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Abstract
There has been dramatic progress in recent years both in efficient calculations and in the interpretation of various x-ray spectroscopies. For example, real-space multiple-scattering theory gives a unified treatment of extended x-ray absorption fine structure, near edge structure, x-ray magnetic circular dichroism and other spectroscopies. Here we discuss the theory of x-ray spectra in the framework of excited state electronic structure. These are closely connected since x-ray spectra are directly related to a Green function for the excited photoelectron in the presence of a core hole. However, corrections to the independent electron approximation are needed to account for many-body effects such as inelastic losses, screening and core-hole effects. We discuss recent approaches for calculating such corrections and show that they can explain some of the remaining discrepancies between theory and experiment.

1. Introduction

Advances in theory over the past decade have revolutionized the technique of extended x-ray absorption fine structure (EXAFS) for local structure determinations. Indeed, the basic theory of EXAFS is now well understood, as discussed in a recent review [1]. Significant progress has also been made both in understanding and in efficient calculations of x-ray absorption near edge structure (XANES), i.e., the structure within about 30 eV of threshold where multiple-scattering (MS) contributions to high or all orders is often important. Here we use the term XAS to refer to EXAFS, XANES, XMCD (x-ray magnetic circular dichroism) and other x-ray absorption spectroscopies. XMCD is strongly dependent on the spin–orbit interaction, which is a primary topic of this conference. There is a close connection between the theory of XAS and excited state electronic structure, since x-ray spectra are directly related to a Green function for the excited photoelectron in the presence of a core hole. One of the main purposes of this paper is to discuss recent advances in the theory of XAS based on this connection. This is done first within a one-electron picture and real space multiple-scattering (RSMS) theory. Second we discuss the need for corrections to the independent particle approximation to better understand the nature of the electronic excitations created in the XAS process and

to improve the calculations. These corrections include the core-hole interaction, the effects of screening of the x-ray field [2] and inelastic losses [3, 4]. In particular we briefly describe recent approaches for treating these many-body effects. These approaches provide a promising alternative to others, e.g., configuration interaction and atomic multiplets [5, 6], since they can treat such many-body effects efficiently in extended systems.

1.1. One-electron theory

The basic single-particle theory of XAS [1, 7] is now fairly well developed and understood. Formally the x-ray-absorption coefficient μ for a given x-ray energy $\hbar\omega$, initial state i and photoelectron energy $E = \hbar\omega + E_i$ is given by Fermi's golden rule,

$$\mu(\omega) \sim \sum_f |\langle i|\boldsymbol{A} \cdot \boldsymbol{p}|f\rangle|^2 \delta(E - E_f), \tag{1}$$

where $\boldsymbol{A} \cdot \boldsymbol{p}$ is the coupling to the x-ray field, and the sum is over unoccupied final states $|f\rangle$. Most practical calculations are based on the dipole approximation and the reduction of the golden rule to a one-electron approximation. However, the question of which one-electron states to use is not unambiguous. Much current work is based on the 'final state rule,' in which the one-particle final states are calculated in the presence of an appropriately screened core hole, and all many-body effects and inelastic losses are lumped into a complex, energy-dependent self-energy or optical potential. This theory is the basis for our XAS/electronic structure code FEFF [1] and many others. Another popular approach for handling these many-body effects is based on atomic multiplets [5, 6]. However, neither of these approaches is fully satisfactory [8]. The one-electron approach ignores particle–hole and correlation effects, while the atomic multiplet theory uses a crystal-field parametrization of solid state effects and ignores delocalized states. Also, one-particle theories neglect intrinsic losses due to the sudden creation of a core hole and hence generally overestimate the amplitude of the fine structure in the spectra [4, 9]. Moreover, such theories also neglect local field effects, i.e., screening of the x-ray field by the system [2].

1.2. Real space Green function (RSGF) formalism

An important formal development in XAS theory is the RSGF approach [7, 10], which illustrates the close connection between XAS and electronic structure. The need to calculate final states in the golden rule—even in the one-electron approximation—is often a severe computational bottleneck, and can only be carried out efficiently for highly symmetric systems such as atoms, small molecules or crystalline solids. However, many systems of interest lack such symmetry. Also band structure methods [11, 12] generally ignore the effects of the core hole which ruin perfect crystalline symmetry unless a super-cell approximation is used. Thus instead of explicitly calculating the final states, it is preferable to calculate the XAS in terms of the photoelectron Green function or propagator in real space, i.e., in terms of the ground state matrix element,

$$\mu(\omega) \sim -\frac{1}{\pi}\text{Im}\,\langle i|\hat{\boldsymbol{\epsilon}} \cdot \boldsymbol{r}' G(\boldsymbol{r}', \boldsymbol{r}, E)\hat{\boldsymbol{\epsilon}} \cdot \boldsymbol{r}|i\rangle. \tag{2}$$

Within MS theory, the propagator $G(\boldsymbol{r}', \boldsymbol{r}, E) = \Sigma_{L,L'} R_L(\boldsymbol{r}') G_{L,L'} R_{L'}(\boldsymbol{r})$, so the expression for μ can be reduced to a calculation of atomic dipole-matrix elements $M_L = \langle i|\hat{\boldsymbol{\epsilon}} \cdot \boldsymbol{r}|L\rangle$ and a propagator matrix $G_{L,L'}$. This matrix $G_{L,L'}$ can be re-expressed formally as a sum over all MS paths that a photoelectron can take away from the absorbing atom and back [1, 7], and thus gives rise to the path expansion for EXAFS. For XANES, however, the MS expansion often

must be carried to all orders (i.e., 'full MS') by matrix inversion [13, 14]. Although carried out in real space, full MS is formally equivalent to 'exact' treatments, e.g., the KKR band structure method [10] including a core-hole potential. The relativistic generalization [15] is similar in form. Relativity is important for the treatment of spin–orbit effects, which are biggest in the atomic cores, but has only weak effects on scattering. In FEFF such relativistic effects are treated with Dirac–Fock atomic calculations [16] and semi-relativistic scattering. Since $G_{L,L'}$ naturally separates into intra-atomic contributions from the central atom and from MS, one obtains $\mu = \mu_0(1 + \chi)$, and hence the structure in μ depends both on the atomic background μ_0 and on the MS signal χ. This result is consistent with the experimental definition of XAFS $\chi = (\mu - \mu_0)/\Delta\mu_0$, where $\Delta\mu_0$ is the jump in the smooth atomic-like background.

1.3. Electronic structure interpretation of XAS

Despite several early efforts at interpreting XANES [17, 18], a fully quantitative analysis is still not well developed. There is also a need for a reliable inverse method of extracting chemical and geometrical structure from XANES. However, there has been some recent progress. Although the XANES signal depends sensitively to the geometrical structure, its behaviour is a direct measure of the excited state electronic structure in a material. The reason is that the local projected density of states (LDOS) ρ is analogous to XAS and shares the same fine structure, i.e., $\rho = \rho_0(1 + \chi)$, and hence $\rho \approx \gamma\mu$ where $\gamma = \rho_0/\mu_0$ is a smooth, atomic ratio. Thus one can extract the LDOS from experimental XAS with this relation. This and similar relations e.g. for the spin density of states, have recently been exploited [19] to interpret charge counts from XANES and spin and orbital moments from XMCD.

1.4. Fast XANES calculations

Due to the need for matrix inversion (which scales in computational time as the cube of system size) in full MS, XANES calculations are much more time consuming than are EXAFS. Indeed, XANES calculations become computationally intractable in the EXAFS regime or for cases (e.g., low Z atoms) where the mean free path is very long. Thus one of the challenges has been to increase the computational speed. Promising methods include the recursion method [20], iterative approaches [21], repartitioning [22] and most recently fast modern Lanczos algorithms [23]. The Lanczos algorithms have the advantage of stability and also automatically yield the full matrix inverse, thus providing significant improvements compared to conventional inversion techniques.

However, much more dramatic reductions can be obtained from parallel computational algorithms, which scale as $A + B/N$, where N is the number of processors. For the code FEFF8.2 $A \cong 0.03$ and $B \cong 0.97$, and hence parallelization can provide one to two orders of magnitude further improvement [23]. This parallelization has been implemented in FEFF8.2 with the MPI (message-passing-interface) protocol [24]. As a result XANES calculations even for very large systems of order 10^3 atoms can now be carried out in less than one cpu hour on parallel computers, e.g., systems with of order $N \approx 32$ processors. With these developments, the computational time bottleneck of XANES calculations has largely been overcome.

2. Local field effects in XAS

Although one-electron theory is quite successful in describing EXAFS and is often a reasonable approximation for XANES [1], it fails dramatically at the $L_{2,3}$ edges of 3d transition metals [25–28]. For example, one-electron theory predicts an L_3/L_2 intensity 'branching ratio' close to 2:1, while the observed ratio varies strongly with atomic number Z and is closer to 1:1

for metals like Ti and V [29]. The source of this effect has been attributed to the effects of the photoelectron/core-hole interaction, which is only included approximately in one-electron models. The trends in the anomalous L_3/L_2 ratio have been explained using atomic models, e.g., configuration-interaction [26] and atomic multiplets [27]. However, such models ignore continuum states and hence are not fully quantitative for solids. A more precise description for solids requires a two-particle Green function, the Bethe–Salpeter equation (BSE) [30–34], which provides a systematic approach for treating correlated particle hole states. However, the BSE involves a non-local, dynamically screened Coulomb interaction between the core hole and photoelectron, which is difficult to model and calculate. Thus considerable efforts are now being made to develop practical alternative approaches for treating these effects [28, 35]. For example, an attractive approach applicable to extended systems uses the time-dependent local density approximation (TDLDA) with static exchange [36–38] and relativistic band structure calculations [28]. While TDLDA with a static exchange–correlation kernel can also explain the trends of the L_3/L_2 branching ratio, significant discrepancies remain compared to experiment. The TDLDA also has a physical interpretation in terms of local screening of the x-ray field by the dielectric response of the system [2]. We have exploited this property by taking advantage of the locality of the screening to simplify the calculations [39]. In particular we have suggested that dynamic screening effects must also be considered which leads to a much better agreement between calculated and observed L_3/L_2 branching ratios.

2.1. TDLDA and BSE

The TDLDA [2, 35] provides an efficient formalism for calculations of electron response functions, including corrections to the independent electron approximation, provided the local exchange approximation is adequate. The TDLDA was originally introduced for atoms, but has since been extended to many other systems [37, 38]. The TDLDA, BSE and TDHF (time-dependent Hartree–Fock) equations are all rather similar since they can be expressed in the form of two-particle Green functions. The main difference lies in the structure of the exchange–correlation kernels $K(\omega)$ in the equations. Thus the TDHF equations use an unscreened non-local particle–hole interaction, while the BSE uses a dynamically screened interaction $W(\omega)$, and TDLDA uses a local, density dependent potential $f_{xc}(\omega)$ derived from density functional theory. Second, both TDLDA and TDHF ignore inelastic losses, while the conventional BSE ignores losses beyond the quasi-particle approximation.

Within the TDLDA or TDHF the XAS can be expressed as an integral over the non-interacting response function $\chi_0(\vec{r}, \vec{r},' \omega)$ and the screened x-ray field $\phi(\vec{r}, \omega)$ [2]

$$\mu(\omega) = -\frac{4\pi\omega}{c} \int d\vec{r}\, d\vec{r}'\, \phi^*(\vec{r}, \omega) \mathrm{Im}\, \chi_0(\vec{r}, \vec{r},' \omega) \phi(\vec{r},' \omega). \tag{3}$$

Equation (3) is equivalent to an analogous expression with ϕ replaced by the external x-ray field ϕ^{ext} and χ_0 by the full response function χ given in matrix notation, regarding $\vec{r}$ and $\vec{r}'$ as vector or matrix indices, by $\chi = [1 - \chi^0 K]^{-1}\chi^0(\omega)$. The field $\phi(\omega)$ consists of the external field $\phi^{ext} \equiv \hat{\epsilon} \cdot \vec{r}$ (in the dipole approximation) plus an induced local field, which (in matrix form) is given by

$$\phi(\omega) = \epsilon^{-1}(\omega)\phi^{ext}(\omega), \qquad \epsilon(\omega) = 1 - K(\omega)\chi^0(\omega). \tag{4}$$

Here $K(\vec{r}, \vec{r},' \omega)$ denotes the particle–hole interaction or TDLDA kernel which contains direct and exchange parts, i.e., $K(\vec{r}, \vec{r},' \omega) = V(\vec{r}, \vec{r}') + f_{xc}(\vec{r}, \vec{r},' \omega)$ where $V = 1/|\vec{r} - \vec{r}'|$ is the Coulomb interaction.

This approach fits well with the the RSMS formalism used in FEFF8. In particular, equation (3) can be reexpressed in a form similar to that of equation (2) in an angular momentum basis,

$$\mu(\omega) = \frac{4\pi e^2 \omega}{c} \sum_{i,LL'} \tilde{M}_{iL}(\omega) \rho_{L,L'}(E) \tilde{M}_{iL'}(\omega), \tag{5}$$

where $E = \omega + E_i - E_F$ is the photoelectron energy. Here both the screening of the x-ray field and the photoelectron–core-hole interaction are included implicitly in the renormalized dipole matrix elements $\tilde{M}_{iL}(\omega) = \langle R_L | \phi | i \rangle$, where $L = (\kappa, m)$ denotes a relativistic angular momentum basis, while the fine structure in ρ is not altered. When screening is negligible, $\tilde{M}_{iL} \to M_{iL}$ and the one-electron result is recovered.

The major difficulty with this approach is the lack of reliable approximations for the dynamic exchange–correlation kernel $K(\omega)$ at x-ray energies, since this is much less well understood than that for the ground state. Most practical TDLDA calculations for optical spectra use the static limit derived from ground state density functional theory, which is appropriate in that limit. Alternatively one can often neglect the exchange–correlation part when the effects are small, setting $f_{xc} = 0$; this is called the RPA (i.e. random phase approximation) [28]. Both of these approaches achieve efficiency by avoiding the non-locality of TDHF or BSE. However, dynamical effects appear to be important at x-ray frequencies [39]. Although the RPA works well for nearly filled d bands (e.g., for Ni) and static exchange works well for nearly empty d bands, neither is adequate for all transition metals. Indeed, by introducing a dynamical model kernel based in part on the behaviour of screening in the BSE at high energies, we were able to explain the behaviour of the anomalous branching ratio over the full range of 3d transition metals, without the complexity of full dynamic-screening calculations.

3. Inelastic losses in XAS

Inelastic losses are crucial to a quantitative theory of XAS [1]. The treatment of such losses in XAS has a long history [3, 9] and generally requires physics going beyond the one-electron and quasi-particle approximations. Two types of loss are usually identified. *Extrinsic* losses occur during the propagation of the photoelectron (giving rise to the photoelectron mean free path) and are caused by the creation of excitations of the system such as plasmons, electron–hole pairs etc. They can be calculated in a quasi-particle approximation from the imaginary part of the photoelectron self-energy. *Intrinsic* losses refer to the creation of similar excitations by the sudden appearance of the core hole, but are similar in nature. These intrinsic losses give rise to the EXAFS many-body reduction factor S_0^2 which is typically about 0.8–0.9. However, since the excitations are quantum mechanically indistinguishable, *interference* between extrinsic and intrinsic losses is also possible. For photoemission spectroscopy, it has been shown [3, 40] that this interference is large near excitation thresholds, where the losses strongly cancel due to the opposite signs of the coupling between the photoelectron and the core hole to excited states.

In this section we describe the recent treatment of inelastic losses and interference by Campbell *et al* [4], which is an extension of the original work by Hedin and Bardyszewski [3]. This approach leads to practical calculations of the XAFS amplitude reduction factor $S_0^2(\omega)$, since the results are formulated in terms of an effective one-particle propagator which includes both losses and interference effects. This propagator contains an asymmetric quasi-particle peak plus a broad energy dependent satellite structure, and hence is an extension of the quasi-particle approximation. The approach is essentially a generalization of the GW self-energy approximation and involves many of the same ingredients. However, the method is more general and can also account for edge-singularity effects and corrections to the final state rule. As in photoemission, there is appreciable cancellation of extrinsic and intrinsic losses by the interference terms near the excitation threshold, while the strength of the primary channel

increases, thus recovering the quasi-particle approximation. Thus the theory also explains both the surprising weakness of multi-electron excitations in the observed XAS [1], and hence the remarkable success of the one-electron (quasiparticle) theory, apart from weak smoothly varying amplitude factors. Moreover, at sufficiently high energies both the extrinsic and the interference contributions become negligible, and the theory crosses over to the sudden-approximation limit, i.e., the theory discussed in [9] with a nearly constant S_0^2.

Here we only briefly outline the basic formalism and qualitative results. One of main results is an expression for the XAS as a convolution of the one-electron spectrum $\mu^{(1)}$ with an energy dependent spectral function $A(\omega, \omega')$ that incorporates all the losses and interference terms,

$$\mu(\omega) = \int_0 d\omega' \, A(\omega, \omega') \mu^{(1)}(\omega + E_c - \omega'). \tag{6}$$

This shows that the main effect of many-body corrections to the one-electron XAS is an energy dependent broadening. Here $A(\omega, \omega')$ is related to an 'effective' one-electron Green function, $A = (-1/\pi)\text{Im}\, g_{\text{eff}}$, while the one-electron XAS is given by

$$\mu^{(1)}(\omega) = \sum_{k' > k_F} |\langle k'|Pd|b\rangle|^2 \delta(\omega - \epsilon_k). \tag{7}$$

An important difference between $\mu^{(1)}$ and the usual one-electron XAS is the presence of the projection operator P in the dipole matrix element. This factor enforces the Pauli principle (suppressing transitions to occupied states) and gives rise to broadened edge-singularity effects. The detailed theory is based on a quasi-boson (oscillator) model Hamiltonian, as discussed in [3]. The Hamiltonian includes couplings between photoelectron and valence electrons V_{pv}, photoelectron and core electrons V_{pc}, and valence electrons and core V_{vc}, as follows:

$$H_{v0} = \sum_n \omega_n a_n^\dagger a_n, \qquad\qquad h' = \sum_{k > k_F} \epsilon_k c_k^\dagger c_k,$$
$$V_{vc} = -\sum_n V_{bb}^n (a_n^\dagger + a_n), \qquad V_{pv} = \sum_{nkk'} [V_{kk'}^n a_n^\dagger + (V_{kk'}^n)^* a_n] c_k^\dagger c_{k'}. \tag{8}$$

The essence of this model is that the electron–hole type excitations are represented by bosons a_n with energies ω_n, and the electron–charge fluctuation coupling is represented by a term linear in the boson operators, as in equation (8). The quantities V^n are fluctuation potentials corresponding to excited states n, and can be obtained from an RPA type dielectric function [41]. With this model Hamiltonian one can solve explicitly for the relation between the ground states of H_{v0}' and H_{v0} with and without a core hole respectively, i.e.,

$$|\Phi_0\rangle = e^{-S}|\Phi_0'\rangle, \qquad S = \frac{a}{2} - \sum_n \frac{V_{bb}^n}{\omega_n} \tilde{a}_n^\dagger, \qquad a = \sum_n \left(\frac{V_{bb}^n}{\omega_n}\right)^2, \tag{9}$$

where $\tilde{a}_n^\dagger$ belongs to $H_{v0}' = \sum_n \omega_n^\dagger \tilde{a}_n^\dagger \tilde{a}_n$. The expansion to second order in the coupling interactions V^n yields

$$g_{\text{eff}}(\omega) = e^{-a} \left[g(\omega) + \sum_n \left(\frac{V_{bb}^n}{\omega_n}\right)^2 g(\omega - \omega_n) - 2\sum_n \frac{V_{bb}^n}{\omega_n} g(\omega - \omega_n) V^n g(\omega) \right], \tag{10}$$

where $g(\omega) \equiv [\omega - h' - \Sigma(\omega) + i\gamma]^{-1}$ is the damped Green function calculated in the presence of a core-hole potential. The above result thus yields an expression for $g_{\text{eff}}(\omega)$ and hence the XAS $\mu(\omega)$ as an expansion in one-particle Green functions, thus avoiding the calculation of correlated many-body final states. The various contributions to the effective spectral function

can be represented as a sum of quasiparticle, interference, intrinsic and extrinsic satellite terms, i.e.,

$$A_{\text{eff}}(\omega, \omega') = [1 + 2a(\omega)]\delta(\omega') + A^{sat}(\omega, \omega'), \tag{11}$$

where $A^{sat}(\omega, \omega') = A_{extr}(\omega, \omega') + A_{intr}(\omega, \omega') - 2A_{inter}^{sat}(\omega, \omega')$. Near threshold the net weight of each of the contributions A_{extr}, A_{inter}^{sat} and A_{intr} is equal to the strength parameter a so that the sum of all of these contributions tends to cancel. Also near threshold, $Z \approx \exp(-a)$ and the interference contribution to the quasi-particle peak $a(\omega) \approx a$. Thus the net strength of the main peak at threshold in this second order theory is close to unity, $Z \exp(-a)(1 + 2a) \rightarrow 1 + O(a^2)$.

It is interesting to examine the effects of inelastic losses and interference on the XAFS spectrum. In the usual MS theory [1], the XAFS spectrum $\chi^{(1)}(\omega)$ is a rapidly oscillating factor in the XAS $\mu^{(1)}(\omega) = \mu_0^{(1)}(\omega)[1 + \chi^{(1)}(\omega)]$, where $\mu_0^{(1)}$ is the generally smooth absorption from the central atom alone. Thus the net effect of the convolution over a normalized and asymmetric spectral amplitude $\tilde{A}_{\text{eff}}(\omega, \omega')$ is clearly a decreased XAFS amplitude and a phase shifted oscillatory signal compared to the one-particle XAFS $\chi^{(1)}$. In particular, the effect on each MS path of length R can be expressed as a 'phasor sum' over the effective spectral function $\tilde{A}_{\text{eff}}$,

$$S_0^2(\omega, R) = \int_0^\omega d\omega' \, \tilde{A}_{\text{eff}}(\omega, \omega') e^{i2[k(\omega-\omega')-k(\omega)]R}. \tag{12}$$

This phasor sum is similar to that derived by Rehr *et al* [9] but contains an energy dependent spectral function $\tilde{A}_{\text{eff}}$ which can be estimated quantitatively, in reasonable agreement with experiment. Qualitatively the behaviour of $S_0^2(\omega, R)$ is as follows: at low energies compared with the excitation energy ω_p, the satellite terms strongly cancel so $A(\omega, \omega') \approx \delta(\omega - \omega')$ and hence $S_0^2(\omega, R) \rightarrow 1$. At high energies, the sudden approximation prevails, and $A \approx A_{qp} + A_{intr}$, which has a strong satellite structure. However, the phase difference between the primary channel and satellite is small at high energies and hence also $S_0^2(\omega, R) \rightarrow 1$. At intermediate energies, however, $|S_0^2(\omega, R)|$ has a broad minimum, which explains why a constant reduction factor is a reasonable approximation. Although the model calculations reported in [4] are based on the relatively crude electron gas dielectric function, they are in reasonable agreement with experiment. Thus this development removes one of the last adjustable parameters in the theory, leading to improved values of coordination numbers from EXAFS experiment.

4. Conclusions

RSGF theory and the FEFF codes now make possible a general treatment of XAS, encompassing both XAFS and XANES as well as a number of other x-ray spectroscopies. The availability of a quantitative theory is key to an interpretation of XAS spectra in terms of local geometrical structure and electronic structure, such as LDOS, and spin and orbital moments. The current state of XAFS is now highly quantitative and widely used. Significant progress has been made in XANES theory and computational algorithms, so one-electron calculations on parallel computers are now both fast and accurate. Moreover, there has been significant progress in understanding corrections beyond the independent-electron approximation, including the treatments of screening of the x-ray field, core-hole effects and inelastic losses. The approaches discussed here illustrate the close connection between XAS and excited state electronic structure. Indeed, the theory of XAS is now progressing beyond the conventional one-electron approximation to a theory of excited states and response functions that accounts for details of two-particle (i.e., particle–hole) excitations. With these developments XANES is beginning to realize its promise as a tool for elucidating chemical and electronic structure.

Acknowledgments

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