

Multiple Scattering Approach to Continuum State with Generally Shaped Potential

Keisuke Hatada, Kuniko Hayakawa, Antonio Tenore, Maurizio Benfatto and Calogero Natoli

INFN Laboratori Nazionali di Frascati, c.p. 13, I-00044 Frascati, Italy

Abstract.

We present a new scheme for solving the scattering problem for an arbitrarily shaped potential cell that avoids the well known convergence problems in the angular momentum expansion of the cell shape function. Tests of the method against analytically soluble model potentials, with and without shape truncation, have been performed with success. By a judicious choice of the shape of the cells partitioning the whole molecular space and use of empty cells when necessary, we set up a multiple scattering scheme that leads to a straightforward generalization of the same equations in the muffin-tin approximation. For example l_{\max} in the angular momentum expansion can still be chosen according to the rule $l_{\max} \sim kR$, where R is the radius of the bounding sphere of the cell and all the matrices appearing in the theory are square matrices.

Keywords: Multiple scattering, non-muffin-tin potential, X-ray absorption

PACS: 71.15.Ap, 61.10.Ht, 61.14.Qp

INTRODUCTION

Multiple scattering (MS) approach has been widely used to solve the Schrödinger (or the associated Lippmann-Schwinger) equation for scattering states. Most practical calculations have been done within the so called “Muffin-Tin (MT) approximation” using cells of spherical shape, inside which the potential is spherically averaged and constant in the interstitial region. However this approximation fails in the description of molecular systems with substantial anisotropy (e.g. systems of biological interest) and surfaces.

The first practical attempt to go beyond MT approximation with arbitrary shaped potential was done by Williams [1]. However it was soon realized that the method presented convergence problems in the angular momentum expansion [2]. One of the difficulties was to solve the Schrödinger equation for arbitrary shaped potential cells.

Therefore several attempts to avoid this problem were done. One approach [3] is to smear the edge of shaped potential, as suggested by Becke [4]. This helps to get convergence, but of course can not provide a correct representation of potential around the edge of the potential, where the anisotropy is most important. Another approach was to use spherical cells, and treat the interstitial region by Born approximation [5, 6].

The present approach instead expands in spherical harmonics the wave function rather than the shaped potential, so that the convergence problem is completely avoided and we can treat arbitrarily shaped potential without any approximation. Together with appropriate

numerical techniques this approach is seen to overcome the historical problem completely.

THEORY

In the multiple scattering scheme for a non-MT, local and real potential, the associated Green’s function can be written in the following way [7, 8],

$$G(\mathbf{r}, \mathbf{r}') = \langle \Phi(\mathbf{r}) | [\tilde{S}E + \tilde{SGS}]^{-1} | \Phi(\mathbf{r}') \rangle \quad (1)$$

$$S_{LL'} = \int_S [J_L(\mathbf{r}) \nabla \Phi_{L'}(\mathbf{r}) - \Phi_{L'}(\mathbf{r}) \nabla J_L(\mathbf{r})] \cdot \mathbf{n} d\sigma$$

$$E_{LL'}^+ = -ik \int_S [H_L^+(\mathbf{r}) \nabla \Phi_{L'}(\mathbf{r}) - \Phi_{L'}(\mathbf{r}) \nabla H_L^+(\mathbf{r})] \cdot \mathbf{n} d\sigma$$

where tilde indicates transposition, $J_L = j_l(r)Y_L(\hat{\mathbf{r}})$ and $H_L^+ = h_l^+(r)Y_L(\hat{\mathbf{r}})$. Here the functions $\Phi_L(\mathbf{r})$ are local solutions of the Schrödinger equation behaving as J_L for $r \sim 0$. They form a complete set of basis functions such that the global scattering wave function can be expanded inside the cell region as $\Psi(\mathbf{r}) = \sum_L A_L \Phi_L(\mathbf{r}) = \sum_{LL'} A_L R_{L'}^L(r) Y_{L'}(\hat{\mathbf{r}})$. For practical computation the sum over L is limited to an $l_{\max} \sim kR$, where R is the radius of the bounding sphere of the potential cell, whereas l'_{\max} is determined by the anisotropy of the wave function, which is much weaker than that of the truncated potential. In practice they can be taken equal. The matrices S and E are integrals over the surface of the potential cell. The matrix G is the usual free electron propagator in the site and angular momentum basis, known as KKR real space structure factors, including the correction due to the presence of an outer sphere, if necessary [9]. In Eq.

(1) the matrix to be inverted is symmetric and independent of the normalization of the basis functions. This expression makes the calculation of Green's function very fast. The absorption cross section can then be written as

$$\begin{aligned}\sigma(\omega) &= -8\pi\alpha\hbar\omega \langle c | \Delta \text{Im}(G) \Delta | c \rangle \quad (2) \\ \Delta &= \boldsymbol{\varepsilon} \cdot \mathbf{r}.\end{aligned}$$

where $|c\rangle$ is a core state.

In our non-MT multiple scattering approach, we partition the space in terms of non overlapping polyhedra such that their bounding sphere do not overlap more than 20 %. In this way the shortest inter-cell vector, joining the origins of nearest neighbor cells, is almost twice larger than any intra-cell vector. This condition insures convergence of the L expansion and the fact that S and E can be taken as square matrices. If necessary, empty spheres can be added to satisfy this condition.

On each scattering site we calculate matrices S and E on the surface of the bounding sphere of the potential cell. Since the potential is zero in the space between the cell and its bounding sphere, the surface integrals in Eq. (1) do not change their value, as is clear from an application of the Green's theorem.

Thus the matrices reduce to non diagonal Wronskians calculated at the radius of the sphere, $S_{LL'} = r_s^2 W[j_l, R_L^{L'}]$, $E_{LL'} = kr_s^2 W[-ih_l^+, R_L^{L'}]$. For spherically averaged potentials, which are used for MT calculation these matrices become diagonal, $S_{LL'} \rightarrow \delta_{LL'} S_l = r_s^2 W[j_l, R_l]$, $E_{LL'} \rightarrow \delta_{LL'} E_l = kr_s^2 W[-ih_l^+, R_l]$ [7].

To solve the Schrödinger equation we do not expand the truncated potential to avoid convergence problems. Instead we discretize the Laplacian operator expressed in polar coordinates and in order to avoid accuracy problems around $\theta = 0, \pi$, we use the relation

$$\begin{aligned}L^2 \Phi_{L'}(\mathbf{r}) &= \sum_L l(l+1) R_L^{L'}(r) Y_L(\hat{\mathbf{r}}) \\ &= \sum_L l(l+1) \left(\int d\hat{\mathbf{r}}' \Phi_{L'}(r, \hat{\mathbf{r}}') Y_L^*(\hat{\mathbf{r}}') \right) Y_L(\hat{\mathbf{r}}).\end{aligned}$$

We observe that, even if the potential has a step, the wave function and its first derivative are continuous, so that the angular momentum expansion is well behaved.

In this way the three-dimensional discretized equation becomes very similar to an one-dimensional equation in the radial variable, which with some numerical trick can be solved by the Numerov method [8] with a log mesh $\rho = \alpha r + \beta \ln r$, to take into account the singularity of the Coulomb potential at the origin. This Numerov method requires less points to be calculated than Runge-Kutta method with the same accuracy. This makes calculation much faster and memory requirement smaller while keeping good accuracy.

We tested the method against analytically soluble separable model potentials, with and without shape truncation, and obtained very good results. [8]

RESULTS

We did some test calculations to check the performance of the method. Fig. 1 shows the result for Li^{2+} free atom. Li^{2+} is an hydrogenic atom with $Z = 3$ for which we know the analytical form of the photoemission cross section [10],

$$\sigma(k) = 4\pi^2 \alpha \frac{2^7}{3} \frac{1}{Z^2} \left(\frac{1}{1 + (\frac{k}{Z})^2} \right)^4 \frac{e^{-4\frac{Z}{k} \tan^{-1}(\frac{k}{Z})}}{1 - e^{-2\pi\frac{Z}{k}}}. \quad (3)$$

We partition the space inside a sphere of radius $R = 8.6$ au into an atomic sphere of 4.15 au and 14 other empty spheres, all truncated so that the resulting polyhedra do not overlap. In this calculation we do not take into account the effect of the outer sphere (G is not corrected for this). We replace instead the potential outside by the value it takes at $R = 8.6$. Apart the small oscillations around the exact result, due to the modification of the potential in the outer sphere region (a constant instead of a Coulomb tail), the comparison is highly satisfactory. This indicates that the partitioning procedure for solving the Schrödinger equation is able to reconstruct the global solution. Also the oscillations due to the truncation of the potential inside each cell cancel each other.

As a second example we consider a Ni atom spherical potential truncated at a radius $R = 3.78$ au. The corresponding cross section is shown in Fig. 2 as a red line. By partitioning the space in a smaller sphere of radius $R = 3$ au and filling the region between the two spheres with 14 empty spheres truncated as in the previous example, we recover the correct cross section (green line). We used $l_{\max} = 5$ (central) and 6 for others. These values are almost the same as for the classical relation $l_{\max} \sim kR$.

CONCLUSION

We have developed a non-MT MS theory which is a straightforward generalization of the usual theory with MT potentials and implemented the code to calculate the cross section for several spectrometers like absorption, photoelectron diffraction and anomalous scattering. The key point in this approach is the generation of the cell solutions $\Phi_L(\mathbf{r})$ for a general truncated potential free of the well known convergence problems of angular momentum expansion. In this way the matrices S and E become square matrices that can be calculated easily as surface integrals on the bounding sphere of the cells parti-

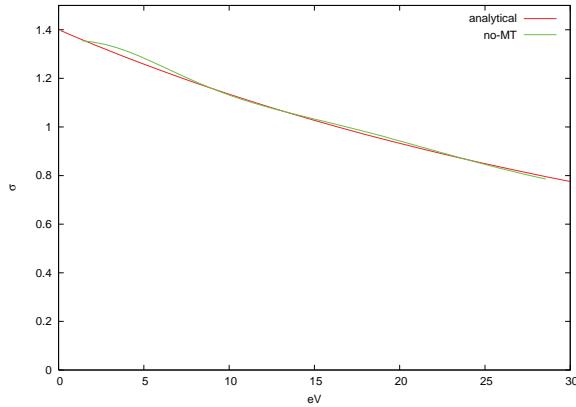


FIGURE 1. Cross section for Li^{2+} with 15 cells compared to the analytical result.

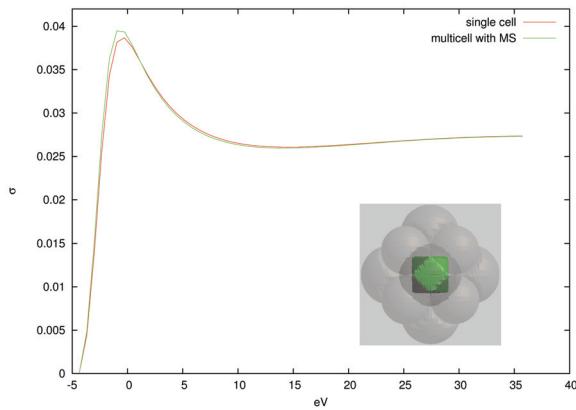


FIGURE 2. Comparison between a single cell and a multi-cell calculation for a Nickel atom.

tioning the space, while the maximum l in the L expansion is still given by the classical relation $l_{\max} \sim kR$. In the near future, we intend to implement this code in the MXAN code [11] to do structure fitting.

ACKNOWLEDGEMENT

One of the author (K. Hatada) wishes to thank Dr. P. Krüger for many useful discussion.

REFERENCES

1. A. R. Williams, and J. van W. Morgan, *J. Phys. C: Solid State Phys.* **7**, 37–60 (1974).
2. Y. Wang, G. M. Stocks, and J. S. Faulkner, *Phys. Rev. B* **49**, 5028–5031 (1994).
3. A. L. Ankudinov, and J. J. Rehr, *Phys. Scr.* **T115**, 24–27 (2005).
4. A. D. Becke, *J. Chem. Phys.* **88**, 2547–2553 (1988).
5. C. R. Natoli, M. Benfatto, C. Brouder, M. F. R. López, and D. L. Foulis, *Phys. Rev. B* **42**, 1944–1968 (1990).
6. D. L. Foulis, R. F. Pettifer, C. R. Natoli, and M. Benfatto, *Phys. Rev. A* **41**, 6922–6927 (1990).
7. C. R. Natoli, M. Benfatto, S. D. Longa, and K. Hatada, *J. Synchrotron Rad.* **10**, 26–42 (2003).
8. K. Hatada, K. Hayakawa, M. Benfatto, and C. R. Natoli, *To be submitted* (2006).
9. T. A. Tyson, K. O. Hodgson, C. R. Natoli, and M. Benfatto, *Phys. Rev. B* **46**, 5997–6019 (1992).
10. H. A. Bethe, and E. E. Salpeter, *Quantum mechanics of one- and two-electron atoms*, Plenum/Rosetta, New York, 1977, p. 304.
11. M. Benfatto, and S. D. Longa, *J. Synchrotron Rad.* **8**, 1087–1094 (2001).