Ψ_k Newsletter

AB INITIO (FROM ELECTRONIC STRUCTURE) CALCULATION OF COMPLEX PROCESSES IN MATERIALS

Number 81 June 2007

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Sponsored by: UK's CCP9
and ESF Psi-k Programme

Contents

1 Editorial

In this newsletter we would like to turn readers' attention to the brief report on a recent graduate school that took place in Bristol (UK) and the scientific highlight of the month. The latter is on "Linear-scaling DFT calculations with the CONQUEST code" by D. R. Bowler (London), A. S. Torralba (London), T. Miyazaki (Tsukuba), T. Ohno (Tsukuba), and M. J. Gillan (London). For the rest, please check the table of content of the newsletter.

The *Networks* have a home page on World Wide Web (WWW). Its *Uniform Resource Locator* (URL) is:

http://psi-k.dl.ac.uk/

The above contains information on the Psi-k 2006/2007 workshops and hands-on courses (subject to funding).

Please submit all material for the next newsletters to the email address below.

The following email addresses, which remain in operation, are repeated for your convenience, and are the easiest way to contact us.

	function
psik-coord@dl.ac.uk	**messages to the coordinators, editor & newsletter**
psik-network@dl.ac.uk	**messages to the whole Ψ_k community**

Dzidka Szotek, Martin Lüders and Walter Temmerman
e-mail: psik-coord@dl.ac.uk

2 Psi-k Training Graduate Schools

2.1 Report on Bristol Training Graduate School

Psi-k Training Graduate School

Walter Temmerman
Daresbury Laboratory United Kingdom

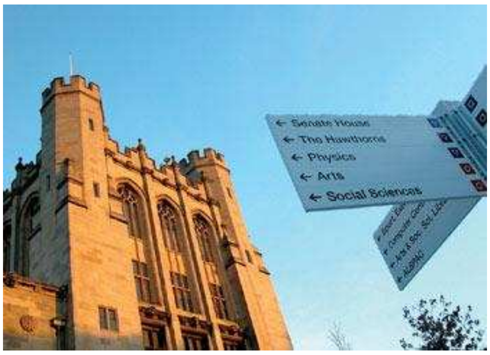
Martin Lueders
Daresbury Laboratory United Kingdom

Z. (Dzidka) Szotek
Daresbury Laboratory United Kingdom

James Annett
HH Wills Physics Laboratory United Kingdom

Workshop Details

Time and location: 25-31 March, 2007, Bristol University, U. K.



Description

This Graduate School is an activity of the Psi-k Training Programme in the EU-funded ’Series of Events’ Marie Curie Conferences and Training Courses. It was funded by MOLSIMU, the Psi-k Programme of the ESF and the EPSRC’s CCP9.

The combined theory-hands-on Graduate School on electronic structure methods took place at Burwalls and the Physics Department in Bristol from Sunday March 25 until Saturday March 31, 2007. There were 20 lectures over 6 days, 10 lectures on theory and 10 lectures on electronic structure methods. The rest was all hands-on experience with relevant codes. The 10 lectures on theory were:

- 3 lectures on Density Functional Theory (DFT) by Hardy Gross
- 3 lectures on many body perturbation theory (MBT) by Rex Godby
- 3 lectures on dynamical mean field theory (DMFT) by Karsten Held
- 1 lecture on the Bethe-Salpether equation (BSE) by Francesco Sottile.

The 10 lectures on methods gave a bird’s eye view of 5 electronic structure methods:

- the plane-wave methods (PW) by Xavier Gonze
- the full potential local orbital method (FPLO) by Manuel Richter
- the linear augmented plane waves (LAPW) by Peter Blaha
- the linearized muffin tin orbital method (LMTO) by Ole Andersen
- the Korringa-Kohn-Rostoker (KKR) method by Hubert Ebert.

Each electronic structure method was introduced by two lectures followed by hands on experience with a modern state of the art code.

Scientific Objectives

The Bristol University Graduate School aimed towards giving masters students and beginning PhD students

- an understanding of the theories underlying electronic structure calculations;

- hands-on experience in electronic structure calculation codes;
- a perspective how these methods are used in state of the art research.

The Graduate School was motivated by

- The importance of electronic structure calculations of materials at the nano scale (such as catalysis, fuel cell research, magnetic recording and spin electronics, semiconductor technology, pharmacy etc.), has resulted in a sharp increase in the number of European groups (including industrial groups) starting with electronic structure calculations; these groups, however, do not have the optimal knowledge expertise for adequate training of their PhD students.
- The field of electronic structure calculations has become so broad that single institutions do not have the expertise to provide training of the entire field; only at the European level this expertise exists.
- The gap between education provided by university lectures and the much higher level of science in real research and at international workshops and conferences is steadily increasing. The school aimed at bridging this gap.
- The combined training and research program, will give young researcher the opportunity to develop in the European Psi-k network at a very early stage of their career.

Report

The Graduate School had 37 participants of which 23 were students. The fundamentals of electronic structure calculations for condensed matter were covered by lectures on density functional theory, on many body perturbation theory, dynamical mean field theory and on the Bethe-Salpether equation. A selection of 5 electronic structure methods and codes was made in order to stress such concepts as pseudopotentials and plane waves, multiple scattering, partial waves and screening, downfolding and minimal basis, local orbitals and linear augmented plane waves. Hands-on exercices complemented these lectures on the electronic structure methods.
The lecture notes can be found under
`http://psi-k.dl.ac.uk/data/Psik-training/psi-k_training2007.html`

Participant List

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Program

Day 1: March 25 2007
Session : 1 Registration and Welcome
16:00 to 20:00 :

Day 2: March 26 2007
Session : 1 DFT I + II (Gross)
09:00 to 10:00 : Presentation
    Gound-state density functional theory: An overview.
        Basic Theorems
10:10 to 11:10 : Presentation
    Gound-state density functional theory: An overview.
        Optimized effective potential method (OPM, OEP)
        Construction of orbital functionals to tackle van der Waals interactions
        Non-collinear OEP
Session : 2 PW I (Gonze)
11:30 to 12:30 : Presentation
    Plane waves and pseudopotentials:
        I. Formalism

        II Iterative techniques

Session : 3 MBT I (Godby)

14:30 to 15:30 : Presentation

- Many-body theory for electronic structure
    - Introduction to many-body perturbation theory
    - The GW approximation (non-SC and SC)

Session : 4 KKR I (Ebert)

15:30 to 16:30 : Presentation

- The Munich SPRKKR program package
    - Introduction
    - Green's functions
    - Scattering theory
    - Angular momentum representation
    - Calculating the scattering path operator

Session : 5 MBT II (Godby)

17:00 to 18:00 : Presentation

- Many-body theory for electronic structure
    - Implementation of GW
    - Spectral properties

Day 3: March 27 2007

Session : 1 PW II (Gonze)

09:00 to 10:00 : Presentation

- Plane waves and pseudopotentials:
    - III Applications
    - IV The ABINIT software

Session : 2 PW: Hands-on

10:30 to 12:30 : ABINIT tutorial session

Session : 3 KKR II (Ebert)

14:30 to 15:30 : Presentation

- The Munich SPRKKR program package
    - The impurity problem
    - Substitutional disordered alloys
    - Relativistic formalism
    - Combination of the KKR with the DMFT
    - Applications

Session : 4 KKR: Hands-on

16:00 to 18:00 : KKR tutorial session

Day 4: March 28 2007

Session : 1 FPLO I + II (Richter)

09:00 to 10:00 : Presentation

- FPLO: Full-potential Loal-orbital approach to electronic structure of solids and molecules
  - Introduction: why yet another DFT solver?
  - Linear combinbation of local orbitals (LCLO) equations and core-valence transformation
  - Optimum local basis: strategies

10:10 to 11:10 : Presentation

- FPLO: Full-potential Loal-orbital approach to electronic structure of solids and molecules
  - Performance and application
  - Summary and licence

Session : 2 FPLO: Hands-on

11:30 to 12:30 : FPLO tutorial session

Session : 3 FPLO: Hands-on

14:30 to 15:30 : FPLO tutorial session

Day 5: March 29 2007

Session : 1 LMTO I + II (Andersen)

09:00 to 10:00 : Presentation

- Muffin tin orbitals
  - Introduction
  - The idea
  - Crystals
  - Muffin tin orbitals: EMTOs, NMTOs

10:10 to 11:10 : Presentation

- Localized minimal basis sets by downfolding and N-ization
  - Wannier functions and tight binding Hamiltonians
  - Metal insulator transition in V_2O_3
  - Superconductivity in hole and eletron doped graphite

Session : 2 LMTO: Hands-on

11:30 to 12:30 : LMTO tutorial session

Session : 3 LMTO: Hands-on

14:30 to 15:30 : LMTO tutorial session

Session : 4 DFT III (Gross)

15:30 to 16:30 : Presentation

- Extensions of density functional theory.
  - Finite temperatures
  - Superconductivity
  - Time dependent DFT
  - Time dependent DFT and Quantum Transport

Session : 5 DMFT I (Held)

17:00 to 18:00 : Presentation

- Dynamical mean field theory
  - DMFT - an introduction
  - LDA + DMFT
  - Beyond DMFT

Day 6: March 30 2007

Session : 1 LAPW I + II (Blaha)

09:00 to 10:00 : Presentation

- The FP-LAPW and APW +lo methods
  - APW Augmented plane wave method
  - Linearization
  - Full-potential
  - Core-semicore and valence states
  - Problems of the LAPW method
  - Extending the basis: local orbitals
  - The LAPW+lo method

10:10 to 11:10 : Presentation

- The FP-LAPW and APW +lo methods
  - The Wien2k software package
  - General remarks on Wien2k
  - w2web GUI (graphical user interface)
  - Program structure
  - Properties with Wien2k
  - Advantages/disadvantages

Session : 2 LAPW: Hands-on

11:30 to 12:30 : LAPW tutorial session

Session : 3 LAPW: Hands-on

14:30 to 15:30 : LAPW tutorial session

Session : 4 DMFT II (Held)

15:30 to 16:30 : Presentation

- LDA + Dynamical mean field theory
  - (Physical) Hamiltonian point of view
  - Spectral density functional point of view
  - Colossal magnetoresistance in $La_{1-x}Ca_xMnO_3$
  - Kinks in $SrVO_3$ and everywhere

Session : 5 DMFT III (Held)

17:00 to 18:00 : Presentation

- Beyond DMFT
  - Cluster extensions
  - Diagrammatic extensions
  - Dynamical vertex approximation DΓA

Results: Hubbard model

Day 7: March 31 2007

Session : 1 MBT III (Godby)

09:00 to 10:00 : Presentation

- Many-body theory for electronic structure
  - GW total energy
  - Vertex correctbions beyond GW

Session : 2 BSE (Sottile)

10:00 to 11:00 : Presentation

- The Bethe-Salpeter equation
  - Spectra in linear response approach
  - The Bethe-Salpeter equation
  - Results

Session : 3 Wrapping Up

11:30 to 12:30 : Discussion

3 News from the ESF Programme

”Towards Atomistic Materials Design”

3.1 ESF Psi-k Programme Wrokshop/Conference Announcements

3.1.1 International Workshop on "Non-Adiabatic Dynamics at Surfaces"

Schloss Reisensburg (close to Ulm, Germany)

22-25 October, 2007

`http://www.fhi-berlin.mpg.de/~behler/Website/reisensburg.htm`

Objectives: Electronically non-adiabatic gas-surface interactions have been discussed in order to account for dissociation dynamics observed in molecular beam experiments, or in the context of electron or light emission during adsorption at metal surfaces. Intimately connected to this are mechanisms of energy dissipation to the bulk solid, which, if hindered, could give rise to controversially debated processes like abstraction or "hot" adatom diffusion. A full quantum-mechanical treatment of these phenomena is severely challenged by the lowered symmetry at the solid surface, by the sheer size and complexity of the systems when considering the extended surface, as well as by the time scales over which it is necessary to follow the coupled atomic and electronic motion. The aim of the workshop is to bring together scientists working on different approaches to dynamics on excited state potential energy surfaces, as well as distinguished experimentalists to discuss and promote advances in this field.

Confirmed Invited Speakers and Discussion Leaders: D. Bird, G. Darling, B. Gadzuk, A. Gross, E.K.U. Gross, E. Hasselbrink, S. Holloway, B. Kasemo, Th. Klüner, R. Kosloff, G.-J. Kroes, O. Kuehn, S. Louie, N. Marzari, E. Pehlke, M. Persico, M. Rohlfing, A. Rubio, T. Van Voorhis, A. Wodtke.

Format and Application: The number of participants is strictly limited to 50. Apart from the formal sessions of invited contributions, there will be a poster session allowing all participants to present their work. The conference fee is 450 Euro and includes full board and lodging.

Applications to participate in the workshop should be sent to Karsten Reuter (reuter@fhi-berlin.mpg.de).

Jörg Behler (ETH Zürich)
Patrick Rinke (FHI Berlin)
Karsten Reuter (FHI Berlin)
Matthias Scheffler (FHI Berlin)

4 News from UK's CCP9 Programme

UK's Collaborative Computational Project 9 (CCP9) on "Computational Studies of the Electronic Structure of Solids"

4.1 UK's CCP9 Workshop Announcements

4.1.1 CASTEP Workshop

17th - 21st September 2007

York University, UK

The CASTEP developer's group are pleased to announce a five-day training workshop on the ab-initio simulation package CASTEP. The workshop will be held at the University of York from the 17th to 21st September 2007.

Lecturers will be

Dr Stewart Clark (Durham University)
Dr Matt Probert (York University)
Dr Matt Segall (BioFocus DPI/Cambridge University)
Dr Phil Hasnip (York University)
Dr Jonathan Yates (Cambridge University)
Dr Keith Refson (STFC Rutherford Appleton Laboratory)
Dr Barbara Montanari (STFC Rutherford Appleton Laboratory)
Professor Mike Payne (Cambridge University)
Dr Johan Carlsson (Fritz-Haber Institute, Berlin)

The aim is to teach the basics of ab-initio atomistic materials simulation using the CASTEP plane-wave pseudopotential code. The workshop will consist of 50% lectures and 50% practical sessions. Topics to be covered include:

* Fundamentals of density functional theory
* DFT in the solid state, kpoints, Brillouin zones
* Plane-wave basis sets
* Pseudopotentials, ultrasoft, norm-conserving and self-consistent
* Simulations using plane-wave DFT
\- geometry optimization
\- molecular dynamics in various ensembles
\- quantum path-integral molecular dynamics
\- ab-initio lattice dynamics and spectroscopy - dielectric properties

- Electric fields, Berry phase and Wannier functions
- NMR properties and chemical shifts

* Ab-initio beyond the LDA and GGA, EXX, hybrid functionals
* Practical aspects of ab-initio calculation
* Application to structural and surface calculations
* Convergence - how to get accurate results

The workshop is suitable for postgraduate students and researchers who wish to learn the methods of plane-wave pseudopotential simulation and CASTEP. We will assume a reasonable knowledge of quantum mechanics applied to the electronic structure of atoms and molecules and a basic knowledge of solid-state physics.

The workshop is aimed primarily at academic researchers but is open to all users and potential users of CASTEP. Applications from academic staff and students will be given priority. The full package includes accommodation for 5 nights from Sun 16-Thu 20 September, breakfast, lunch and refreshments. There will be a conference dinner on the evening of Thursday 20, but no other evening meals are included.

Rates are:

	Incl. Conference Dinner	Excl. Conference Dinner
Residential	£500.00	£470.00
Non-residential	£220.00	£190.00

Some bursaries may be available to assist with fees for applicants who do not have grant or training funds to cover the workshop. This will be awarded on a discretionary basis, but may not cover the full costs, as funds are limited.

Details of the applications procedure and bursaries can be found on the CASTEP web site

http://www.castep.org.

Please note that the 2006 workshop was fully subscribed within 10 days of applications opening.

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5 General Workshop/Conference Announcements

5.1 Gordon Conference on Time-dependent density-functional theory

Colby College, Waterville, Maine, USA

July 15-20, 2007

Chairs: Carsten A. Ullrich and Kieron Burke

http://www.grc.uri.edu/programs/2007/timeden.htm

Time-dependent density-functional theory (TDDFT) provides an efficient, elegant, and formally exact way of describing the dynamics of interacting many-body quantum systems, circumventing the need for solving the full time-dependent SchrÃűdinger equation. In the 20 years since it was first rigorously established in 1984, the field of TDDFT has made rapid and significant advances both formally as well as in terms of successful applications in chemistry, physics and materials science. Today, TDDFT has become the method of choice for calculating excitation energies of complex molecules, and is becoming increasingly popular for describing optical and spectroscopic properties of a variety of materials such as bulk solids, clusters and nanostructures. Other growing areas of applications of TDDFT are nonlinear dynamics of strongly excited electronic systems and molecular electronics.

The purpose and scope of this Gordon Research Conference is to provide a platform for discussing the current state of the art of the rapidly progressing, highly interdisciplinary field of TDDFT, to identify and debate open questions, and to point out new promising research directions. The conference will bring together experts with a diverse background in chemistry, physics, and materials science.

Application deadline: June 24, 2007

To contact the organizers, please email ullrichc@missouri.edu.

5.2 Summer School "Multiscale Modelling in Materials Science and Engineering"

July 23 - 28, 2007

Landhotel Kallbach, Eifel Mountains, Germany

This Summer School gives a broad introduction to materials modelling and to three or four modelling techniques spanning the range from finite elements down to electronic structure, with the opportunity of hands on experience and expert guidance.

The deadline for registration is now June 15.

Please forward this information to any students you think would profit from it.

See the website for details:

http://www.idealeague.org/summerschool2007/

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5.3 Computational Molecular Science (CMS) Conference

22nd-25th June 2008

The Royal Agricultural College, Cirencester, U. K.

We are organizing a conference to promote and explore the best of UK Computational Molecular Science. Our basic aim is to bring together the best practitioners in the field, with a broad and inclusive interpretation of ’computational molecular science’.

Plenary talks will be given by Jean-Pierre Hansen, Martin Head-Gordon, Martin Karplus, Michael Klein and Mike Robb. Details of the meeting can be found at

http://www.chm.bris.ac.uk/cms,

and if you are interested in attending, please register your interest there.

Fred Manby
Jeremy Harvey
Neil Allan
Gabriel Balint-Kurti
Adrian Mulholland

5.4 CECAM Workshop on "Modelling the structures and reactivity of silica and water: from molecule to macroscale"

17-19th September, 2007

Lyon, France

We would like to draw your attention to a three-day workshop: ’Modelling the structures and reactivity of silica and water: from molecule to macroscale’ CECAM (European Centre for Atomic and Molecular Calculation) Lyon, France from 17-19th September, 2007.

We invite you to register your attendance and abstracts for talks/posters at:

http://www.simbioma.cecam.org/

Confirmed invited speakers at the meeting are

- Prof. Jim R. Chelikowsky, University of Texas at Austin, USA
- Prof. Julian D. Gale, Curtin University of Technology, Perth, Australia
- Prof. Sherwin J. Singer, Ohio State University, USA

At the webpage you can register by signing in with your name, affiliation and email. After which, you may then access the MatBioSim pages where you can register your participation at the workshop and upload your abstract and preferences.

If any further details and/or assistance is required please feel free to email the organisers.

Looking forward to seeing you in September.

Stefan Bromley (University of Barcelona, s.bromley@qf.ub.es)
Ben Slater (The Royal Institution of Great Britain, ben@ri.ac.uk)

6 General Job Announcements

Ph.D. Positions

Imperial College London, United Kingdom

Applications are invited for PhD studentships (starting October 2007) to be supervised by academics in the Thomas Young Centre for Theory and Simulation of Materials

(http://www.thomasyoungcentre.org)

at Imperial College London. The Thomas Young Centre is a stimulating environment for interdisciplinary research projects, usually jointly supervised.

Our main research activities are in the following areas and prospective candidates are encouraged to contact members of the academic staff working in their fields of interest:

- Development and applications of first principles (ab initio) methods for simulating at the atomic scale, including linear scaling methods for large systems, polarisation, molecular dynamics and thermodynamics
- Electronic structure of matter and the dynamics of electrons
- Development of semi-empirical methods of atomistic simulation, with applications to complex and amorphous structures, defects and interfaces in materials
- Applications to nanomaterials and nanotechnology

These studentships are fully funded via the EPSRC DTA award for candidates that meet the EPSRC criteria of having been been ’ordinarily resident’ in the UK for the past 3 years. For nationals of EU member states who are not UK residents this funding only covers tuition-fees.
(http://www.epsrc.ac.uk/PostgraduateTraining/DoctoralTrainingAccounts)

Please see http://www.jobs.ac.uk/jobfiles/UA785.html for further details.

Dr Peter Haynes (pdh1001@cam.ac.uk)
Dr Andrew Horsfield (a.horsfield@imperial.ac.uk)
Dr Arash Mostofi (arash.mostofi@gmail.com)
Dr Paul Tangney (PTTangney@lbl.gov)

Postdoctoral Positions

Computational Materials Science in Advanced Industrial Science and Technology (AIST)

Osaka, Japan

Two postdoctoral positions are available in Research Institute for Ubiquitous Energy Devices (UBIQEN) in AIST-Kansai, Osaka, Japan

(`http://unit.aist.go.jp/ubiqen/english/index_e.html`).

The subjects are:

1) First-principles calculations of the adhesive and mechanical properties of metal/carbide and/or metal/nitride interfaces, and

2) First-principles calculations of the microscopic nature of ionic liquids and ionic liquid/metal interfaces.

The subject 1) will be performed in the group of Dr. Masanori Kohyama, and the subject 2) will be performed in the group of Dr. Hajime Matsumoto in close cooperation with Dr. M. Kohyama and Dr. Shingo Tanaka. Each subject will be performed in collaboration with experimental studies in UBIQEN or AIST. The candidates will need experiences in density- functional theory calculations and a strong interest on materials science. For the subject 1), the candidate is desirable to have an interest on mechanical properties in micro- and nano-scales, and for the subject 2), he/she is desirable to have an interest on ionic liquids or electrochemistry.

Both posts will start from Sep. 1 or Aug. 1, 2007.

The period of both posts is basically one year, although it can be extended to three years according to the achievements in the first year. Salary range is 4500,000 - 5000,000 yen per year.

Interested candidates should submit their CV, including a list of publications and a reference letter, by e-mail, to Dr. M. Kohyama, m-kohyama@aist.go.jp , for the subject 1), and to Dr. H. Matsumoto, h-matsumoto@aist.go.jp, for the subject 2). Candidates havsinge interests in both of the subjects, should submit their CV to both of the above addresses.

The deadline of the submission is 10 July.

Dr. Masanori Kohyama
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National Institute of Advanced Industrial Science and Technology
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`http://staff.aist.go.jp/m-kohyama/English%20top.html`

Ph. D. Position in Computational Materials Modelling
Department of Physics, University of Antwerp (Belgium)

A PhD position is available at the materials modelling group of the Department of Physics at the University of Antwerp (Belgium). The research will be on the study of the phase stability of Ge-Sb-Te alloys which are used for optical data storage ("Blue Ray" disk) by first-principles (DFT) electronic structure calculations. Candidates should have a degree in physics, chemistry or engineering. A good knowledge of condensed matter physics, statistical physics and computational physics is an advantage. They should also be familiar with programming in Fortran or C and working with the Linux operating system.

Consideration of candidates will begin immediately and will continue until the position is filled.

Interested candidates should send their applications including CV and academic record, preferably via electronic mail, to:

Dirk Lamoen
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Postdoctoral Position

"First-Principles Based Modeling of Alloys for Nuclear Applications"

University of Wisconsin, Madison, USA

A postdoctoral position is available immediately in the group of Dane Morgan in the Department of Materials Science and Engineering at University of Wisconsin, Madison. The research will be in the general area of combining First-Principles (DFT) and standard and kinetic Monte Carlo methods to model thermodynamics, diffusion, and evolution of radiation damage in multicomponent alloys of interest for nuclear applications. Familiarity with DFT methods and alloy thermodynamic and kinetic modeling is essential. The appointment is initially for one year with possible extension. Interested applicants should send CV (preferably in PDF format) and contact information for at least 3 references to Dane Morgan at ddmorgan@wisc.edu. Consideration of candidates will begin immediately and will continue until the position is filled.

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Madison, WI 53706-1595
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Fax (department): 608-262-8353
Email: ddmorgan@wisc.edu
`Web: www.engr.wisc.edu/mse/faculty/morgan_dane.html`

Postdoctoral Position

Materials Department and the Solid State Lighting and Energy Center University of California, Santa Barbara (UCSB)

A postdoctoral position in Computational Materials Physics is available to work with Prof. Chris Van de Walle in the Materials Department and the Solid State Lighting and Energy Center at the University of California, Santa Barbara (UCSB). Candidates should have experience with electronic structure and condensed matter theory. They should also have a keen interest in materials physics and a motivation to interact with experimentalists. Good communication skills (writing papers, making presentations) are required.

The project will encompass one or more of the following areas: first-principles calculations (density-functional theory) for surfaces, interfaces, and point defects; development/application of techniques to overcome band-gap problems; and modeling of device structures, including Schroedinger-Poisson simulations and/or k.p calculations of band structure.

Applications should include: (1) Curriculum Vitae, (2) Publication List, (3) One-page summary of accomplishments to date, and their significance, (4) Names and contact information (including email) of three references.

Professor Van de Walle's group works on a variety of topics ranging from new materials for solid-state light emitters to hydrogen-storage materials. The Solid State Lighting and Energy Center, directed by Profs. S. Nakamura and S. DenBaars, comprises more than 50 researchers, including faculty, visitors, postdocs and graduate students, and is focused on developing novel technologies for solid-state light emitters and energy conversion. The UCSB campus offers a unique environment, both in terms of collaborative research and natural beauty. Competitive salaries are offered, based on qualifications and experience.

More information about UCSB, about the Solid State Lighting and Energy Center, and about the Materials Department can be found at www.ucsb.edu,

http://ssldc.ucsb.edu,

and www.materials.ucsb.edu.

Information about Prof. Van de Walle's research group can be found at

`www.mrl.ucsb.edu/~vandewalle`.

For more information or to apply, please contact Prof. Chris Van de Walle (vandewalle@mrl.ucsb.edu).

Chris G. Van de Walle
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Post-doctoral position in "Electronic Structure Theory"

University of Osnabrueck, Germany

A positions for a post-doctoral researcher is available at the University of Osnabrueck, in the "Electronic Structure of Condensed Matter" group headed by Prof. Dr. Michael Rohlfing.

The prospective candidate is expected to work on the electronic structure of condensed matter, described by state-of-the-art ab-initio computational approaches. Possible topics include excited electronic states, many-body perturbation theory, modern developments of density-functional theory, short-time dynamics, surface physics, and nano-scale physics. A solid background in computational solid-state physics or computational chemistry is required.

The position includes moderate teaching obligations. Therefore some knowledge of German is required, enabling to communicate physics to undergraduate students.

Salary and social benefits follow the "Entgeltgruppe 13" (similar to the now outdated "BAT IIa" classification) common at German universities. An initial contract could be for three years, with possible extension. The University of Osnabrueck offers the possibility of pursuing a Habilitation for further academic qualification.

For further information, visit our websites at http://www.physik.uni-osnabrueck.de/

and

http://www.physik.uni-osnabrueck.de/rohl/

The position is available immediately and applications will be considered until the position is filled. Further inquiries and applications (including a CV, names and addresses of up to three references, summary of research interests, and list of publications) should be directed to Prof. Dr. Michael Rohlfing (Michael.Rohlfing@uni-osnabrueck.de).

Research Fellow

Atomistic Simulation Centre
School of Mathematics and Physics
Queen's University Belfast, U. K.

Ref: 07/W595A

This post is available at the Atomistic Simulation Centre (http://titus.phy.qub.ac.uk), for two years starting on 1 November 2007, to pursue research, as part of an ongoing project, on the time-dependent simulation of correlated electron-ion dynamics and inelastic conduction in atomic-scale wires.

Applicants must hold or be about to obtain a relevant PhD and have proven experience and track record in one of the following areas: (i) theory and numerical simulation of inelastic transport in nanostructures, (ii) theory and quantum-mechanical modelling of electron-ion interactions in nanoscale structures, (iii) first-principles electronic-structure theory.

Salary scale: GBP 25,138 - 34,793 per annum (including contribution points)

Closing date: 4.00 pm, Friday 15 June 2007

JOB PURPOSE

To pursue research, as part of an ongoing project, on the time-dependent simulation of correlated electron-ion dynamics and inelastic conduction in atomic-scale wires. This two-year research post is part of an ongoing collaboration between QUB, Imperial College London and University College London on correlated electron-ion dynamics in three areas: nanoscale conductors (QUB), molecular systems (UCL), and radiation damage (IC). The project at QUB focuses on the dynamical simulation of inelastic quantum transport in nanowires, to model in real time processes such as the local heating of atomic vibrations under current flow and the characteristic signature of this heating on the electronic current. Our method in its present form is described in

Journal of Physics: Condensed Matter 17 (2005) 4793, Journal of Physics: Condensed Matter 19 (2007) 196201.

Two specific directions for ongoing and future work are the inclusion of electron-electron screening at an appropriate approximate level, and a comparison of the method with NEGF in the SCBA. We accordingly are looking for a person with a strong theoretical and computational background in one or more of the following areas: inelastic quantum transport, first-principles electronic structure, and electron-ion interactions in nanostructures. Other aspects of the post include regular research meetings between the teams from the three universities above, and maintenance, development and management of computational resources.

FOR APPLICATION DETAILS PLEASE VISIT

http://www.jobs.ac.uk/jobfiles/DC762.html

AND FOLLOW THE LINKS FROM THERE.

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POSTDOCTORAL POSITION OPENING

Theoretical Chemistry of Reactivity, Spectroscopy and Catalysis

Laboratory of Chemistry, CNRS and Ecole Normale Supérieure de Lyon, France

"Adsorption, diffusion of carbon and model catalytic growth of nanotubes on alloys"

A postdoctoral position is opened in the field of theoretical modeling of reactivity at catalytic surfaces in the Laboratory of Chemistry of the Ecole Normale Supérieure de Lyon, starting from September 2007. In the recent years, the field of carbon nanotube chemistry has developed rapidly. Several experimental and theoretical works have been devoted to explore the growth of these nanotubes, particularly on nickel. A key step is the diffusion of the carbon atoms formed on the surface by dissociation of precursors. With the aim of finding new catalysts efficient for the growth of the nanotubes, alloy catalysts will be studied both experimentally and theoretically. In the laboratory of Chemistry, the theory group has gained expertise throughout the years for adsorption properties and reactivity at metal or oxide surfaces. It is worth mentioning that this group is involved in several European research networks such as IDECAT, MONET, EUROSIM (see

`http://www.ens-lyon.fr/CHIMIE/Fr/Groupes/RCS/RCS_home.html`).

The successful candidate will perform periodic calculations based on the density-functional theory for the study of the carbon behavior on transition metal alloy surfaces (adsorption, absorption, diffusion and model catalytic growth of nanotubes). The applicant should have a PhD in theoretical chemistry and/or condensed matter theory. Experience with calculations of periodic systems would be appreciated. The project is part of a National Research Agency contract (ECLAT, "ECLAirage arriàre à nanoTubes de carbone d'écrans LCD à basse consommation") in collaboration with three other French partners. The position is funded with a net salary of 2039 Euros per month. The Ecole Nationale Supérieure de Lyon provides an outstanding environment for research and teaching with an important permanent staff of researchers in chemistry and physics, and with a large number of graduate students and postdoctoral fellows

(see http://www.ens-lyon.fr for more details).

Lyon is a nice town where the life is pleasant. The city is famous for its gastronomy. Please send a cover letter and a CV to Dr Philippe Sautet or Dr Francoise Delbecq. Recommendation letters will be requested after a preliminary selection.

Dr Philippe Sautet
Laboratoire de Chimie, UMR CNRS 5182
Ecole Normale Supérieure de Lyon 46 Allée d'Italie
F-69364 Lyon Cedex 07, France
Tel (33) 4 72 72 81 55
Email: philippe.sautet@ens-lyon.fr

Dr Francoise Delbecq
Laboratoire de Chimie, UMR CNRS 5182

Ecole Normale Supérieure de Lyon 46 Allée d’Italie
F-69364 Lyon Cedex 07, France
Tel (33) 4 72 72 81 55
Email: francoise.delbecq@ens-lyon.fr

PostDoc Position Available at LAAS-CNRS

LAAS-CNRS, 7 av. du Colonel Roche, 31077 Toulouse, France

An 18 month post doctoral position in Atomic Scale Modelling and Simulation is available at the Laboratoire d'Analyse et d'Architecture des Systemes (LAAS-CNRS), Toulouse, France, from 1st of October 2007. The position is supported by an ANR (French National Research Agency) contract entitled: 'Atomic Scale Simulation of SiGe systems for microelectronics: oxidation, starin, diffusion' The five following organizations are participating to this project : (i) Laboratoire de simulation atomistique (`L_Sim`), CEA, Grenoble, (ii) LAAS-CNRS, Toulouse, (iii) Centre de Recherche en Matiere Condensee et Nanosciences (CRMCN-CNRS), Marseille, (iv) Laboratoire de Simulation et Caracterisation des Procedes, CEA, Grenoble, (v) Modelling Department, STMicroelectronics, Crolles.

The goal of this project is to supply the technology engineers with the appropriate numerical models so that they will be able to control the manufacturing steps concerned with the oxidation, the implantation, or the thermal annealing of these SiGe nano-devices. These models will be designed using state-of-art atomistic simulation tools (ab initio calculation, molecular dynamics and kinetic Monte Carlo simulations) and will be checked by comparison with experimental results. The implementation of these models in industrial simulation tools will be the final step of the project.

The research project will concern the multi-scale modelling of the oxidation process of SiGe alloys combining DFT calculations and Kinetic Monte Carlo simulations. The objective of DFT calculations will be to determine the chemical reaction pathways, including the enthalpy changes and activation barriers. The Monte Carlo simulations carried on the basis of an existing software package are intended to reproduce the process in real experimental conditions and to validate the proposed models.

We are looking for a candidate with a PhD in Physics or Chemistry, having substantial experience in DFT calculations, some knowledge of Monte Carlo simulations and a strong interest in Materials Science. Interested candidates should submit their CV to Mehdi DJAFARI ROUHANI, LAAS-CNRS, 7, Ave. Colonel Roche, 31077 Toulouse, France (djafari@laas.fr)

Post-doctoral Position

"Electronic simulations by quantum Monte Carlo"

SISSA, Trieste, Italy

Position for a post-doctoral fellow is available at the DEMOCRITOS National Simulation Center, SISSA Trieste, in the group headed by Prof. Sandro Sorella.

The prospective candidate should mainly work on developments and applications of Quantum Monte Carlo techniques to Carbon based compounds and/or Hydrogen at high pressures, and/or ab-initio simulation of High-Tc materials.

Applications should be sent by e-mail to sorella@sissa.it, with complete CV in attachment.

The deadline for applications is September 7.

Post-Doctoral Position in Condensed Matter Physics

"Development of multiscale simulations schemes for material science applications"

University of Lyon 1, France

A post-doc position is now available for one year at the "Laboratoire de Physique de la Matière Condensée et Nanostructures", University of Lyon 1 (France). The applicant will work in the modeling group on the development and application of the LOTF technique, a QM/MM molecular dynamics scheme. This technique has already been applied to brittle fracture and dislocation dynamics in silicon. Further developments will be carried on by the successful candidate to :

(1) extend the application of the method to polyatomic systems and
(2) use the LOTF technique as an acceleration scheme for the geometry optimization in ab-initio simulations.

Applications will focus on material science problems like fracture mechanics and the study of "plastic events" in glasses.

The applicants should hold a PhD in physics and possess a good background in solid state physics. Coding skills in F90 and/or C++ programming languages are required as well as the will to be involved for the period in scientific code development.

This work is founded by the french government through the ANR framework and it includes collaborations with others theoretical groups in Grenoble and Paris.

The net salary after the application of all taxes will approximately amount to 1800 euros per month.

Applicants should send to the contact below a detailed CV and one or two representative publications.

Contact :

Tristan Albaret
Laboratoire de Physique de la Matière Condensée et Nanostructures
UMR5586 UniversitÃl’ Lyon 1/CNRS

Email : tristan.albaret@lpmcn.univ-lyon1.fr
Phone : +33(0)4 72 43 15 65
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Group website :
`http://lpmcn.univ-lyon1.fr/theorie/site/index.php`

ANR (LN3M) website :
`http://www-drfmc.cea.fr/sp2m/L\_Sim/LN3M/index.html`

7 Abstracts

Energy gaps and interaction blockade in confined quantum systems

K. Capelle[1,2], M. Borgh[2], K. Karkkainen[2] and S.M. Reimann[2]
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Abstract

Many-body effects in confined quantum systems pose a challenging problem due to the simultaneous presence of particle-particle interactions and spatial inhomogeneity. Here we investigate universal properties of strongly confined particles that turn out to be dramatically different from what is observed for electrons in atoms and molecules. We show that for a large class of harmonically confined systems, including small quantum dots and optically trapped atoms, *many-body* particle addition and removal energies, and energy gaps, can *accurately* be obtained from *single-particle* eigenvalues. Transport blockade phenomena are related to the derivative discontinuity of the exchange-correlation functional. This implies that they occur very generally, with Coulomb blockade being a particular realization of a more general phenomenon. In particular, we predict *van-der-Waals blockade* in cold atom gases in traps.

(Phys. Rev. Lett. (2007), accepted, arXiv:cond-mat/0702246)
Contact person: Klaus Capelle (capelle@ifsc.usp.br)

Luther-Emery Phase and Atomic-Density Waves in a Trapped Fermion Gas

Gao Xianlong[1], M. Rizzi[1], Marco Polini[1], Rosario Fazio[1,2], M. P. Tosi[1],
V. L. Campo, Jr.[3], and K. Capelle[4]
[1] *NEST-CNR-INFM and Scuola Normale Superiore, Pisa, Italy*
[2] *International School for Advanced Studies (SISSA), Trieste, Italy*
[3] *Centro Internacional de Física da Matéria Condensada, Universidade de Brasília, Brazil*
[4] *Departamento de Física e Informática, Instituto de Física de São Carlos,*
Universidade de São Paulo, 13560-970 São Carlos, SP, Brazil

Abstract

The Luther-Emery liquid is a state of matter that is predicted to occur in one-dimensional systems of interacting fermions and is characterized by a gapless charge spectrum and a gapped spin spectrum. In this Letter we discuss a realization of the Luther-Emery phase in a trapped cold-atom gas. We study by means of the density-matrix renormalization-group technique a two-component atomic Fermi gas with attractive interactions subject to parabolic trapping inside an optical lattice. We demonstrate how this system exhibits compound phases characterized by the coexistence of spin pairing and atomic-density waves. A smooth crossover occurs with increasing magnitude of the atom-atom attraction to a state in which tightly bound spin-singlet dimers occupy the center of the trap. The existence of atomic-density waves could be detected in the elastic contribution to the light-scattering diffraction pattern.

(Phys. Rev. Lett. 98, p. 030404 (2007))

Contact person: Klaus Capelle (capelle@ifsc.usp.br)

Simple implementation of complex functionals: scaled selfconsistency

Matheus P. Lima[1], Luana S. Pedroza[1], Antonio J. R. da Silva[1], A. Fazzio[1],
Daniel Vieira[2], Henrique J. P. Freire[2] and K. Capelle[2]
[1] *Instituto de Física, Universidade de São Paulo, São Paulo, Brazil*
[2] *Departamento de Física e Informática, Instituto de Física de São Carlos,*
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Abstract

We explore and compare three approximate schemes allowing simple implementation of complex density functionals by making use of selfconsistent implementation of simpler functionals: (i) post-LDA evaluation of complex functionals at the LDA densities (or those of other simple functionals); (ii) application of a global scaling factor to the potential of the simple functional; and (iii) application of a local scaling factor to that potential. Option (i) is a common choice in density-functional calculations. Option (ii) was recently proposed by Cafiero and Gonzalez. We here put their proposal on a more rigorous basis, by deriving it, and explaining why it works, directly from the theorems of density-functional theory. Option (iii) is proposed here for the first time. We provide detailed comparisons of the three approaches among each other and with fully selfconsistent implementations for Hartree, local-density, generalized-gradient, self-interaction corrected, and meta-generalized-gradient approximations, for atoms, ions, quantum wells and model Hamiltonians. Scaled approaches turn out to be, on average, better than post-approaches, and unlike these also provide corrections to eigenvalues and orbitals. Scaled selfconsistency thus opens the possibility of efficient and reliable implementation of density functionals of hitherto unprecedented complexity.

(J. Chem. Phys. 126, p. 144107 (2007))
Contact person: Klaus Capelle (capelle@ifsc.usp.br)

Entanglement of strongly interacting low-dimensional fermions in metallic, superfluid and antiferromagnetic insulating systems

V. V. Franca and K. Capelle
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Universidade de São Paulo, 13560-970 São Carlos, SP, Brazil

Abstract

We calculate the entanglement entropy of strongly correlated low-dimensional fermions in metallic, superfluid, and antiferromagnetic insulating phases. The entanglement entropy reflects the degrees of freedom available in each phase for storing and processing information, but is found not to be a state function in the thermodynamic sense. The role of critical points, smooth crossovers, and Hilbert space restrictions in shaping the dependence of the entanglement entropy on the system parameters is illustrated for metallic, insulating, and superfluid systems. The dependence of the spin susceptibility on entanglement in antiferromagnetic insulators is obtained quantitatively. The opening of spin gaps in antiferromagnetic insulators is associated with enhanced entanglement near quantum critical points.

(Phys. Rev. A 74, p. 042325 (2006))
Contact person: Klaus Capelle (capelle@ifsc.usp.br)

Bethe-Ansatz density-functional theory of ultracold repulsive fermions in one-dimensional optical lattices

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[4] *Physics Department, University of California, Davis, California 95616, USA*
[5] *Institut für Theoretische Physik III, Universität Stuttgart, 70550 Stuttgart, Germany*

Abstract

We present an extensive numerical study of the ground-state properties of confined repulsively interacting fermions in one-dimensional optical lattices. Detailed predictions for the atom-density profiles are obtained from parallel Kohn-Sham density-functional calculations and quantum Monte Carlo simulations. The density-functional calculations employ a Bethe ansatz based local-density approximation for the correlation energy that accounts for Luttinger-liquid and Mott-insulator physics. Semianalytical and fully numerical formulations of this approximation are compared with each other and with a cruder Thomas-Fermi-type local-density approximation for the total energy. Precise quantum Monte Carlo simulations are used to assess the reliability of the various local-density approximations, and in conjunction with these provide a detailed microscopic picture of the consequences of the interplay between particle-particle interactions and confinement in one-dimensional systems of strongly correlated fermions.

(Phys. Rev. B 73, p. 165120 (2006))

Contact person: Klaus Capelle (capelle@ifsc.usp.br)

Phase diagram of harmonically confined one-dimensional fermions with attractive and repulsive interactions

V. L. Campo, Jr.[1,2] and K. Capelle[2]
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[2] *Departamento de Física e Informática, Instituto de Física de São Carlos,*
Universidade de São Paulo, 13560-970 São Carlos, SP, Brazil

Abstract

We construct the complete U-μÎij phase diagram for harmonically confined ultracold fermionic atoms with repulsive and attractive interactions (μÎij is the chemical potential and U the interaction strength). Our approach is based on density-functional theory, and employs analytical expressions for the kinetic and correlation energy functionals, permitting us to obtain closed expressions for all phase boundaries and characteristic lines of the phase diagram, both for repulsive and attractive interactions.

(Phys. Rev. A 72, p. R-061602 (2005))

Contact person: Klaus Capelle (capelle@ifsc.usp.br)

Construction of model dielectric functions for two and three dimensional electron liquids from density functionals

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Abstract

The Thomas-Fermi (TF) approximation for the static dielectric function of a three-dimensional (3D) electron liquid can be derived by minimizing the TF local-density approximation for the kinetic-energy functional. Here we show that this connection between energy functionals and model dielectric functions is not an artifact, but a general paradigm. Four examples are worked out in detail, by calculating the model dielectric functions that follow, respectively, from (i) exchange corrections to TF theory in 3D, i.e., TF-Dirac theory, (ii) further correlation corrections to TF-Dirac theory in 3D, (iii) TF theory in two dimensions (2D), and (iv) exchange corrections to TF theory in 2D. Each of these cases has certain interesting features, revealing connections between independent many-body methods, that are discussed in some detail. As a by-product of these investigations we also find that a common textbook statement about the long-wavelength ($k \to 0$) limit of the random-phase approximation is not fully correct.

(Phys. Rev. B 73, p. 045133 (2006))

Contact person: Klaus Capelle (capelle@ifsc.usp.br)

Dimensional scaling of ground-state energies: Fermi liquid and Hubbard model

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Abstract

A simple, physically motivated, scaling hypothesis, which becomes exact in important limits, yields estimates for the ground-state energy of large composed systems in terms of the ground-state energy of its building blocks. The concept is illustrated for the electron liquid, and the Hubbard model. By means of this scaling argument the energy of the one-dimensional half-filled Hubbard model is estimated from that of a two-site Hubbard dimer, obtaining quantitative agreement with the exact one-dimensional Bethe-Ansatz solution, and the energies of the two- and three-dimensional half-filled Hubbard models are estimated from the one-dimensional energy, recovering exact results for $U \to 0$ and $U \to \infty$ and coming close to quantum Monte Carlo data for intermediate U.

(Phys. Rev. B 73, p. 113111 (2006))
Contact person: Klaus Capelle (capelle@ifsc.usp.br)

Chiral magnetic order at surfaces driven by inversion asymmetry

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Abstract

Chirality is a fascinating phenomenon that can manifest itself in subtle ways, for example in biochemistry (in the observed single-handedness of biomolecules) and in particle physics (in the charge-parity violation of electroweak interactions). In condensed matter, magnetic materials can also display single-handed, or homochiral, spin structures. This may be caused by the Dzyaloshinskii-Moriya interaction, which arises from spin-orbit scattering of electrons in an inversion-asymmetric crystal field. This effect is typically irrelevant in bulk metals as their crystals are inversion symmetric. However, low-dimensional systems lack structural inversion symmetry, so that homochiral spin structures may occur. Here we report the observation of magnetic order of a specific chirality in a single atomic layer of manganese on a tungsten (110) substrate. Spin-polarized scanning tunnelling microscopy reveals that adjacent spins are not perfectly antiferromagnetic but slightly canted, resulting in a spin spiral structure with a period of about 12 nm. We show by quantitative theory that this chiral order is caused by the Dzyaloshinskii-Moriya interaction and leads to a left-rotating spin cycloid. Our findings confirm the significance of this interaction for magnets in reduced dimensions. Chirality in nanoscale magnets may play a crucial role in spintronic devices, where the spin rather than the charge of an electron is used for data transmission and manipulation. For instance, a spin-polarized current flowing through chiral magnetic structures will exert a spin-torque on the magnetic structure, causing a variety of excitations or manipulations of the magnetization and giving rise to microwave emission, magnetization switching, or magnetic motors.

(Nature **447**, 190 (2007))
Contact person: Stefan Blügel (s.bluegel@fz-juelich.de)

Angle-dependent Ni^{2+} x-ray magnetic linear dichroism: Interfacial coupling revisited

Elke Arenholz
Advanced Light Source, Lawrence Berkeley National Laboratory
Gerrit van der Laan
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Rajesh V. Chopdekar and Yuri Suzuki
Department of Materials Science and Engineering, UC Berkeley

Abstract

Using x ray magnetic linear dichroism (XMLD) for magnetometry requires detailed knowledge of its dependence on the relative orientation of polarization, magnetic moments, and crystallographic axes. We show that Ni^{2+} $L_{2,3}$ XMLD in cubic lattices has to be described as linear combination of two fundamental spectra $-$ not one as previously assumed. The spectra are calculated using atomic multiplet theory and the angular dependence is derived from crystal field symmetry. Applying our results to Co/NiO(001) interfaces, we find perpendicular coupling between Ni and Co moments.

Published in *Physical Review Letters* **98**, 197201 (2007).
Manuscript available from g.vanderlaan@dl.ac.uk.

Resonant Inelastic X-ray Scattering from magnetic systems with angular resolution and polarization analysis of the scattered beam: Results on metallic Co, Fe, and Co ferrite at the $L_{3,2}$ edges

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N. B. Brookes
European Synchrotron Radiation Facility, Grenoble, France

Abstract

We present experimental results on Resonant Inelastic X-ray Scattering (RIXS) in perpendicular geometry excited with circularly polarized x-rays at the Co $L_{3,2}$ edges in Co ferrite ($\mathrm{CoFe_2O_4}$) and Co metal and at the Fe $L_{3,2}$ edges in Fe metal. In this geometry with magnetic samples the incident x-ray beam is perpendicular to the magnetization and the magnetic dichroism is only present in RIXS. We study the $3s$-RIXS channel terminating in an inner shell $3s$ hole and extra $3d$ electron ($2p^6 3d^n \rightarrow 2p^5 3d^{n+1} \rightarrow 2p^6 3s^1 3d^{n+1}$). The work is based on the measurement of the spectra vs. incident photon energy and integrated over the scattered photon energy. We present data resolved in linear polarization of the scattered beam for scattering at 45° and data summed over the outgoing polarizations and taken vs. the scattering angle ϕ. The results show common features in both metals and ionic system: the dichroism scales as $\sin 2\phi$ while the spectral shape remains constant. The dichroism is maximum when the outgoing linear polarization is in the scattering plane and zero when the outgoing linear polarization is perpendicular to the scattering plane. The presence of the dichroism is due to the breaking of the mirror symmetry of the geometry consisting of the helicity vector of the incident radiation, the sample magnetization and the linear polarization of the scattered beam. This is expected in general when the scattering occurs without rearrangement in the intermediate state. It is noteworthy that this occurs also in the metallic systems, where the scattering takes place with rearrangement due to a spin dependent screening of the intermediate state core hole. This shows that this rearrangement does not require a more complex vector system in its description. The results show the relation between the selection of the scattering angle and the measurement of the polarization of the scattered radiation. We also present results from a geometry where the dichroism is absent in the emission integrated over outgoing polarization but where it is observed when this polarization is selected.

Published in Physical Review B **75**, 184408-1/9 (2007).
Manuscript available from g.vanderlaan@dl.ac.uk.

Element specific investigation of ultrathin $Co_2MnGa/GaAs$ heterostructures

Jill S. Claydon and Sameh Hassan
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Department of Physics, Technical University of Denmark, Lyngby, Denmark
Yongbing B. Xu
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Gerrit van der Laan
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Abstract

We have used x-ray magnetic circular dichroism to study the element specific magnetic properties of ultrathin films of the Heusler alloy Co_2MnGa at room temperature. Nine films were grown by molecular beam epitaxy on GaAs substrates and engineered to vary in stoichiometry as $Co_{1.86}Mn_{0.99}Ga$, $Co_{1.95}Mn_{0.98}Ga$, and $Co_{1.97}Mn_{0.96}Ga$, with thicknesses of 5.3, 7.6, and 9.7 nm, and were capped with Al to prevent oxidization. Sum rule analysis revealed magnetic moments significantly lower than the values predicted theoretically, especially in the case of the Mn total magnetic moment. The results do not support the hypothesis that a large magnetic moment is transferred from Co to Mn, and may suggest that diffusion and reacted layers at ultrathin thicknesses can effect the establishment of a full Heusler structure.

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Theoretical study of isoelectronic $\mathrm{Si_nM}$ clusters (M = Sc^-, Ti, V^+; n=14-18

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Abstract

We study, from first-principles quantum mechanical calculations, the structural and electronic properties of several low-lying energy equilibrium structures of isoelectronic $\mathrm{Si}_n\mathrm{M}$ clusters (M = Sc^-, Ti, V^+) for n=14-18. The main result is that those clusters with n = 16 are more stable than its neighbors, in agreement with recent experimental mass spectra. By analyzing the orbital charge distribution and the partial orbital density of states, that special stability is rationalized as a combination of geometrical (near spherical cage-like structure for n=16) and electronic effects (*l-selection rule* of the spherical potential model). The structures of the two lowest energy isomers of $\mathrm{Si}_{16}\mathrm{M}$ are nearly degenerate, and consist in the Frank-Kasper polyhedrom and a distortion of that polyhedrom. The first structure is the ground state for M=V^+, and the second is the ground state for Ti and Sc^-. For the lowest energy isomers of clusters $\mathrm{Si}_n\mathrm{M}$ with n=14-18, we analyze the changes with size, n, and impurity, M, of several quantities: binding energy, second difference of total energy, HOMO-LUMO gap, adiabatic electron affinity, addition energy of a Si atom, and addition energy of a M impurity to a pure Si_n cluster. We obtain good agreement with available measured adiabatic electron affinities for $\mathrm{Si}_n\mathrm{Ti}$.

(Submitted to Physical Revew B)

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On the accuracy of first-principles lateral interactions: Oxygen at Pd(100)

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Abstract

We employ a first-principles lattice-gas Hamiltonian (LGH) approach to determine the lateral interactions between O atoms adsorbed on the Pd(100) surface. With these interactions we obtain an ordering behavior at low coverages that is in quantitative agreement with experimental data. Uncertainties in our approach arise from the finite LGH expansion and from the approximate exchange-correlation (xc) functional underlying the employed density-functional theory energetics. We carefully scrutinize these uncertainties and conclude that they primarily affect the on-site energy, which rationalizes the agreement with the experimental data. We also investigate the validity of the frequently applied assumption that the ordering energies can be represented by a sum of pair terms. Restricting our LGH expansion to just pairwise lateral interactions, we find that this results in effective interactions which contain spurious contributions that are notably larger than any of the uncertainties e.g. due to the approximate xc functional.

(accepted at: Phys. Rev. B)

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Non-adiabatic Effects in the Dissociation of Oxygen Molecules at the Al(111) Surface

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Abstract

The measured low initial sticking probability of oxygen molecules at the Al(111) surface that had puzzled the field for many years was recently explained in a non-adiabatic picture invoking spin-selection rules [J. Behler *et al.*, Phys. Rev. Lett. **94**, 036104 (2005)]. These selection rules tend to conserve the initial spin-triplet character of the free O_2 molecule during the molecule's approach to the surface. A new locally-constrained density-functional theory approach gave access to the corresponding potential-energy surface (PES) seen by such an impinging spin-triplet molecule and indicated barriers to dissociation which reduce the sticking probability. Here, we further substantiate this non-adiabatic picture by providing a detailed account of the employed approach. Building on the previous work, we focus in particular on inaccuracies in present-day exchange-correlation functionals. Our analysis shows that small quantitative differences in the spin-triplet constrained PES obtained with different gradient-corrected functionals have a noticeable effect on the lowest kinetic energy part of the resulting sticking curve.

(submitted to: Physical Review B)
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Spectral broadening due to long-range Coulomb interactions in the molecular metal TTF-TCNQ

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Abstract

We employ density-functional theory to calculate realistic parameters for an extended Hubbard model of the molecular metal TTF-TCNQ. Considering both intra- and intermolecular screening in the crystal, we confirm the importance of the suspected longer-range Coulomb interactions along the molecular stacks, as well as inter-stack coupling. Contrary to past belief, these terms do not lead to the formation of a Wigner lattice, but simply broaden the spectral function.

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Correlation-Driven Charge Order at a Mott Insulator - Band Insulator Digital Interface

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Abstract

To study digital Mott insulator $LaTiO_3$ and band insulator $SrTiO_3$ interfaces, we apply correlated band theory (LDA+U) to (n,m) multilayers, $1 \leq n, m \leq 9$ using unit cells with larger lateral periodicity. If the on-site repulsion on Ti is big enough to model the Mott insulating behavior of undistorted $LaTiO_3$ the charge imbalance at the interface is found in all cases to be accommodated by disproportionation (Ti^{4+} + Ti^{3+}), charge ordering, and Ti^{3+} d_{xy}-orbital ordering, with antiferromagnetic exchange coupling between the spins in the interface layer. Lattice relaxations lead to conducting behavior by shifting (slightly but importantly) the lower Hubbard band, but the charge and orbital order is robust against relaxation.

(submitted to: Phys. Rev. Lett., (in press))
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Density-functional theory calculations of bare and passivated triangular shaped ZnO nanowires

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Abstract

We employ density functional theory within the generalized-gradient approximation to investigate infinitely long [0001] ZnO nanowires. We report on atomic relaxations, formation energies and electronic structure of bare and hydrogen passivated ZnO wires with triangular cross-sections. We find that surface reconstruction plays an important role in stabilizing the nanowires. We show that the band gap can be tuned by changing the wire diameter and by passivation with hydrogen. While bare and completely passivated wires are semiconducting, wires with intermediate hydrogen passivation exhibit metallic behavior.

(Appl. Phys. Lett., accepted)
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Tuning ferromagnetism in Mn-Zn-O by intrinsic defects

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Abstract

In this work we employ density-functional theory (DFT) within the generalised-gradient approximation (GGA) to study the structural and electronic properties of Mn-Zn-O systems. We investigate the role of vacancies in the bulk phases of Zn-doped Mn_2O_3 and Mn-doped ZnO. We find that Zn incorporation in Mn_2O_3 does not induce ferromagnetic behaviour and therefore cannot be responsible for the observed ferromagnetism in Mn-doped ZnO films. We also show that oxygen vacancies in Mn-doped ZnO favours anti-ferromagnetism, whereas Zn vacancies stabilises ferromagnetic behaviour.

(submitted to Journal of Physics: Condensed Matter)
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8 SCIENTIFIC HIGHLIGHT OF THE MONTH: "Linear-scaling DFT calculations with the CONQUEST code"

Linear-scaling DFT calculations with the CONQUEST code

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Abstract

We outline the main ideas underlying the CONQUEST code for first-principles modelling of systems containing many thousands of atoms, focusing on the algorithms used to achieve linear-scaling of the cpu and memory requirements with number of atoms, and the strategies for implementing the algorithms so as to achieve good parallel scaling on parallel computers. We note that the code can be run at different levels of precision, ranging from empirical tight-binding, through *ab initio* tight-binding, to full *ab initio*. Very recent technical developments implemented in the code are outlined. We give illustrations of physical systems currently being studied with the code, ranging from biologically important molecules to Ge hut clusters on Si (001), including structural relaxation on systems of over 20,000 atoms using electronically self-consistent density-functional theory. Arrangements for obtaining and learning to use the code are also noted.

1 Introduction

It is now over 15 years since the first proposals were made for doing DFT calculations so that the amount of memory and number of cpu cycles needed are proportional to the number of atoms, rather than scaling as N^2 or worse [1–7]. These ideas stimulated a flurry of activity, and in the middle 1990's it was more or less obligatory for every condensed-matter electronic-structure conference to include a section on 'linear-scaling' or '$O(N)$' methods. This activity rather quickly led to efficient practical codes for linear-scaling tight-binding calculations, but it gradually became clear that there were many practical difficulties in achieving the same thing for density functional theory. Not the least of these difficulties was that of making the calculations run efficiently on large parallel computers, so that they scaled linearly not only with the number of atoms but (inversely) with the number of processors. The consequence was that the effort to develop linear-scaling DFT codes died away to rather a low level, and the subject started to disappear from the conference programmes. Nevertheless, the persistent efforts of a few research groups have recently started to bear fruit, so that practical codes for performing DFT calculations on very large complex systems are now becoming available [8–12]. CONQUEST is one of these codes.

We have published many papers over the past 12 years about the principles underlying CONQUEST [8,13–18], so the main purpose of this article is to give an update about recent progress, and particularly about the large-scale practical calculations that are now becoming possible. However, to make the article self-contained, we start by recalling the main ideas. We will then give a summary of how the computational effort is distributed across processors on parallel machines. Then we give some recent practical examples from unpublished or only partially published work, including exploratory calculations on the important enzyme dihydrofolate reductase, and large-scale structural relaxation calculations on Ge/Si hut clusters performed on the Earth Simulator on systems of over 20,000 atoms.

2 Principles of the CONQUEST code

2.1 Theory

The reasons why traditional DFT calculations scale poorly with N are well known. The number of occupied Kohn-Sham orbitals must clearly be proportional to N. But each orbital $\psi_n(\mathbf{r})$ extends over the entire volume of the system, which is also proportional to N. This means that the amount of stored information and the number of operations needed to manipulate it are proportional to N^2. However, all the usual implementations require an operation equivalent to calculating the scalar product $\langle \psi_m | \psi_n \rangle$ of all pairs of occupied orbitals, and the cpu time for this is proportional to N^3. The prefactor is small, but for very large systems this N^3 scaling will dominate. However, Kohn's 'near-sightedness' principle [19] tells us that it should be possible to do much better than this, and that $O(N)$ performance should be achievable. The amount of information stored in an N-atom system is not really proportional to N^2; it is just that the usual manner of doing things incurs an enormous degree of redundancy in the way the information is represented.

With DFT, the near-sightedness principle is expressed by the locality of the Kohn-Sham density matrix $\rho(\mathbf{r}, \mathbf{r}')$. Recall that if the Kohn-Sham occupied orbitals (eigenfunctions of the Kohn-Sham equation) are already known, then $\rho(\mathbf{r}, \mathbf{r}')$ is defined as:

$$\rho(\mathbf{r}, \mathbf{r}') = \sum_n \psi_n(\mathbf{r}) \psi_n(\mathbf{r}')^\star \; . \tag{1}$$

The nearsightedness principle says that there is quantum coherence only between nearby positions, or, more exactly: $\rho(\mathbf{r}, \mathbf{r}') \rightarrow 0$ as $|\mathbf{r} - \mathbf{r}'| \rightarrow \infty$. But the variational principle of DFT can be formulated in terms of the density matrix [7]: the DFT ground state is obtained by minimising the total energy E_{tot} with respect to $\rho(\mathbf{r}, \mathbf{r}')$, subject to the 'weak idempotency' condition that the eigenvalues of ρ should all lie between 0 and 1. Linear scaling is then obtained by minimising E_{tot} with respect to ρ, subject to the constraint that $\rho(\mathbf{r}, \mathbf{r}') = 0$ for $|\mathbf{r} - \mathbf{r}'| > r_c$, where r_c is a chosen cut-off distance. The amount of information stored in $\rho(\mathbf{r}, \mathbf{r}')$ is then manifestly $O(N)$. These ideas are implemented in CONQUEST, with the additional constraint that $\rho(\mathbf{r}, \mathbf{r}')$ be 'separable' (the number of its non-zero eigenvalues is finite), so that:

$$\rho(\mathbf{r}, \mathbf{r}') = \sum_{i\alpha, j\beta} \phi_{i\alpha}(\mathbf{r}) K_{i\alpha, j\beta} \phi_{j\beta}(\mathbf{r}') \; . \tag{2}$$

The functions $\phi_{i\alpha}(\mathbf{r})$, which we refer to as 'support functions', are chosen to be non-zero only within spherical regions of radius R_{reg} centred on the atoms ($\phi_{i\alpha}(\mathbf{r})$ is the αth support function on atom i). Effectively, the matrix $K_{i\alpha, j\beta}$ is the density matrix in the (non-orthogonal) basis of support functions.

In practice, then, the idea is to express the total energy in terms of the density matrix given by eqn (2), and to minimise it with respect to the K-matrix and the $\phi_{i\alpha}(\mathbf{r})$ support functions, subject to the conditions of (i) weak idempotency, and (ii) constant electron number. In doing this, the support functions should in principle be freely varied within their spherical regions, and for this purpose they need to be represented in terms of some chosen basis functions. Before discussing that, though, we address the more difficult question of how to ensure weak idempotency. It goes without saying that we are not allowed to diagonalise the density matrix, because that would be an $O(N^3)$ operation, and we would have achieved nothing. There are several ways of enforcing weak idempotency, but the present implementation in CONQUEST is a combination of the technique of Li, Nunes and Vanderbilt (LNV) [33] and Palser and Manolopoulos [34], both of which are related to McWeeny's 'purification' scheme [35]. In the LNV technique, the matrix K is represented in terms of an 'auxiliary' density matrix L as:

$$K = 3LSL - 2LSLSL \; , \tag{3}$$

where S is the overlap matrix of support functions: $S_{i\alpha,j\beta} = \langle \phi_{i\alpha} | \phi_{j\beta} \rangle$. In order to ensure $O(N)$ scaling, a spatial cut-off is imposed on the L-matrix, so that $L_{i\alpha,j\beta} = 0$ when the distance between atoms and i and j exceeds a chosen cut-off R_L. Alternative methods for enforcing weak idempotency could, of course, also be used.

In order to obtain a scheme that is equivalent to standard DFT, we must allow the support functions $\phi_{i\alpha}(\mathbf{r})$ to be freely varied within their spherical regions. This means that they must be represented in terms of some basis set. We have two completely different ways of doing this in CONQUEST, and which basis set one chooses depends on what one is trying to achieve. If plane-wave precision is desired, then it is essential to use a basis set that is in some sense equivalent to plane waves. The obvious difficulty is that the support functions are localised, so if one literally uses plane waves, then it is undesirable that they should extend over the entire system. The solution we have adopted is to use a finite-element basis that is quite closely equivalent to plane waves. (It is interesting here to compare with the plane-wave methods that have been used to solve this same problem in the ONETEP CODE [10].) On the other hand, if plane-wave precision is not needed, the other option on CONQUEST is to use numerical pseudo-atomic orbitals, as is done in some other codes, notably SIESTA [9, 29] and PLATO [39, 40].

The finite-element scheme we use to obtain plane-wave precision represents the $\phi_{i\alpha}(\mathbf{r})$ in terms of piecewise continuous polynomials, using a technique sometimes referred to as B-splines. Full details of the scheme, with demonstrations of its effectiveness, are presented in a published report [20], so here we give only a brief summary. Suppose first that we have a continuous function $f(x)$ in one dimension, which we wish to represent. The B-spline basis consists of localised functions $\theta_s(x)$, centred on the points of a grid, whose nodes are at positions $X_s = sa$, where a is the grid spacing. The basis functions are all images of each other, displaced by an integer number of grid spacings, so that $\theta_s(x) = \theta_0(x - X_s)$. The basis function $\theta_0(x)$ vanishes identically outside the range $-2a < x < 2a$. Inside this range, it is assembled from cubic polynomials:

$$\theta_0(x) = \begin{cases} 1 - \frac{3}{2}(x/a)^2 + \frac{3}{4}|x/a|^3 & \text{if} \quad 0 < |x| < a \\ \frac{1}{4}(2 - |x|/a)^3 & \text{if} \quad a < |x| < 2a \\ 0 & \text{if} \quad 2a < |x| \end{cases} \tag{4}$$

and has the property that it and its first two derivatives are continuous everywhere. In fact, the only discontinuities are in the third derivative at the points $|x| = 0$, a and $2a$. The representation of a continuous function

$$f(x) \simeq \sum_s b_s \theta_s(x) \tag{5}$$

can be made arbitrarily precise by systematically reducing the grid spacing a. This is exactly analogous to increasing the plane-wave cut-off $G_{\max}$ when taking a plane-wave calculations to convergence.

In fact, there is a close relationship between B-spline and plane-wave basis sets. The $\theta_s(x)$ basis functions can be used to form Bloch-like functions $\chi_k(x)$ by the unitary transformation:

$$\chi_k(x) = \sum_s e^{ikX_s} \theta_s(x) \ . \tag{6}$$

To obtain the full set of distinct χ_k functions, k should be restricted to the range $-\pi/a < k < \pi/a$. As $|k| \to 0$, the functions become identical to plane waves, and in fact they rather precisely reproduce plane waves except near the ends of the interval $(-\pi/a, \pi/a)$. This means that B-splines with grid spacing a are nearly equivalent to plane waves with cut-off $G_{\mathrm{max}} = \pi/a$.

In practice, of course, we work in three dimensions, and the three-dimensional B-splines $\Theta_s(\mathbf{r})$ are defined as Cartesian products:

$$\Theta(\mathbf{r} - \mathbf{R}_s) = \theta(x - X_s)\theta(y - Y_s)\theta(z - Z_s) \ , \tag{7}$$

where (X_s, Y_s, Z_s) are the Cartesian components of $\mathbf{R}_s$, and the support functions are represented as:

$$\phi_{i\alpha}(\mathbf{r}) = \sum_s b_{i\alpha s} \Theta_s(\mathbf{r} - \mathbf{R}_{is}) \ . \tag{8}$$

In the current scheme, the blip-grid on which the $\Theta_s(\mathbf{r})$ are sited is defined separately for each atom, and moves with that atom. To enforce the vanishing of $\phi_{i\alpha}(\mathbf{r})$ outside the support region, we include in eqn (8) only those $\Theta_s(\mathbf{r})$ that are non-zero only for points within the region. The reason for making the blip-grid move with the atom is that this ensures that each $\phi_{i\alpha}(\mathbf{r})$ is represented always in terms of the same set of basis functions.

Blip functions therefore give us a scheme that is closely related to plane waves, but at the same time respects the strict localisation of the support functions. It also shares another feature with plane waves, and that is that as the blip spacing is decreased, the computational effort grows linearly only with the number of blip functions. This is because the number of blip functions that are non-zero at each point in space does not increase as a decreases.

The alternative basis set of numerical pseudo-atomic orbitals provided in CONQUEST is similar in spirit to the ones used in the SIESTA [9, 29] and PLATO [39, 40] codes.

2.2 Implementation

In CONQUEST, the search for the ground-state is organised into three loops. In the innermost loop, the support functions and electron density are fixed and the ground-state density matrix is found, either by varying L or by diagonalisation. In the middle loop, self-consistency is achieved by systematically reducing the electron-density residual, i.e. the difference between the input and output density in a given self-consistency cycle. In the outer loop, the energy is minimised with respect to the support functions, $\phi_{i\alpha}$. This organisation corresponds to a hierarchy of approximations: when the inner loop alone is used, we get the scheme known as non-self-consistent *ab initio* tight binding (NSC-AITB), which is a form of the Harris-Foulkes approximation [22–25]; when the inner two loops are used, we get self-consistent *ab initio* tight binding (SC-AITB); finally, if all loops are used, we have full *ab initio*. In this last case, we recover the exact DFT ground state as the region radius R_{reg} and the L-matrix cut-off R_L are increased. For non-metallic systems, the evidence so far is that accurate approximations to the ground state are obtained with quite modest values of the cut-offs [9, 13]. For the non-self-consistent ground-state search of the inner loop, as well as operating in $O(N)$ mode, CONQUEST can find the ground state directly by diagonalisation, using the SCALAPACK package, which allows efficient parallelisation of the diagonalisation. Since this scales as $O(N^3)$, this will only be appropriate for relatively small systems, but it provides an important tool for testing the outer parts of the ground-state search, and for exploring the convergence of the $O(N)$ algorithm with the cut-off on the L-matrix.

For calculations at the level of full *ab initio* accuracy, the convergence of the outer loop (optimising the support functions with respect to their basis functions) is well-conditioned provided appropriate pre-conditioning measures are taken; these have been discussed both for blips in the context of CONQUEST [26, 27] and for psinc functions in the context of ONETEP [28]. We note that CONQUEST can be run in a mode analagous to SIESTA, where pseudo-atomic orbitals are used and no optimisation is performed; in this case, the outer loop is not performed.

We have recently found that the self-consistency search (the middle loop described above) can be accelerated by use of the Kerker preconditioning. This idea, which is well-known in the plane-wave community, removes long wavelength changes in the charge density during mixing. It is applied in reciprocal space, as a prefactor:

$$f(q) = \frac{q^2}{q^2 + q_0^2} \tag{9}$$

Then the charge is mixed using a Pulay or Broyden (or related) scheme [21] with the prefactor applied to the residual or output charge after transformation to reciprocal space. The mixing includes a parameter, A, which determines how aggressive the mixing is (with the input charge density for iteration $n + 1$ given by $\rho_{in}^{n+1} = \rho_{in}^{n} + Af(q)R_n$, with R_n the residual from iteration n).

While performing the search for self-consistency, we must monitor the residual. We define the following dimensionless parameter which is used to monitor the search:

$$d = \frac{\langle |R(\mathbf{r})|^2 \rangle^{1/2}}{\bar{\rho}}, \tag{10}$$

$$\langle |R(\mathbf{r})|^2 \rangle = \frac{1}{V} \int \mathrm{d}\mathbf{r}\, |R(\mathbf{r})|^2 \,, \tag{11}$$

where V is the simulation cell volume and we use the usual definition of residual, $R(\mathbf{r}) = \rho_{\mathrm{out}}(\mathbf{r}) - \rho_{\mathrm{in}}(\mathbf{r})$, the difference between the output and input charge densities. The quantity d is then the RMS value of $R(\mathbf{r})$ normalised by dividing by the *average* charge density in the system, $\bar{\rho}$. Note that, for systems containing large amounts of vacuum, the criterion for convergence will need to be altered when compared to bulk-like environments. This criterion may be coupled with a monitor on the largest value of residual on an individual grid point $\mathbf{r}_l$, $R_{\mathrm{max}} = \max_l |R(\mathbf{r}_l)|$

The scheme we have outlined is closely related to the methods used in SIESTA [9, 29], OpenMX [11] and ONETEP [10]. The main differences are: (i) the basis sets chosen (SIESTA uses fixed PAOs, while OpenMX uses optimized orbitals and ONETEP psinc functions); (ii) the method of finding the ground state density matrix (Siesta uses the constrained search technique [3–5], OpenMX the divide-and-conquer [30] or BOP [31] and ONETEP either penalty functional [19, 32] or LNV [33]); (iii) the technique of 'neutral-atom potentials' [9, 29], used by SIESTA and OpenMX, which allows calculation of matrix elements to be performed very efficiently for localised, atomic-like basis sets.

2.3 Forces on the ions

In order to perform structural relaxation or molecular dynamics of materials with an electronic structure technique, the algorithms for calculating the forces $\mathbf{F}_i$ on the ions must be the exact derivatives of the total ground state energy, E_{GS}, with respect to the positions, $\mathbf{r}_i$, such that $\mathbf{F}_i = -\nabla_i E_{\mathrm{GS}}$. One of the advantages of DFT, within the pseudopotential approximation, is that it is easy, in principle, to achieve this relationship between the forces and the energy. Since the CONQUEST formalism allows the calculation of the total energy at different levels of accuracy, some care is needed in the formulation of the forces to develop a scheme that works at all levels of this hierarchy. It is also important to ensure that it works equally well (and accurately) for both the diagonalisation and $\mathcal{O}(N)$ modes of operation implemented in CONQUEST.

We recall the Harris-Foulkes expression [22, 23] for the total energy, which is often applied when self-consistency is not sought, but which at self-consistency is identical to the standard Kohn-Sham expression for total energy. The expression is:

$$E_{\mathrm{GS}} = E_{\mathrm{BS}} + \Delta E_{\mathrm{Har}} + \Delta E_{\mathrm{xc}} + E_{\mathrm{C}}, \tag{12}$$

with E_{C} the Coulomb energy between the ionic cores, and the band-structure energy, the double-counting Hartree and exchange-correlation energies defined as:

$$\begin{aligned}
E_{\mathrm{BS}} &= 2\sum_n f_n \epsilon_n && (13)\\
&= 2\mathrm{Tr}[KH] && (14)\\
\Delta E_{\mathrm{Har}} &= -\frac{1}{2}\int d\mathbf{r}\, n^{\mathrm{in}}(\mathbf{r}) V_{\mathrm{Har}}^{\mathrm{in}}(\mathbf{r}) &&\\
\Delta E_{\mathrm{xc}} &= \int d\mathbf{r}\, n^{\mathrm{in}}(\mathbf{r}) \left(\epsilon_{\mathrm{xc}}(n^{\mathrm{in}}(\mathbf{r})) - \mu_{\mathrm{xc}}(n^{\mathrm{in}}(\mathbf{r}))\right) . && (15)
\end{aligned}$$

Here, $n^{\mathrm{in}}(\mathbf{r})$ is the *input* charge density used (normally a superposition of atomic charge densities if a non-self-consistent scheme is used, or the self-consistent charge density if self-consistency is used). This expression is very useful when comparing forces at different levels of approximation.

At the empirical TB level, the ionic force is a sum of the band-structure part $\mathbf{F}_i^{\mathrm{BS}}$ and the pair-potential part $\mathbf{F}_i^{\mathrm{pair}}$, the former being given by [24]:

$$\mathbf{F}_i^{\mathrm{BS}} = -2\mathrm{Tr}\left[K\nabla_i H - J\nabla_i S\right] , \tag{16}$$

where K and J are the density matrix and energy matrix respectively [24]. It is readily shown that in the $\mathcal{O}(N)$ scheme of LNV, and in some other $\mathcal{O}(N)$ schemes, the same formula for $\mathbf{F}_i^{\mathrm{BS}}$ is the exact derivative of the $\mathcal{O}(N)$ total energy.

In NSC-AITB (Harris-Foulkes), the forces can be written in two equivalent ways. The way that corresponds most closely to empirical TB is:

$$\mathbf{F}_i = \mathbf{F}_i^{\mathrm{BS}} + \mathbf{F}_i^{\Delta\mathrm{Har}} + \mathbf{F}_i^{\Delta\mathrm{xc}} + \mathbf{F}_i^{\mathrm{ion}} , \tag{17}$$

where $\mathbf{F}_i^{\mathrm{BS}}$ is given by exactly the same formula as in empirical TB. The contributions $\mathbf{F}_i^{\Delta\mathrm{Har}}$ and $\mathbf{F}_i^{\Delta\mathrm{xc}}$, which arise from the double-counting Hartree and exchange-correlation parts of the NSC-AITB total energy, have been discussed elsewhere [24]. The final term $\mathbf{F}_i^{\mathrm{ion}}$ come from the ion-ion Coulomb energy. This way of writing $\mathbf{F}_i$ expresses the well-known relationship between NSC-AITB and empirical TB that in the latter the pair term represents the sum of the three contributions $\Delta\mathrm{Har} + \Delta\mathrm{xc} + \mathrm{ion} - \mathrm{ion}$. The alternative, and exactly equivalent, way of writing $\mathbf{F}_i$ in NSC-AITB is:

$$\mathbf{F}_i = \mathbf{F}_i^{\mathrm{ps}} + \mathbf{F}_i^{\mathrm{Pulay}} + \mathbf{F}_i^{\mathrm{NSC}} + \mathbf{F}_i^{\mathrm{ion}} . \tag{18}$$

Here, $\mathbf{F}_i^{\mathrm{ps}}$ is the "Hellmann-Feynman" force exerted by the valence electrons on the ion cores; $\mathbf{F}_i^{\mathrm{Pulay}}$ is the Pulay force that arises in any method where the basis set depends on ionic positions; $\mathbf{F}_i^{\mathrm{NSC}}$ is a force contribution associated with non-self-consistency, and is expressed in terms of the difference between output and input electron densities; $\mathbf{F}_i^{\mathrm{ion}}$, as before, is the ion-ion Coulomb force. Exactly the same formulas represent the exact derivative of E_{tot} in both diagonalisation and $\mathcal{O}(N)$ modes.

In both SC-AITB and full AI, the force formula is:

$$\mathbf{F}_i = \mathbf{F}_i^{\mathrm{ps}} + \mathbf{F}_i^{\mathrm{Pulay}} + \mathbf{F}_i^{\mathrm{ion}} , \tag{19}$$

which differs from the second version of the NSC-AITB formula eqn (18) only by the absence of the non-self- consistent contribution $\mathbf{F}_i^{\mathrm{NSC}}$, as expected.

The above hierarchy of force formulas has been implemented in CONQUEST, and extensive tests have ensured that the total energy and the forces are exactly consistent within rounding-error precision [17].

2.4 Parallel operation

The principle of near-sightedness and the idea of parallel computation fit each other as a glove fits a hand. Since different regions of space are independent of each other as far as quantum coherence is concerned, there is a natural mapping of $O(N)$ calculations onto an array of processors. CONQUEST was written from the outset as parallel code, and a large part of the development effort has been concerned with techniques for achieving good parallel scaling. The parallelisation techniques have been described in detail elsewhere [8, 14, 36], so we give only a brief summary. There are three main types of operation that must be distributed across processors:

- the storage and manipulation of support functions, e.g. the calculation of $\phi_{i\alpha}(\mathbf{r})$ on the integration grid starting from blip- or PAO-coefficients, and the calculation of the derivatives of E_{tot} with respect to these coefficients, which are needed for the ground-state search;
- the storage and manipulation of elements of the various matrices (H, S, K, L, etc...);
- the calculation of matrix elements by summation over domains of points on the integration grid, or by analytic operations (for certain integrals involving PAOs and blips).

Efficient parallelisation of these operations, and the elimination of unnecessary communication between processors, depend heavily on the organisation of both atoms and grid points into small compact sets, which are assigned to processors [36]. When the code runs in $\mathcal{O}(N)$ mode, matrix multiplication takes a large part of the computer effort, and we have developed parallel multiplication techniques [36] that exploit the specific patterns of sparsity on which $\mathcal{O}(N)$ operation depends.

2.5 Recent technical progress

The implementation outlined above was already in place, and the practical $O(N)$ performance of the code was demonstrated several years ago. However, until fairly recently the range of systems to which the code could easily be applied was rather limited. However, in the past two years we have greatly enhanced its functionality and ease of use, in preparation for public release later this year. We have now standardized the pseudopotentials used in the code on the Troullier-Martins form [37]. The reason for this choice is that these pseudpotentials are used in a number of plane-wave/pseudopotential codes, such as ABINIT [38]. This makes it rather convenient to cross-check CONQUEST results against standard plane-wave calculations. If one chooses to use PAO basis sets in CONQUEST, it is necessary to generate the PAO's using the standard pseudopotentials. The code for doing this has been adapted from the PLATO code [39, 40]

Any practical DFT code needs to be able to use a range of available exchange-correlation functionals. To make this possible, we have recently implemented the PBE form of generalized-gradient approximation (GGA) [41], with PW92 parameterization [42] for the local part. The gradient calculations are done following the scheme of White and Bird [43], which is formally exact on a grid, and involves the computational of only four Fast Fourier Transforms (FFT's). The linearity of the scheme preserves $O(N)$ operation. In order to keep the ability of the code to perform structural relaxation with non-self-consistent Harris-Foulkes calculations, the original computation of forces had to be adapted to the newly implemented GGA functional. As we will report elsewhere [44], we are able to maintain the condition that the forces are exact derivatives of the total energy, and the number of FFT's remains equal to four.

We mentioned above that the division of atoms and grid points into compact groups is important in achieving good parallel efficiency. The way this was done in early versions of the code is summarised above. However, those methods turned out to be inefficient for problems in which a significant part of the system consists of empty space – a common situation when dealing with surface problems. We have now been able to develop more sophisticated procedures, which significantly improve the efficiency.

In applications of nano-devices, a crucial physical effect is often the transport of electrons, and the exchange of energy between the ionic and electronic sub-systems. These are effects that are not included in conventional first-principles molecular dynamics (m.d.) techniques, which explicitly or implicitly enforce the Born-Oppenheimer approximation, that the electronic sub-system adiabatically follows the motion of the ions. Recently, an important extension of m.d. has been developed, known as "correlated electron-ion dynamics" (CEID) [45], in which the quantum spread of the ions is included *via* a small-amplitude moment expansion. With CEID, it is possible to make direct numerical simulations of, for example, inelastic current-voltage spectroscopy in atomic wires. An ambition for the future is to implement CEID within the CONQUEST code, and we are currently formulating the strategies needed to do this.

3 Technical tests

Much of the hard work involved in developing any large code goes into demonstrating that it really achieves what it is intended to achieve, that it is reasonably robust, and that it runs efficiently on appropriate platforms. In the case of a linear-scaling DFT code like CONQUEST, the issues that must be addressed include the following: (i) does the code actually achieve parallel scaling with respect to the number of atoms? (ii) does it achieve good parallel scaling on parallel computers, and at what typical numbers of processors does the quality of the scaling start to deteriorate? (iii) if we go to basis-set convergence, and if we go to the limit of large support-region radius R_{reg} and large L-matrix cut-off, does it recover standard plane-wave results (using the same pseudopotentials, obviously)? (iv) how rapid is the convergence with respect to R_{reg} and R_L? (v) how rapid is the ground-state search for large systems? (vi) how rapid is the search for self-consistency for large systems? (vii) how rapid is structural relaxation for large systems?

The issue of scaling with respect to number of atoms and number of processors on large parallel computers was studied already 10 years ago, when we demonstrated excellent scaling of both kinds on systems of up to $\sim 15,000$ atoms using computers having up to ~ 512 processors [14]. More recently, we have done extensive tests on the Earth simulator, the results of which will be published soon. We have also presented the results of test on convergence with respect to R_{reg} and R_L. As an illustration of the search for self-consistency, we show in Fig. 1 the decrease of the self-consistency residual as a function of iteration number for an amorphous Si cluster of 343 atoms, which was specifically designed as a challenge to self consistency, because it is close to being metallic. The results show rather rapid monotonic convergence to self consistency, and generally we find similar behaviour also for much larger systems. As an illustration of the ground-state search for very large systems, we show in Fig. 2 the deviation of the energy from the exact ground-state value as a function of iteration number for a 23,000-atom Ge hut cluster on Si (001) (see below for more details of this system). For fuller discussion of the many other technical issues referred to above, our published papers should be consulted.

4 Scientific applications

In the immediate future, we expect the most important applications of CONQUEST to be in the area of biomolecular systems and nano-systems (there are, of course, close links between the two types of systems). In all cases, it is clearly essential to build up experience with $O(N)$ methods, starting with relatively small systems, where we can cross-check against the results of more standard codes. For nano-systems, we started this learning process with simple tests on semiconductor surfaces [17], and we are now making exploratory calculations on much larger and more complex systems. For biomolecules, we are still at the stage of tests on systems of a few hundred atoms.

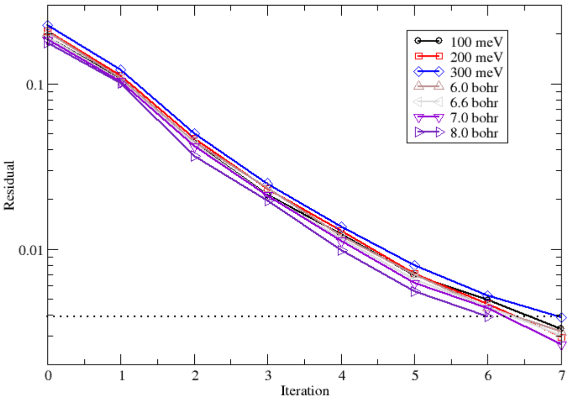

Figure 1: Residual during self-consistency search for different R_{reg}. System treated is an amorphous Si cluster (see text).

In preparation for large-scale calculations on DNA systems, we are currently making extensive tests with CONQUEST on single DNA bases and on DNA base pairs, and comparing with results obtained with other codes, including SIESTA, VASP and GAUSSIAN. As expected, we find excellent agreement for the equilibrium bond lengths of covalently bonded atoms. Results of these tests will be published in the near future [46].

We are also performing tests on the important enzyme dihydrofolate reductase (DHFR), whose function in living organisms is to catalyze the reduction of dihydrofolate to produce tetrahydrofolate. The latter is an important molecule in metabolism. In particular, it is an essential cofactor in one-carbon transfer reactions. As a consequence, DHFR, which is the only enzyme that synthesizes it, has receive much attention, for example as a target for anti-malarial drugs. Although the specific substrate for DHFR is dihydrofolate (DHF), in some species the enzyme also catalyzes, very inefficiently and less specifically, the reduction of folate, a precursor of DHF.

The reasons why DHFR is specific for DHF remain unclear. LDA DFT calculations of the active site suggested that enzyme-induced polarization of the substrates may be a cause for the preference, at least in the *Escherichia coli* enzyme. Indeed, one study [47] found large electron density differences (EDD) between the density of DHF when bound to the enzyme with respect to that in vacuum. However, results from MP2 calculations, although qualitatively supportive for a role of polarization, are less conclusive [48, 49].

All existing studies used a point-charge model for the bulk protein, restricting the quantum mechanical (QM) calculations to a few atoms at the active site. Hence, the quantitative discrepances between different studies may be due to that limitation of the models, rather than to the different QM methods employed. Since DHFR is a relatively small protein (159 amino acids in *Escherichia coli*, or about 3000 atoms), we decided to assess such posibility by using Conquest to perform LDA DFT calculations in extended models of the active site, with the ultimate goal of including the whole of the protein. Thus, we did not model bulk protein in any way, since its effect was expected to become obvious as the size of the model increased.

Our preliminary results on portions of the protein of up to 300 atoms show that indeed larger models are quantitatively closer to MP2 results than to the original LDA calculations. We found larger polarization on DHF than on folate, and only DHF displayed polarization on the bond susceptible of hydrogenation, consistent with the observed specificity (see Fig. 3). Furthermore, calculations on different conformations of the protein agree with experimental evidence regarding the mechanism.

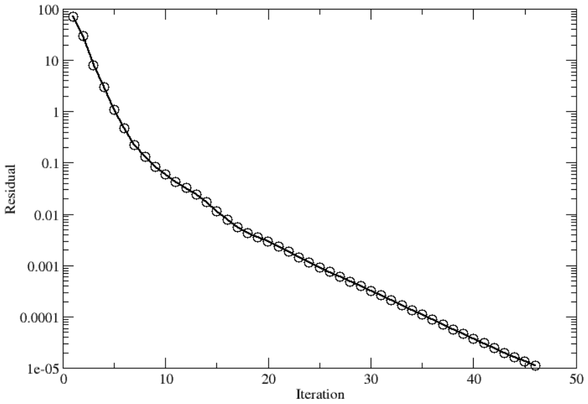

Figure 2: Convergence during energy minimisation with respect to density matrix elements (inner loop of ground-state search) for 23,000-atom Ge hut cluster on Si (001).

In particular, the presence of some amino acids of the so-called Met20 loop seems to be essential for catalysis, as represented by polarization on the hydrogenable bond of the substrate. Moreover, those amino acids must be occluding the active site for polarization to be observed, as expected in the proposed mechanism [50].

Turning now to the application of CONQUEST to nano-systems, we summarise our recent progress in investigating the three-dimensional (3D) structures formed when Ge is deposited on the Si (001) surface. The Ge/Si (001) has been extensively studied, because it is a prototypical example of hetero-epitaxial Stranski-Krastanov growth. When Ge atoms are deposited on Si (001), growth initially occurs layer by layer, up to a critical thickness of about three monolayers (ML). Strain due to the lattice mismatch is relieved by the formation of regularly spaced rows of dimer vacancies in the two-dimensional (2D) structure, resulting in the $2 \times N$ structure. Deposition of further Ge leads to another strain-relief structure, 3D pyramid-like structures known as "hut clusters" [51]. Recently, we have studied this transition from 2D to 3D structures, using CONQUEST.

Usually, the stability of 3D structures is governed by (i) the lowering of strain energy in the clusters and the underlying substrate, and (ii) the energy increase arising from the formation of facets. Theoretical approaches used so far have used continuum elasticity theory to describe the strain energy, with DFT being used only for the surface energies [52, 53]. For the Ge/Si system, the four facets of the hut cluster are well established to be $\{105\}$ surfaces, and the structure of these surfaces has recently been clarified by DFT calculations [54, 55]. Note that the typical side-length of hut clusters is about 150 Å, and deposition of additional Ge leads to the formation of other 3D structures called "domes", having steeper facets. Interestingly and importantly, the DFT calculations show that the strained Ge (105) surface is more stable than strained Ge (001). This means that the surface energy may actually *stabilise* the structure. If the surface contribution to the overall energy is small or favours the 3D structure, contributions from the edges where the facets meet each other and the wetting layer may also affect the stability of the 3D structure. In addition, as the area of the facets of the experimentally observed Ge hut cluster is not large, the evaluation of the surface part itself is doubtful. For these reasons, the validity of previous theoretical approaches is uncertain, especially for small hut clusters. To overcome these problems, we are using CONQUEST to model the entire hut cluster, together with the wetting layer and the Si substrate.

In preparation for CONQUEST calculations on the full system, we first performed DFT calculations on the Ge (105) surface, including test calculations also on the unstrained and strained Ge

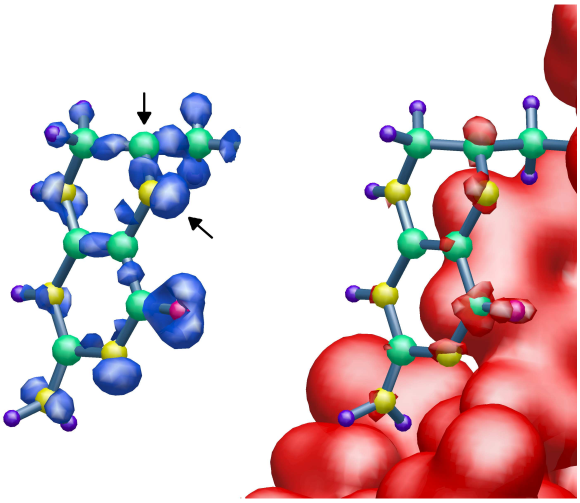

Figure 3: Electronic density difference plot for dihydrofolate (DHF) upon binding to the enzyme dihydrofolate reductase (± 0.001 electron/bohr). Charge deficiency (with respect to the density of DHF in vacuum) is shown in blue; charge excess is red. The enzyme induces polarization on N5 and C6 atoms (marked with arrows), and electronic density withdrawal from the bond linking them. These effects are consistent with the catalyzed reaction, namely, protonation of N and hydride transfer to the bond, and are much weaker for the very inefficient reduction of folate, a secondary substrate (not shown).

bulk [56]. Since the size of this system is relatively small, we can employ diagonalisation in this case. We have clarified the accuracy of the various DFT methods explained above for the unstrained and strained Ge systems. We have also confirmed that full DFT calculations performed with CONQUEST using cubic-spline basis sets are accurate enough for the study of the strained Ge (105) surface. The conditions need for $O(N)$ calculations to achieve good accuracy for this system have also been established.

Using these results, we have performed $O(N)$ DFT calculations on the entire Ge/Si (001) hut clusters. At the non-self-consistent level, we have performed structual optimisation on systems of different sizes. The largest system treated so far, shown in Fig. 4, contains ~ 23000 atoms, and we found that structure optimisation is robust even for such large systems. We have examined three structural models of the Ge hut cluster having different facet or edge structures, and we have compared their energies with those of the $2 \times N$ reconstructions with $N = 4$, 6 and 8. The results, to be reported in detail elsewhere [56,57], show that the 2D structure is more stable for small coverages of Ge atoms, but the 3D hut structure becomes more stable when the coverage exceeds 2.6 monolayers, in agreement with experimental observation.

5 Distribution of the CONQUEST code

We plan that the CONQUEST code will be released under a GNU General Public License by the end of 2007. At the time of writing (end of May 2007), we are in the beta-testing phase, and the code has been released to a small set of carefully chosen users, who will work with us to apply the code to their own scientific problems. A short tutorial course on the practical use of CONQUEST will be held at CECAM $7-8$ September 2007, and there is funding to support the attendance of participants. For more details, please go to `www.cecam.fr` and click on ‘tutorials’.

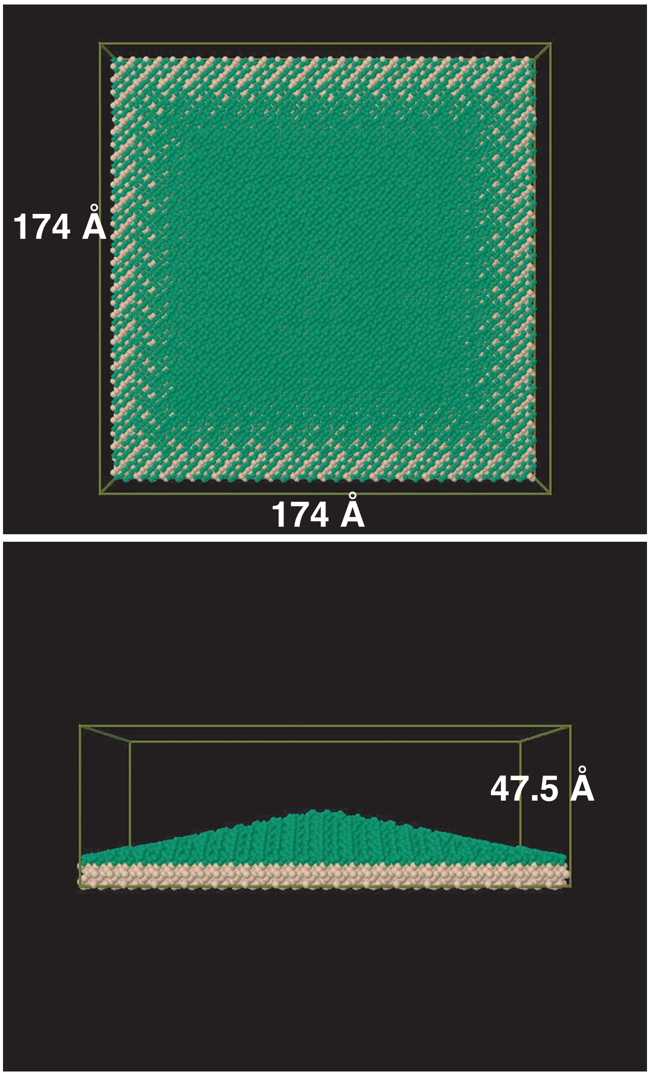

Figure 4: Atomic geometry of largest Ge/Si (001) hut cluster used for structural relaxation with CONQUEST DFT calculations. Upper and lower panels shows plan and side views, respectively. Pink and green spheres represent Si and Ge atoms. Dimensions of periodically repeated cell in surface plane and normal to surface are marked.

6 Summary

The main ideas underlying linear-scaling DFT were established in the early 1990's. However, the realisation of these ideas in practical codes has required the solution of a large number of technical problems concerning basis sets, the enforcement of linear scaling in the calculation of the ground-state density matrix, efficient manipulation of sparse matrices having the patterns of sparsity associated with spatial locality in three dimensions, and implementation of the algorithms on large parallel computers. Some of these problems admit of more than one solution, and the codes that have appeared so far, including CONQUEST, SIESTA, ONETEP and OPEN-MX, differ in important ways. We have tried to show here how the CONQUEST code has now passed beyond the stage of feasibility studies, and can now be applied to real scientific problems concerning biomolecular and nanoscale systems. Comparisons with the results of standard codes for relatively small systems of a few hundred atoms are demonstrating the realibility of the methods. At the same time, it is clear that structural relaxation at different levels of precision, using both self-consistent and non-self-consistent calculations, is becoming a practical proposition for systems containing more than 20,000 atoms.

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