Effects of electronic correlation on x-ray absorption and dichroic spectra at L2,3 edge

L Pardini, V Bellini and F Manghi

CNR—Institute of Nanosciences—S3, Via Campi 213/A, I-41125 Modena, Italy
and
Dipartimento di Fisica, Università di Modena e Reggio Emilia, Via Campi 213/A,
I-41125 Modena, Italy

E-mail: franca.manghi@unimore.it

Received 19 January 2011, in final form 16 March 2011
Published 9 May 2011
Online at stacks.iop.org/JPhysCM/23/215601

Abstract

We present a new theoretical approach to describe x-ray absorption and magnetic circular dichroism spectra in the presence of electron–electron correlation. Our approach provides an unified picture to include correlations in both charged and neutral excitations, namely in direct/inversion photoemission where electrons are removed/added, and photoabsorption where electrons are promoted from core levels to empty states. We apply this approach to the prototypical case of the L2,3 edge of 3d transition metals and we show that the inclusion of many-body effects in the core level excitations is essential to reproduce, together with satellite structures in core level photoemission, the observed asymmetric lineshapes in x-ray absorption and dichroic spectra.

The excitation due to x-ray absorption is a complex phenomenon where many-body effects may play a major role. The independent-particle picture has been shown to be inadequate in describing features of x-ray absorption spectra (XAS) in transition metals [1] and their compounds [2, 3] where electron–electron (e–e) interactions are known to be non-negligible. To account for these failures various theoretical methods have been developed that differ in how the e–e Coulomb interaction is taken into account. They range from atomistic approaches, where configuration–interaction methods are used to solve the many-body Hamiltonian either in a parameterized form [2, 4–6] or ab initio [7, 8], to solid state first-principles schemes that properly include the structure of valence electrons [9–11] but lose some of the atomic many-body effects that can be relevant to the physics of the process.

In this paper we present a new approach that treats on the same footing the localized and itinerant character of electrons in a solid, exploiting on one side the first principles calculations of the band structure and on the other side the localized picture to treat many-body effects associated with e–e interactions. We will show that the on-site interaction between core and valence electrons, responsible for satellite structures in core level photoemission spectra, gives rise to asymmetric lineshapes in XAS and x-ray magnetic circular dichroism (XMCD) spectra, in agreement with experiments. Application to the prototypical case of absorption from the L2,3 edge in 3d transition metals is presented.

Within the independent-particle scheme the x-ray absorption is described as the addition of one electron–hole (e–h) pair to a non-interacting Fermi sea. In the language of many-body theory, this corresponds to approximating the two-particle polarization propagator to zeroth order. It is possible to improve this approach by substituting the bare particle and hole propagators with the dressed ones. Except for vertex corrections, this would be the exact two-particle propagator. This picture is very physical in the sense that the creation of the e–h pair due to x-ray absorption can be visualized as the removal of one core electron in the presence of the valence continuum and its addition to the conduction band, a sort of superposition of photoemission and inverse photoemission spectra, plus possible e–h interactions. We will not include this e–h coupling responsible for excitonic effects in the present discussion, focusing on the modifications induced by e–e interaction in the electron removal and addition.

Even neglecting excitonic effects we are left with a very hard task, namely the calculation of hole and particle
operators of an interacting many-particle system. This is even more difficult here since we are dealing with two processes that, from the point of view of e–e interactions, are very different: on one side the removal of one electron from an inner core state with atomistic interactions resulting in multiplet structures that, in most cases, survive the band formation; on the other side the addition of one electron in an itinerant conduction state where local short range e–e interactions coexist with hopping from site to site. An approach that can treat these two apparently opposite situations in a unique way is based on the generalized Hubbard model where the different strength of localization can be taken into account in terms of different $U$ and $J$ parameters and different bandwidths (finite and zero bandwidth for valence states and non-dispersive inner core energy levels, respectively). In the present case the Hubbard Hamiltonian can be usefully partitioned into core (c) and valence (v) contributions:

$$\hat{H} = \hat{H}_c + \hat{H}_v.$$  \hspace{1cm} (1)

The first term describes valence states in terms of single-particle band eigenvalues ($\epsilon_{i\sigma\nu}$) and of on-site Coulomb ($U_n\nu$) and exchange ($J_{\nu\sigma\nu'}$) interactions:

$$\hat{H}_v = \sum_{i\nu\sigma\nu'} \epsilon_{i\nu\sigma} \hat{n}_{i\nu\sigma} + \frac{1}{2} \sum_{i\nu\sigma\nu'} (U_{\nu\nu'} - J_{\nu\nu\nu'}) \hat{n}_{i\nu\sigma} \hat{n}_{i\nu\sigma'}.$$

Here $i$ is the site index. Similarly

$$\hat{H}_c = \hat{H}_{cc} + \hat{H}_{cv},$$

where

$$\hat{H}_{cc} = \sum_{i\sigma\sigma'} \epsilon_{i\sigma\sigma} \hat{n}_{i\sigma\sigma} + U_{cc} \hat{n}_{i\sigma\sigma} \hat{n}_{i\sigma\sigma'},$$

$$\hat{H}_{cv} = \frac{1}{2} \sum_{cv} \sum_{\sigma\sigma'} (U_{\nu\nu'} - J_{\nu\nu\nu'}) \hat{n}_{i\nu\sigma} \hat{n}_{i\nu\sigma'}.$$

Here $\hat{n}_{i\sigma\sigma} = \hat{a}_{i\sigma\nu} \hat{a}_{i\sigma\nu}^\dagger$, $\hat{n}_{i\nu\sigma} = \hat{c}_{i\nu\sigma} \hat{c}_{i\nu\sigma}^\dagger$ are the number operators in the Bloch and localized basis, respectively. $k, n$ identify wavevector and band index, $\alpha = v/c$ the valence/core orbital and $i$ the site. The creation–destruction operator in the two bases are connected by the standard transformation

$$\hat{a}_{k\alpha}^\dagger = \frac{1}{\sqrt{N}} \sum_{\sigma} \sum_{\nu} C_{\alpha k\sigma}^\dagger(k) e^{i k R} \hat{c}_{i\nu\sigma},$$

$$\hat{a}_{k\alpha} = \frac{1}{\sqrt{N}} \sum_{\sigma} \sum_{\nu} C_{\alpha k\sigma} e^{-i k R} \hat{c}_{i\nu\sigma}^\dagger,$$

where $C_{\alpha k\sigma}$ are the orbital coefficients of the eigenstates obtained by band structure calculation. The general expression for a multi-band Hubbard Hamiltonian in the Bloch basis and its definition for core and valence states is reported in [12]. In particular, for $\hat{H}_v$ we get

$$\hat{H}_v = \frac{1}{2} \sum_{kk'} \sum_{\sigma\sigma'} \sum_{nn'} (U_{\nu\nu'} - J_{\nu\nu\nu'}) \times C_{\alpha k\sigma}^\dagger C_{\alpha k'\sigma'} \hat{a}_{k\alpha} \hat{a}_{k'\alpha} + \hat{a}_{k\alpha} \hat{a}_{k'\alpha}^\dagger \hat{a}_{k\alpha'} \hat{a}_{k'\alpha'}^\dagger.$$

Notice that $\hat{H}_v$ includes both core–core ($U_{cc}$) and core–valence ($U_{cv}$, $J_{cv}$) e–e interaction. In the present case we are interested in $L_{2,3}$ edge excitations in 3d transition metals, therefore we will consider Coulomb and exchange integrals involving 2p and 3d orbitals.

The orbital character of the valence band comes into our scheme through the $d$ orbital coefficients $C_{\nu\sigma\nu}^R$ of equation (3) obtained in our case by ab initio spin-polarized band structure calculation. Both core and valence states have been calculated within the full-potential linearized plane-wave method (FLAPW) as implemented in the WIEN2K code [13]. Spin–orbit coupling has been included in order to reproduce a non-zero total orbital momentum that is one of the quantities that can be extracted from dichroic spectra. For core states the relativistic effects are accounted for by solving the Dirac equation while for valence states the spin–orbit coupling is treated by perturbation theory [14]. The core hole is not included at this level and the band structure calculation is performed for the perfect crystal—the so-called initial-state picture. The idea, common to all the many-body approaches based on Green’s functions and propagators, is that the addition of the core hole and of the perturbing potential associated with it is automatically included in the propagators in terms of self-energy corrections.

The ab initio band structure results could also be used to estimate the $U$ and $J$ parameters: the bare on-site valence–valence and core–valence Coulomb and exchange interactions can be explicitly calculated using the core and valence wavefunctions and properly scaled to account for screening effects. This procedure has been applied to the evaluation of core–core integrals in transition metal oxides assuming a static effective dielectric constant [15]. Various ab initio estimates of on-site valence–valence Coulomb and exchange integrals have been recently proposed for 3d transition metals, either within a constrained density functional approach [16] or as dynamically screened on-site integrals [17]. The results depend on the procedure adopted and the range of variation in the parameters (1–5 eV) remains the same as reported previously in the literature [18]. In the present calculation $U$ and $J$ have been used as adjustable parameters, with values for valence–valence within the above-mentioned range, tuned to optimize the agreement between theory and experiment. Their values are reported in table 1. These values for the valence–valence interactions give an accurate description of the quasi-particle band dispersion probed by angular resolved photoemission [12, 19, 20]. The same is true of core–core interactions that have been fixed to reproduce the satellite position in core level photoemission spectra (see figure 1 on core level photoemission).

When dealing with charged excitations where one electron is removed from a core level or added to an empty valence

Table 1. Coulomb and exchange integrals (in eV) describing the interaction between valence (3d) and core (2p) states.

|        | $U_{cc}$ | $J_{cc}$ | $U_{cv}$ | $J_{cv}$ |
|--------|----------|----------|----------|----------|
| Fe     | 1.5      | 0.9      | 0.8      | 0.1      |
| Co     | 2.1      | 0.9      | 1.8      | 0.2      |
| Ni     | 2.0      | 0.9      | 2.5      | 0.2      |
that are responsible for just a rigid shift in the core hole excitation energy—no multiple scattering involved.

The 3BS approach has been implemented to treat both core [15, 21] and valence spectra [12, 22]; it allows us to calculate energy- and spin-dependent complex self-energies \( \Sigma_\sigma^{c/v}(\omega) \) and from them spectral functions for core and valence states given by

\[
A_\sigma^{c/v}(\omega) = \frac{1}{\pi} \text{Im} \frac{1}{\omega - \epsilon_\sigma^{c/v} - \Sigma_\sigma^{c/v}(\omega)}.
\]

Note that, for valence states, the spectral function depends on the band index and \( k \)-vector: \( A_\sigma^v(\omega) \equiv A_{k\sigma}^v(\omega) \), the \( k \) and band index dependence coming from \( \epsilon_\sigma^v \equiv \epsilon_{k\sigma}^v \) and possibly from the self-energy.

Let us start from the core hole excitation. Within the present approach the hole self-energy turns out to be [12, 21]

\[
\Sigma_\sigma^c(\omega) = \int_{E_F}^{+\infty} n_{d-\sigma}(\epsilon)[U_{cv} - T_{hh}^{cv}(\omega - \epsilon)] \, d\epsilon \\
+ \int_{E_F}^{+\infty} n_{d\sigma}(\epsilon)[(U_{cv} - J_{cd}) - T_{hh}^{cv}(\omega - \epsilon)] \, d\epsilon \\
\times (1 + (U_{cv} - J_{cv})\tilde{A}_\sigma(\omega - \epsilon)) \, d\epsilon.
\]

Here \( n_{d\sigma}(\epsilon) \) is the \( d \) contribution to the valence density of states of spin \( \sigma \). The hole–hole scattering associated with the on-site interactions is described by \( T \) matrices, \( T_{hh}^{cv} \) and \( T_{hh}^{cv} \), for scattering between antiparallel and parallel spin holes respectively; similarly \( A_\sigma(\tilde{A}_\sigma) \) includes antiparallel (parallel) e–h scattering [21].

Figure 1 shows the calculated spectral functions for the 2p core level of Fe, Co and Ni obtained assuming the \( U \) and \( J \) values of table 1 with binding energies adjusted to the experimental values [23]. Since our calculated self-energy is responsible for an intrinsic broadening identical at the two edges, to reproduce the observed different lifetimes at the two edges we have added extra broadening \( \delta = 0.5 \) eV and \( \delta = 1.5 \) eV for 2p_{3/2} and 2p_{1/2}, respectively. The spectral functions reproduce the essential features of the core photoemission data for transition metals where a main peak is always followed by a satellite structure at higher binding energies. This structure is the fingerprint of e–e correlation, being commonly attributed to the admixture of different single-particle configurations: not just the ground state with one core electron missing but also the shake-up states where electrons are promoted to higher energy levels. These physical processes are contained in our many-body description based, as previously mentioned, on an extension to the solid state of the configuration–interaction scheme.

We turn now to valence states. The self-energy correction to a valence band level \( \epsilon_{k\sigma}^v \) is slightly more complicated with respect to the core one, reflecting the complex valence band structure where different orbitals are inextricably hybridized (for a detailed description of the valence self-energy see [12]).

The effect of correlation on empty states is shown in figure 2 for iron where the electron spectral functions are shown along high symmetry directions of the Brillouin zone. Notice that only some of the empty bands (the minority
spin ones of d orbital character) are affected by self-energy corrections, mainly in terms of lifetime broadening. The overall effect of correlation on empty states is, however, very small, and even smaller for cobalt and nickel where d states are almost fully occupied.

The response of interacting electrons to the creation of an e–h pair due to x-ray absorption is connected to these hole and particle spectral functions: within the single-particle approach the absorption cross section is just the joint density of core and valence states modulated by the dipole matrix elements:

\[ \mu_0^\pm (\omega) \propto \sum_{kn} |D_{ckn}^\pm|^2 \sum_\sigma \text{Im } \chi_{ck0}^\sigma (\omega) \]  

(6)

with

\[ \text{Im } \chi_{ck0}^\sigma (\omega) = \int_{-\infty}^{\infty} \delta (\Omega - \epsilon_{co}) \delta (\omega + \Omega - \epsilon_{kn}) d\Omega. \]

One effect of many-body correlation is to replace this joint density of states with the convolution of hole and particle spectral functions. Formally this corresponds to calculating a two-particle polarization propagator \( \chi_{cv}(\omega) \), where the bare particle and hole propagators are substituted with the dressed ones:

\[ \mu_0^\pm (\omega) \propto \sum_{kn} |D_{ckn}^\pm|^2 \sum_\sigma \text{Im } \chi_{ck0}^\sigma (\omega) \]  

(7)

with

\[ \text{Im } \chi_{ck0}^\sigma (\omega) = \int A^c_\sigma (\Omega) A_{kn0} (\Omega + \omega) d\Omega. \]

\( D_{ckn}^\pm \) appearing both in equations (6) and (7) is the matrix element of the electric dipole moment over the core and valence states:

\[ D_{ckn}^\pm = \sum_{m_j, m_r} \langle \Psi_{kn}^c | \hat{e}_{m_j}^\pm e_r | \Psi_{kn}^c \rangle \]  

(8)

with \( \hat{e}_{m_j}^\pm \) the polarization vector (left/right) of the incident photon, \( e \) the electron charge, and \( \Psi_{kn}^c \) and \( \Psi_{kn} \) the spin–orbit split core and valence eigenstates, respectively. The XMCD signal is obtained as the difference \( \mu^+ (\omega) - \mu^- (\omega) \).

Figure 3 shows the calculated absorption (a) and dichroic (b) spectra for Fe, Co and Ni calculated both with and without self-energy corrections, compared with experimental data [24, 25]. We notice that in most cases the inclusion of many-body effects improves the agreement with experimental XAS spectra, making the lines more asymmetric. What makes lineshapes asymmetric is the presence of shake-up satellite structures in the hole spectral functions. These structures are essential to also recover asymmetric lineshapes in XMCD spectra. Since in our calculation the L2 and L3 lines have the same lineshape (the self-energy in our calculation arises from the core–valence interaction which is the same at the two edges), the only difference being their width, it is not surprising that the asymmetry in the dichroic lines is the same at the two edges. In the case of nickel where both peaks in the measured dichroic spectrum present the same pronounced asymmetry, the inclusion of e–e correlation improves the agreement between theory and experiment. For iron and cobalt, in contrast, we are able to reproduce rather well the dichroic lineshape at the L2 edge but less accurately the L3 one, which turns out to be experimentally rather symmetric and more similar to the uncorrelated result. The asymmetry of the L2 edges increases from Fe to Ni, in agreement with the corresponding trend in the core–valence electronic correlation described by \( U_{sd} \) (see table 1).

As we mentioned at the beginning, what is still missing in this description is the e–h attraction responsible of excitonic effects. These effects can be included by considering the two-particle eigenvalue problem assuming the excited states of the \( N \)-particle interacting system to be a superposition of single-particle states with one core hole and an electron above the Fermi level. This is the so-called Tamm–Dancoff approximation (TDA) [26] and is at the core also of the 3BS scheme applied here to describe the charged excitations—just one e–h pair added in this case to the \( N \pm 1 \)-particle interacting system. TDA has been used to solve the Bethe–Salpeter equation (BSE) and treat excitonic effects in valence–valence transitions [27] and more recently extended to x-ray absorption from core states [10, 11, 28]. In most cases the dressed one-particle propagators have been obtained within the GW approximation [29]. In the present case we are interested in a regime of high e–e correlation where a perturbative approach like GW is supposed to be less appropriate, being unable to reproduce satellite structures that dominate the core level spectra. A non-perturbative method such as the 3BS approach would be more adequate and we are presently testing the extension of our theory in this direction. In this way it will be possible to treat more appropriately the case of highly correlated materials where e–e correlations are responsible not only for strong quasi-particle renormalization, correctly described within the Hubbard model and 3BS, but also strong excitonic effects.

A further difference between the present approach and the \( ab \) \textit{initio} methods based on either GW + BSE [10, 28] or the time-dependent local density approximation [1] is the treatment of the e–e interaction: in these schemes the electrons interact through the full long range, dynamically screened Coulomb potential while in our approach only the short range part of the Coulomb interaction is considered, in the spirit of the Hubbard model. The implicit assumption, common to
Figure 3. Absorption (left panels) and dichroic (right panels) spectra of Fe, Co and Ni. Theoretical spectra, with (QP) and without (SP) self-energy corrections, are compared with experimental ones [24, 25] represented by gray areas.

most approaches used to describe e–e correlation in strongly correlated materials, is to attribute many-body effects to just the on-site interaction, the long range part being included at the mean-field level in the band calculation. This assumption seems particularly reasonable in the case of the strongly localized core states but in practice leads to the introduction of adjustable parameters. This has been, up to now, a shortcoming of most of the approaches based on the Hubbard model, with the advantage of allowing for solutions beyond the perturbation limit.

The configuration–interaction scheme is another general method that allows us to include many-body effects in XAS and XMCD [4, 7, 8, 30]. This approach is quite attractive for core excitations due to their localized character and has provided an accurate description of experimental results, its main disadvantage being the need to rely on finite clusters. A genuine solid state description may be more appropriate when the energy scale of the interactions is of the same order of magnitude as the valence bandwidth or when, in spite of the strongly localized character of the electron states and of the interactions, the relaxation process following the creation of a core hole in one particular site involves many nearby atoms, ruling out a purely atomistic description. In these situations an approach like the one we have proposed here may be useful since full details of the valence and conduction band structure are included together with on-site interaction between localized (core) and itinerant (valence) states. Apart from these general statements it is difficult to identify unambiguously the solid state effects in the simulated spectra. For sure in a periodic system, Fermi level and ground state properties such as the fractional occupancies of d electrons are obtained naturally and accurately and fractional occupancies are related to the intensity of the dichroic signal. All the same we believe that the identification of solid state effects in the simulated
spectra would be possible only by a direct comparison with cluster-CI results, obtained possibly with increasing numbers of cluster atoms.

In summary, we have shown that many-body effects due to e–e interactions can be included in the description of x-ray absorption and dichroic spectra by replacing the joint density of states appearing in the absorption cross section with a convolution of (core) hole and (valence) electron spectral functions. Whenever e–e correlations modify significantly hole and electron spectral functions we expect non-negligible effects in the absorption spectra as well. In the case of 3d transition metals these modifications are essentially associated with the shake-up structures that appear in the core level photoemission spectra as a residue of atomic multiplets.

References

[1] Ankudinov A L, Nesvizhskii A I and Rehr J J 2003 Phys. Rev. B 67 115120
[2] Kotani A 2008 Phys. Rev. B 78 195115
[3] Shim J H, Haule K and Kotliar G 2009 Europhys. Lett. 85 17007
[4] de Groot F 2005 Coord. Chem. Rev. 249 31
[5] Jo T and Sawaizky G 1991 Phys. Rev. B 43 8771
[6] van der Laan G and Thole B T 1992 J. Phys. Chem. A 4 4148
[7] Ikeno H, de Groot F M F, Stavitski E and Tanaka I 2009 J. Phys.: Condens. Matter 21 104208
[8] Krueger P 2010 Phys. Rev. B 81 125121
[9] Soininen J A and Shirley E L 2001 Phys. Rev. B 64 165112
[10] Olovsson W, Tanaka I, Mizoguchi T, Puschnig P and Ambrosch-Draxl C 2009 Phys. Rev. B 79 041102(R)
[11] Laskowski R and Blaha P 2010 Phys. Rev. B 82 205104
[12] Manghi F, Bellini V and Arcangeli C 1997 Phys. Rev. B 56 7149
[13] Blaha P, Schwarz K, Madsen G, Kvasnicka D and Luitz J 2001 WIEN2k, An Augmented Plane Wave + Local Orbitals Program for Calculating Crystal Properties ed K Schwarz (Wien: Techn. Universität) (ISBN 3-9501031-1-2)
[14] Kuneš J, Novák P, Diviš M and Oppeneer P M 2001 Phys. Rev. B 63 205111
[15] Rozzi C A, Manghi F and Calandra C 2005 Phys. Rev. B 72 125106
[16] Cococcioni M and de Gironcoli S 2005 Phys. Rev. B 71 035105
[17] Miyake T, Aryasetiawan F and Imada M 2009 Phys. Rev. B 80 155134
[18] Steiner M M, Albers R C and Sham L J 1992 Phys. Rev. B 45 13272
[19] Sanchez-Barriga J J et al 2009 Phys. Rev. Lett. 103 267203
[20] Sanchez-Barriga J J et al 2010 Phys. Rev. B 82 104414
[21] Rozzi C A, Manghi F and Arcangeli C 2000 Phys. Rev. B 62 4774(R)
[22] Monasta S, Manghi F, Rozzi C A, Arcangeli C, Wetli E, Neff H-J, Greber T and Osterwalder J 2002 Phys. Rev. Lett. 88 246402
[23] Moulder J F, Stickle W F, Sobol P E and Bomben K D 1993 Handbook of X-Ray Photoelectron Spectroscopy (Eden Prairie, MN: Perkin-Elmer, Physical Electronics Division)
[24] Chen C T, Sette F, Ma Y and Modesti S 1990 Phys. Rev. B 42 7262
[25] Chen C T, Idzerda Y U, Lin H J, Smith N V, Meigs G, Chaban E, Ho G H, Pellegrin E and Sette F 1995 Phys. Rev. Lett. 75 152
[26] Rohlfing M and Louie S G 2000 Phys. Rev. B 62 4927
[27] Onida G 2002 Rev. Mod. Phys. 74 601
[28] Rehr J, Soininen J and Shirley E L 2005 Phys. Scr. T115 207
[29] Hedin L 1965 Phys. Rev. 139 A796
[30] Krueger P and Natoli C R 2004 Phys. Rev. B 70 245120
[31] Amadon B, Biermann S, Georges A and Aryasetiawan F 2006 Phys. Rev. Lett. 96 066402