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Scaling Properties of Algorithms in Nanotechnology[1]

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Extended Abstract

1. Introduction: At the present time, several technologies are pressing the limits of microminiature manufacturing. In semiconductor technology, for example, the Intel Pentium Pro (which is used in the DoE ASCI 'red' parallel supercomputer system) and the DEC Alpha 21164 (which is used in the CRAY T3E) both are fabricated using 0.35 micron process technology. Recently Texas Instruments (TI) announced the availability of 0.25 micron technology chips by the end of 1996 and plans to have 0.18 micron devices in production within two years. However, some significant challenges lie down the road. These include the skyrocketing cost of manufacturing plants, the 0.1 micron foreseeable limit of the photolithography process, quantum effects, data communication bandwidth limitations, heat dissipation and others.

Some related microminiature technologies include micro-electromechanical systems (MEMS), opto-electronic devices, quantum computing, biological computing and others.

All of these technologies require the fabrication of devices whose sizes are approaching the nanometer level. As such they are often collectively referred to with the name "nanotechnology". Clearly nanotechnology in this general sense is destined to be a very important technology of the 21st century. The ultimate dream in this arena is 'molecular nanotechnology' [1], in other words the fabrication of devices and materials with most or all atoms and molecules in a pre-programmed position, possibly placed there by "nano-robots". This futuristic capability will probably not be achieved for at least two decades. However, it appears that somewhat less ambitious variations of molecular nanotechnology, such as devices and materials based on "buckyballs" and "nanotubes" may be realized significantly sooner, possibly within ten years or so. Even at the present time, semiconductor devices are approaching the regime where quantum chemical effects must be considered in design [2].

2. Molecular nanotechnology: However they are manufactured, the design and analysis of nanometer-scale systems presents a formidable computational challenge. Simulations need to be performed for structures containing between several hundred and several billion atoms. These simulations involve processes such as chemical synthesis controlled by a mechanical systems with atomic-scale precision, which thereby enables direct positional selection of reaction sites. Perhaps the ultimate computational challenge in nanotechnology is to simulate entire molecular assemblies of 100 million atoms or more. Simulations of such assemblies will require a hierarchy of approximations of varying accuracies, since the most accurate methods available are necessarily limited in scope to small number of atoms even if we generously extrapolate future computational capabilities. An overview of the most commonly used approximate methods is as follows:

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2.1 Quantum mechanical *ab-initio* methods: Quantum mechanical theories [3] can be classified as relativistic (originally formulated by Dirac) and non-relativistic (originally formulated by Schrodinger). For the atoms of greatest importance to nanosystem design, namely light elements such as H, C, N, O, F, relativistic effects on valance electrons are negligible. Therefore, computational chemistry methods seek solutions to the non-relativistic Schrodinger equation describing bound, time invariant systems. The solution of the Schrodinger equation is very difficult, and exact analytical solutions exist only for two-body problems such as a hydrogen atom with a proton and an electron. In fact, the Schrodinger equation cannot be solved exactly even for a hydrogen molecule. The goal of computational chemistry is thus to solve the Schrodinger equation within the what is known as the Born-Oppenheimer approximation. Calculated quantities of interest to nanotechnology researchers include equilibrium geometries, potential energy surfaces (PES), infrared and Raman spectra, excited state energies, dipole moments and polarizabilities. It may be noted that in quantum mechanical computations, there is no a *priori* concept of a chemical bond. Some of the most commonly used schemes for these computations are as follows:

2.1.1 Full configuration interaction (FCI): FCI is the most accurate method to compute the physical quantities of interest. In this method, careful mixing of multiple wave functions including the excited states amounts to incorporating electron correlations. However, the set of possible configurations becomes so large that the complexity of FCI is of the order of $(10\,N)!$ where N is number of atoms, and where we assume 10 basis functions in an atom. As a a result, FCI computations converge slowly and are very expensive. Thus this method can be used only for systems with one or two atoms.

2.1.2 CCSD(T): Since the FCI method is not feasible for most problems, the coupled-cluster singles and doubles (CCSD) method, with a perturbational estimate of the connected triple excited CCSD(T) method, is probably the most accurate and practical approach in use today. The computational complexity of CCSD(T) is proportional to $(10\,N)^7$ where N is number of atoms. This method can only be used for systems with up to about 20 atoms.

2.1.3 CCSD: The computational complexity of CCSD(T) can be reduced by ignoring the triple excited states. The computational complexity of CCSD is proportional to $(10\,N)^6$ where N is number of atoms. This method can only be used for systems with up to about 30 atoms.

2.1.4 MP2: Another approximation is the Moller-Plesset second-order perturbation theory (MP2). The computational complexity of MP2 is on the order of $(10\,N)^5$ where N is number of atoms. This method can be used for up to about 40 atoms.

2.1.5 DFT: The density functional method has complexity $(10\,N)^4$ and can be used for somewhat larger systems, up to about 50 atoms.

2.2 Scaling of *ab-initio* methods: The scaling of several available computational *ab-initio* methods is shown in Figure 1. We have omitted the FCI method as even for $N=2$ the computational complexity is 20!. It is clear from this figure that quantum mechanical based methods can exhaust the computing capabilities of even the most advanced supercomputers, in spite of the fact that the computation of the required matrix elements is embarrassingly parallel. As a result, highly accurate *ab-initio* calculations are almost impossible. In other words, *ab-initio* methods could conceivably be used to compute the PES of larger nano-scale systems, but the computational complexity is beyond the capabilities of present-day supercomputers.

3. Molecular mechanics (MM): The limitations of the *ab-initio* methods in terms of accuracy, computational cost, and scalability motivate the popularity of empirically based models, such as MM schemes [4]. In MM methods the Born-Oppenheimer potential is approximated in the terms of the molecular geometry. Unlike *ab-initio* methods, MM methods use the concept of bonds, which are used to model the PES. This PES is analytically developed from the input of small scale *ab-initio* methods in conjunction with experimental data.

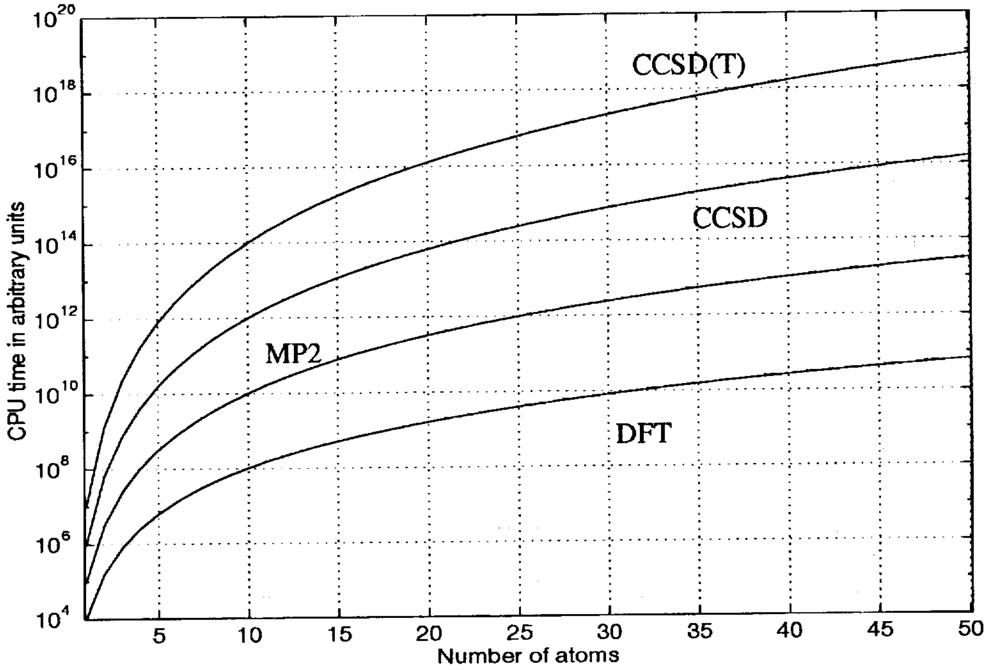

Figure 1: Computational requirements of various ab-initio methods.

3.1 Scaling of MM methods: In MM methods, a one finds a local minimum on the PES using Newton methods, which have computational complexity that scale as N^3 and memory requirements that scale as N^2, where N is the number of atoms. Recently a new algorithm has been developed with computational complexity N^2 and memory requirement $N^{1.5}$. The PES of a ground-state system determines its mechanical properties. For designing nano-scale systems, MM methods on modest-sized molecular assemblies will be feasible once we have computers capable of performing at one Tflop/s (10^{12} floating-point operations per second) or greater. Larger assemblies will require systems that can perform at more than one Pflop/s (10^{15} floating-point operations per second).

4. Non-statistical molecular dynamics (MD): In the non-statistical MD approach, one starts with a set of initial conditions and then integrates the equations of motion using a PES. Statistical results (for example thermal distribution) are then computed after integrating the system for a long time. The price one has to pay for not using a statistical distribution is that one has to integrate for a very long time. Using this approach one can obtain both equilibrium and dynamic properties.

4.1 Scaling of MD methods: The complexity of MD involving long-range forces is of the order of N^2. The complexity of MD using fast-multipole expansion methods is of the order of $NlogN$. The scaling of different MD methods is shown in Figure 2. The complexity of MD involving only short-range forces is of the order of N.

5. Monte Carlo (MC): Unlike MD where we specify the values of the parameters N, V and E, in MC methods one specifies N, V and T. One generates random moves and samples with either classical statistical mechanics (CSM) or quantum statistical mechanics (QSM). In CSM, one computes a distribution of positions and velocities, whereas in QSM one computes the distribution of quantum states.

5.1 Hybrid MC: The HMC approach was first used in lattice field theory in 1987. This method is about an order of magnitude faster with improved volume dependence.

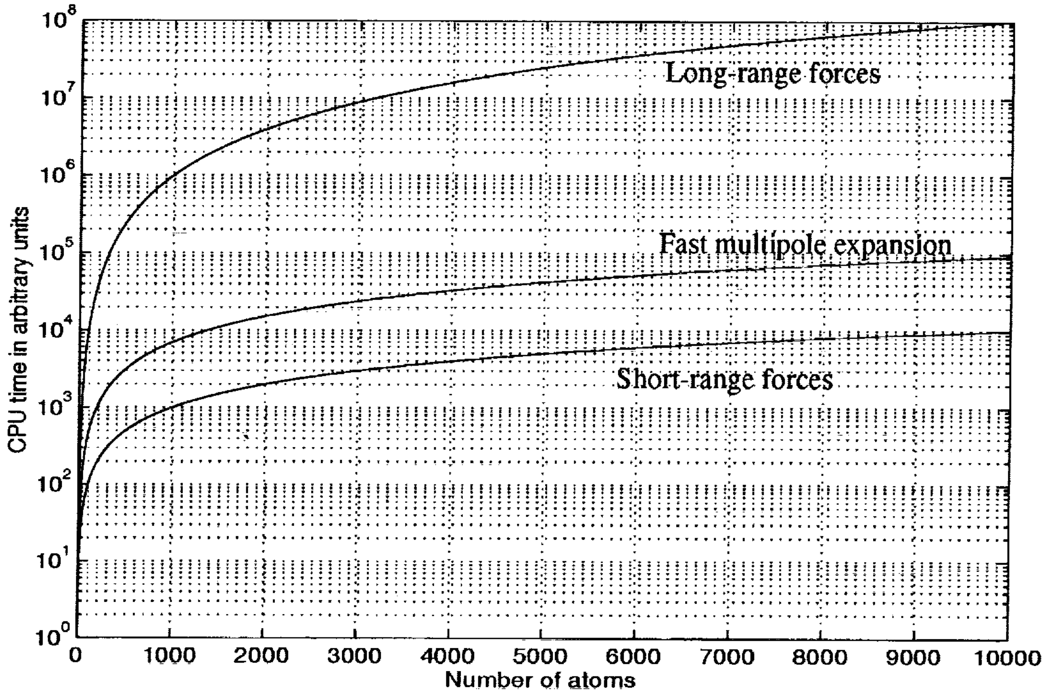

Figure 2: Computational requirements of various MD methods.

6. Exotic algorithms: Recently, various exotic algorithmic approaches have been explored for attacking computational chemistry problems. These include neural networks, fuzzy logic and genetic algorithms [5]. The neural network method for performing function approximation, is a model-free, data driven technique. The scaling is only related to the size of the input data set and on the method used to optimize the connection weights. Generally the input is given as a matrix and the training speed scales proportional to the size of the matrix: for second order methods it is *O(2N)* and for first *O(N)*. Again this is only for the training of the neural network. Once trained the prediction phase is trivial. For MD simulations of interest in nanotechnology, depending on what one is interested in modeling, one can primarily use the neural network method as a means of extrapolating in variable space (initial conditions such as energy, positions, and momenta as well as total time). Recently, neural networks techniques have been used to compute the energy transfer from CH overtones in a polyethylene molecule. In this case the variables used as input to the neural network were: temperature, pressure, initial energy of the overtone, and time. Given a number of MD trajectories which span the range of interest for those variables, the neural network could then accurately predict the behavior of a trajectory for conditions not simulated by the MD method. Genetic algorithms in particular have the potential of reducing the costs of some methods by an order of magnitude or more. Thus such schemes are likely to find more widespread usage in computational nanotechnology during the next decade.

7. Computational Strategy: For nano-scale design work to be feasible at all, less accurate but faster methods must be used. Benchmark calculations have shown that the complete-active-space self-consistent-field (CASSCF) method with MP2 correlation included is quite accurate for a small number (20-30) of atoms. The PES is computed using CASSCF. The computed PES is then converted to some analytical form using molecular mechanics models. Molecular mechanics methods are based on the following assumptions: nuclei and electrons are lumped together into an atom and treated like particles; atoms are assumed to be spherical, with radii and net charge obtained from either theory or experiment; interactions are assumed to be of springs or classical potentials; interactions determine the spatial distribution of atoms and their energies. This potential is then used in MD computations. Classical MD methods involve solving Hamilton's equations of motion for each atom in the system with respect to every other atom.

The forces acting on an atom are a combination of forces due to bonds, van der Waals forces, and Coulomb forces. The calculation of the Coulomb forces is typically the most computationally intensive because each atom interacts electrostatically with all the other atoms in the system. Several methods are available for dealing with resonant and non-resonant systems for multidimensional systems.

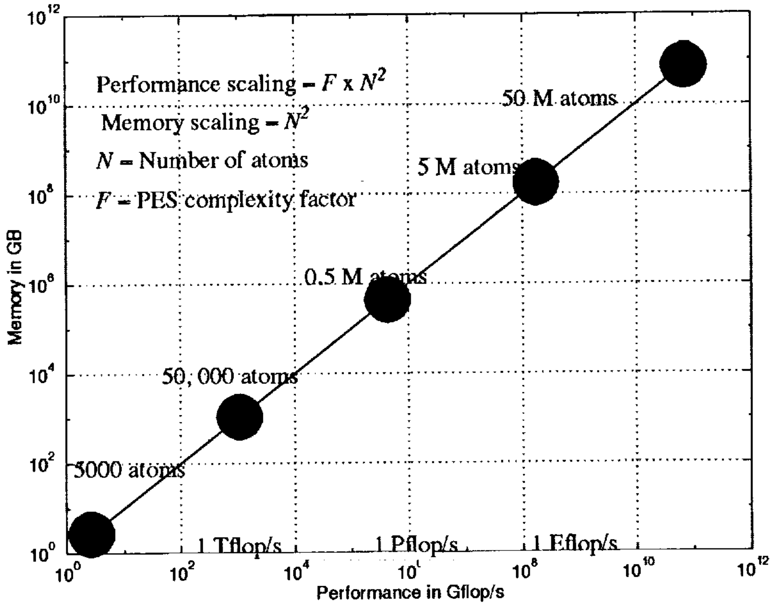

Figure 3: Estimated required computing power in Gflop/s vs. required memory in GByte.

Since the computational requirements for molecular nanotechnology are so large, it is clear that highly parallel computing systems will be required to perform the needed calculations in a reasonable time. With regards to parallelization techniques, there are two classes of methods that need to be considered. The first is characterized by short-range (local) interactions (i.e., each atom interacts only with other atoms that are within some cut-off distance). Many solids are modeled in this way because of electronic screening effects or because long-range interactions are truncated to avoid more costly computations. The local nature of the forces means that the computational cost scales linearly with the number of atoms. There are several related approximate methods such as the fast multipole expansion method and the cell multipole method. The second type is characterized by long-range (global) interactions (i.e., each atom interacts with very other atom). This is necessary when atoms undergo large displacements over the duration of the simulation. In a solid, such displacements can result from diffusion, impurities, dislocations, surface defects, or phonon scattering. A phonon is a quantum of acoustic energy. Thermal excitations in an elastic continuum are described as population of phonons. Phonon scattering is a phenomenon in which mechanical motions disturb phonon distribution by reflection. Such phenomena have significant computational impact, because each atom's neighbors must be tracked as the simulation progresses to take full advantage of the force locality.

These two classes of algorithms are implemented on parallel computers using two different decomposition schemes: atom decomposition and spatial decomposition. Assuming the above outlined strategy (*Ab-initio* + CASSCF + MD), we have estimated the computing power and disk space needed to perform long-range MD simulations for systems of interest to nanotechnologists. The results are shown in Figure 3.

8 Conclusions

It is clear from estimates such as those in Figure 3 that dramatic improvements in simulation capabilities will be required if the projected future needs of nanosystem design and analysis are to be met. Improvements in innovative hardware must be matched by new algorithms to enable computational scientists to expand the boundaries of computational capabilities. It appears that parallel supercomputers with Tflop/s and even Pflop/s performance levels will be required for molecular nanotechnology to achieve its full potential [6]. Systems with this power may also be required for more modest variations of nanotechnology, such as future-generation semiconductors, opto-electronic systems, micro-electromechanical systems, and "buckyball" and "nanotube" systems. Given the key role that Tflop/s and Pflop/s computers will likely play in the development of these advanced technologies, it is clear that efforts leading to the realization of these very-high performance computer systems should be a high priority.

References

[1] Drexler K. E., *Nanosystems: Molecular Machinery, Manufacturing and Computation*, 1992, John Wiley & Sons, Inc.

[2] Saini S. and Bailey D. H. (Eds.), *Proceedings of Semiconductor Device Modeling Workshop*, March 28-29, 1996, NAS-NASA Ames Research Center, Moffett Field, California.

[3] Lawley K. P., (Ed.), *Advances in Chemical Physics: Ab Initio Methods in Quantum Chemistry*, Vols. 67 and 69, (Wiley, New York, 1987).

[4] Bukert U. and Allinger N. L., *Molecular Mechanics*, ACS Monograph 177, Washington, DC, American Chemical Society.

[5] Hertz J., Krogh A. and Palmer R.G., *An Introduction to the Theory of Neural Networks*, Addison-wesley, 1991.

[6] Saini S., "Petaflops Computing and Computational Nanotechnology", *Nanotechnology*, (in press) 1996.