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Real-space multiple-scattering approach to XANES

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The historical development of ideas in x-ray absorption and multiple scattering theory that lead to real space, multiple scattering (RSMS) calculations of XANES is reviewed. The RSMS method for both XANES and electronic structure calculations has several advantages with respect to other approaches. Recently developed RSMS codes now provide a way to interpret XANES in terms of structural and electronic information. The sensitivity of XANES calculations to muffin-tin potential construction, self-consistency and self-energy is demonstrated for the Ti K edge of PbTiO₃. Future RSMS electronic structure codes require several improvements, such as non-spherical potentials and inclusion of many body effects in order to achieve more quantitative agreement with experiment.

Keywords: XANES, electronic structure, multiple scattering theory

1. Key developments in x-ray absorption and multiple scattering theory

Multiple scattering theory (MST) was first formulated by Lord Rayleigh in 1892 for the theories of conductivity and sound in the quasistationary case (Rayleigh, 1892). He also introduced the expansion of the potential in terms of spherical harmonics, which proved to be very useful in many applications of MST due to its fast convergence properties. Kasterin strongly developed the MST of sound and generalised it to arbitrary wavelengths (Kasterin, 1896). The possibility to use this theory for other types of waves was first realised by Ewald, who applied Kasterin's work to electromagnetic waves and developed expression for optical dispersion (Ewald, 1916). Koringa also used Kasterin's ideas to develop the first approach to the electronic structure calculations based on MST (Koringa, 1947), which is now known as the Koringa-Kohn-Rostoker (KKR) band structure method. Originally MST for electrons was developed for the case of non-overlapping muffin-tin potentials, but its generalisation to the case of arbitrary potential shape was suggested by Williams & Morgan (1972).

The RSMS approach was formulated by Beeby for the study of electronic structure of disordered materials (Beeby, 1967). Interestingly, all components of the RSMS approach were known separately by 1962. They can be found in the classical textbooks on quantum mechanics (Messiah, 1962). The principal difference of RSMS from other multiple scattering methods is that it concentrates on the study of the Green's function and not the wave function. Beeby noticed, that for disordered materials the Green's function is much more

convenient to work with, since the electronic density is linearly proportional to the imaginary part of Green's function, but is proportional to the square of the wave function. The RSMS approach is closely related to the KKR and Scattered Wave (Johnson, 1966) approaches, also based on MST. However, in the last two methods the wave function is calculated, while within RSMS method the Green function is calculated using MST. Thus the treatment of bound states for the clusters is drastically different within the SW and RSMS method. The calculation of the wave function is avoided within RSMS method. The RSMS approach utilises analytic properties of the Green function to calculate electron density from integration in the complex energy plane, which may also include Fermi-Dirac statistics for finite temperature (Wildberger, 1995).

The theory of XAFS was first developed by Kronig. In his first work he suggested the long range order (LRO) interpretation of XAFS in crystalline materials; i.e. the fine structure in x-ray absorption is determined by the features of the band structure (Kronig, 1931). In his second paper he developed a short range order (SRO) theory for the molecules within a single scattering plane wave approximation (Kronig, 1932). Within SRO, XAFS is due to interference of the original photoelectron wave and the waves scattered from the neighbours. The history of XAFS before 1975, including the details of the controversy between LRO and SRO and development of EXAFS formula (Sayers, 1971), is well described by von Bordwehr (1989).

The RSMS approach of Beeby has been developed to obtain first RSMS expressions for x-ray emission (Gyorffy, 1971) and x-ray absorption (Schaich, 1973). The RSMS expression includes multiple scattering and curved wave effects, absent in the single scattering plane wave SRO theory of Kronig and has no restriction to point scattering. Schaich has shown that starting from the same formula both LRO and SRO expressions for XAFS can be derived, and therefore there is no contradiction between the SRO and LRO interpretations of XAFS.

The significance of many body effects in the theory of x-ray absorption was first raised by Mahan (1967). He showed that due to the creation and screening of a core hole in the x-ray absorption process, a singularity at the absorption edge may arise. However the significance of other many body effects for XAFS was not realised until after 1975. Von Barth & Grossmann (1977) have shown that most of the core-hole screening effect can be accounted for by the "final state rule", that reduces the many body problem to single electron calculations. Lee & Beni (1977) demonstrated the necessity of including the self-energy (extrinsic losses) in the calculation of x-ray absorption. Rehr et al. (1978) first pointed out the importance of intrinsic losses, known as shake up or multielectron processes in atomic theory. Hedin (1989) proposed that the interference between intrinsic and extrinsic losses can strongly reduce the imaginary part of the self-energy near the onset of an extrinsic excitation (such as plasmon).

The calculations of XANES with cluster MST (RSMS or SW method) usually omit one or another important theoretical ingredient of those just mentioned. The purpose of this paper is to discuss the ways to achieve more accurate XANES calculations, using RSMS FEFF8 (Ankudinov, 1998) calculations as an example.

2. Calculations of XANES with RSMS formula.

The RSMS approach is equivalent to the Scattered Wave (SW) approach for continuum states and real energies. The SW formula for XAFS can be considered as a particular case of the RSMS formula for real energies. Many of the ingredients of the calculations are the same and the code written within the SW approach can be converted into a RSMS code and vice versa. The principal difference in calculations appears only for the bound states. Within SW one will calculate the wave function of the bound state and its eigenenergy. Within RSMS one would calculate the Green's function on a contour in the complex energy plane around the eigenenergy.

Several codes for the calculation of XANES using the RSMS or SW method have been developed: CONTINUUM (Natoli, 1980), DLXANES (Durham, 1981), FEFF (Rehr, 1992) and several Rostov-on-Don codes (Vedrinskii, 1974; Soldatov, 1991; Nikiforov, 1994). The only code that consistently implements the RSMS approach is FEFF, which recently has been extended to include the self-consistent potential also via the RSMS method (Ankudinov, 1998). All these codes calculate XANES using MST for clusters, but differ in details of the implementation of the RSMS formula for x-ray absorption. There were many successful XANES calculations with RSMS formula starting from the pioneering work of Vedrinskii et al. (1974). Typically, these calculations show good qualitative agreement with experiment that allow structural and electronic interpretation of the XANES peaks. The calculations were extended for spin-polarised XANES (Soldatov, 1994) and x-ray magnetic circular dichroism (Ankudinov, 1995).

The main advantage of using the RSMS approach is that it is a very practical way to treat disordered systems (Beeby, 1967). Also the Green's function, calculated with RSMS, is a central quantity for many body theory and therefore may provide an effective way to include additional many body effects in the future. Adding an imaginary part to the energy is equivalent to a Lorentzian broadening of the density of states. Thus by doing calculations in the complex energy plane one can avoid very small energy step for the density of states calculation, which is typical for band structure calculations, and save time in calculations.

The RSMS and SW calculations are usually done with atomic overlap potential (Mattheiss, 1964), which is further approximated by the muffin-tin form with a Norman automated prescription for the ratio of muffin-tin radii (Norman, 1974). Typically the overlapping muffin-tin spheres are used with an overlap factor of 10-15% (Jepsen & Andersen, 1995). Calculations are usually done with the final state rule and the self-energy within the Dirac-Hara or Hedin-Lundqvist model (Hedin, 1965). The intrinsic losses and interference of extrinsic and intrinsic losses are typically neglected, since the cancellation effect is expected (Fujikawa, 1993). The imaginary part of Hedin-Lundqvist self-energy is also often neglected, since it is also expected to be suppressed by the interference term.

XANES calculations depend much stronger on the details of potential construction than calculations in EXAFS region. The similar sensitivity of calculations to the muffin-tin approximation, self-consistency and self-energy is demonstrated below, using FEFF8 (RSMS) XANES calculations for PbTiO_3 , as an example. The calculations are

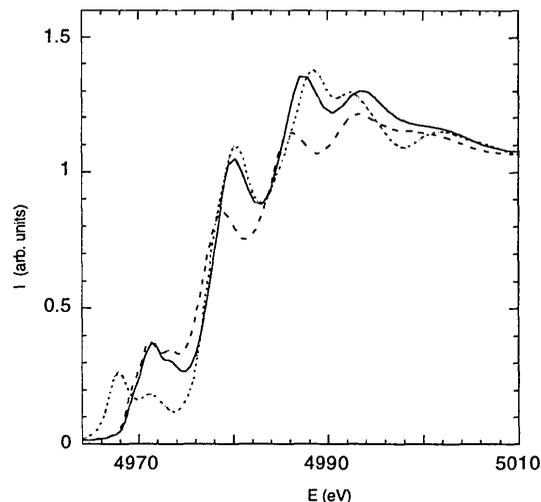


Figure 1

Non self-consistent (atomic overlap potential) calculations of XANES for PbTiO_3 with Hedin-lundqvist self-energy and two choices for muffin tin radii: Norman (solid) and matching point (dashes) prescriptions. Experiment is shown by short dashes and was shifted to match the peak position at 4980 eV.

made for a low temperature distorted structure, reported by x-ray diffraction study (Sicron, 1994). The Ti K-edge XANES is calculated for a 147 atom cluster around the absorbing atom.

Figure 1 shows the results of non self-consistent calculations with two different prescriptions for choosing muffin-tin radii: Norman and matching point. Within the Norman prescription one first finds the Norman radii, which is the radius of electrically neutral sphere around each atom. These radii are scaled so that the muffin-tin spheres are just touching. Within the matching point prescription one chooses muffin-tin radii so as to reduce jumps in potential for the touching geometry. Both prescriptions seem physically reasonable. However, the Norman prescription usually shows much better agreement with experiment. This is demonstrated for PbTiO_3 on Fig.1. The same effect was previously shown for GeCl_4 molecule (Natoli, 1980). The sensitivity to the choice of muffin-tin radii suggests, that the muffin-tin approximation should be avoided if possible. The multiple scattering theory is not restricted to the muffin-tin potential, and the full potential extension for XANES calculations was suggested by Natoli et al. (1986). The first calculations using this theory were performed by Foulis, Pettifer and Sherwood (1995) for the Cl_2 molecule, and showed much better agreement with experiment than muffin-tin calculations.

The results of adding self-consistency to calculations can be seen by comparing Fig. 1 and Fig. 2. The result shown by the solid line on Fig. 2 differs from that on Fig. 1 only due to inclusion of self-consistency. It shows much better agreement for the double peak around 4990 eV, but the overall agreement with experiment is of the same quality. The necessity to include both self-consistency and the full potential for a better quantitative agreement between calculations and experiment was clearly demonstrated for Cl_2 molecule (Foulis, 1995).

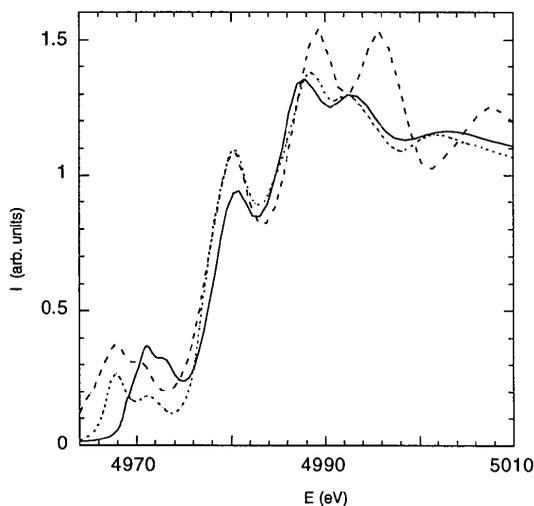


Figure 2

Self-consistent calculations of XANES for PbTiO_3 with Norman prescription for muffin-tin radii and two types of self-energy: Hedin-Lundqvist (solid) and Dirac-Hara (dashes). Experiment is shown by short dashes and was shifted to match the peak position at 4980 eV.

However, the effect of self-energy on XANES calculations is similar in magnitude to that of muffin-tin approximation and self-consistency. This is demonstrated on Fig. 2, where the solid line represents the calculations with Hedin-Lundqvist self-energy model, while the dashed one with Dirac-Hara. One can see that Hedin-Lundqvist model is much better above 4985 eV, while Dirac-Hara is definitely better below. Both models are Local Density Approximations (LDA) for the self-energy. Self-energy calculations can be improved by using the GW approximation (Hedin, 1965). This has already been implemented for calculations of ground state properties (Aryasetiawan & Gunnarson, 1998) and showed much better agreement with experiment than similar LDA calculations.

3. Conclusions.

The main advantages of the RSMS approach to electronic structure and XANES calculations are that it is applicable to ordered and disordered systems, and it provides a natural way to include many body effects. This is essential for several materials of important practical applications (high temperature superconductors, colossal magnetoresistance materials), which lack translational invariance. The XANES calculations with the RSMS formula typically show good qualitative agreement with experiment, which allows interpretation of the experimental data in terms of electronic and atomic structure. The calculated XANES intensities show similar sensitivity to the self-consistency, the self-energy and the details of muffin-tin potential construction. In order to make XANES a reliable structural probe, a better quantitative agreement between calculations and experiment is needed. In order to achieve such agreement the future calculations should be done with a self-consistent full potential MST and a better self-energy model.

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