_{2,3}$ edge NEXAFS, Fig. 1.

In particular, our concern is show how the concepts of angular momentum coupling and recoupling [6,7] and intermediate coupling [8] lead to the complex NEXAFS spectra; however, we will not use the mathematical formalism of Clebsch–Gordon algebra [9]. An important quantum mechanical principle at the foundation of our analysis is that the final states for core-level ionizations and excitations cannot be represented by a single Slater determinant but must be treated with a many-body formulation. In our, and in many other treatments, the many-body approach involves describing the wavefunctions, WF's, as a summation of Slater determinants or, equivalently, of configuration state functions [2,3,10–13]. A many-body effect that is especially important for NEXAFS is the angular momentum coupling of the open shell electrons. This coupling may be within the open valence, the 3d shell of Fe cations, and within the open core shell, the 2p shell for the $L_{2,3}$ NEXAFS edge, as well as between these shells. When the valence shell coupling changes from the angular momentum coupling in the ground state, we describe this as an angular momentum recoupling. There is also spin–orbit splitting; for the core levels, it is important to distinguish between the $j = \ell + \frac{1}{2}$ and the $j = \ell - \frac{1}{2}$ spin–orbit split shells. The two limits of angular momentum coupling are Russell-Saunders, RS, coupling [14] where the total orbital angular momentum, L, and the total spin angular momentum, S, are good quantum numbers, and j–j coupling [15] where the spin–orbit splitting dominates. It is common, especially when core holes are present, that neither the RS nor the j–j limits will dominate and the determinants will mix in such a way that the coupling is intermediate. We will describe both effects of angular momentum recoupling as well as the departures from pure j–j coupling as intermediate angular momentum coupling. In Section 2, we will discuss the details of the many body effects considered and the criteria that we use to measure the extent of the intermediate coupling. We also consider selection rules for transitions from the ground state to the NEXAFS core-excited final states. In later sections, we apply these measures to characterize the ground and excited states and their contributions

to the NEXAFS spectra. The concept of the mixing of multiplets in the final NEXAFS excited states is well known and this mixing has been taken into account. This is especially true for treatments that start from non-relativistic solutions and then add spin–orbit interactions; see, for example, Refs. [16,17]. Our work is unique in that we use the presence of multiplets as a physical tool to understand the properties of the excited states rather than primarily as a mathematical tool to obtain wavefunctions for the excited states [9,16,17].

In this paper, we consider core excitation in the isolated Fe^{3+} cation and the $L_{2,3}$ edge NEXAFS spectra obtained for transitions to these excited states. Fe cations as found in ionic crystals, especially oxides, are important for geochemical processes where the distinction between Fe(II) and Fe(III) may be quite important [18,19] and for catalysis where they may often be used as supports; see for example, Ref. [20]. It is clear that the environment of the cations will have an impact on the NEXAFS spectra [2] and that this impact must be taken into account for a predictive understanding of the chemical significance of the features of the NEXAFS spectra. One method that has been used to take the crystalline environment of complexes into account is to represent the crystals with embedded clusters. For a discussion of cluster models of metal complexes used for the analysis of core-level ionization see, for example, Ref. [12] and for the analysis of NEXAFS edges see, for example, Ref. [16,17]. However, there is strong evidence that the methods that we develop to analyze and interpret the spectra of the Fe^{3+} cation can also be applied for the analysis of materials models that take the oxide environment into account. The main reason that our methods are appropriate for complex systems is that the physical properties that are the basis of these methods, spin–orbit splitting and angular momentum coupling, hold for all point groups. We have chosen to make our first application with atomic symmetry since the analysis is more straightforward and simpler with the higher atomic symmetry [21]. This simplicity allows us to tune our theoretical approaches and to explain them in a compact fashion.

The next section of the paper, Section 2, presents an explanation of the theoretical concepts used to analyze the relativistic wavefunctions in terms of the angular momentum coupling and to determine the intensities of the X-Ray absorption transitions. It also describes the computational methods used. In Section 3, the methods developed in Section 2 are used to show that the lowest, $^6S_{5/2}$, level of Fe^{3+} is very well described as a RS multiplet. In Section 4, the characteristics of these excited states are analyzed. In particular, the relationship between the contribution of the dipole allowed RS multiplet to an intermediate coupled excited level and the NEXAFS intensity of that level is established. Finally, in Section 5, our conclusions are summarized

2. Theoretical concepts and computational methods

Our methods involve using WF's to describe the initial and final, core-excited states. As we explain below, with this choice angular momentum coupling, especially intermediate coupling, can be treated in a natural fashion. We use four component spinors obtained as solutions of the Dirac-Hartree–Fock equations for the average of configurations of the $3d^5$ initial, and $2p^5 3d^6$ final, core excited, configurations of Fe^{3+} [22]. (Here, and in the remainder of the paper, we show only the open shells of a configuration.) These spinors are eigenfunctions of j^2 and j_z. (Note that we use lower case j^2 and j_z to describe the angular momentum of spinors and upper case J^2 and J_z to describe the angular momentum of many-electron wavefunctions.) The use of spinors optimized for an average of configurations makes it possible to determine a large set of wavefunctions with different degeneracies and different J^2 and J_z from a single Hamiltonian matrix, accomplished using the COSCI