

# Towards Petacomputing in Nanotechnology

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**ABSTRACT:** *The ability to design nano-structured materials presents significant future scientific and technological opportunities. To realize this potential realistic quantum mechanical simulations of real nanomaterials are required. These usually involve large problem sizes in the range of thousands to millions of atoms. Interestingly, recent advances in the locally self-consistent multiple scattering (LSMS) method, a first principles order-N scaling technique specifically implemented to exploit massively parallel computing, are making the direct quantum simulation of nano-structures possible. In this paper we show that this effectively accomplishes the first step towards understanding the electronic and magnetic structure of nanoparticles with dimension size as large as 5 nanometers (nm). We demonstrate, as an example, the electronic and magnetic structure calculated for an iron nanoparticle embedded in iron aluminide crystal matrix. We also indicate to what extent future petaflop computing systems may enable the study of the dynamics of the magnetic switching process.*

**KEYWORDS:** petaflop, order-N, LSMS, *ab initio*, nanoparticle, CRAY XT3

## 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. Even though the making of nanomaterials appeared rather early in human history, for example the use of nanoparticles as decorative pigments can be traced back to Roman times, precision manufacturing of nanomaterials of desired shape and size did not become possible until the 1980s following breakthroughs in atomic scale synthesis and characterization. The discovery of Fullerenes – novel forms of carbon – and the invention of the scanning tunneling microscope (STM) – which allows imaging and manipulation of individual atoms – were two of the events that sparked a whole new science. Notably, these two breakthroughs both resulted in Nobel Prizes; the former in Chemistry (1996) and the latter in Physics (1986). Clearly, the ability to design materials at the nanoscale holds significant future scientific and technological opportunities.

The excitement that nanoscience and technology has engendered is based on the fact that nanostructured

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 this complexity, realizing the ultimate potential of nanoscience 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 two-three decades there has been significant progress in our ability to calculate the properties of materials at the first principles – quantum – level. These advances have largely been based on the local density approximation (LDA) to density functional theory (DFT); a theory for which Walter Kohn received the 1998 Nobel Prize in Chemistry (along with John Pople). However, nanoscience places new demands on these first principles methods because of the large numbers of atoms that are present in even the simplest of nanostructures – to set the scale recall that a 5nm cube of Fe contains the order of 12,000 atoms. In this paper we report on one approach to scaling up of current LDA-DFT methods to this regime.

The locally self-consistent multiple scattering (LSMS) method is an *ab initio* order- $N$  scaling technique (Wang *et al.*, 1995). It is specifically implemented to exploit massively parallel computing and to make first principles quantum simulations of systems which contain large numbers of atoms possible. Previously, the method has been used to simulate  $\sim 10^3$  atoms. Here, based on a new implementation of the method, we report on the first steps towards the direct simulation of the physical properties of a realistic model of a nanoparticle; namely, the calculation of the electronic and magnetic structure of an iron nanoparticle embedded in an iron-aluminide crystal matrix. We also indicate to what extent future petaflop computing systems may enable the study of the dynamics of the magnetic switching process.

This paper is organized as follows. The next section is a short discussion of theoretical approaches to materials science simulation. It is followed by a brief description of the LSMS method. We show the parallel performance and linear scaling properties of the method. The application of the LSMS method to the electronic and magnetic structure of nanoparticles is demonstrated in section 4, followed by an outlook of how petaflop computing may assist us to study more complex problems in nano-structured materials.

## 2. Approaches to Materials Simulation

Materials simulation is to perform experiments with a computer rather than laboratory instruments. Though the results of such simulations have to be validated by real experiment, it is known that in many cases we may rely on them as much as on the true experimental values. The information generated from these simulation methods can in principle be used to fully characterize the physical and chemical properties of the system. In addition simulation is an invaluable tool to interpret the results of complex experimental probes of material properties.

There are in general two broad classes of methods for calculating the inter-atomic interaction potential: quantum and classical. The former, because they are based on the most fundamental description of matter, have the potential to be highly accurate and unbiased. The most rigorous implementations of the quantum formalism, so called *ab initio* methods, do not require any experimental data other than a handful of basic physical constants (speed of light, electron mass, elementary charge, etc). Classical methods, on the other hand, derive a model for the energy function, or inter-atomic interaction potential, which is then fitted to some basic experimental observations or, in recent years, first principles quantum mechanical calculations for simple systems. Even though any particular empirical model need not be derivable from more rigorous theory, say quantum, good models should have a sound scientific justification to yield useful results. Obviously, the parameters entering into the functional

form must be known in advance for all types of atoms (or molecules) comprising the system; finding these can itself be a difficult task. In general classical approaches are less accurate and system specific than *ab initio* methods but, because of their relative simplicity, are applicable to much larger systems ( $10^6$ - $10^9$  atoms) using standard Monte-Carlo and Molecular Dynamics techniques.

The density-functional theory (Hohenberg and Kohn, 1964; Kohn and Sham, 1965) based *ab initio* methods were originally developed to provide physical insight about the electronic structure for crystalline solid state materials. After decades long improvement, they have become an important tool in the theoretical prediction of physical properties and in aiding the interpretation of new experimental results. Their applications can be widely seen in physics, chemistry, biology, and materials science, for the study of structural, electronic, and dynamical properties of large molecules, chemical complexes, defects in metals, and random alloys. The reason for their utility lies both in the ability of *ab initio* methods to treat systems of relatively large sizes compared to other non-empirical approaches (e.g. quantum chemical approaches), and in the systematic and relatively high of accuracy that can be achieved over wide classes of materials and materials properties..

*Ab initio* electronic structure calculations generally involve a self-consistent process that cycles between two stages: solving the Kohn-Sham one-electron Schrödinger equation (Kohn and Sham, 1965) to obtain the electron and magnetization densities; and solving the Poisson equation to obtain the electrostatic potential and hence DFT one-electron potential. The self-consistent process iterates until the ground state is found. In DFT all of the complicated many electron interactions, that make solving the many electron Schrodinger equation so difficult, are encapsulated in an exchange/correlation potential and energy density which, while formally an exact mapping, is unknown. Within the LDA (Hedin and Lundqvist, 1971; von Barth and Hedin, 1972) and generalized gradient approximation (Perdew and Wang, 1986; Perdew *et al.* 1996) (GGA) approximations are made to this exact exchange correlation potential that render the theory tractable while still retaining high accuracy.

Modern *ab initio* electronic structure calculation techniques are capable of determining fundamental electronic 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 form of the one-electron effective potential in the Kohn-Sham equations (all electron, pseudopotential) and according to the basis functions used in its solution. These latter 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. Currently, the most popular *ab initio* method for the electronic structure calculation is probably the plane-wave based pseudopotential method.

A theoretical approach to materials simulation usually starts with constructing a unit cell that repeats itself along  $x$ ,  $y$ , and  $z$  directions to fill the entire 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 [ $O(N_a^3)$ ]. In plane-wave based *ab initio* methods, for example, the orthogonalization step scales as  $N^2 \times N_p$ , where  $N$  is the number of Kohn-Sham orbitals and  $N_p$  is the number of plane waves, and the electron density calculation step using FFT scales as  $N \times N_p \times \log N_p$ . Note that both  $N$  and  $N_p$  are proportional to  $N_a$ . Since the steps involving  $O(N \times N_p \log N_p)$  scaling have a dominant pre-factor, for a moderate number of atoms, the electronic structure calculation scales approximately as  $O(N_a^2 \log N_a)$ . However, for large  $N_a$ , the computing time spent on the orthogonalization step, which essentially scales as  $O(N_a^3)$ , will become dominant. 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. Fortunately, much effort has been made since early 1990s to develop approximate methods to solve the electronic structure of large unit cell systems with an acceptable computational cost. The result is the so-called order- $N$  methods, for which the computational effort of the methods scale linearly with respect to the number of atoms in the unit cell.

### 3. Locally Self-consistent Multiple Scattering (LSMS) Method

The LSMS method (Wang *et al.*, 1995) is an order- $N$  all-electron approach to *ab initio* electronic structure calculations. By all-electron, we mean that electronic states for both valence and core electrons are treated on equal footing – in contradistinction to pseudopotential methods where core electrons are not explicitly treated. In particular, the LSMS method is based on real space multiple scattering theory (Korringa, 1947; Kohn and Rostoker, 1954) (MST) in that the electron, under the influence of the DFT-LDA (or GGA) potential, sees each atom in the crystal as a scatterer, and the electronic movement is treated as a multiple scattering problem. In the framework of MST, the Green function for the Kohn-Sham one-electron Schrödinger equation is readily given in such a convenient algebraic expression (Faulkner and Stocks, 1980) that its numerical calculation is clearly feasible; particularly when advantage is taken of the analytic properties of the Green's function.

An advantage of using the Green function is that it makes the calculation of the crystal wave functions unnecessary, and, as a result, there is no need for the time-consuming orthogonalization and normalization procedure. 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.

In general, given the Green function, the electron density and the magnetic moment density in the vicinity of the  $i^{\text{th}}$  atom can be conveniently obtained as follows:

$$\rho_i(\mathbf{r}) = -\frac{1}{\pi} \text{Im Tr} \int_{-\infty}^{\varepsilon_F} d\varepsilon \underline{G}_i(\mathbf{r}, \mathbf{r}; \varepsilon), \quad (1)$$

$$\mathbf{m}_i(\mathbf{r}) = -\frac{1}{\pi} \text{Im Tr} \int_{-\infty}^{\varepsilon_F} d\varepsilon [\underline{G}_i(\mathbf{r}, \mathbf{r}; \varepsilon) \cdot \underline{\sigma}],$$

where the Green function  $\underline{G}_i(\mathbf{r}, \mathbf{r}; \varepsilon)$  is a  $2 \times 2$  matrix in the spinor space and is calculated in the vicinity of atom  $i$ . The  $x$ ,  $y$ , and  $z$  components of vector  $\underline{\sigma}$  are the corresponding Pauli matrix, and  $\varepsilon_F$  is the Fermi energy. The energy integration usually takes place along an energy contour in the upper half complex plane to avoid the singularities of the Green function on the real energy axis. In non-magnetic cases, the Green function matrix is reduced to a scalar function, and the magnetic moment density is simply zero. For ferromagnetic states, the Green function matrix is diagonal in the frame of references that the  $z$ -axis is along the magnetization direction, and the computational procedure can be much simplified by carrying out a spin-polarized calculation, for which the Green function for spin up and spin down states is decoupled and is calculated separately. For non-collinear magnetic states, the Green function matrix is non-diagonal and its calculation, also known as a spin-canted calculation, usually takes four times longer than

the spin-polarized calculation and eight times longer than a non-spin-polarized one.

Of course use of MST Green's function methods does not, *a priori*, circumvent the  $O(N_a^3)$  scaling. This is due to the fact that obtaining the multiple-scattering matrix still requires inverting a matrix whose size is proportional to the number of atoms in the unit cell. The crux to making multiple scattering theory order- $N$  scaling is 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 (Kohn, 1996). Technically, this approximation is implemented as follows: we draw a sphere (or LIZ), with a 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 use equation (1) to 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. Firstly, 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. Secondly, 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. Thirdly, since the only global operations are trivial sums to calculate the total charge in the system and hence the electron chemical potential, the code is highly parallel.

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 (Ujfalussy *et al.*, 1998). Recent applications of the LSMS method include the study of core state chemical shifts in intermetallic alloys (Faulkner, Wang, and Stocks, 1998), the investigation of non-collinear magnetism in Fe (Stocks, *et al.*, 1998) and INVAR alloys (Wang, *et al.*,

1998), the calculation of magnetic structure of multilayers (Oparin *et al.*, 1999; Stocks *et al.*, 2002), the determination of energetics of quasi-crystal aluminides (Widom, *et al.*, 2000), and the magnetic structure of Fe-based bulk amorphous metals (Wang *et al.*, 2003.)

The LSMS method was originally developed in the mid-1990s. A detailed description of the method can be found in the literature. In its original implementation, the LSMS code was designed to associate each atom in the unit cell with a processor on a massively parallel processing (MPP) supercomputer. This design is convenient to implement, but has one obvious limitation: the problem size can not exceed the maximum number of available processors. This one (atom) to one (processor) mapping, however, was necessary in the early days because of the limited computing power and memory size of MPP processors of that time – Intel IPSC/35, /75 and /150 series and Intel Paragon. Because of the tremendous increases in both processor speed and memory size since the 1990s, eliminating the one-to-one mapping limitation in the original implementation became an urgent task. Recently, we have redesigned the code entirely to make better use of modularization and, most importantly, to allow flexible association between atoms and processors such that multiple atoms can be mapped onto one processor.

This new code has been tested for portability on a variety of computer systems with different combination of hardware architectures, operating systems, and compilers. Its performance on CRAY XT3 and Compaq AlphaServer at Pittsburgh Supercomputing Center is shown in figure 1, where the computing time for the electronic structure calculation for a ferromagnetic Fe nanoparticle embedded in FeAl matrix is plotted against the number of processors employed in the calculation. This is a spin-polarized calculation and data is shown for the first five iterations towards self-consistency. The nanoparticle is about 5 nm wide along the diagonal, and contains 4286 Fe atoms arranged on a body centered cubic (bcc) lattice. The FeAl matrix is in B2 binary alloy structure. There are 8192 atoms, including both Fe and Al, in total, and the LIZ for each atom is chosen to include 26 neighboring atoms (or 3 neighboring shells). With 4 atoms on each processor, this calculation completed in less than 500 seconds on 2048 processors of a CRAY XT3 machine.

#### 4. Electronic Structure Calculation for Magnetic Nanoparticles

Magnetic nanoparticles are of great interests to us because of their potential applications in data storage and magneto-electronics industry. The data storage and magneto-electronics industries are developing ever smaller magnetic structures and are already in the nanometer regime. Of critical importance for magnetic storage is the length of time for which a magnetic bit,

once written, is stable at operating (room) temperature. Ideally this should be several years; typically 10 years is used as the industrial design criterion. Quite generally the stability of the (ferromagnetic) moment orientation (up/down or 0/1) against thermal fluctuations depends on the particle volume and an anisotropy constant (that pins the moment along some crystallographic direction). Thus, as the particle volume decreased in the drive for increased storage density, the moment orientation becomes increasingly unstable. This gives rise to increased noise, false response, and long-term memory loss. Thus understanding the relationship between materials properties and magnetic stability is of crucial importance.

Another motivation for our interests in magnetic nanoparticles is related to permanent magnets where the energy product, the area under the second quadrant of the hysteresis loop, needs to be as large as possible. Unfortunately, conventional permanent magnets have energy products that are only a fraction, less than 50%, of what is thought to be possible. Here exchange-spring magnets (Zeng, *et al*, 2003), nanocomposites made of nanoparticles of magnetically hard and soft phases that interact via magnetic exchange coupling, are promising candidates. However, the requirement that both the hard and soft phases are controlled at the nanometer scale, to ensure efficient exchange coupling, poses significant preparation challenges. Clearly, new techniques, both experimental and theoretical, are required for characterizing the magnetic structures and the exchange couplings on nanometer size scales and over a wide range of time scales, from picoseconds to years.

Fortunately, the latest advances in LSMS method now made the direct quantum mechanical simulation of magnetic nanoparticles a realistic possibility. Here we make a preliminary report of our ongoing studies of magnetic nanoparticles using LSMS method. In particular, we considered magnetic Fe nanoparticles embedded in an iron-aluminide matrix. More specifically, we considered a Fe nanoparticle embedded in a stoichiometric FeAl binary compound having a B2 (CsCl) structure. The Fe nanoparticle itself is in bcc lattice structure, and has the same lattice constant, 2.868 Å, as the FeAl matrix. The nanoparticle, whose shape is shown in figure 2, 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.

As a proof-of-concept demonstration, we performed the first five iterations of a spin-polarized LSMS calculation for the Fe-nanoparticle in FeAl-matrix system described above. We also simplified the calculation by making the atomic sphere approximation (ASA) to the potential in which the one-electron potential around each atom is assumed to be spherically symmetric within an atomic sphere whose size is equal to the atomic volume (or Wigner-Seitz volume in 1 atom per unit cell case). This is a reasonable approximation for most simple and

transition metals. In this preliminary calculation, we choose the LIZ for each atom to include only 26 neighboring atoms – somewhat too small to give well converged moments but sufficient for demonstration purposes. The calculation is performed on 1,600 processors, with 10 atoms per processor, and the job is finished in less than 20 minutes.

We present the calculated results in figures 2, 3, and 4. Figure 2 shows the shape of the nanoparticle, as well as the distribution of the local magnetic moment associated with the individual atoms comprising the nanoparticle. The magnitude of these local moments is encoded in the coloring of the Fe atoms – shown as balls. The reddish colored balls represent the atoms with larger moment, and the gray colored balls represent the atoms with smaller moment. Figure 3 is a sliced view of the charge distribution within the nanoparticle and the atoms of the surrounding FeAl matrix. The amount of net charge on each atom is color-coded. The silver colored balls in the interior region of the nanoparticle represent the Fe atoms with the very few excess electrons (i.e. are charge neutral), the dark blue colored balls in the boundary region represent those Fe atoms gaining a significant amount of electrons, and the green colored balls in the FeAl matrix represent the Al atoms which lose a significant number of electrons to Fe.

A more detailed picture of the charge distribution and the moment distribution is shown in Figure 4, 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. Not surprisingly, we see that atoms in the center of the nanoparticle have essentially the same amount of magnetic moment as in the bulk and carry no extra charges. Note that the Fe moment in the bcc Fe is expected to be 1.85 Bohr Magnetons ( $\mu_B$ ) if we use the same LIZ size (27 atoms) for the bulk calculation. Moving away from the center, we observe that the excess amount of electrons on each Fe atom in the nanoparticle increases gradually but the magnetic moment essentially stays the same until around 13 Å from the center, where both excess electrons and magnetic moment values start to drop. More dramatic changes are seen in the region of the boundary between the nanoparticle and the matrix. While all the Al atoms lose electrons to Fe atoms and carry very little magnetic moment (in an opposite direction to the moment on Fe atoms), the Fe atoms can either gain or lose electrons depending on the location, and their magnetic moment varies from atom to atom, again, depending on the atom location. A further study is necessary to determine the underlying mechanism that correlates the charge and moment of the Fe atoms with the location on the boundary. Finally, deep into the FeAl matrix, each Fe atom carries approximately 1.0  $\mu_B$  moment.

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 nanocomposites or nano-structured devices in which each nanoparticle is treated as a point particle with proper charge and multipole moment, determined from the quantum mechanical calculation, can also be built.

## 5. Towards Petaflop Computing

In summary, *ab initio* calculations employing LSMS method are clearly possible for the large unit cells necessary for modeling interfaces, surfaces, defects, and especially, the 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 of several nanometers.

Despite these early successes with our new code it is clear that nanotechnology, especially new discoveries in nano-structured spintronic devices, pose challenges that go much beyond the capability we just demonstrated. To meet the challenges, we are required to develop computational techniques capable of characterizing the electronic and magnetic structures on sub-hundred nanometers length scales and over a wide range of time scales. Evidently, going from several nanometers to sub-hundred nanometers, an order of magnitude increase in length scale, increases the problem size from tens of thousands to millions of atoms, and consequently increases the computational cost by a factor of hundreds, even assuming the continued order- $N$  scaling of our methods – an assumption that will require considerable effort to realize. In addition to the challenges in terms of the length scale requirement, we are also facing the challenges in terms of the time scale requirement which can range from picoseconds, for the simulation of the magnetic moment rotation, to tens of nanoseconds or more, for the simulation of nanoparticle movement. Clearly, the success of direct quantum mechanical simulation of nanostructured electronic devices relies on the birth of petaflop computing technology.

To be prepared for the new dawn in high-performance computing technology, we need to make advances on two “work-fronts”. One is *ab initio* spin-dynamics simulation, which is necessary for the physical systems with non-collinear magnetic structure and for the study of moment dynamics resulting from thermal effects and/or switching by an external field. Statically, non-collinear magnetic structure evidently exists in large varieties of materials, ranging from those as simple as metallic Cr to those as complex as magnetic amorphous alloys. Past efforts to develop LSMS method with the ability to perform spin-canted calculations have enabled

the study of non-collinear magnetic structure in  $\gamma$ -Fe (Stocks *et al*, 1996) and Fe-rich FeNi alloys (Wang *et al*, 1997). Especially, the implementation of constrained local moment model (Stocks *et al*, 1998) in LSMS method allows for *ab initio* spin dynamics simulation (Antropov *et al*, 1996) and makes it possible to determine complex magnetic structure of the ground state from the first principles. This work-front needs to be pushed further by applying *ab initio* spin-dynamics simulation to such complex problems as magnetic domain wall movement, exchange coupling between magnetic nanoparticles or between magnetic nanoparticle and substrate, and etc.

The other work-front is *ab initio* molecular dynamics simulation. In the earlier implementation of LSMS method, either a muffin-tin or an ASA approximation has to be used. These approximations assume the one-electron potential and the electron density are spherically symmetric around each atom. These approximations work well if the target physical system possesses a regular underlying lattice and is dominated by the metallic bonding. Lately, full-potential multiple scattering theory has been implemented to allow electronic structure calculations without these shape approximations for the potential and density. Given the full-potential capability, this latest version of the LSMS code will make possible not only the calculation for the structures involving strong covalent bonding, such as nanoparticles of semiconductors and insulators, but also the determination of the force acting on each atom.

Being able to calculate the force in a straightforward manner is an essential requirement for the structural relaxation and molecular dynamics simulation. Considering the fact that the core electrons can be treated in a simplified scheme that results in a spherical core charge, we handle the electrostatic force from the core electrons in the manner described by Papanikolaou (Papanikolaou *et al*, 1997). The resulting expression for the force is a straightforward function of the electron density and the dipole part of the one electron potential:

$$\mathbf{F}_i = Z_i \cdot \left[ \nabla v_i^{\text{Coul}}(\mathbf{r}) \right]_{r=0} - \int d^3r \rho_i^{\text{core}}(r) \nabla v_i(\mathbf{r}), \quad (2)$$

where  $Z_i$  the atomic number of atom  $i$ ,  $v_i^{\text{Coul}}(\mathbf{r})$  is the Coulomb part of the one-electron potential  $v_i(\mathbf{r})$  in the vicinity of the atom, and  $\rho_i^{\text{core}}(r)$  is the spherical component of the core electron density. A careful analysis of this expression reveals that if we expand the potentials in terms of the spherical harmonics, the only non-zero contributions to the two terms in the force expression are from the  $l = 1$  components. Since the spherical harmonic expansions of the potential and density are actually used in the multiple scattering theory implementation, it turns out the force can readily be calculated. With the help of *ab initio* molecular dynamics simulation, it is possible to

study such problems like the underlying mechanism for the self-assembly of nanoparticles. Ultimately, coupling first principles MD and first principles spin dynamics opens previously unimagined areas to first principles studies and will usefully occupy even multi-petaflop computers.

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### Ferromagnetic Fe nanoparticle in B2 FeAl matrix

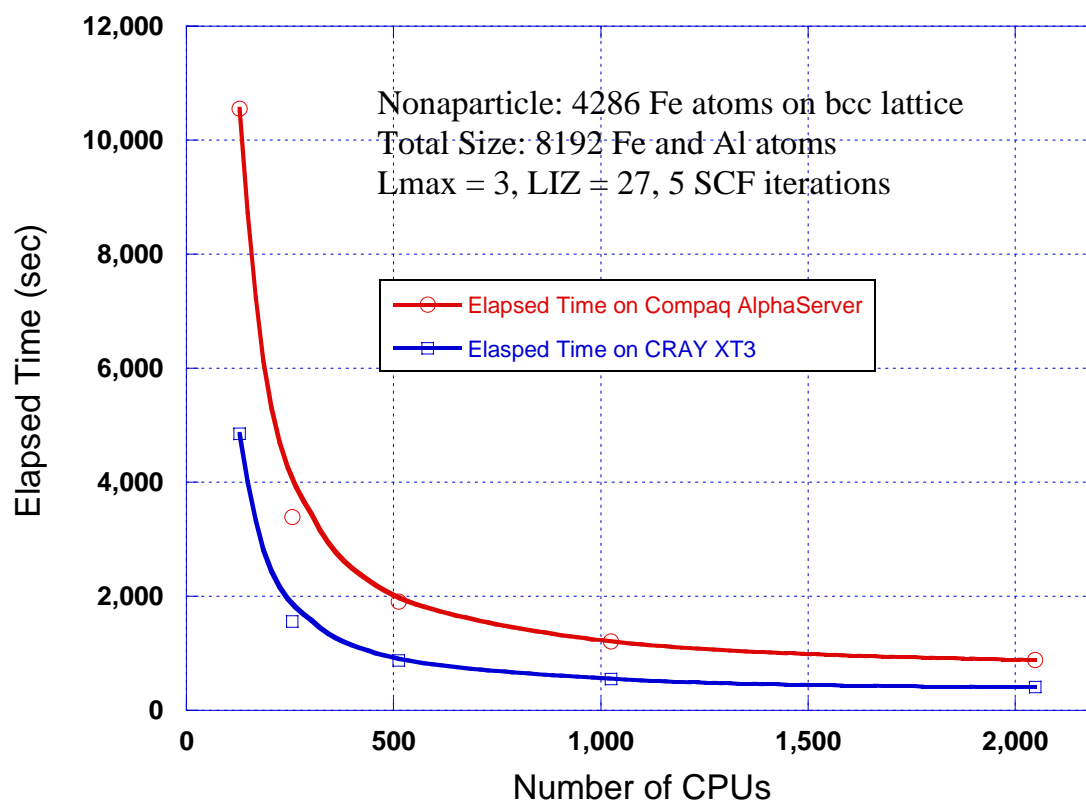


Figure 1. The scaling of LSMS code on CRAY XT3 and Compaq AlphaServer systems. The measurement is performed at Pittsburgh Supercomputing Center.

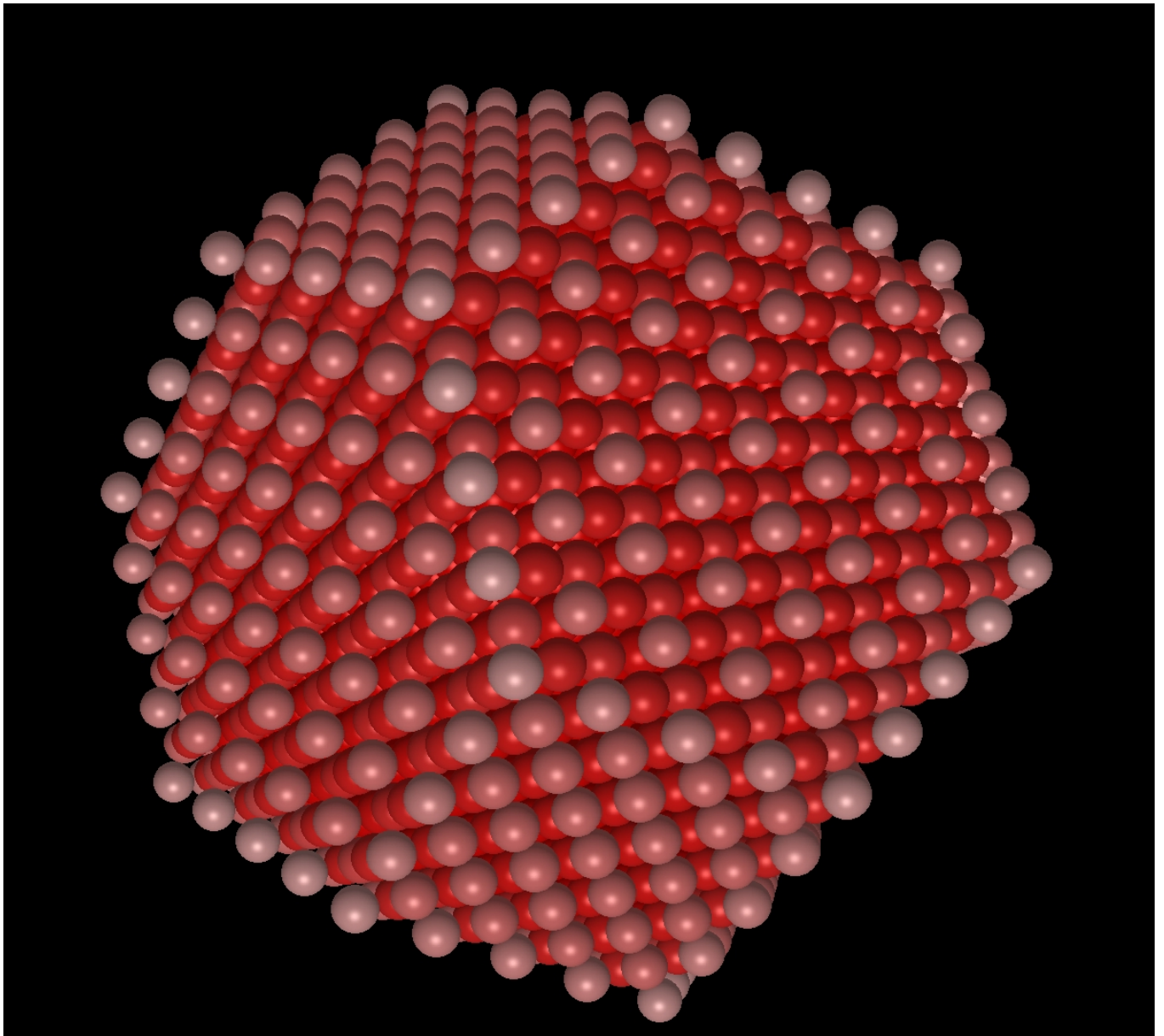


Figure 2. Magnetic Fe nanoparticle that contains 4409 Fe atoms, represented by the colored balls, located on a body centered cubic lattice. The characteristic size of this particle is about 5 nm. The magnitude of the magnetic moment on each atom is coded in the coloring of the balls. The reddish colored balls represent the atoms with larger moment, and the gray colored balls represent the atoms with smaller moment.

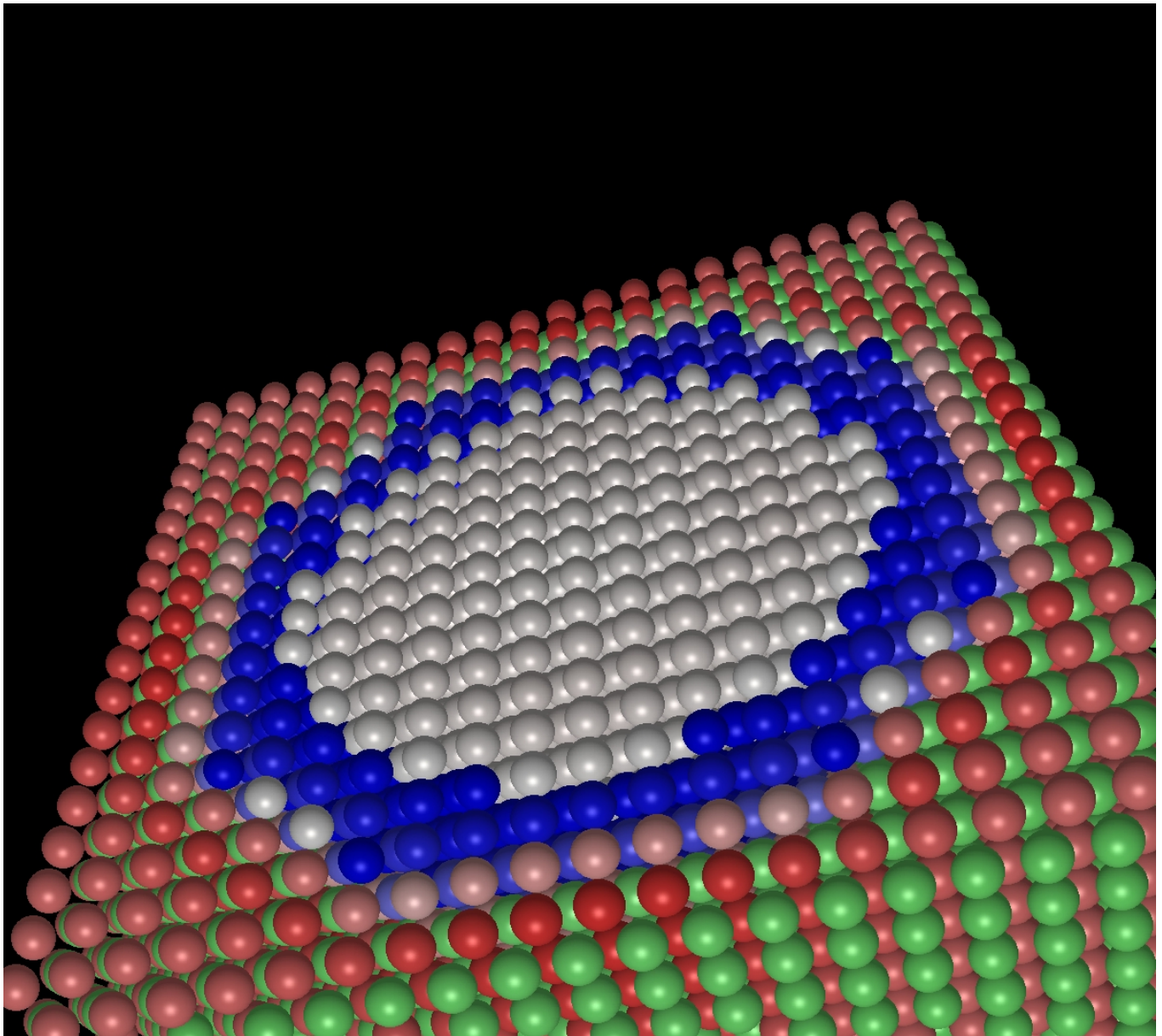


Figure 3. A sliced view of the magnetic Fe nanoparticle together with the surrounding FeAl matrix. The charge distribution within the nanoparticle and its surrounding atoms is indicated by the color change from the center to the edge. The silver colored balls in the interior region of the nanoparticle represent the Fe atoms with very little excess electrons, the dark blue colored balls in the boundary region represent those Fe atoms gaining a significant amount of electrons, and the green colored balls represent the Al atoms which lose a significant amount of electrons to Fe.

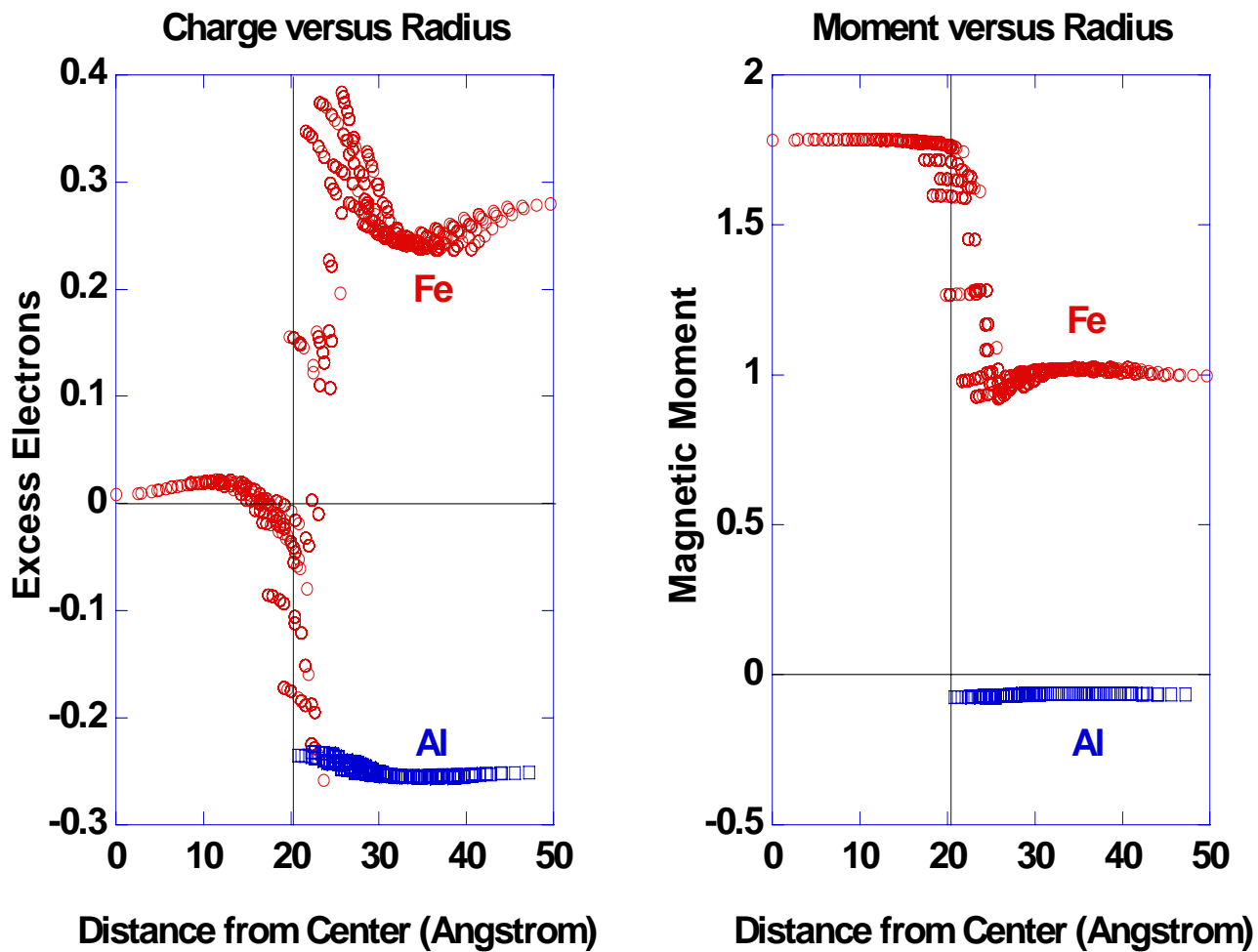


Figure 4. The number of excess electrons (left) and the magnetic moment (right) on each of 16,000 atoms are plotted versus the atom distance from the center of the nanoparticle. The red circles are the data point from Fe atoms, and the blue squares are the data point for Al atoms.