PROGRESS IN SCF-SW-XALPHA AB INITIO XANES CALCULATIONS FOR CHROMIUM HEXACARBONYL BASED ON GENERAL NON-MUFFIN-TIN POTENTIALS

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Abstract

We describe progress towards the performance of SCF-SW-Xalpha calculations of photo-absorption cross-sections based on the theory of Natoli et al. for non-muffin-tin potentials. A crucial requirement is the accurate modelling of the electron-molecule potential using spherical harmonic expansions. We describe how this has been achieved and what difficulties are encountered. In the particular case of our model compound, chromium hexacarbonyl, we show what muffin-tin calculations produce and show that we may expect significant improvements from a non-muffin-tin calculation. Finally, we comment on the programming problems involved in these computations.

Introduction

The calculation of X-ray absorption near-edge structure (XANES) for covalently-bonded, open-structured materials has been hitherto rather unsatisfactory. At best, the agreement with experiment has been only qualitative. Considerable evidence points to the muffin-tin (MT) approximation for the electron-molecule potential as the main source of error. It is thus our purpose to perform ab initio calculations of XANES based on general, non-MT potentials for these materials. The immediate task therefore is to develop computer code realising the theory of C.R. Natoli, M. Benfatto and S. Doniach (1985, submitted for publication). This is a task of considerable complexity and to date we have made only limited progress. Our experience so far however, convinces us that the problem is quite tractable and that even for a small computer like our VAX 11/750 meaningful calculations can be done on medium-sized molecular clusters (~10 to 15 atoms), within certain limitations.

The theory underlying our approach to non-MT calculations is an extension of the self-consistent field scattered-wave Xalpha (SCF-SW-Xalpha) method developed by Johnson and others (see e.g. [1]), and extended to continuum states according to [2]. In the above theory of Natoli et al. the usual partitioning of the molecular space is retained, i.e. non-overlapping atomic spheres centred on the nuclear positions with an outer sphere enclosing them. However, in

the atomic spheres and outside the outer sphere we retain higher
multipole terms for the potential than the usual monopole term. In
the remaining interstitial region we replace the usual constant value
by a multipole expansion about the molecular centre. The use of such
a potential model affords a much better representation of the actual
case, but results in a considerable increase of algebraic
complication.

Model Compound and MT Calculations

Our present target is to perform a non-MT calculation for the chromium
K-edge spectrum in chromium hexacarbonyl. This model compound has
several features which make it a useful test of theory. It is a
system which has been studied several times using different
approaches. Thus we can compare our results with those readily
available from the literature. Additionally, the bonding in this
system is of general interest in coordination chemistry. From our
point of view it is interesting because of its similarity to metal
centres in biological systems such as enzymes.
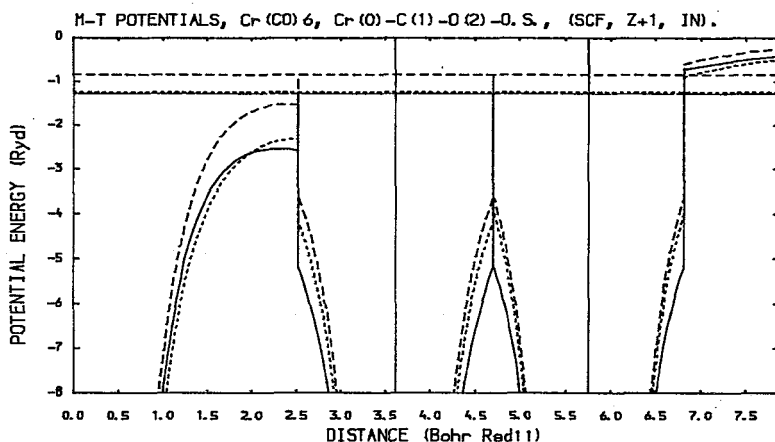

Fig. 1   Three different final state potentials used for the
          continuum calculations. Potentials are plotted along a
          traverse from the chromium nucleus, through the carbon and
          oxygen nuclei (full vertical lines), to some distance
          outside the outer sphere. The self-consistent ionized
          potential is denoted by the full curve; the Z+1
          approximation by the fine broken curve and the initial
          overlapped free atom potential by the coarse broken curve.
          The horizontal lines for each potential represent the
          constant value of the interstitial potential.

As far as calculations are concerned, the most important point is that
the MT approximation is particularly poor for chromium hexacarbonyl.
This can be seen from Fig. 1 where we show three potentials used for
the ionized final states in the calculation of photoabsorption
cross-sections. Although the SCF potential is the one normally used,
it is interesting to compare the results with calculations based on
the initial, overlapped free-atom potential and a Z+1 approximation to
the ionized potential. The structure of chromium hexacarbonyl was
taken from the literature (i.e. octahedral symmetry with d(Cr-C)=3.61
a.u. and d(C-O)=2.15 a.u.) and the MT spheres chosen so that nearest
neighbours touched with the potential matched at the C-O contact point

COMPARISON (THEOR./EXP.), Cr K-edge, Cr (CO) 6.
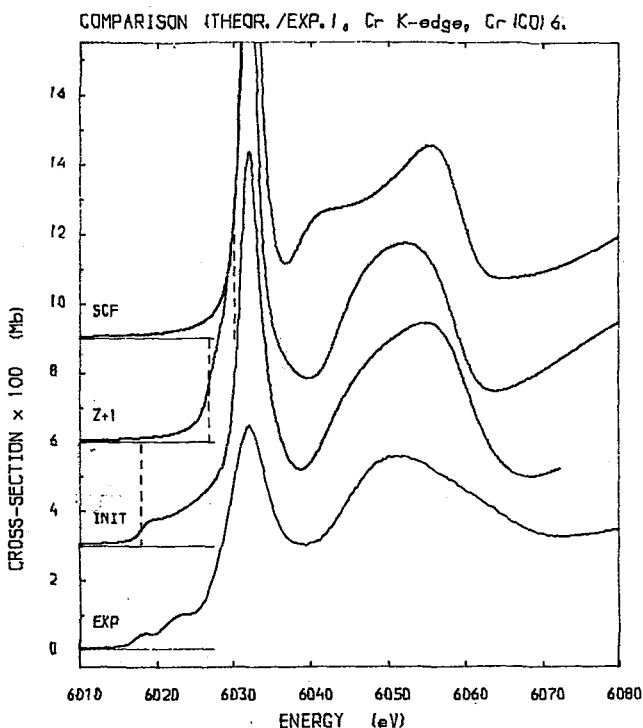
Fig. 2 Comparison of the three MT · based spectra with an experimental curve. Theoretical curves have been placed so that the first continuum peaks are aligned in energy. In the SCF case, for which total energies are available, this necessitated an upward shift of 59.8 eV. Bound states have been ignored. The theoretical cross-section curves were convoluted with Lorentzians of 1.5 eV FWHM to model the effects of core hole lifetime and monochromator resolution. The broken vertical lines associated with the theoretical spectra mark the positions of the continuum threshold. The main peaks in the SCF and Z+1 cases reach 0.208 and 0.164 Mb respectively. The experimental curve has been normalised to the McMaster et al. value of 42.025 kb.

(R(Cr)=2.52 a.u., R(C)=1.09 a.u. and R(O)=1.06 a.u.). One should particularly note the large potential discontinuities (~3 to 4 Ryd.) at the C and O sphere boundaries, the SCF case being the worst. An outer sphere of radius R(O.S.)=6.81 a.u. encloses the cluster just touching the oxygen spheres.

In Fig. 2 we see spectra calculated with these potentials compared with an experimental spectrum. We follow the general methods described in [3] and [4]. The average amplitudes of the theoretical curves are roughly correct, but the size of the oscillations are much too large, the first peak especially so. The gross features of the experimental spectrum are reproduced i.e. a narrow peak followed by a flatter wider peak. We notice that the worst case seems to be the SCF one, indicating that the projection of the potential onto a MT form between iterations is such a severe constraint that the benefits of self-consistency are nullified. We can see therefore that a more

accurate representation of the potential should produce significant
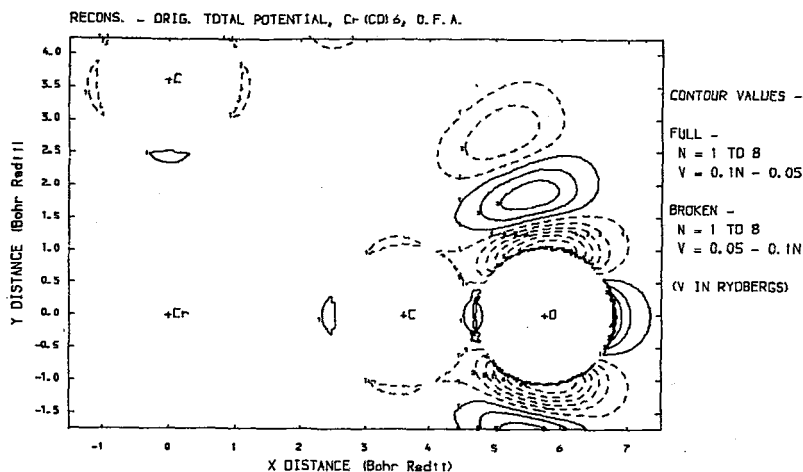improvements.

Non-MT Programs

In the MT case several main programs are used. Initially the program
MOLPOT is used to generate a (MT) potential from the superposition of
free-atom charge densities. The program ENERGY searches for electron
energy eigenvalues and eigenfunctions in this initial potential. The
potential and accurate eigenvalues are then passed to the program SCF
to begin the iteration to self-consistency.   Finally, using the
self-consistent initial potential and final excited potentials the
program CONTNM is used to calculate photoabsorption cross-sections.
This basic scheme is being followed for the non-MT case with the
writing of the corresponding programs MLPSHX, ENESHX, SCFSHX and
CNTSHX.

The current state of progress on the programs is shown in Fig.   3.
MLPSHX is completed and produces good results. ENESHX is nearing
completion. It is planned to write CNTSHX next, bypassing SCFSHX for
the present.   In this way we can obtain an immediate idea of the
effects of the inclusion of non-spherical components in the potential.
Fortunately, there is a great deal of similarity between parts of
ENESHX, SCFSHX and CNTSHX, so that the writing of the last two will be
much quicker than the first.   However, in SCFSHX one needs to
normalise states and generate a new potential at each iteration, which
will be a very difficult problem.
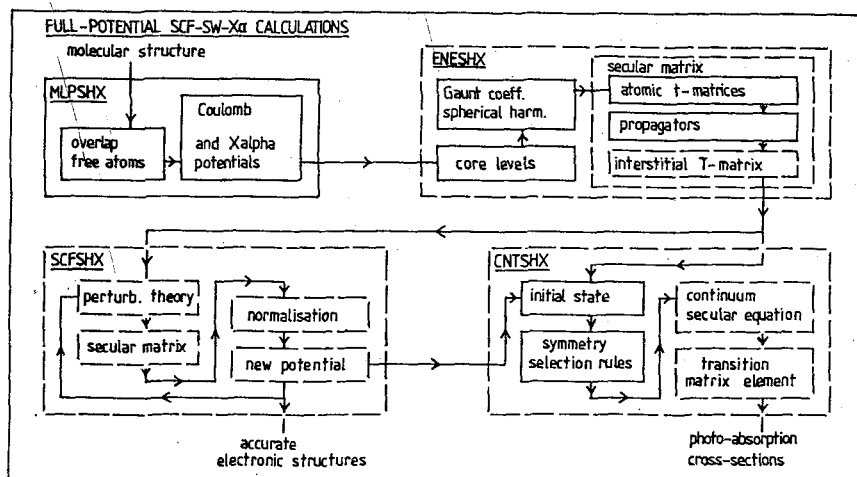
Fig. 3   Flow chart of the non-muffin-tin calculational scheme.   We
          follow the same overall pattern as with the MT case. First,
          we generate an initial potential from overlapped free-atom
          charge densities using MLPSHX. The program ENESHX is then
          used to search for energy eigenvalues in this potential.
          The eigenvalues and potential can then be passed to SCFSHX
          to start the generation of self-consistent potentials and
          eigenvalues; or passed directly to CNTSHX for the
          calculation of continuum states and photo-absorption
          cross-sections.   Only those parts of the calculations
          significantly different from the MT case are indicated.
          Broken lines indicate the present degree of completeness of
          the programs.

An important part of the present calculations is the use of molecular point symmetry to reduce the size of the matrix equations involved. MLPSHX superimposes free atoms to produce radial functions for the symmetrised spherical harmonic expansions (SHX's) of electron density, Coulomb potential, Xalpha potential and total electron-molecule potential. Advantage has been taken of the spherical symmetry of the free atoms to reduce the surface integrals to one-dimensional integrals. The most difficult problem however, is the calculation of the Xalpha part of the potential since this involves calculating a SHX of the cube root of another SHX. Currently, we perform the actual surface integrals using 60 of the total 70 minute program running time. A direct algebraic technique, if such existed, using the SHX components, would be preferable. The results of MLPSHX can be seen in Fig. 4 and are a considerable improvement over the MT case.

RECONS. _ ORIG. TOTAL POTENTIAL, Cr (CO) 6, O. F. A.

CONTOUR VALUES -

FULL -
N = 1 TO 8
V = 0. 1N - 0.05

BROKEN -
N = 1 TO 8
V = 0. 05 - 0. 1N

(V IN RYDBERGS)

Fig. 4 Contour plot of the difference between the total potential reconstructed from truncated spherical harmonic expansions in the various parts of the molecular space, and that obtained directly from the overlapped free atoms. Full contours are positive and broken contours are negative. The plot plane is through the atomic nuclei shown. The maximum l-values are as follows: l=20 for the interstitial region; l=10 for the chromium atom and l=5 for the carbon and oxygen atoms.

Conclusions

Currently we can generate SHX's for the various regions of the cluster partition that provide an accurate model of the potential. This model is good out to the second shell of coordinating atoms and very good for the first shell. Although we have used l(max)=20 for the interstitial region in Fig. 4, a value of 14 is not much worse.

At the current stage of progress on ENESHX we have found that the storage requirements (~0.5 to 0.6 megabytes) are easily within the limits of our computer. For CNTSHX we estimate that about 1 to 1.5 Mbytes will be necessary.

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[4] KUTZLER, F.W., NATOLI, C.R., MISEMER, D.K., DONIACH, S. and HODGSON, K.O., Journal of Chemical Physics 73 (1980) 3274-3288.