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Integrating the QMR Method with First Principles Material Science Application Code*

N. M. Nachtigal[†] W. A. Shelton[‡] G. M. Stocks[§] D. M. C. Nicholson[¶]
Y. Wang^{||}

Abstract

First principles methods are used to aid the material designers and metallurgists in the investigation and design of new materials. These methods suffer from a divergent $O(N^3)$ scaling which restricts the problem sizes that can be addressed. It will be demonstrated that the $O(N^3)$ scaling problem can be overcome by employing real-space multiple scattering techniques to calculate the scattering properties, combined with the QMR algorithm. By incorporating the QMR method into our real-space multiple scattering code, we observed $O(N)$ scaling for the large problem sizes of interest. This advancement will provide researchers with the necessary tools to treat large systems.

1 Introduction

The design of new technologically advanced materials is of extreme importance to the industrial and economical competitiveness of the U.S. The modern design of new materials makes use of local-density approximation (LDA) based, first principles electronic structure calculations. These methods are parameter-free methods, requiring no experimental input. This means they are predictive methods that can be accurately used to calculate materials properties.

The development of LDA-based, first principles electronic structure methods that scale linearly with the number N of atoms in the system grows is necessary because current methods exhibit $O(N^3)$ scaling, which renders the study of large systems comprised of hundreds of atoms computationally intractable. The $O(N^3)$ scaling arises in LDA methods due to either a eigenvalue-eigenvector solve or a matrix inversion. Our problem concerns the latter and by incorporating the quasi-minimal residual (QMR) method into the our real space multiple scattering code, we are able to achieve $O(N)$ scaling for the problem sizes of interest.

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[†]Oak Ridge National Laboratory, Oak Ridge, TN 37831-6367.

[‡]Oak Ridge National Laboratory, Oak Ridge, TN 37831-6367.

[§]Oak Ridge National Laboratory, Oak Ridge, TN 37831-6014.

[¶]Oak Ridge National Laboratory, Oak Ridge, TN 37831-6014.

^{||}Oak Ridge National Laboratory, Oak Ridge, TN 37831-6014.

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2 Local Density Approximation

The density functional theory (DFT) is an exact method for calculating the energetics of an electron system in the field of the atomic nuclei within a single-particle framework[6]. This theory in principle includes all of the many-body quantum mechanical effects of electron exchange (Pauli-exclusion principle or exchange energy) and correlation.

A central result of the theory is that the total energy of the system yields the correct ground-state energy at its minimum. At the heart of this formalism is the calculation of a non-local, exchange-correlation potential that accounts for the many-body effects of electron exchange and correlation. However, the non-local exchange-correlation potential is unknown, requiring further approximation.

The local-density approximation to density functional theory is a technique for treating the non-local exchange-correlation potential within a mean-field theoretical framework, resulting in a set of single-body Schrödinger-like equations (Kohn-Sham equations) with an effective potential containing a local exchange-correlation potential [8]:

$$(1) \quad [-\nabla^2 + V^{eff}(\vec{r})]\psi(\vec{r}, \epsilon) = \epsilon\psi(\vec{r}, \epsilon).$$

It should be noted that the DFT-LDA theory is a ground-state theory. The eigenvalues of the Kohn-Sham equations only represent the true eigenvalues of the system in its ground state and are not the true eigenvalues for the excited states.

3 Real-Space Multiple Scattering

The real-space multiple scattering method is based on multiple scattering theory. It is similar in spirit to the Korringa, Kohn and Rostoker (KKR) method [9][7][10][4][5]. The KKR method makes use of scattering theory to calculate the scattering path operator, which is used to construct the single-site, site-diagonal, Green's function and is written in the angular momentum representation as

$$G^\alpha(\vec{r}, \vec{r}, \epsilon) = \sum_{L, L'} [Z_L^\alpha(\vec{r}, \epsilon) \tau_{LL'}^{\alpha, 00}(\epsilon) Z_{L'}^\alpha(\vec{r}, \epsilon) - Z_L^\alpha(\vec{r}, \epsilon) J_{L'}^\alpha(\vec{r}, \epsilon) \delta_{LL'}],$$

where $\epsilon \equiv$ is the complex energy, and

$Z_L^\alpha(\vec{r}, \epsilon) \equiv$ regular single-site wave function of the α^{th} atomic specie;

$J_L^\alpha(\vec{r}, \epsilon) \equiv$ irregular single-site wave function of the α^{th} atomic specie;

$\tau_{LL'}^{\alpha, 00}(\epsilon) \equiv$ single-impurity scattering-path operator of the α^{th} atomic specie. The scattering path operator $\tau_{LL'}^{00}(\epsilon)$ relates the outgoing wave from one site into an incident wave on another and includes all possible scattering paths (multiple scattering). However, instead of calculating the scattering properties of the infinite periodic system, the real-space multiple scattering method includes only a finite set of atoms in the system. The real-space multiple scattering technique calculates $\tau_{LL'}^{00}$ (scattering properties) for each atom in the unit cell and is expressed in general, in matrix notation as,

$$(2) \quad \tau^{ij}(\epsilon) = t^i(\epsilon) \delta_{ij} + \sum_k t^i(\epsilon) g^{i,k}(\vec{R}, \epsilon) \tau^{kj}(\epsilon)$$

where \vec{R} is a real-space translation vector. The physical properties of the system are determined by the site-diagonal scattering path operator $\tau^{00}(\epsilon)$ which leads to,

$$(3) \quad \tau^{00} = [I - t(\epsilon)g(\vec{R}, \epsilon)]^{-1}t(\epsilon).$$

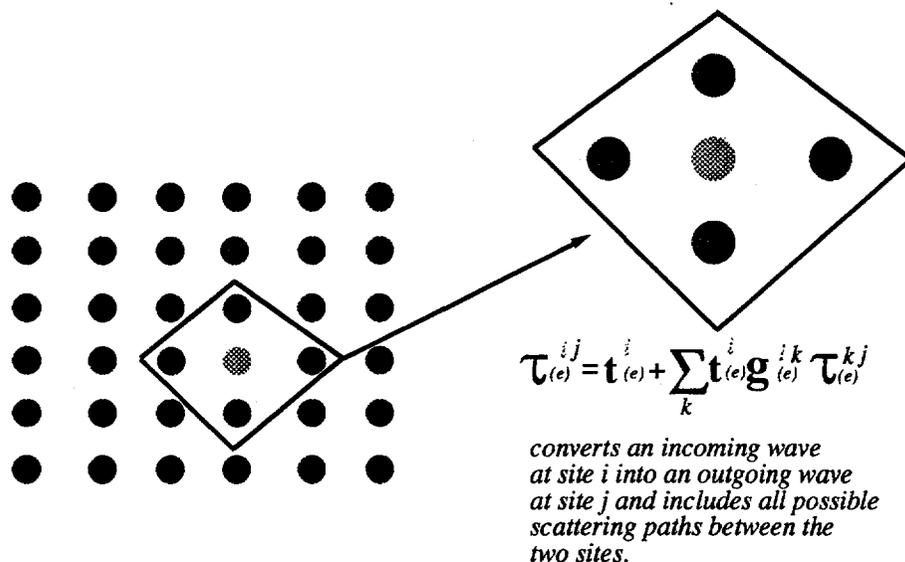


FIG. 1. Schematic display of the real-space multiple scattering method. The atom at the center of the prescribed boundary calculates its scattering properties by including only those atoms which fall within the boundary.

This results in a single inverse of a large matrix at a given energy to calculate τ^{00} . A schematic representation of this process is shown in Figure 1. The solution to Poisson's equation and the total energy of the system is performed by including all the atoms in the unit cell.

The advantage of this method, in the context of this study, is that it is a straightforward procedure to increase the system size. For certain systems, such as Molybdenum, it can require hundreds of atoms in the system in order to obtain accurate results (1600×1600 double precision complex matrix). Whereas, in the KKR method this same problem results in a small one atom per unit cell investigation. However, the results of the analysis do not depend on which code is used. The physics of the problem is the same for both codes and both codes are based on multiple scattering theory. Hence, the results of the analysis are invariant with respect to the codes.

4 Use of QMR

For this study, we were interested in investigating the use of the quasi-minimal residual (QMR) methods for the solution of the linear system in Equation (3). The QMR method was proposed by Freund and Nachtigal[3]. It is an iterative method for the solution of general non-Hermitian linear systems, based on selecting a quasi-minimal residual iterate

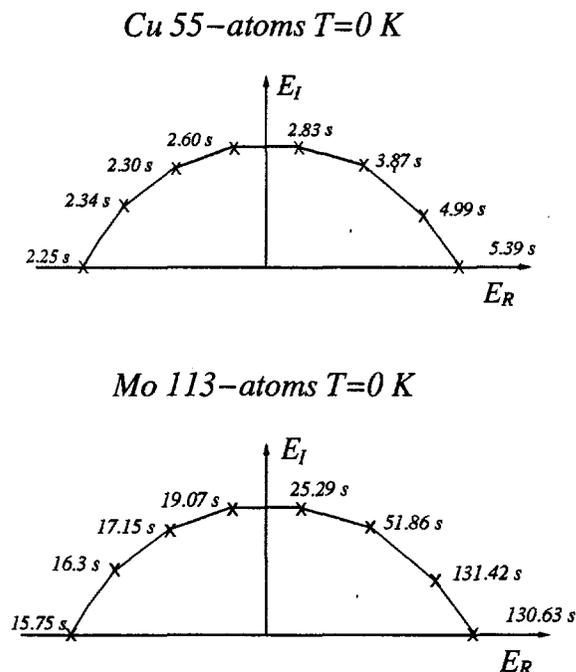


FIG. 2. Time required to solve for the inverse for each energy on the contour.

from a Krylov space built using the look-ahead Lanczos algorithm[2]. The particular variant used was the transpose-free QMR method (TFQMR), proposed by Freund[1]. Unlike the original QMR method, the TFQMR algorithm does not require a multiplication with the transpose of the matrix at each step. However, the TFQMR is currently implemented without look-ahead, which means that it is susceptible to possible breakdowns. In our examples, we have not encountered any difficulties with the method, probably due to the few number of iterations required to solve the linear systems. The quasi-minimal residual algorithms have several properties that make them appealing: the underlying Lanczos process requires little and almost constant work and storage per iteration. In addition, the use of a quasi-minimization problem to define the iterates gives a smooth and almost monotonically decreasing convergence behavior. For further details on the quasi-minimal residual methods, we refer the reader to the references.

5 Results

We have compared two different methods for computing the inverse of a matrix associated with performing electronic structure calculations on face-centered cubic (fcc) Copper and body-centered cubic (bcc) Molybdenum. The first is a direct method based on an LU-factorization and the second is the TFQMR method.

These two atomic elements were chosen because of their different physical dependencies on the multiple scattering at the Fermi energy (highest occupied electronic state in energy) and the number of atoms (cluster size) that are necessary to accurately calculate the physical properties of the system. It will be shown that these physical dependencies can have a dramatic effect on the rate of convergence of the TFQMR method, but that the effects are system dependent and obviously do not effect a direct method.

In Figure 2 is displayed the time required to solve for the inverse for each energy on

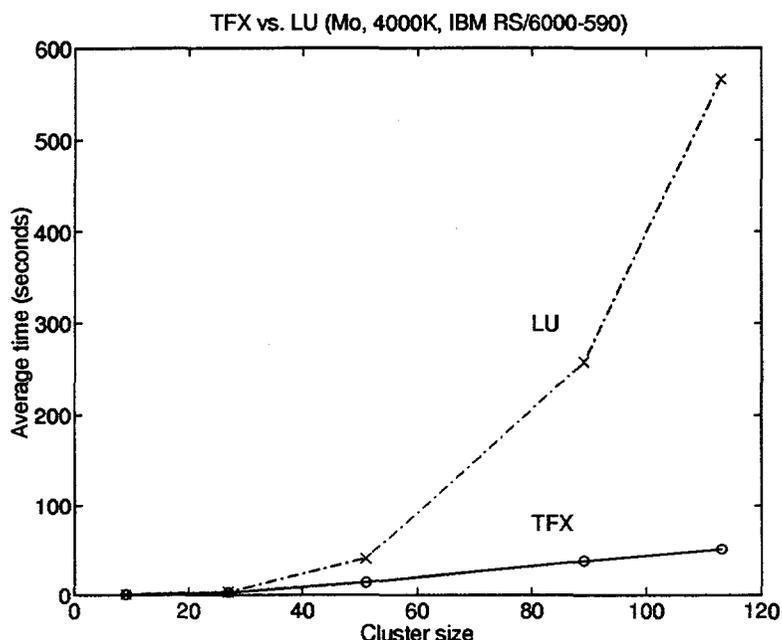


FIG. 3. Comparison of timings for QMR vs. LU for various cluster sizes for Molybdenum.

the contour for a specific cluster size. Notice, that the time increases as one approaches the Fermi energy (top of the contour) for both elements but, Molybdenum exhibits a substantial increase in time as compared to Copper. This is to be expected because Molybdenum has d-states (d-resonances) at the Fermi energy which require higher order multiple scattering terms and hence, more iterations. In addition, to accurately calculate this type of behavior and other physical properties of the system requires larger cluster sizes. This exemplifies the dependency of the efficiency of the TFQMR method with respect to the type of system to be investigated.

In Figure 3 is the timing versus system size for the LU-based algorithm and the TFQMR method for Molybdenum. As expected, the LU-based algorithm displays cubic behavior. However, the TFQMR method exhibits near linear behavior in a regime where one would expect quadratic behavior (hundreds of atoms which translates into 1600×1600 double precision complex matrix). This unexpected result illustrates the robustness of the TFQMR method and as importantly, means that it may be possible to study even larger systems than was anticipated.

6 Conclusions

The effectiveness of the TFQMR method coupled with its efficient use of memory makes it a highly effective algorithm that will enable material scientists to investigate large scale problems which would otherwise be untenable due to the poor N^3 scaling of direct methods. In addition, the unexpected $O(N)$ scaling of the TFQMR algorithm makes it even more competitive than had been expected.

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