

# Teraflop Computing for Nanoscience

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***Abstract:** Over the last three decades there has been significant progress in the first principles methods for calculating the properties of materials at the quantum level. They have largely been based on the local density approximation (LDA) to density functional theory (DFT). However, nanoscience places new demands on these first principles methods because of the thousands to millions of atoms present in even the simplest of nano-structured materials. Recent advances in the locally self-consistent multiple scattering (LSMS) method are making the direct quantum mechanical simulation of nano-structured materials possible. The LSMS method is an order-N approach to first principles electronic structure calculation. It is highly scalable on massively parallel processing supercomputers, and is suited for performing large unit cell simulations to study the electronic and magnetic properties of materials with complex structure. In this presentation, we show that the LSMS accomplishes the first step towards understanding the electronic and magnetic structure of nano-structured materials with dimension size close to 10 nanometers (nm). As an example, we describe a 16,000 atom calculation of the electronic and magnetic structure calculated for an iron nanoparticle embedded in iron aluminide crystal matrix.*

**Keywords:** Teraflop, nanoscience, nanoparticle, *ab initio*, order-N, LSMS

## 1. Introduction

Nanotechnology – which refers to research and development activities at the 1 to 100 nanometer scale (1 nanometer =  $10 \text{ \AA} = 10^{-9}$  meter) – is one of the most rapidly growing areas of materials R&D. Clearly, the ability to design materials at the nanoscale holds significant future scientific and technological opportunities due to the fact that nano-structured materials can have physical and chemical properties that are characteristic of neither isolated atoms nor their bulk counterparts. Indeed the special confinement characteristic of nanoparticles can even result in the emergence of totally new physical phenomena. Given the complexity of the problem, realizing the ultimate potential of nano-structured materials will require understanding of the atomic interactions which underpin these new structures and phenomena – interactions that are mediated by electrons and which, therefore, are fundamentally quantum mechanical.

Over the last 2-3 decades there has been significant progress in our ability to calculate the properties of materials at the quantum level. These advances have largely been based on the local (spin) density approximation (LDA) [1] or generalized gradient approximation (GGA) [2] to density functional theory (DFT) [3], a theory for which Walter Kohn received the 1998 Nobel Prize in Chemistry. However, nanoscience places new demands on these *ab-initio* methods because of the large numbers of atoms that are present in even the simplest of nanostructures, an example of which is a 5 nm cube of iron that contains the order of 12,000 atoms. Fortunately, recent advances in the locally self-consistent multiple scattering (LSMS) method [4], an *ab-initio* order-N scaling technique specifically implemented to exploit massively parallel computing, are making the direct quantum simulation of nano-structured materials possible. Previously, this method has been used to simulate  $\sim 10^3$  atoms. Here, based on a new

implementation of the method and our preliminary results on the calculation of the electronic and magnetic structure of an iron nanoparticle embedded in iron-aluminide crystal matrix, we are taking the first steps toward the direct quantum mechanical simulation of the physical properties of a realistic model of nanoparticles.

## 2. Computational Methodology

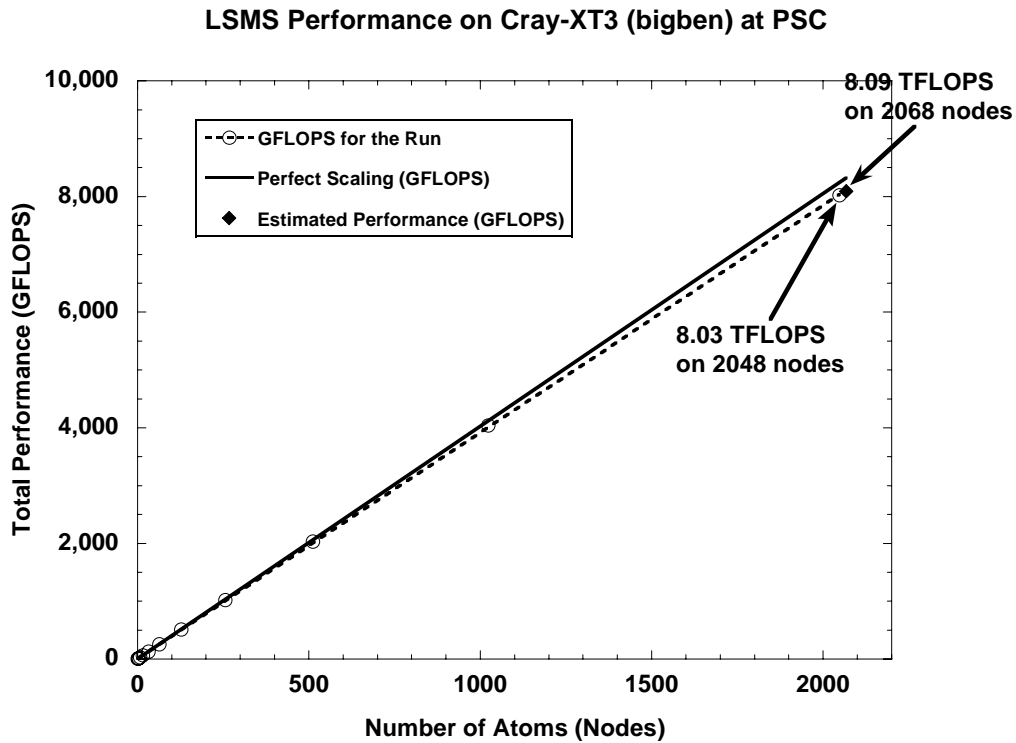
At the atomic length scale, modern *ab initio* electronic structure calculation techniques are capable of determining fundamental electric and magnetic properties, such as electrical conductivity, magnetic moments, exchange interactions, and magneto-crystalline anisotropy, of bulk materials or atom clusters. There exist several DFT based *ab-initio* methods. They are usually classified according to the technique used to solve the Kohn-Sham one-electron Schrödinger equation [1] or according to the representation used for the electron density, potential, and wave function solutions (the Kohn-Sham orbitals). Here, the representation refers to the kind of the basis functions used to expand the Kohn-Sham orbitals. These usually fall into two broad classes: local atomic-like orbitals (e.g. Gaussian-type functions, linear-muffin-tin orbitals) and plane-waves. Of course, it is possible to avoid using a basis function representation altogether by numerically solving the Schrödinger equation on grids or finite elements. The choice of the technique and the basis functions is made to minimize the computational costs and ease the programming efforts, while maintaining a sufficient numerical accuracy.

A theoretical approach to materials simulation usually starts with constructing a unit cell that repeats itself along  $x$ ,  $y$ , and  $z$  directions to fill all space. The unit cell consists of the constituent atoms in a predetermined proportion and in a real space distribution to mimic the atomic composition and spatial arrangement in the actual material. A fundamental problem arises, however, with conventional *ab-initio* methods when applied to unit cells containing a large number of atoms ( $>100$ ). That is the amount of computational work, or more precisely, the number of floating point operations, increases as the third power of the number of atoms ( $N_a$ ) in the unit cell [ $O(N_a^3)$ ]. Another problem with conventional *ab-initio* methods is the lack of efficient schemes for parallel implementation, especially when the number of atoms is large, mainly due to the fact that the dominating computational tasks are global in nature.

Because of the problems mentioned above, applying conventional *ab-initio* methods to the electronic structure calculation for nanostructured materials is obviously prohibitive. Efforts have been made since early 1990s to develop order- $N$  methods, for which the computational cost scales linearly with the number of atoms in the unit cell.

The LSMS method [4] is an order- $N$  all-electron approach to *ab-initio* electronic structure calculations. By all-electron we mean that the electronic states for both valence and core electrons are treated on equal footing, in contrast to most pseudopotential methods where core electrons are not explicitly treated. The LSMS method is based on real space multiple scattering theory (MST) [5, 6] in which the electron, under the influence of the DFT-LDA (or GGA) potential, sees each atom in the crystal as an independent scatterer. The MST equations describe the propagation of the electrons in the material. The Green's function for the Kohn-Sham one-electron Schrödinger equation is given by a convenient algebraic expression [7]. When advantage is taken of the analytic properties of the Green's function, numerical calculations are quite feasible. Using the Green function makes the calculation of the crystal wave functions unnecessary, and, as a result, there is no need for time-consuming orthogonalization and normalization procedures. Another advantage is that the only global operation required for obtaining the Green function is the calculation of a multiple scattering matrix for each atom. It is, however this step that accounts for the major portion of the floating point operations of the entire electronic structure calculation.

Use of Green's function methods does not circumvent the  $O(N_a^3)$  scaling because obtaining the multiple scattering matrix still requires inverting a matrix whose size is proportional to the number of atoms in the unit cell. Order- $N$  scaling is achieved with an approximation that neglects multiple scattering processes around an atom if they involve atoms from a distance greater than some cut-off radius ( $R_{LIZ}$ ). The space within  $R_{LIZ}$  is called local interaction zone (LIZ). The idea behind this approximation is based on the observation that the scattering processes involving far away atoms influence the local electronic states less and less as the distance from the scatter under study is increased – an example of nearsightedness [8]. Technically, this approximation is implemented as follows: we draw a sphere (or LIZ), with a



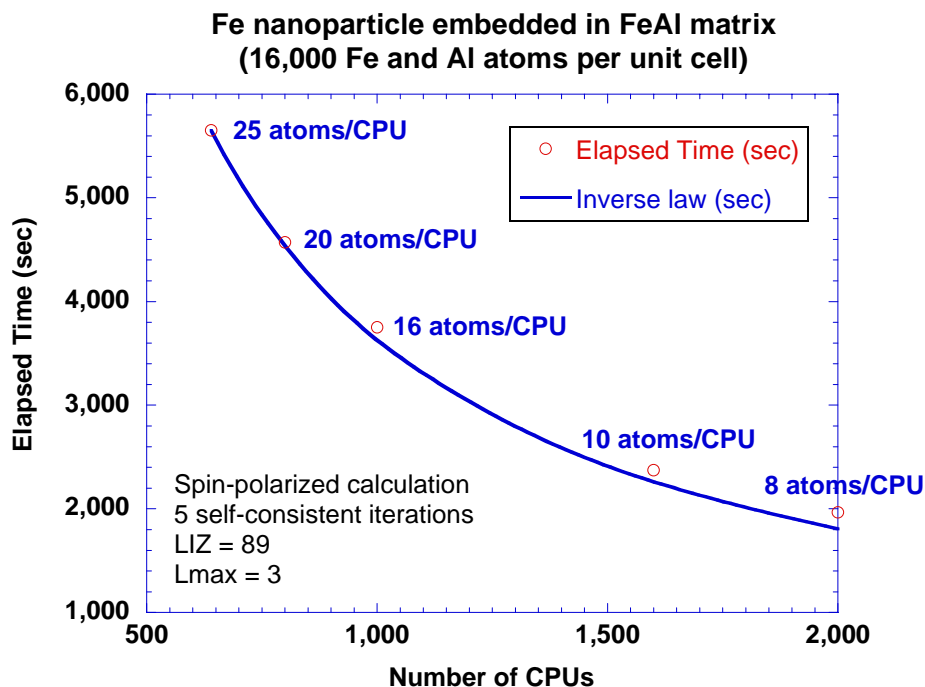
**Figure 1.** The order- $N$  scaling of LSMS code on CRAY XT3. The performance test is a set of non-collinear spin-canted calculations for bcc Fe with 1, 2, 4, 8, 16, 32, 64, 128, 256, 512, 1024, and 2048 atoms, respectively. Each atom is mapped onto a node. The measurement is performed at Pittsburgh Supercomputing Center. With  $LIZ = 137$  atoms, the code achieved 8.03 teraflops on 2048 nodes.

predefined radius, around atom  $i$ , we calculate the multiple scattering matrix only for the multiple scattering processes involving the atoms enclosed by the sphere, and we calculate the Green function and then compute the electron and magnetic moment density in the vicinity of the atom. This procedure is repeated for each atom in the unit cell.

The LSMS method described above has three obvious advantages. First, the time cost for calculating the Green function for an atom does not depend on the number of atoms in the unit cell, rather it depends on the size of the LIZ, i.e., the number of atoms included in the sphere mentioned above and since we only have to repeat the Green function calculation for each atom, the time cost for the entire electronic structure calculation only scales linearly with respect to the number of atoms in the unit cell. Second, parallelism is intrinsic to the method since the Green function calculation for each atom and each energy point along the complex contour is essentially independent. Consequently, there are no global operations involved in the process of calculating the Green function. Finally, since the only global operations are

trivial sums to calculate the total charge in the system and hence the chemical potential, the code is highly parallel.

It should be mentioned in this connection that the Coulomb interactions are treated without approximation, and hence are not order- $N$ . They are not time consuming because they are easily calculated for supercells using the Madelung matrix.



**Figure 2.** The strong scaling (or Amdahl scaling) of LSMS code measured on CRAY XT3. The same kind of electronic structure calculation (an Fe nanoparticle embedded in FeAl matrix with 16,000 Fe and Al atoms in the unit cell) is performed on 640, 800, 1000, 1600, and 2000 nodes, respectively. The solid curve is the ideal strong scaling curve, and the circles represent the actual elapsed time.

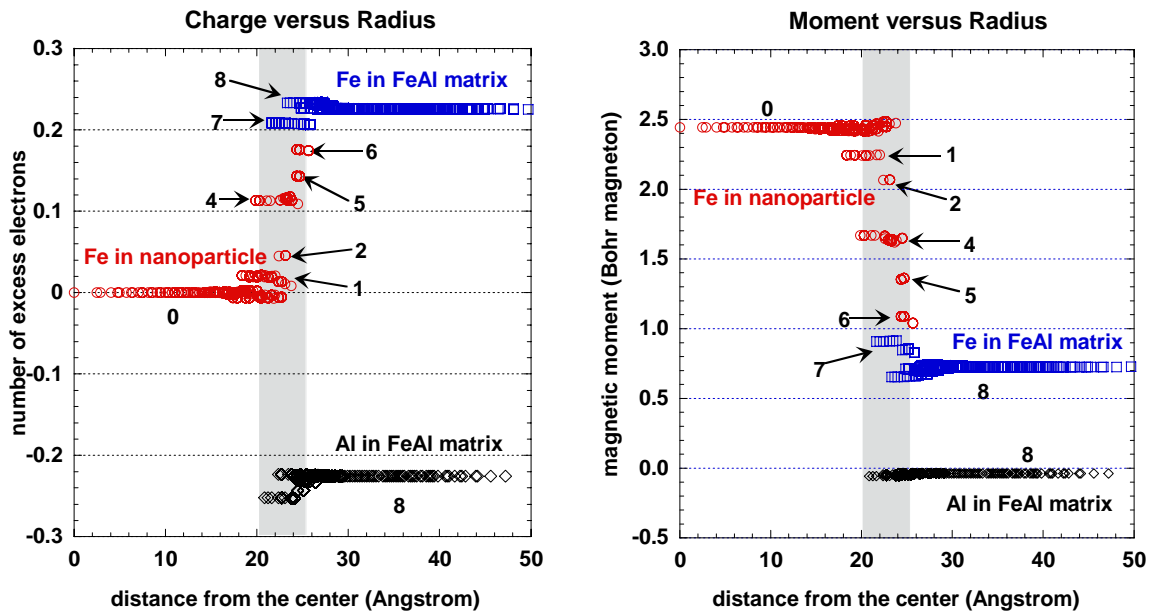
The LSMS method has proved to be a very useful tool for the study of the electronic and magnetic structures of substitutional and amorphous alloys. The source code of this method became the first scientific application to pass the teraflop computing speed barrier while investigating the magnetic properties of a non-collinear magnetic structure of 1458 iron atoms [9]. The latest measurement of its order- $N$  property on Cray-XT3 is shown in figure 1, in which the number of float operations is plotted against the number of nodes employed in the calculation. Pushing the LIZ size to an extreme (including 136 neighboring atoms), where the entire calculation is dominated by the BLAS routine ZGEMM because of large size of the large multiple scattering matrix ( $3472 \times 3472$  double complex matrix), we are able to run LSMS at 80% of the peak performance of the system. The results of strong scaling measurement of LSMS code on a Cray XT3 are shown in figure 2. In this plot, the elapsed time for a fixed size problem, the electronic structure calculation for a magnetic Fe nanoparticle embedded in FeAl matrix with 16,000 atoms altogether, is measured against the number of nodes employed. The ideal strong scaling curve (solid line) representing 100% parallel efficiency is also shown. Departure from the ideal strong scaling at the large number of CPUs usually indicates the existence of the serial components, i.e., tasks that can not

be parallelized, and such other factors as the latency for communication, the time spent in performing I/O, etc.

### 3. Results

In our recent study of magnetic nanoparticles using LSMS method, we considered magnetic Fe nanoparticles embedded in an Iron-Aluminide matrix, a stoichiometric binary compound having a B2 (CsCl-type) crystal structure. The Fe nanoparticle has the bcc lattice structure and the same lattice constant, 2.868 Å, as the FeAl matrix. The nanoparticle contains 4,409 Fe atoms, and its diameter (the length between the diagonal corners) is about 5 nm. The surrounding matrix contains 11,591 Fe and Al atoms. Altogether, the unit cell contains 16,000 atoms.

We performed self-consistent spin-polarized LSMS calculation for the system described above. We chose the LIZ for each atom to include 88 neighboring atoms (7 neighboring shells), which is large enough to give converged magnetic moment value for Fe atoms in pure bcc Fe and B2-FeAl binary compound of the same lattice constant ( $a_0 = 2.868 \text{ \AA}$ ). The calculation was performed on 1,600 processors, with 10 atoms per processor.



**Figure 3.** The number of excess electrons (left) and the magnetic moment (right) on each of 16,000 atoms are plotted versus the atom distance from the center of Fe nanoparticle (~ 5 nm in diameter). The Fe nanoparticle is made of 4409 iron atoms (circles) and the surrounding medium is a FeAl intermetallic compound, made of 11591 iron (squares) and aluminum (diamonds) atoms. The shaded area represents the boundary region of the nanoparticle. The number pointed to the data points represents the number of unlike nearest neighbors of the corresponding atoms.

The calculated charge and magnetic moment distribution is shown in Figure 3, where 16,000 data points, each of which corresponds to the number of excess electrons or the magnetic moment on each atom, are plotted against the atom distance measured from the center of the nanoparticle. The shaded region in the figures depicts the boundary region of the nanoparticle. Not surprisingly, we see that atoms in the center of the nanoparticle essentially carry no extra charges and have a magnetic moment at  $2.454 \mu_B$ , which is very close to  $2.433 \mu_B$ , the Fe moment in pure bcc Fe of the same lattice constant. Moving away from the center until the boundary region between the nanoparticle and the surrounding medium, most Fe atoms are gaining electrons. Interestingly some Fe atoms have a slightly larger moment than those in the center region. More dramatic changes are seen in the boundary region. While all the Al atoms lose electrons to Fe atoms and carry small magnetic moments (in an opposite direction to the moment on Fe atoms), most Fe atoms gain (and some Fe atoms lose) electrons. The magnetic moment varies from atom to atom, depending on the atom location. A detailed picture of the charge and moment distribution of the Fe atoms in the boundary region will be discussed in the next section. Finally, deep into the FeAl matrix, each Fe atom carries 0.225 excess electrons gaining from Al atoms and has approximately  $0.72 \mu_B$  magnetic moment. In comparison, the Fe atom in B2-FeAl binary compound carries 0.223 excess electrons and  $0.715 \mu_B$  magnetic moment.

## 4. Discussions and Summary

It is not surprising that atoms in the center region of the nanoparticle and the region in the matrix but away from the nanoparticle have properties similar to the corresponding bulk, even though their charge and magnetic moment are less than 1% different from the bulk value due to the existence of the boundary region. The charge and moment distribution in the boundary region, as depicted by the shaded area in figure 3, shows a step-like pattern. This step-like pattern can be easily explained by the unlike nearest neighbor model, a qualitative model that states that, in binary alloys, the charge and moment value on each atom is proportional to the number of unlike nearest neighbors. Careful analysis reveals that those atoms associated with the data points on a given step have the same number of unlike atoms as the nearest neighbor. In figure 3, each of the steps is indicated by a number showing the actual number of unlike nearest neighbors for the all the atoms associated with the step. Note that in the center region of the nanoparticle, Fe atoms have 0 unlike nearest neighbors (i.e., Al atoms), and in the matrix region away from the nanoparticle, both Fe and Al atoms have 8 unlike nearest neighbors (i.e., Al and Fe atoms, respectively). The Fe atoms in the boundary region are those on or near the facets, edges, and corners of the nanoparticle, which is in a polyhedron shape resembling the Wigner-Seitz cell of bcc lattice. Depending on their location in the boundary region, these Fe atoms may have 1-7 Al atoms as the nearest neighbors. The Fe atoms with the same number of Al atoms as the nearest neighbor carry a similar charge and magnetic moment. The more Al atoms in their nearest neighbor, the more electrons they gain and the less magnetic moment they carry.

A quantitative picture of the charge and the moment distribution in the boundary region can be described by the linear relation between the charge and the Madelung potential shift due to long range electrostatic interaction [12] and the linear relation between the moment and the local exchange field. We will examine these relations in our future publication.

Knowing the charge and moment distribution within a nanoparticle helps to understand the size effect as well as the effect of the surrounding environment. It also helps to determine the electrostatic interaction and the exchange coupling between nanoparticles. A multi-scale model for complex nano-composites or nano-structured devices in which each nanoparticle is treated as a point particle with proper charge and multipole electric moment, determined from the quantum mechanical calculation, can also be built.

In summary, *ab-initio* calculations employing the LSMS method are clearly possible for the large unit cells necessary for modeling nano-structured materials while allowing a rigorous treatment of their

electronic and magnetic properties. In particular the new multi-atom/processor LSMS method implemented on multi-teraflop high-performance computing technology has enabled us to perform the first *ab-initio* calculations of physical systems of a length scale in the range of 1 to 10 nanometers.

## 5. Acknowledgment

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