**FPMS: full potential multiple scattering**

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A full potential multiple-scattering (FPMS) code based on a real-space FPMS theory that is free from the drawbacks that have previously been believed to be necessary (in particular the need to expand cell-shape functions in spherical harmonics and the use of rectangular matrices) has been implemented under conditions for space partitioning that are less restrictive than those previously applied and are valid for both continuum and bound states. This approach eliminates the drawbacks of multiple-scattering theory in the muffin-tin approximation (MTA), while preserving its ease and simplicity of application. Tests of the program show that it is able to reproduce known solutions of the Schrödinger equation with very good accuracy. Applications to the spectroscopy of low-dimensional systems, such as 1D chain-like systems, 2D layered systems and 3D diamond structure systems, where the MTA is known to give very poor results, show a decisive improvement towards agreement with experiment. The default mode of the code uses superimposed atomic charge densities and works satisfactorily in most applications, but with the help of the "ES2MS" interface, which is incorporated into the program, self-consistent charge densities derived from the VASP program can also be used. The program has also been incorporated into the photoelectron diffraction code MsSpec and parallelized for energy points.

1. Introduction

Multiple-scattering (MS) theory is and has been one of the techniques of choice for solving the Schrödinger equation (SE) owing to its suggestive description of the electronic structure of solids and spectroscopic response functions, which appeals to our physical intuition. It is implemented by partitioning the space into non-overlapping domains (cells), solving the differential equation separately in each of the cells and then assembling the partial solutions together into a global solution that is continuous and smooth across the whole space and satisfies the given boundary conditions. It was originally proposed by Korringa and by Kohn and Rostoker (KKR) as a convenient method for calculating the electronic structure of solids (Korringa, 1947; Kohn & Rostoker, 1954) and was subsequently extended to the calculation of bound states of polyatomic molecules by Slater & Johnson (1972) and of continuum states by Dill & Dehmer (1974).

A characteristic feature of the method is the complete separation of the dynamical aspect of the system under study, as embodied in the cell scattering power, from the structural aspect of the problem, reflecting the geometrical positions of the atoms in space. Another advantage of the theory is that one can write an explicit form of the Green’s function (GF; the solution of the SE with a delta-like source term), which is essential for the description of many properties of the systems under investigation.
For ease of computation, the KKR method has traditionally been implemented within the so-called muffin-tin (MT) approximation, in which the potential is spherically averaged inside non-overlapping spheres (usually containing a physical atom) and takes a constant value in the interstitial region (see Fig. 1(a)). However, it is known that this approximation is only good for close-packed systems and works poorly for covalently bonded and low-dimensional systems, such as surfaces, sparse and/or layered systems and diamond-like structures (Hatada et al., 2007, 2009, 2010; Xu et al., 2015). Moreover, the introduction of empty spheres to reduce the interstitial volume does not mitigate the problem (Andersen, 1975). Although in some cases the introduction of empty spheres improves the calculations for X-ray absorption fine structure (XAFS) and density of states (DOS) in bulk systems, where an angle-integrated feature is probed, it still generates spurious peaks in angle-resolved low-energy photoelectron diffraction spectra owing to the unphysical diffraction caused by the potential discontinuities between the physical and artificial scatterers.

Owing to the poor performance of the MT approximation for both bound and continuum states, investigations to overcome this approach started quite early. In their pioneering work, Williams & Morgan (1974) reformulated the MS theory for arbitrary local potentials by partitioning the space with space-filling truncated cells and successfully applied this method to a model of crystalline silicon for which exact numerical solutions were available. The introduction of empty cells (ECs) was found to be necessary for the diamond-type lattice of silicon in order to adequately represent the potential in regions of substantial anisotropy and to satisfy geometrical constraints imposed by the re-expansion of the free GF around two sites. This way of partitioning the space is illustrated in Fig. 1(b), as opposed to the MT partition depicted in Fig. 1(a). Figs. 2(a) and 2(b) show a schematic representation of the potential in the two cases.

Williams and Morgan showed that the practical implementation of the method did not imply large increases in computation with respect to the MT approach. The only point of difference was the calculation of the single-site scattering power ($T_{LL'}$ matrix; no longer diagonal in the angular momentum indexes), for which they developed the variable-phase method to solve the SE for the truncated cell potential. However, the implications of the truncation of the angular momentum expansion that is necessary in the numerical implementation of the method, posing convergence problems, were not analysed and remained unanswered.

The need to expand the truncated potential (or, equivalently, the cell-shape function) in spherical harmonics (SH; giving rise to the well known Gibbs phenomenon, as in Fourier expansion), the need to converge ‘internal’ sums arising from

![Figure 1](a) A typical model of the muffin-tin approximation for a four-atom molecule. Inside atoms A–D, the potential, represented by contour lines of constant value, is spherically averaged, while the interstitial potential is constant. (b) Representation of the full potential model with space-filling cells. Empty cells (ECs) were placed at spots where the potential is not negligible. An outer sphere (OS) can be placed when the potential does not decrease rapidly enough to be negligible.

![Figure 2](a) MT case, (b) full potential case.
the re-expansion of the free GF around two sites, entailing the unwanted feature of the introduction of rectangular matrices, the geometrical restrictions on the space-partitioning cells induced by this re-expansion, the solution of a fairly complicated system of coupled differential equations to determine the local (cell) solutions (based on the phase function method) and the question of the angular momentum convergence of the whole theory have all contributed to the slow progress and application of full potential MS (FPMS) theory. In the few cases in which FPMS theory has been applied, the general attitude has been the empirical approach used by Williams & Morgan (1974). The reader is referred to Gonis & Butler (2012), and references therein, for a discussion used by Williams & Morgan (1974). The reader is referred to Gonis & Butler (2012), and references therein, for a discussion.

In Hatada et al. (2010), we presented the derivation of a real-space FPMS theory that is free from the drawbacks described above (in particular the need to expand cell-shape functions in SH and rectangular matrices) and is valid for both continuum and bound states under conditions for space partitioning that are less restrictive than those applied previously. This approach provides a straightforward extension of MS theory in the MT approximation.

We have implemented the FPMS code based on this theory.

2. Theory

One of the key ingredients of our approach to FPMS (Hatada et al., 2010) is a new scheme to generate local basis functions for the truncated potential. Starting from the SE written in polar coordinates, after elimination of the radial first derivative, the local solution \( P_L(r) = r\Phi_L(r) \) satisfies the equation

\[
\frac{d^2}{dr^2} + E - V(r, \hat{r}) P_L(r, \hat{r}) = \frac{1}{r} \hat{L}^2 P_L(r, \hat{r}),
\]

(1)

where \( \hat{L}^2 \) is the angular momentum operator, the action of which on \( P_L(r, \hat{r}) \) can be calculated in terms of the SH \( Y_{L\ell}(\hat{r}) \) as

\[
\hat{L}^2 P_L(r, \hat{r}) = \sum_{L'} \ell' (\ell' + 1) r R_{L'L}(r) Y_{L\ell}(\hat{r}),
\]

(2)

and \( V(r, \hat{r}) \) is the truncated cell potential, which coincides with the true potential inside the cell and is zero outside. As usual, here and in the following, \( L = l, m \). The index \( L \) of \( P_L(r) \) is reminiscent of its behaviour at the origin: \( \lim_{r \to 0} P_L(r) \propto J_L(r) = j_l(r)Y_{L\ell}(\hat{r}) \), where \( j_l(r) \) is the Bessel function of index \( l \) (Williams & Morgan, 1974). Its expansion in SH does not pose convergence problems, since it is continuous with its first derivative; however, we do not expand the potential. Equation (2) in the variable \( r \) is similar to a second-order equation with an inhomogeneous term. Accordingly, we have modified Numerov’s method to solve it. We have checked that the method works by comparison with known solutions of the SE (Hatada et al., 2010).

This method of generating \( P_L(r) \) is simple, fast, efficient and valid for any shape of the cell, and reduces the number of SH in the expansion of the scattering wavefunction to a minimum. The cell \( T \) matrix is then calculated as a surface integral over the cell-bounding sphere of a Wronskian-like combination of this solution with Hankel and Bessel functions.

It can then be shown that the global solution \( \Psi(r) \) of the SE inside a particular cell \( \Omega \), with centre \( \mathbf{R} \), and local coordinates \( r = r - \mathbf{R} \), can be represented as a linear combination of local solutions \( \Phi_L(r) \) as

\[
\Psi(r) = \sum_L A_L^r \Phi_L^r(r).
\]

(3)

By inserting this local solution into the Lippmann–Schwinger integral equation (LSE) associated with the SE (Williams & Morgan, 1974; Hatada et al., 2010) and partitioning the integral over the whole space into integrals over the various cells, the differential problem is transformed into an algebraic condition for the coefficients \( A_L^r \),

\[
A_L^r = I_L^r + \sum_{jL'} \sum_{L''} G_{L''L'}^{jL'} T_{L''L'}^{jL'} A_{L''}.
\]

(4)

Here, the inhomogeneous term \( I_L^r \) originates from the incoming plane wave \( \exp(i\mathbf{k} \cdot \mathbf{r}) \) in the case of a scattering solution and is zero for bound states. Moreover, the partial wave propagators \( G_{L''L'}^{jL'} \) come from the two-centre decomposition of the free GF in the LSE and are known in MS theory as KKR structure factors. They depend only on the location of the centres of the various cells in space. In contrast to previous approaches, we have avoided the double-series expansion of the free GF around two centres, so that the angular momentum indexes \( L \ell \) are the same as those of the \( T \) matrix \( T_{L''L'}^{jL'} \) and originate from the function \( R_{L''L'}(r) \) in equation (2). As a consequence, the MS matrix \( \mathbf{I} + \mathbf{GT} \) can be considered to be square and we have been able to show that as \( l \to \infty \) its inverse exists, providing firm ground for the use of FPMS theory as a viable method for electronic structure calculations and spectroscopic response functions, with the ease and versatility of the corresponding MT theory. The truncation parameter in the SH expansion is given by the classical relation \( \ell_{\text{max}} = kr_R \), where \( k \) is the electron wavevector and \( r_R \) is the radius of the bounding sphere of the scattering cell.

3. The program

3.1. Features and capabilities

The FPMS code (Hatada et al., 2005) focuses on the calculation of XANES spectra, but can also calculate projected DOS and resonant X-ray elastic scattering (Subíás et al., 2007). It incorporates part of the ES2MS code (Xu et al., 2016), which is an interface to use the charge densities and potentials generated by electronic structure codes, notably LMTO (Andersen, 1975) and VASP (Kresse & Joubert, 1999). FPMS is incorporated into the MXAN code (Hayakawa et al., 2007; the FP-MXAN code) to perform structural fitting of XANES spectra without the need for the MT approximation (Hatada & Hayakawa, 2011). FPMS has an option to print out \( T \) matrices to feed the input of the MsSpec code (Sébilleau et al., 2011) so that one can perform full potential calculations for photoelectron diffraction. Point-group symmetries can be specified in order to reduce the computational cost
considerably. Truncation of cells may be checked with an interactive animation based on an OpenGL library (Segal & Akeley, 2010; see Fig. 3)

3.2. Requirements

The code is platform-independent: it can run on Linux, Windows and Mac OS X. A prepared executable is provided only for the serial mode and is standalone; no additional programs or libraries are required. The parallel version must be compiled by users on their own platform. For compilation, one needs Fortran 2003 compilers, OpenGL, MPI (Message Passing Interface Forum, 1994), LAPACK (Anderson et al., 1990) and BLAS (Blackford et al., 2002).

4. Examples

For electronic and structural studies of materials, it is important to go beyond the MT approximation, especially for systems with open structures such as layers or a diamond structure. Fig. 4 shows a comparison of MT and full potential (FP) calculations with experimental data obtained by an electron energy loss (EEL) technique (Hatada et al., 2009). It is known that EEL spectra, in the limit of small momentum transfer and high energy of the incoming beam, can be described as an absorption spectrum in the dipole approximation, with polarization given by the momentum transfer vector. We see that MT calculation gives a very poor result.

In Fig. 5 (Xu et al., 2015), the graphene experimental spectrum (Pacilé et al., 2008) is shown along with the present calculations performed for different potential approximations. The SCF potential has been transferred from the VASP code. The radius of the cluster is 30 Å; indeed, it is rather large owing to the need to describe the focusing effect of the chain-like structure of C atoms. As in Fig. 3, the graphene layer is covered by layers of ECs from both sides. It is obvious that the FP calculations (non-SCF-FP or SCF-FP) agree much better with experiment than the MT calculation (SCF-MT). The differences between non-SCF-FP and SCF-FP spectra are small, indicating that self-consistency affects XANES much less than FP corrections.

5. Future perspectives

5.1. Optimization

In the latest version of FPMS, we introduced a new way of partitioning the MS matrix for inversion. On an Intel Xeon E5-2650 V2 2.6 GHz eight-core CPU, the computation time per energy point for a copper cluster of 233 atoms with \( l_{\text{max}} = 6 \) was 203 s without partitioning, reducing to 13.5 s with

Figure 4
Unpolarized absorption cross section of \( L_{2,3} \) edges for \( \alpha \)-quartz, showing a comparison of the MT and FP calculations with the experimental data (Hatada et al., 2009).

Figure 5
Comparison (Xu et al., 2015) between calculated polarized C K-edge XANES of graphene with a cluster of radius 30 Å and the experimental data from Pacilé et al. (2008). \( \alpha \) is the angle between the electric field and the \( xy \) plane. Since \( \alpha = 74^\circ \), \( \sigma \simeq 0.924\sigma_x + 0.076\sigma_y \). Dashed vertical lines show the peak experimental positions. SCF and non-SCF represent the results of calculations using self-consistent and non-self-consistent potentials in the full potential (FP) and muffin-tin (MT) version of multiple-scattering theory.

Figure 3
(a) Positions of C atoms (blue spheres) and empty cells (green spheres) for graphene. (b) and (c) show schematic diagrams of the graphene cluster with space-filling cells viewed along the \( z \) and \( y \) axis, respectively. The colours are as in (a) (Xu et al., 2015).
partitioning, with a gain of a factor of 15. We expect an even larger gain for larger clusters.

5.2. Other spectroscopies

A UPS (ultraviolet photoemission spectroscopy) code is under development using FPMS. Implementations for STMs (scanning tunnelling microscopes) and BEEMs (ballistic emission electron microscopes) are also in progress.

References


