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Massively Parallel Density Functional Theory Calculations of Large Transition Metal Clusters

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Abstract: We report on *ab initio* density functional theory (DFT) calculations of structural properties of large elementary transition metal clusters with up to 561 atoms, corresponding to a diameter of about 2.5 nm, which is a relevant size for practical applications. The calculations were carried out on an IBM Blue Gene/L supercomputer, showing that reasonable scaling up to 1024 processors and beyond can be achieved with modern pseudopotential plane wave codes.

Keywords: Density-functional Theory, magnetic nanoparticles, transition metal clusters, massively parallel computing

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Introduction

Transition metal nanoparticles are of growing interest for technological applications. Especially iron and its alloys are of primary concern. So are regular arrays of $L1_0$ ordered FePt particles with a diameter of 4 nm and below considered as a recording medium for magnetic data storage [1]. FeCo particles are discussed as carriers for magnetically guided transport of drugs in the human body [2]. Although of lesser practical importance, investigations of elementary transition metal clusters are indispensable prerequisites for the understanding of the properties of alloyed systems. Due to the complexity of the potential energy surfaces, general procedures to obtain the ground state structures (like simulated annealing) are impracticable for larger cluster sizes on an *ab initio* basis. On the other hand, classical molecular dynamics simulations are lacking reliable model potentials for many elements of interest.

With the help of state-of-the-art massively parallel supercomputers, spin-polarized quantum mechanical calculations of nanoparticles consisting of several hundred transition metal atoms including full structural relaxations have become feasible, providing valuable information about structure and magnetism of these objects. This is of special interest, since modern transmission electron imaging methods provide resolutions on the atomic scale [3], allowing a direct comparison between theory and experiment. Within this contribution, we report on *ab initio* geometrical optimizations of large elementary clusters with up to 561 atoms and discuss the scaling behavior of the DFT code on the IBM Blue Gene/L supercomputer.

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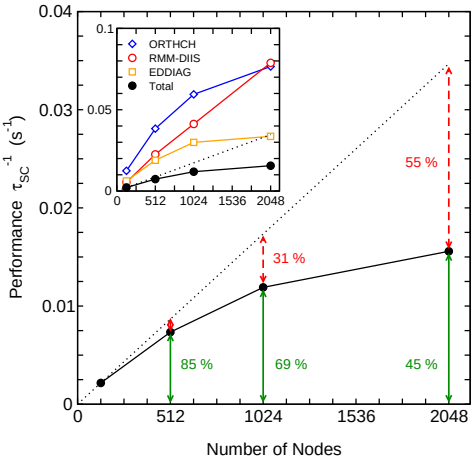

Figure 1: Scaling behavior of a cluster with 561 Fe atoms on the IBM Blue Gene/L. The performance (inverse average computation time for an electronic self consistency step) τ_{SC}^{-1} is shown as a function of the number of nodes (black circles). The dashed lines describe the ideal scaling behavior. The open symbols in the inset refer to the scaling of selected subroutines (see text).

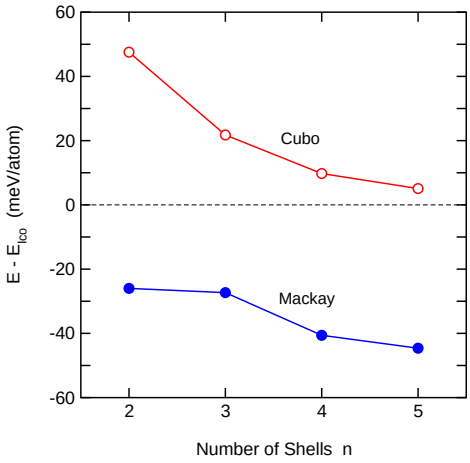

Figure 2: Energy of the cuboctahedral (open symbols) and shell-wise Mackay transformed (filled symbols) iron clusters as compared to the energy of the icosahedral isomers for different numbers of closed geometric shells. As opposed to the cuboctahedra, the shell-wise Mackay transformed clusters are lower in energy throughout all inspected cluster sizes.

Technical aspects

DFT calculations were performed using the Vienna Ab initio Simulation Package (VASP) [4] applying a plane wave basis set for the wavefunctions of the valence electrons and the augmented wave (PAW) approach [5] for the interaction with the nuclei and the core electrons. For the exchange-correlation functional the generalized gradient approximation (GGA) was used in the formulation of Perdew and Wang [6]. Reciprocal space integration was restricted to the Γ-point. Geometrical optimizations were carried out on the Born-Oppenheimer surface using the conjugate gradient method. Parallelization is implemented in the VASP code using calls to the Message Passing Interface (MPI) library, parallel linear algebra routines (e. g., the eigensolver) are used from the ScaLAPACK library. The installation on the IBM Blue Gene/L did not require major changes in the code.

The peculiarity of the IBM Blue Gene/L concept is the huge packing density, which allows 1024 double processor nodes with a peak performance of 5.6 GFlops to be placed into one rack (for an overview, see [7]). To allow sufficient air cooling, power consumption was kept low by reducing the clock frequency of the CPUs and providing only a limited amount of main memory (512 MB) per node. The hardware allows the memory to be divided between both CPUs ('virtual node' mode) or to be dedicated to one processor alone, while the other takes care of the communication requests ('communication coprocessor' mode). Scalability is increased by a threefold high-bandwidth, low-latency network.

Although DFT calculations are generally considered to be demanding with respect to memory and I/O bandwidth, we can show that large systems can be handled efficiently on the Blue Gene/L. Figure 1 demonstrates that the VASP code can achieve 69 % of the ideal performance on 1024 processors for $N = 561$. In this case, however, the coprocessor mode had to be used sacrificing one half

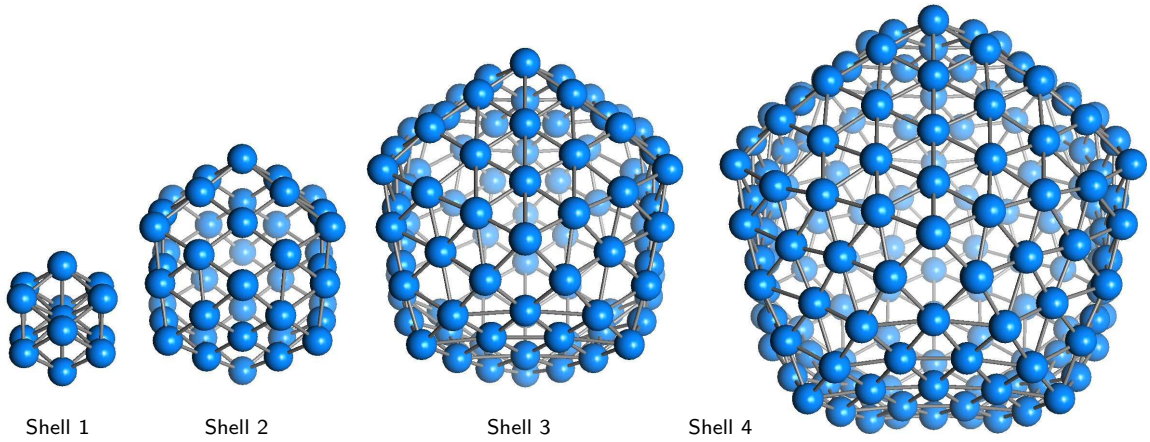

Figure 3: Image of a shell-wise Mackay-transformed Fe_{309} cluster ($n = 4$) after structural relaxation. For clarity, each shell is depicted separately. One can clearly see that the innermost shell (1) possesses the typical six square faces of a cuboctahedron, while at the outermost shell (4) only triangular faces appear and the fivefold icosahedral symmetry axis (center) is almost retained. The shell-wise Mackay-transformed structure is $\Delta E = 40.6\,\mathrm{meV/atom}$ lower in energy than a fully relaxed icosahedron.

of the potential peak performance. Especially the optimization of the trial wavefunctions according to the residual vector minimization scheme (labeled 'RMM-DIIS' in Fig. 1) scales nearly perfectly, even at the largest processor numbers under consideration. However, with increasing number of processors, its computation time gets outweighed by other routines ('EDDIAG' and 'ORTCH') providing the calculation of the electronic eigenvalues, subspace diagonalization and orthonormalization of the wavefunctions, making use of linear algebra routines from the ScaLAPACK library and performing fast Fourier transforms.

Results

We primarily focused on structures with closed atomic shells, i. e. icosahedra and cuboctahedra, which exist for the so called magic atom numbers:

$$N = \frac{1}{3}(10n^3 + 15n^2 + 11n + 3) = 13, 55, 147, 309, 561, \ldots \quad ,$$

where n is the number of closed geometric shells. It was first pointed out by Mackay [8] that a continuous transition path exists between icosahedra and cuboctahedra of the same size. During this transformation the common edges of six pairs of triangular surfaces of the icosahedron elongate and the surfaces turn into the same plane, forming the six squares of the cuboctahedron. Recently, it has been shown [9] that the ground state of Fe_{55} is neither icosahedral nor cuboctahedral. Instead, the lowest energy is found for an isomer which is partially transformed along the Mackay-path. Each shell transforms to a different degree with the outer shell retaining practically icosahedral shape and the innermost shell transforming into a more or less cuboctahedral shape. Comparison of the energies between the isomers (Fig. 2) confirms that this trend also holds for larger clusters, e. g., for Fe_{309} (cf. Fig. 3) where the transformed structure is $\Delta E = 40.6\,\mathrm{meV/atom}$ lower in energy than a fully relaxed icosahedron as compared to $\Delta E = 26.0\,\mathrm{meV/atom}$ in the case of Fe_{55} [9].

Although the energy differences are remarkable, a shell-wise Mackay-type deformation is not a general property of transition metal clusters. Calculations of 147-atom cobalt and nickel clusters

reveal that the Mackay-state is not stable for these elements and the clusters transform back into nearly perfect icosahedra during the structural relaxation process.

Conclusions

We demonstrated that state-of-the-art supercomputer systems are capable of efficiently performing *ab initio* geometric optimizations of nanometer-sized transition metal clusters containing several hundred atoms within the framework of density functional theory. With these calculations we showed that shell-wise Mackay transformed structures are favorable for large Fe clusters, while they seem to be unstable for Co or Ni nanoparticles. Further calculations of structural and magnetic properties of binary alloy systems with relevance for technical applications (like FePt) are currently underway.

Acknowledgment

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