UCRL-CR- 116369
B239763

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October 20, 1994

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Full Potential Multiple Scattering Theory

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Abstract

A practical method for performing self-consistent electronic structure calculations based upon full-potential multiple-scattering theory is presented. Solutions to the single site Schroedinger equation are obtained by solving coupled channel integral equations for a potential which is analytically continued out to the circumscribing sphere. This potential coincides with the full cell potential inside each atomic cell. Scattering matrices and wavefunctions for the full cell potential are obtained from surface Wronskian relations. The charge density is obtained from the single particle Green's function. This Green's function is computed using the cell scattering matrices and wavefunctions using the layer multiple scattering theory. Self consistent solutions require a solution at each iteration to the Poisson equation. The Poisson equation is solved using a variational cellular method. In the approach a local solution to each cell is augmented by adding a series of regular harmonics (solutions to Laplace's equation). Minimizing the coulomb energy, subject to continuity of the potential across all cell boundary provides an expression for the coefficients of the regular harmonics. This method is applied to BCC Nb. Calculated properties converge well in angular momentum and show comparable accuracy to full potential linearize muffin-tin orbital calculations.

Introduction

Electronic structure theory provides a framework for accurately predicting many properties of condensed matter systems, including for example, ground state crystal structures, elastic constants, and formation energies. In order to be able to predict many of these properties in geometries in which the atoms are not close packed, then the electronic structure technique should be a full potential method. Electronic structure techniques based upon multiple scattering theory have a number of attractive features: the ability to treat defects such as interfaces, surfaces and point defects, and the ability to treat disorder through the use of the coherent potential approximation. Unfortunately, these methods have been implemented almost exclusively within the muffin-tin approximation which is only suitable for a close packed atomic arrangement. There is a clear need to extend these techniques to a full potential treatment. In a self-consistent electronic structure calculation, one needs to solve both the Schroedinger and Poisson equations. These equations are rather similar and will be solved using similar methods. The aim of the work is to produce a self-consistent full-potential electronic structure program based upon multiple scattering theory and implemented within the layer Korringa-Kohn-Rostoker formalism.

The central quantity in a self-consistent electronic structure calculation is the charge density. The charge density is obtained from the trace of the imaginary part of the single particle Green's function. This Green's function is calculated from multiple-scattering theory.

Solution of the Schroedinger Equation

Single Site Schroedinger Equation

The first step in formulating a self-consistent multiple-scattering based theory is a solution of the single site Schroedinger equation for a full-cell potential. Two approaches were tried. The first used an angular momentum expansion of the step function to force the cell potential to vanish outside the cell. Coupled integral equations were solved for this potential out to the bounding sphere. Scattering matrices were found by matching at the bounding sphere radius. This method, which has been suggested by other researchers, turned out to have such bad convergence as to be impractical. A second approach was therefore adopted. In this alternative method, the potential entering the coupled integral equations was not chopped by the step function, but rather was analytically continued out to the bounding sphere, and thus only represents the true crystal potential inside the cell. It can be shown that outwards integration of the Schroedinger equation with suitable choice of boundary conditions inside the muffin-tin radius yields solutions that are identical to converged solutions obtained for the chopped potential. Convergence and stability of these solutions was significantly better since the Gibbs oscillation caused by the step function was avoided. Numerical tests in two-dimensions showed that provided convergence was achieved the two solutions gave identical values inside the cell. Scattering matrices and wavefunctions were obtained through surface Wronskian integrals which were found numerically. A stable numerical algorithm using Romberg extrapolation appropriate for two-dimensional surface integration was developed to deal with numerical difficulties associated with the surface integrals.

Multiple Scattering Theory

Once a stable solution to the single-site Schroedinger equation has been found, the Green's function can be obtained using multiple scattering theory. I chose to implement a layer multiple scattering theory since one of the future objects is to have a theory applicable to interfaces and surfaces as well as to bulk materials. Possible basis-set and internal summation convergence issues do not seem to cause problems for the full-cell Green's function. The calculation of the non-spherical charge density posed no computational problems. Full use of available symmetry was used to save on CPU time and storage.

Self Consistent Solutions and the Poisson Equation

Self-consistent solutions to the Schroedinger equation require that the output charge density is used to construct a new potential. When input and output potentials are the same then a self-consistent solution has been achieved. A Broyden mixing scheme was adapted to speed up the rate of convergence, which was typically achieved in ten iterations. The construction of the new potential from the charge density involves two terms: (1) the exchange correlation potential, and (2) the Coulomb potential. The former is obtained directly from the charge density. The angular momentum expansion of this potential was found using a Gaussian quadrature technique. The Coulomb potential is found from a solution of Poisson's equation.

The Poisson equation has been solved using three different cellular approaches: the conventional multipole structure constant summation resulting from multiple-scattering theory; a Green's function cellular method; and a variational cellular method [1]. The last of these techniques appears to have the best numerical convergence and has been implemented in the full potential electronic structure code. In the cellular treatment, space is divide up into a collection of cells, where a local solution to the Poisson equation is found be direct integration. This solution is only required to satisfy the Poisson equation within its cell.

The global solution can be found as a sum of this local solution plus a sum of regular solutions to Laplace's equation. In the multiple-scattering approach, the coefficients of the regular harmonics are given as the product of a structure constants and multipole moments. Slow convergence of internal sums in this method was observed, making it not as efficient computationally as the other two approaches that were tried.

The Green's function cellular method uses the fact that the coefficients can also be expressed as surface integrals by use of Green's theorem. Now careful choice of origin of expansion allows all the surface contributions except those on the cell of interest to vanish. This leads to a nearest neighbor set of linear equations. The convergence of this approach is similar to that found from the multiple-scattering theory method provided the internal sums were converged. Thus, because of the lack of internal sums this approach is superior.

The best approach numerically is the variational cellular method. This method chooses the unknown coefficients in such a way as to minimize the Coulomb energy of the system subject to a smooth continuous solution across the cell boundaries. Since it has been derived from the variational principle, the errors in the Coulomb energy are expected to be small, and at a given basis set size it is expected to be the "best" solution. This was found to be the case. More details about these methods can be found in reference [1].

Total Energy Calculations

The total energy was found in the usual way from the sum of kinetic, Coulomb and exchange-correlation. The volume integrals over the unit cell are found using the step function approach, though in future these will be replaced by the surface integration method since then only one integration technique will be required.

Test Calculations

The programs have been extensively tested on BCC Nb, a metal which has also been studied using other full potential methods. Figure 1 shows the results of energy volume curves for different values of l-truncation. Convergence is seen to be excellent. The lattice constant while slightly smaller than experiment is very close to that found with a full potential linearized muffin-tin orbital method. The shorter lattice constant reflects the well known overbinding of the local density approximation. The calculated bulk modulus is 1.65 MBar which is close to the experimental value of 1.70 Mbar. Agreement of 10% is usually regarded as excellent.

Conclusions

During the year at LLNL significant progress was made on the development of a full-potential electronic structure program. A code was completed and resides on athens at LLNL. This code is of course a beta version and it is expected to be improved over the coming year. In particular a better user interface and algorithmic efficiencies are expected. Testing on Nb showed that stable accurate algorithms have been developed and results appear comparable to those obtained from the full potential linearized muffin-tin orbital method. Much of the work has addressed the practical aspects in particular convergence and stability of algorithms. Full potential multiple scattering theory has had a long history without a true full-potential self-consistent implementation where numerical accuracy and stability have been addressed.

References

[1] X.-G. Zhang, W. H. Butler, J. M. MacLaren and J. van Ek, Phys. Rev. B in press.
[2] J. M. MacLaren, J. van Ek, A. Gonis, X.-G. Zhang, and W. H. Butler to be published.

Figure Caption
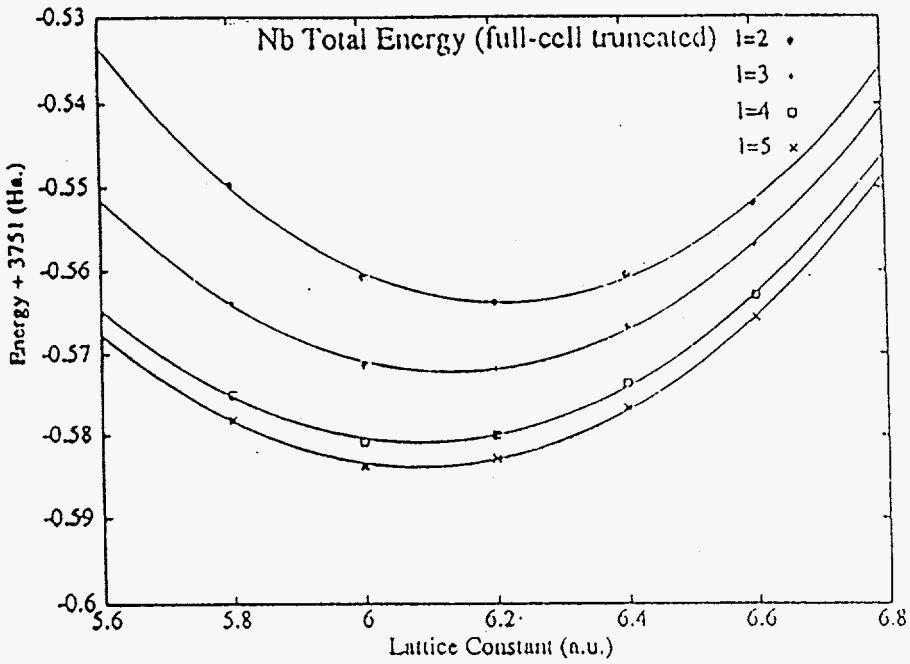
Figure 1 Energy volume curve for BCC Nb for l=2,3,4, and 5.