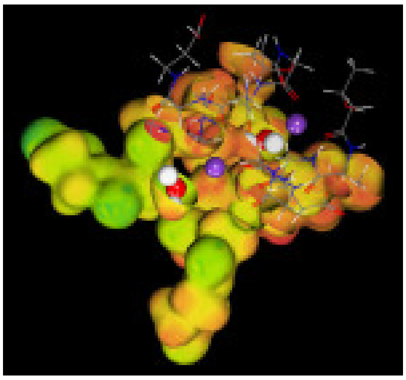
Workshop Report

Linear-scaling ab initio calculations: applications and future directions



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1 Workshop Details

1.1 Details

Timing
Number of days : 4
Start : 2007-09-03
end : 2007-09-06

Location of the activity
CECAM
46 allé e d'Italie
69007 Lyon
France

1.2 Description

The study of properties and of processes in materials, frequently hinges upon understanding phenomena which originate at the atomic level. In such cases the accurate description of the interactions between large numbers of atoms is critical and in turn requires the accurate description of the electrons which play a crucial role in the bonding of atoms into molecules, surfaces and solids. This can only be achieved by solving the equations of quantum mechanics. These equations are too complicated to solve exactly; however their solutions can be approximated by computational techniques. The most accurate – but also most computationally demanding – are the "ab initio" techniques which do not use any empirical adjustable parameters. Amongst them, the Density Functional Theory (DFT) formulation of quantum mechanics stands out as an excellent compromise between accuracy and computational efficiency. However, the applicability of ab initio techniques is severely limited by poor scaling: the computational effort needed to perform an ab initio calculation increases with (at least) the third power of the number of atoms, N. This cubic-scaling bottleneck limits the number of atoms we can study to a few hundred at most, even on parallel supercomputers. To overcome this length-scale limitation, a number of researchers worldwide have been pioneering the development of a novel class of ab initio methods with linear-scaling or "Order N" (O(N)) computational cost which nevertheless retain the same high level of accuracy as the conventional approaches. While physically motivated, such methods have proved particularly hard to develop as they introduce highly non-trivial localisation constraints. Nevertheless, many major obstacles have been overcome and a number of O(N) methods (SIESTA, CONQUEST, ONETEP, etc.) for ground state DFT calculations on systems with a gap (e.g. molecules, semiconductors and insulators) are now available and have reached a state of maturity that allows them to be used to study ”real” materials. The particular focus of this workshop is therefore to look forward to what can be achieved in the next few years. Our aim is twofold: (1) As O(N) methods are currently extending the applicability of DFT calculations to problems involving biomolecules and nanostructures they are leading to completely new levels of understanding of these systems. This CECAM meeting will give us the opportunity to make an appraisal of such large-scale simulations and their potential to connect more directly to experiments. (2) We also want to examine the options for extending linear-scaling to problems that cannot be treated by ground-state DFT but require other, more complex approaches. These include methods for treating metallic systems, excited states and wavefunction-based theories for including electronic correlation. Finding ways to transform these methods to linear-scaling cost, and hence extent their applicability to the nano-scale, is the next big challenge that the community of developers of large-scale electronic structure methods is beginning to face. We hope that this workshop will stimulate these major new O(N) methodological developments by bringing together the leading groups in the development of O(N) DFT methods with the leading groups in the development of metal and excited-state or wavefunction-based methods. Strong emphasis during the workshop will be given to discussion in order to promote the exchange of ideas between different communities (Physics, Chemistry, Materials Science, Biochemistry) which are all interested in large-scale applications with ab initio accuracy but are approaching them from different perspectives.

2 Requested Support

CECAM

ESF

CCP9

Psi-k

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Workshop Report

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INFM Democritos, Trieste, Italy Italy

4 Presentation List

Wavelets as a basis set for electronic structure calculations and electrostatic problems

Stefan Goedecker

University of Basel, Switzerland

Abstract

Wavelets and scaling functions form a systematic basis set that is localized in real space. I will explain how the functions are defined and how basic hamiltonian matrix elements can be calculated in this basis. I will compare wavelet basis sets with plane wave and Gaussian basis sets and show performance results for a standard (i.e. cubically scaling) wavelet based electronic structure code. In addition I will also demonstrate the usefulness of scaling functions to solve electrostatic problems under various boundary conditions.

A DFT study on the structural stability of Ge 3D nanostructures on Si(001) using CONQUEST

Tsuyoshi Miyazaki

National Institute for Materials Science (NIMS), Japan

Abstract

We report our recent theoretical study on the heteroepitaxial growth of Ge on Si(001) using our linear-scaling DFT code CONQUEST. The system is of great importance because it is a prototypical system for strained, Stranski-Krastanov growth and has a technological interest for optoelectronic devices. Although DFT simulations on these systems are highly desirable, they had been impossible as the systems include more than ten thousand atoms. We will demonstrate that it is now possible to perform DFT calculations on such large and scientifically important systems. We have succeeded in employing DFT structure optimisation on the systems containing about 23,000 atoms. We will show that 3D cluster is more stable than the 2xN (2D) structure for large coverage of Ge atoms. In the talk, we will also present 1) summary of the theory behind the code and its practical implementations, 2) the performance and opening plan of the code, and 3) our on-going study on DNA systems using CONQUEST. The present work has been done in collaboration with M. Todorovic (NIMS), A. S. Torralba (UCL) and V. Brazdova (UCL), and is partly supported by the Grant-in-Aid for Scientific Research on Priority Areas from MEXT.

A linear scaling three dimensional fragment method for ab initio calculations

Lin-Wang Wang

Lawrence Berkeley National Laboratory, United States

Abstract

We will present a new linear scaling 3 dimensional fragment (LS3DF) method for ab initio electronic structure calculations. While the long range electostatic interaction is calculated via a global Poisson equation, the near-sighted quantum mechanical energy is calculated based on a divide-and-conquer method. A novel scheme is used to patch up the divided fragments with both postive and negative signs which cancels out the artificial boundary effects of the division.

The LS3DF has excellent numerical agreements with direct local density approximation (LDA) calculations with accuracy of 3 meV/atom for total energy, 0.2% for charge density and 10^{-5} a.u. for atomic forces. It can be used to simulate systems with tens of thousands of atoms, and the method scales linearly to thousands of processors. We will also present calculation results for the dipole moments of quantum dots using this LS3DF method. They shed lights on a decade old problem for the total dipole moments and internal electric fields inside quantum dots.

A miscellaneous overview of SIESTA algorithms

Jose M. Soler
Universidad Autonoma de Madrid, Spain

Abstract

I will review some details of miscellaneous algorithms, used in SIESTA, related to linear scaling and to large scale simulations. There are recent developments, like the MOSAICO method of Seijo and Barandiaran (JCP 121, 6698 (2004)), as well as various works in progress. Among them, an O(N) implementation by Ordejon to find the chemical potential on the fly, an efficient implementation by Soler of the Van der Waals functional of Dion et al (PRL 92, 246401 (2004)), and a suite of linear scaling algorithms implemented by Gale's group.

Ab initio molecular dynamics with linear scaling: foundations and applications

Eiji Tsuchida
Research Institute for Computational Sciences, AIST, Japan

Abstract

In recent years, much effort has been devoted to the development of linear scaling algorithms like the density-matrix minimization method, divide-and-conquer method, and the orbital minimization method (OMM). In particular, OMM is suited for systematic basis sets in real space, such as finite-element and finite-difference methods. In the presence of localization constraints on the orbitals, however, a naive implementation of OMM often suffers from poor convergence of the total energy. We show that this drawback can be overcome by imposing additional constraints on the orbitals, thus eliminating the near redundancy associated with unitary rotation of the orbitals. We also present our results on the Born-Oppenheimer molecular-dynamics simulation of liquid ethanol consisting of 1125 atoms.

References

[1] E. Tsuchida and M. Tsukada, ”Large-Scale Electronic-Structure Calculations Based on the Adaptive Finite-Element Method”, J. Phys. Soc. Jpn. 67, pp.3844-3858 (1998).
[2] E. Tsuchida, ”Augmented Orbital Minimization Method for Linear Scaling Electronic Structure Calculations”, J. Phys. Soc. Jpn. 76, 034708 (2007). Preprint available from http://arxiv.org/abs/cond-mat/0608024.

Ab initio transport calculations in defected carbon nanotubes using O(N) techniques

Blanca Biel

CEA/LETI-MINATEC/D2NT/LSCDP, France

Abstract

In this talk I will present recent results on ab initio transport calculations in defected carbon nanotubes [1,2]. A combination of the local orbital first principles Fireball code with standard Green's functions techniques is used to analyze the transport properties of long tubes (up to one micron) with realistic disorder. The efficiency of these linear scaling methods allows a statistical study of the conductance averaged over a large sample of defected nanotubes and thus the comparison with experiment.

References

[1]Tuning the conductance of single-walled carbon nanotubes by ion irradiation in the Anderson localization regime
Gomez-Navarro et al., Nature Materials 4, 534 (2005)
[2]Anderson localization in carbon nanotubes: Defect density and temperature effects
Biel et al., Phys.Rev.Lett. 95, 266801 (2005)

Accurate O(N) first-principles DFT calculations using finite differences and confined orbitals

Jean-Luc Fattebert
Lawrence Livermore National Research Laboratory, United States

Abstract

Representing the electronic structure in Density Functional Theory (DFT) by a set of localized wave functions discretized on a real-space mesh essentially leads to a linear scaling of the computational cost with the size of the physical system. This can be achieved by formulating the DFT energy functional in terms of general non-orthogonal orbitals which are then optimized under localization constraints (spatial confinement). Multigrid preconditioning and a block version of Anderson's extrapolation scheme are used to accelerate convergence towards the ground state. For localization regions — constraints — large enough, truncation error can be reduced to a value smaller than discretization error and achieve the level of accuracy of a Plane Waves calculation. Accuracy is improved by allowing for flexible localization regions that can adapt to the system. This also reduces problems with local minima and enables energy conserving Born-Oppenheimer molecular dynamics simulations. Our implementation of this approach scales on hundreds of processors and becomes competitive with Plane Waves codes around 500 atoms for dense systems.

This work was performed under the auspices of the U.S. Department of Energy by University of California Lawrence Livermore National Laboratory under contract No. W-7405-Eng-48.

References

[1] J.-L. Fattebert and F. Gygi, Phys. Rev. B 73, 115124 (2006)
[2] J.-L. Fattebert and F. Gygi, Comput. Phys. Comm. 162, 24 (2004)
[3] J.-L. Fattebert and J. Bernholc, Phys. Rev. B 62. 1713 (2000)

An O(N) time-domain algorithm for TDDFT

Guan Hua Chen
Hong Kong University, China

Abstract

An O(N) algorithm for time-dependent density-functional theory is developed to evaluate the optical responses of large molecular systems. The two-electron Coulomb integrals are evaluated with the fast multipole method, and the calculation of exchange-correlation quadratures utilizes the locality of exchange-correlation functional and the integral pre-screening technique. Instead of many-body wave function, the equation of motion is solved for the reduced single-electron density matrix in the time-domain. Based on its ”nearsightedness”, the reduced density matrix cutoffs are employed to ensure that the computational time scales linearly with the system size. Different time-domain integration methods will be presented and compared.

CONQUEST: A Linear Scaling DFT Code

David R. Bowler
University College London, United Kingdom

Abstract

We will present recent developments and applications of the Conquest O(N) DFT code. After giving an overview of the methodology behind the technique, recent changes will be presented, including an automatic partitioning scheme for simple parallelisation which scales well up to several hundred processors will be described. An overview of recent applications to biochemical problems will be given, along with details of future developments planned and the full release of the code following the present beta testing process.

References

[1] D. R. Bowler, T. Miyazaki, and M. J. Gillan, J. Phys.:Condens. Matter 14, 2781 (2002).
[2] D. R. Bowler, R. Choudhury, M. J. Gillan, and T. Miyazaki, phys. stat. sol. b 243, 989 (2006).
[3] M. Gillan, D. Bowler, A. Torralba, and T. Miyazaki, Comput. Phys. Commun. 117, 14 (2007).

Density Functional Embedding for Molecular Systems

Marcella Iannuzzi
Paul Scherrer Institute, Switzerland

Abstract

Molecular dynamics (MD) simulations combined with electronic structure calculations are exremely powerful to describe the physical/chemical properties and macroscopic behaviors of materials from on atomistic level. Structural transformation involving electronic structure rearrangements, as breaking and forming of chemical bonds, can be observed. Moreover, the many-body effects are also included, which is of particular importance in the study of molecular liquids, where they play a crucial role. The choice of Density functional Theory (DFT), rather than more accurate ab-initio levels of theory, is often mandatory when one wants to simulate large systems in combination with first-principles MD. However, due to the high computational costs, large model systems and long time-span simulations are often not affordable, even by DFT within the Kohn–Sham (KS) formalism. We introduce a DFT-based embedding method for the study of molecular systems in condensed phase. The system is partitioned in molecular subunits, which are individually treated at standard KS level by calculating the electronic density on small molecular grids. The necessary correction to include intermolecular interactions is

introduced by an embedding potential derived from orbital-free DFT using kinetic energy functionals. The method leads to a linear scaling electronic structure approach that maps naturally onto massively parallel computers. Molecular dynamics simulations of water at room conditions result in a liquid with unstructured second solvation shell. The application tomore weakly interacting molecular systems, like liquid acetronile, shows extremely satisfactory agreement between the full KS approach and the embedding approach.

References

M. Iannuzzi, B. Kirchner, J. Hutter, Chem. Phys. Lett., 421, 16-20, (2006).
P. Cortona, Phys. Rev. B, 44, 8454 (1991).
J. Wesolowski, J.Chem.Phys., 106, 8516 (1997).
J. Neugebauer, et al., J. Chem. Phys., 122, 094115 (2005).
J. Vandevondele et al., Comp. Phys. Comm., 167, 103 (2005).

Exact embedding of local defects in crystals using Maximally Localized Wannier Functions

Eric Cancès
CERMICS - ENPC, France

Abstract

By means of rigorous thermodynamic limit arguments, we derive a new variational model providing exact embedding of local defects in insulating or semiconducting crystals. A natural way to obtain variational discretizations of this model is to expand the perturbation of the periodic density matrix generated by the defect in a basis of precomputed maximally localized Wannier functions of the host crystal. This approach can be used within any semi-empirical or Density Functional Theory framework.

References

E. Cancès, A. Deleurence and M. Lewin, A new approach to the modelling of local defects in crystals: the reduced Hartree-Fock case, Preprint math-ph/0702071

E. Cancès, A. Deleurence and M. Lewin, Density Functional Theory for local defects in crystalline materials, Preprint arXiv:0706.0794

Faster GW calculations in larger model structures using ultralocalized nonorthogonal Wannier functions

Paolo Umari
INFM Democritos, Trieste, Italy, Italy

Kernel optimisation and the physical significance of optimised local orbitals in the ONETEP code

Peter Haynes
Imperial College London, United Kingdom

Abstract

This presentation focusses on methods and applications of the ONETEP code, in which the density-matrix is represented in terms of a sparse density-kernel and a set of local orbitals (nonorthogonal generalised Wannier functions or NGWFs) optimised in situ. The density-kernel optimisation procedure employed within the ONETEP code is examined, with an emphasis on the need for a stable algorithm. Particular attention is paid to the use of penalty functionals and methods for enforcing the normalisation constraint. An examination of the physical significance of the NGWFs is made for the case of application to nanotubes, focussing on the description of low-lying conduction band states.

References

1. P D Haynes, A A Mostofi, C-K Skylaris and M C Payne, Psi-k Newsletter 72, 78-91 (December 2005)
2. C-K Skylaris, P D Haynes, A A Mostofi and M C Payne, J. Chem. Phys. 122, 084119 (2005)

3. C-K Skylaris, P D Haynes, A A Mostofi and M C Payne, J. Phys.: Condens. Matter 17, 5757-5769 (2005)

Large scale electronic structure calculation theory and several applications

Takeo Fujiwara
Center for Research and Development of Higher Education, University of Tokio, Japan

Abstract

We have developed the fundamental theory and practical methods for large-scale electronic structure calculations. The method is based upon the short range tight-binding Hamiltonian. Several methodologies, without calculating eigenfunctions, are rigorously of linear-scale scheme with total atom number and tested in systems of up to 10^7 atoms. Among them, the Krylov subspace method is applicable both to insulators or semiconductors and metals. Furthermore, the accuracy can be controlled with monitoring the residual vectors during the MD simulation. We will also present applications, including formation model of gold helical multishell nanowires. The model can explain the magic number of the helical gold nanowires in the multishell structure. The reconstruction from ideal non-helical to realistic helical nanowires consists of two stages: dissociations of atoms on the outermost shell from atoms on the inner shell and slip deformations of atom rows generating (111)-like structure on the outermost shell.

Large-scale calculations with the tight-binding (screened) KKR method

Rudolf Zeller
IFF, Forschungszentrum Juelich, Germany

Abstract

The basic features of the full-potential KKR Green-function method are presented and its differences compared to wavefunction methods are discussed. The screening transformation leading to a tight-binding form with exponentially decaying structure constants is explained and its accuracy and suitability for large scale electronic-structure calculations is illustrated.

Linear Scaling Calculations with the Divide-and-Conquer Approach and with Non-orthogonal Localized Orbitals

Weitao Yang

Department of Chemistry, Duke University, United States

Abstract

Recent development and application of linear scaling approaches with the divide-and-conquer approach and with non-orthogonal localized orbitals will be reviewed. The divide-and-conquer approach is the foundation for many recent approximate and efficient fragment approaches for large systems. Non-orthogonal orbitals and the associated variational principles have the potential to be most efficient for accurate linear scaling calculations, because non-orthogonal orbitals provide most compact description of electronic degrees of freedom.

Local Correlation Theory and Electronic Delocalization

Joseph Subotnik
Tel-Aviv University, Israel

Abstract

The theory of local correlation has been applied to many interesting chemical examples over the years, beginning with the early local MP2 work Peter Pulay in the early 1980's, evolving into the linear-scaling local coupled cluster work of Schutz and Werner around 2000. Most examples thus far, however, has focused on molecules in the ground state with tightly bound electrons, where the one electron density matrix decays quickly in space. In this presentation, we will address a class of more difficult examples, including both anions and transition states where some electronic correlations are expected to be long-range. Within the context of new approximations, we will show that even such cases can be treated by local approximations which are in fact linear-scaling.

Maximally-Localised Wannier Functions as Building Blocks for Large-Scale Electronic Structure Calculations

Arash A. Mostofi
Cavendish Laboratory, United Kingdom

Abstract

We combine large-scale, ab initio electronic structure calculations and the maximally-localised Wannier function (MLWF) approach in order to study the electronic properties of complex nanostructures. MLWF provide an accurate, localised, minimal basis set in which to diagonalise the Hamiltonian. In the MLWF basis, Hamiltonians for large, complex systems can be constructed directly from the short-ranged Hamiltonians of smaller constituent units by performing full first-principles calculations on either periodically-repeated or isolated fragments. We apply our approach to the case of DNA helices. The effects of sequence, twist-angle, and solvation environment on the electronic structure are investigated. This work opens the way to obtaining a more detailed understanding of charge transport and conductance in DNA, bringing closer the prospect of engineering its electronic structure for use in nano-electronic circuits and biotechnology applications.

O(N) Krylov subspace method for large-scale ab initio electronic structure calculations

Taisuke Ozaki
Japan Advanced Institute of Science and Technology (JAIST), Japan

Abstract

I will present a unified approach [1] bridging the divide-conquer (DC) method [2] and recursion method [3] for ab initio O(N) electronic structure calculations based on non-orthogonal localized basis functions. In the unfiied approach, a detailed short range and an effective long range contributions to the electronic structure are taken into account by solving an embedded cluster defined in a Krylov subspace of each atom. The convergence properties of the method will be discussed by systematic test calculations for metals, semiconductors, and molecular systems. I will also address applicability and difficulty of the method in applications.

References

[1] T. Ozaki, Phys. Rev. B 74, 245101 (2006).
[2] W. Yang, Phys. Rev. Lett. 66, 1438 (1991).
[3] T. Ozaki and K. Terakura, Phys. Rev. B 64, 195126 (2001).

ONETEP: Linear-scaling DFT with plane waves

Chris-Kriton Skylaris
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Abstract

I will present an overview of the ONETEP (Order-N Electronic Total Energy Package) code [1] for Density Functional Calculations with computational cost that increases linearly with the number of atoms. ONETEP exploits the locality of the single-particle density matrix inherent in non-metallic materials by optimising directly nonorthogonal generalised Wannier functions (NGWFs) expressed in terms of periodic cardinal sine (PSINC) basis functions [2]. The PSINC basis is equivalent to a plane wave basis set, and near-complete basis accuracy can be achieved by improving it systematically via a single parameter. Its properties make it ideal for imposing localisation in real space with linear-scaling cost. ONETEP has been developed as a parallel code [3] able to run on an arbitrary number of processors, allowing plane wave calculations with thousands of atoms to be performed. Results of applying the method to nanostructures [4] and biomolecules [5] will be presented.

References

[1] C.-K. Skylaris, P. D. Haynes, A. A. Mostofi and M. C. Payne. J. Chem. Phys. 122 (2005) 084119
[2] C.-K. Skylaris, A. A. Mostofi, P. D. Haynes, O. Dieguez and M. C. Payne. Phys. Rev. B 66 (2002) 035119.
[3] C.-K. Skylaris, P. D. Haynes, A. A. Mostofi and M. C. Payne. Phys. Stat. Sol. (b). 243(5) (2006) 973.
[4] C.-K. Skylaris, P. D. Haynes, A. A. Mostofi and M. C. Payne. J. Phys.: Condens. Matter. 17 (2005) 5757.
[5] L. Heady, M. Fernandez-Serra, R. L. Mancera, S. Joyce, A. R. Venkitaraman, E. Artacho, C.-K. Skylaris, L. Colombi Ciacchi and M. C. Payne. J. Med. Chem. 49 (2006) 5141.

Partial linear scaling for quantum Monte Caro calculations on condensed matter

Mike Gillan
University College London, United Kingdom

Abstract

The quantum Monte Carlo (QMC) method offers considerably greater accuracy than density functional theory (DFT) for condensed matter calculations, and it is starting to be quite widely used, in spite of its greater cost. I will give a brief summary of the two kinds of QMC, variational Monte Carlo (VMC) and diffusion Monte Carlo (DMC), nothing that DMC is generally needed in practice. The problem of basis sets will be mentioned, and it will be explained how the B-spline basis used in the Conquest O(N) DFT code has allowed a considerable improvement in efficiency of the QMC code CASINO. Then, I wil show how the concept of localised orbitals that is crucial for many O(N) DFT methods can also be applied to QMC, though it leads to only partial O(N) operation.

Partition-of-unity finite element method for large, accurate electronic-structure calculations of metals

John E. Pask
Lawrence Livermore National Laboratory, United States

Abstract

Over the past few decades, the planewave (PW) pseudopotential method has established itself as the dominant method for large, accurate, density-functional calculations in condensed matter. However, due to its global Fourier basis, the PW method suffers from substantial inefficiencies in parallelization and applications involving highly localized states, such as those involving 1st-row or transition-metal atoms, or other atoms at extreme conditions. Modern real-space approaches, such as finite-difference (FD) and finite-element (FE) methods, can address these deficiencies without sacrificing rigorous, systematic improvability but have until now required much larger bases to attain the required accuracy. Here, we present a new real-space FE based method which employs modern partition-of-unity FE techniques to substantially reduce the number of basis functions required, by building known atomic physics into the basis, without sacrificing locality or systematic improvability. Initial results show order-of-magnitude improvements relative to current state-of-the-art PW and adaptive-mesh FE methods for systems involving localized states such as d- and f-electron metals and/or other atoms at extreme conditions.

This work was performed under the auspices of the U.S. Department of Energy by University of California, Lawrence Livermore National Laboratory under Contract W-7405-Eng-48.

Peta-scalable Reactive Molecular Dynamics Simulation of Mechanochemical Processes

Aiichiro Nakano
University of Southern California, United States

Abstract

We have designed scalable parallel algorithms for first principles based simulations of mechanochemical processes on emerging petaflops architectures based on unified divide-and-conquer (DC) algorithmic and tunable hierarchical cellular decomposition (CD) parallelization frameworks.

The DCCD frameworks expose maximal data locality and have achieved parallel efficiency as high as 0.998 for 1.06 billion-atom reactive force-field molecular dynamics (MD) and 11.8 million-atom (1.04 trillion electronic degrees-of-freedom) quantum-mechanical (QM) MD in the framework of the DC density functional theory (DFT) on adaptive multigrids, in addition to 134 billion-atom nonreactive MD, on 131,072 IBM BlueGene/L processors. We have also used the DCCD frameworks for automated execution of adaptive hybrid DFT/MD simulation on a Grid of 6 supercomputers in the US and Japan, in which the number of processors changed dynamically on demand and tasks were migrated according to unexpected faults. I will present the application of the frameworks to study: (1) shock and reactive nanojets in energetic materials; and (2) damage of glasses in corrosive environment. I will also discuss the extension of time scales for these simulations based on a space-time-ensemble parallel (STEP) approach.

Recent developments and applications of the real-space multigrid (RMG) method

Jerzy (Jerry) Bernholc
North Carolina State University, United States

Abstract

We describe several new developments and applications of multigrid-based methods in large-scale, massively parallel electronic structure calculations: (i) The ability to simulate solvent effects in fully quantum mechanical calculations at much reduced cost through a hybrid approach that combines ab initio Kohn-Sham DFT and orbital-free (OF) DFT. The KS DFT is used to describe the chemically active part of the system and its first solvation shells, while the OF DFT is used to treat the rest of the solvent. The OF solvent molecules are assumed to be rigid and have frozen electron densities, which allows for their efficient treatment. The OF DFT method is fully O(N) and capable of handling about a hundred thousand solvent molecules on current parallel supercomputers, while taking only about 10% of the time required for performing a DFT calculation on the chemically active solvated part. Solvent molecules can seamlessly move between the full DFT and OF DFT regions during quantum molecular dynamics simulations, and both electrostatic and exchange-correlation contributions are evaluated in the entire simulation box. This methodology has already been applied to simulating prion proteins in solution and identifying their initial agglomeration mechanisms. (ii) The DFT part of the RMG code parallelizes well on 4096 CPUs and reaches over 8 teraflops, even when ultrasoft pseudopotentials are used, (iii) We have refined the quantum transport part of the code and applied it to large organic molecules between semiconducting and metallic leads, such as porphyrins and rotaxanes, examining negative differential resistance and switching mechanisms.

Semiclassical approach to density functional theory

Kieron Burke
University of California Irvine, United States

Abstract

I will present a novel approach to density functional theory,one that explains the accuracy and origins of modern generalized gradient approximations in terms of semiclassical approximations [1,2]. I will use semiclassics to show a path toward how both the density and the non-

interacting kinetic energy can be found as functionals of the potential.

References

[1] Relevance of the slowly-varying electron gas to atoms, molecules, and solids J. P. Perdew, L. A. Constantin, E. Sagvolden, and K. Burke, Phys. Rev. Lett. 97, 223002 (2006).

[2] Generalized gradient approximation for solids and their surfaces J. Perdew, A. Ruzsinszky, G.I. Csonka, O.A. Vydrov, G.E. Scuseria, L.A. Constantin, X. Zhou, and K. Burke, arXiv:0707.2088

Toward efficient wavefunction based linear scaling energy minimization

Valery Weber
University Zurich, Switzerland

Abstract

We will present an efficient direct energy functional minimization algorithm for electronic structure theory. The technique provides a computationally very efficient tool that requires only few matrix multiplies per self-consistent-field iteration. We propose to exploit the invariance property of the total energy, through unitary transform, to generate “on the fly” sparse wavefunction. To achieve this goal, we propose the use of a sparseness function based on the l1-norm. Sparsity of the wavefunction will be discussed for some large systems.

Towards a Linear Scaling Car-Parrinello-like Approach to Born-Oppenheimer Molecular Dynamics

Thomas Kühne
ETH Zürich, Switzerland

Abstract

We present a new method [1] to accelerate density functional theory-based ab-initio molecular dynamics simulations. In the spirit of the Car-Parrinello [2] approach, the method circumvents the need to perform fully self-consistent electronic structure calculations. However, in contrast to the original scheme, large integration time steps can be used. Deviations from the Born-Oppenheimer surface are small and more importantly, constant. Nevertheless, the incomplete energy minimization and the use of a non-sym- plectic integrator for the electronic degrees of freedom induces a small dissipative drift. Inspired by ideas of Krajewski and Parrinello [3] we show how this can be rigorously corrected using a properly modified Langevin equation, which leads to a correct sampling of the Boltzmann distribution. The inherently required friction term is low enough, so that even the dynamics is correctly reproduced.

Applying our new method we have been able to gain some insights into the temperature induced phase-change mechanism of Ge2Sb2Te5$, by predicting its still unknown amorphous phase [4]. The validity of our calculations and the agreement of our findings with experiment will be discussed.

In addition, we would like to report on our efforts to extend this method towards linear scaling, based on the finite-temperature grand-canonical potential for non-interacting fermions [5]. Similar to evaluating path-integrals in imaginary time, this expression can be factorized into multiple, but much easier problems [6]. The resulting algorithm does not rely on the ability

to localize the orbitals, so that even metals can be treated. However, solving them exactly in O(N) is only possible for quasi-1D systems, or at the presence of statistical noise, approximately in higher dimensions. We briefly outline, that by accepting insignificant truncation errors and via exploiting analytically derived smooth limits, one can circumvent explicitly calculating the catchiest terms of the factorization. In this way, it is possible to calculate efficiently the one-particle density matrix in an accurate and deterministic manner, compatible with the aforementioned method. Initial results on TB Hamiltonians will be presented.

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[5] A. Alavi, J. Kohanoff, M. Parrinello and D. Frenkel, Phys. Rev. Lett. 73, 2599 (1994).
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Wavelets as a basis set for linear scaling electronic structure calculations

Mark Rayson
University of Basel, Switzerland

Abstract

Daubechies wavelets and scaling functions form an orthogonal systematic basis set that is localised in real space. A linear scaling algorithm using this basis set will be presented. The wavelet basis (the ’systematic kernel’) is used to represent a smaller set of localised basis functions (the ’subspace kernel’) that can be optimised to achieve systematic convergence. Details of the parallel implementation of the systematic kernel will also be given. Furthermore, algorithms for the subspace kernel, including the recent ’recursive bisection density matrix method’ [1], will be discussed.

References

[1] M. J. Rayson, Phys. Rev. B 75, 153203 (2007)

5 Program

Day 1: Sept. 03 2007

Session : 1 Applications to nanostructures and biomolecules
09:00 to 09:15 : Welcome

09:15 to 10:00 : Presentation
A DFT study on the structural stability of Ge 3D nanostructures on Si(001) using CONQUEST
Tsuyoshi Miyazaki

10:00 to 10:45 : Presentation
Large scale electronic structure calculation theory and several applications
Takeo Fujiwara

10:45 to 11:15 : Coffee Break

11:15 to 12:00 : Presentation
Density Functional Embedding for Molecular Systems
Marcella Iannuzzi

12:00 to 12:45 : Presentation
ONETEP: Linear-scaling DFT with plane waves
Chris-Kriton Skylaris

12:45 to 14:15 : Lunch Break

14:15 to 15:00 : Presentation
Maximally-Localised Wannier Functions as Building Blocks for Large-Scale Electronic Structure Calculations
Arash A. Mostofi

15:00 to 15:45 : Presentation
A linear scaling three dimensional fragment method for ab initio calculations
Lin-Wang Wang

15:45 to 16:15 : Coffee Break

16:15 to 17:00 : Presentation
Peta-scalable Reactive Molecular Dynamics Simulation of Mechanochemical Processes
Aiichiro Nakano

17:00 to 17:45 : Presentation
Recent developments and applications of the real-space multigrid (RMG) method

Jerzy (Jerry) Bernholc

Day 2: Sept. 04 2007

Session : 2 Energy minimisation functionals and algorithms
09:00 to 09:45 : Presentation
CONQUEST: A Linear Scaling DFT Code
David R. Bowler

09:45 to 10:30 : Presentation
Kernel optimisation and the physical significance of optimised local orbitals in the ONETEP code
Peter Haynes

10:30 to 11:00 : Coffee Break

11:00 to 11:45 : Presentation
A miscellaneous overview of SIESTA algorithms
Jose M. Soler

11:45 to 12:30 : Presentation
Wavelets as a basis set for electronic structure calculations and electrostatic problems
Stefan Goedecker

12:30 to 14:00 : Lunch Break

14:00 to 14:45 : Presentation
Wavelets as a basis set for linear scaling electronic structure calculations
Mark Rayson

14:45 to 15:30 : Presentation
O(N) Krylov subspace method for large-scale ab initio electronic structure calculations
Taisuke Ozaki

15:30 to 16:00 : Coffee Break

16:00 to 16:45 : Presentation
Toward efficient wavefunction based linear scaling energy minimization
Valery Weber

16:45 to 17:30 : Presentation
Accurate O(N) first-principles DFT calculations using finite differences and confined orbitals
Jean-Luc Fattebert

17:30 to 18:15 : Presentation
Linear Scaling Calculations with the Divide-and-Conquer Approach and with Non-orthogonal Localized Orbitals
Weitao Yang

Day 3: Sept. 05 2007

Session : 3 Linear-scaling methods in dynamics simulations or beyond DFT and ground state properties
09:00 to 09:45 : Presentation
An O(N) time-domain algorithm for TDDFT
Guan Hua Chen

09:45 to 10:30 : Presentation
Local Correlation Theory and Electronic Delocalization
Joseph Subotnik

10:30 to 11:00 : Coffee Break

11:00 to 11:45 : Presentation
Ab initio molecular dynamics with linear scaling: foundations and applications
Eiji Tsuchida

11:45 to 12:30 : Presentation
Towards a Linear Scaling Car-Parrinello-like Approach to Born-Oppenheimer Molecular Dynamics
Thomas Kühne

12:30 to 14:00 : Lunch Break

14:00 to 14:45 : Presentation
Partial linear scaling for quantum Monte Caro calculations on condensed matter
Mike Gillan

14:45 to 15:30 : Presentation
Exact embedding of local defects in crystals using Maximally Localized Wannier Functions
Eric Cancès

15:30 to 16:00 : Coffee Break

16:00 to 16:45 : Presentation
Faster GW calculations in larger model structures using ultralocalized nonorthogonal Wannier functions
Paolo Umari

16:45 to 17:45 : Discussion

20:00 to 22:00 : Dinner

Day 4: Sept. 06 2007

Session : 4 Other approaches for linear-scaling, including methods for metals
09:00 to 09:45 : Presentation
Partition-of-unity finite element method for large, accurate electronic-structure calculations of metals
John E. Pask

09:45 to 10:30 : Presentation
Semiclassical approach to density functional theory
Kieron Burke

10:30 to 11:00 : Coffee Break

11:00 to 11:45 : Presentation
Ab initio transport calculations in defected carbon nanotubes using O(N) techniques
Blanca Biel

11:45 to 12:15 : Presentation
Large-scale calculations with the tight-binding (screened) KKR method
Rudolf Zeller

12:15 to 12:30 : Closing word

6 Organizer's report

6.1 Conclusions.

This has been a landmark workshop for linear-scaling electronic structure theory. After more than a decade of intense activity to solve a multitude of technical difficulties, a number of groups worldwide have now developed linear-scaling first principles quantum mechanics methods which are approaching a level of maturity. Even though a number of reliability issues remain to be solved, these codes are already being used in challenging problems which involve thousands of atoms and provide new insights. Very interesting applications were presented in this workshop with O(N) codes, involving surfaces, nanostructures, biomolecules and materials. The workshop served the role of a forum for reviewing the current state-of-the-art in O(N) methods, discussing recent, ongoing and future developments, and was attended by some 46 participants.

There is currently a major effort under way in the further development and improvement of linear-scaling DFT approaches. The richness of ideas and activity in the field is reflected in the multiplicity of methods and their variants on which several groups are working. Talks in this area included Krylov subspace approaches, 3D fragment methods, MD simulations with O(N) calculation of the potential energy surface, combinations of density mixing and linear-scaling energy functionals, combinations of penalty functionals and linear-scaling energy functionals, linear-scaling implementations of dispersion energy functionals, methods based on wavelet basis sets, efficient methods for O(N) calculations with Gaussian basis sets, and divide-and-conquer approaches with functionals that obey an absolute-minimum principle.

Current O(N) approaches for ground state DFT make use of the nearsightedness principle which they impose by using some set of localised functions. These are expected to be able to describe the ground state which is made up of the occupied Kohn-Sham states. However, in contrast with conventional cubic-scaling techniques, recent tests show that O(N) approaches are not in general able to describe most unoccupied states, except in the case of approaches which employ localised Wannier-type states optimised in situ. While no formal physical meaning can be attributed to these states, in practice they are often useful in the calculation of various experimental observables (with perturbative approaches) or the incorporation of corrections for effects such as the self-interaction error which is present in most exchange-correlation functionals.

While their computational demands obviously increase linearly, O(N) first principles approaches are nevertheless computationally demanding and careful consideration should be given to a particular problem before attempting to use an O(N) approach to solve it. It should be noted that not all problems that involve thousands of atoms require O(N) first principles approaches for their solution. There are nevertheless a multitude of cases involving nanostructures, biomolecules, materials and surfaces where the insight into the accurate description of atomic interactions that

O(N) approaches can provide is invaluable. First principles calculations with millions of atoms will also become possible in the near future and will be invaluable for at least a niche of problems that cannot be studied in depth using other means.

New, promising approaches for the extension of linear-scaling beyond ground state DFT were presented. Many of these approaches are currently at an embryonic stage. Significant problems remain to be overcome to allow their use in applications on materials and perhaps it will take a decade for this to happen. However, progress is being made, and this workshop provided the opportunity to present the current state of these approaches and discuss future directions for theoretical and algorithmic developments. The approaches that were discussed involved time-dependent DFT, coupled-cluster singles and doubles (CCSDT), Car-Parrinello approaches, quantum Monte Carlo, exact defect-embedding techniques, GW theory, finite element methods for metallic systems and Green function based methods for electronic transport calculations.

6.2 Recommendations.

The current state of development of linear-scaling techniques can be compared to the situation of classical potential approaches in the 1970's: the benefits that these methods can offer in research are tremendous; however these methods are not yet developed at a level that allows them to be used by inexperienced users on a routine basis. Specialist knowledge is required when using linear-scaling algorithms as the choices of cut-offs and other parameters are not yet fully automated and an inexperienced user can compromise the accuracy and increase dramatically the cost of the calculation through inappropriate choices. Training of the users through close collaboration with developers at the initial stages of a project is therefore ideally needed when using such methods, and also in related tasks such as the preparation of inputs and the post-processing of the large amounts of data that are generated.

While it is clear that single-core processors are approaching atomic limits and therefore their speed will no longer increase, the increase in computer power according to Moore's law is likely to continue thanks to the availability of multi-core processors and the trend to incorporate more cores per processor. The computational requirements of linear-scaling techniques, albeit linear, remain high and all such techniques need to be (and usually have been) designed with parallel computers in mind. Parallelisation strategies remain crucial and some attention will need to be given to make algorithms suitable to the emerging parallel architectures where calculations will be routinely run on tens of thousands of cores on machines with multicore processors. Taking advantage in this way of the relentless increase in computing power will mean that in the near future we will be able to perform first principles calculations on millions of atoms.

As linear-scaling techniques are making total energy calculations possible in systems involving many thousands of atoms, there is the desire to use them in molecular dynamics simulations, e.g. in calculations of free energies. However, these techniques address only the length-scale issues and in simulations the time-scales (which are already significantly smaller than those that can be addressed by molecular mechanics approaches) that can be reached are often too small for most applications. It is therefore suggested that some effort should be made in combining linear-scaling approaches with techniques for sampling rare events, as this will allow effective exploration of phase space for many applications.

Healthy competition between research groups worldwide and specialised workshops every 2-3 years have played a catalytic role for the development of the linear-scaling methods that are available today. For example, exchanges of opinions between developers during the present workshop have led to the emergence of consensus on various complex technical issues such as the relative benefits and deficiencies of the several proposed energy expressions and basis sets in the context of O(N) calculations. For the continuation of progress, it is important that the dialogue between O(N) groups (and now also the growing user base of their methods) to continue in the future and meetings (conferences) of the community should take place every couple of years.

Many unsolved issues remain. On the one hand the existing ground-state linear-scaling methods need to be developed further and applied to a wide range of problems to reach a stage where their reliability and wealth of functionalities would be comparable to those of conventional cubic-scaling methods. On the other hand, the currently embryonic efforts in the community to extend linear-scaling to new areas such as metallic systems, excited states and correlated wavefunction-based methods need to be supported as these approaches have the potential to provide valuable insights in many bio and nano materials-related problems.

7 Key references

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