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Development of the full potential multiple scattering method

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Multiple scattering (MS) approach has been widely used to solve the Schrödinger equation (SE) (or the associated Lippmann-Schwinger equation) both for scattering and bound states. Most practical calculations have been done within the so called ``Muffin-Tin (MT) approximation'' using cells of spherical shape, inside whicht he potential is spherically averaged and constant in the interstitial region. However the MT approximation cannot properly describe a great number of physical systems, ranging from open lattices to molecular systems with substantial anisotropy (*eg*. systems of biological interest), to surfaces and interfaces.

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 (AM) expansion. [2] One of the difficulties was to solve the Schrödinger equation (SE) for arbitrarily shaped potential cells.

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. [3]

We have tested the present Full potential multiple scattering (FP-MS) scheme against the analytical solution of the absorption cross section for hydrogen-like atoms in the case of the Li^{2+} atom (Z=3). Even though the potential is spherically symmetric in the whole space with respect to the atomic center so that it is easy to reproduce numerically the cross section, this is not obvious in the MS scheme To this purpose we have partitioned 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 and such that their bounding sphere do not overlap more than 40%. To calculate the contribution of the outer sphere we integrated inwardly the Coulomb potential. Fig. 1 shows the almost exact agreement between the analytical and the numerical result, indicating that the partitioning procedure for solving the SE is able to reconstruct the global solution. Moreover the oscillations due to the truncation of the potential inside each cell (shown by the solution for a truncated central sphere with radius 4.15 au) cancel each other, showing that at a common boundary the overall solutions inside two adjacent cells are continuously smooth. For this test a value of $l_{max} = 4.15\sqrt{3} \sim 8$ was taken at the end of the energy interval $E_{max} = 3$ Ryd.

Fig. 2a shows an application of the method to the calculation of the Ge K-edge absorption spectrum of the tetrahedral molecule $GeCl_4$ [4]. The MT approximation could never reproduce the first bump after the main transition. Its appearance is due to the introduction of the anisotropy of the potential inside the atoms and the presence of four empty Voronoi cells completing the BCC unit cell. An $l_{max} = 4$ was sufficient to reach convergence of the spectrum, as verified by using higher l values up to $l_{max} = 10$ (Fig. 2b).

In conclusions we have developed a FP-MS scheme which is a straightforward generalization of the usual theory with MT potentials and implemented the code to calculate the cross section for several spectroscopies like absorption, photo-electron diffraction and anomalous scattering. The key point in this approach is the generation of the cell solutions $\varphi_L(\mathbf{r})$ for a general truncated potential free of the well known convergence problems of AM expansion together with an alternative derivation of the MSE which allows us to treat the matrices S and E as square, with only one truncation parameter given by the classical relation $l_{max} \sim kR$. At variance with what usually stated, there are hints that this truncation procedure

converges [5]. At the same time we have provided an efficient and fast method for solving numerically a partial differential equation of the elliptic type in polar coordinates which can also be used to solve the Poisson equation.

References

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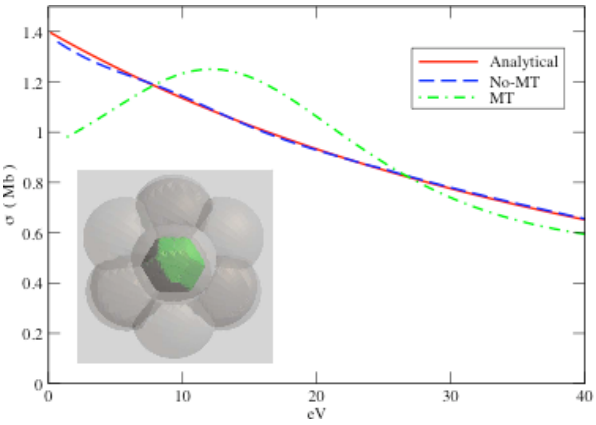

FIG. 1. Cross section for Li^{2+} with 15 cells compared to the analytical result. The solution for a MT central sphere is also shown.

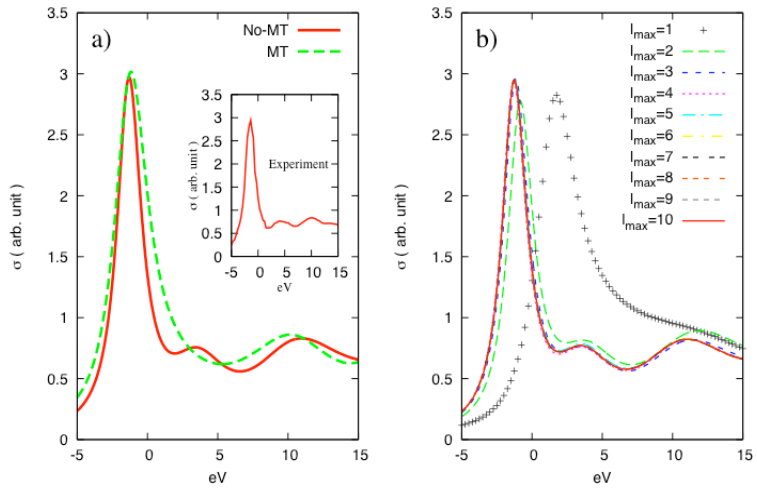

FIG. 2. (a) Cross section for $GeCl_4$ molecule with nine scattering cells located at the sites of a BCC lattice, compared with the MT result and experiment. (b) Study of its convergence rate as a function of l_{max} up to $l_{max} = 10$.