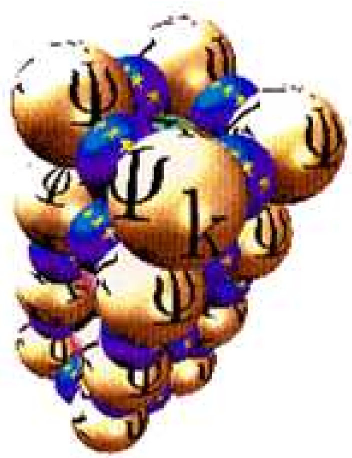
Ψ_k Newsletter

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

Number 91 February 2009



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Sponsored by: UK's CCP9
and Psi-k

Contents

1 Editorial

In this first Psi-k Newsletter of 2009 we repeat information on the Psi-k Portal and in particular how to receive and distribute the Psi-k related information to the whole Psi-k community. In addition we remind our readers of uploading complete reports on the Psi-k workshps and other meetings to the Psi-k Resources on the Portal.

As usual, this newsletter contains job and workshop announcements, workshop reports, and abstracts of newly submitted or recently published papers. In addition, in this issue we also have some information on the Atomisticx Toolkit for those who know of it or might be interested in.

The scientific highlight article of this issue is by James R. Chelikowsky (Austin) and Yousef Saad (Minneapolis) on "Using Chebyshev-Filtered Subspace Iteration Methods to Solve the Kohn-Sham Problem"

For further details, please check the table of content.

The *Uniform Resource Locator* (URL) for the Psi-k webpage is:

http://www.psi-k.org.uk/

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

The email address for contacting us and for submitting contributions to the Psi-k newsletters is

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

Dzidka Szotek, Martin Lüders and Walter Temmerman

2 General News

2.1 Uploading Information to Psi-k Portal

Psi-k Portal

As already mentioned in the past newsletters, the Psi-k Portal is the only means for distributing and receiving Psi-k related information. We do not advise using 'Mailtool' facility on the Portal, as it does not allow to store the distributed information on the Psi-k Portal in the Psi-k Announcements' pool. Thus it cannot be seen by anybody who chooses to check for the new announcements on the Portal.

Since uploading information to the Psi-k Portal seems to give problems to some users, below we repeat the steps one needs to follow to successfuly upload e. g. an announcement to the Psi-k Announcements folder and have it distributed by e-mail to all the Portal members.

1. **'Login to Psi-k Portal'**, accessed from http://www.psi-k.org, by clicking on the former while on the Psi-k web page
2. While already on the Psi-k Portal click on **'Psi-k Announcements'**
3. Click on **'Add'** to get a window for uploading an announcement and then fill in all the required fields
4. Hyperlinks have to be added to any URLs of the web pages ocurring in the body of the announcement by clicking on the option above the main text window, which looks like **'binnacles on a blue ball'** and typing the URL into the subsequently opened field
5. **Add Attachements**, if any, by pressing this option
6. When all is typed and filled, then press **'Preview'** to see if all looks right
7. If yes, then for **'Email Notification'** choose **'High - All Participants'**
8. **Don't do** anything about 'Access' or 'Availability' please, and leave them as they are by default
9. Press **'Add Announcement'**, and all is done.

2.2 Uploading Reports on Workshops and Other Events to Psi-k Portal

It has been our long-term practice to publish in the Psi-k Newsletters reports on all workshops/meetings supported by the Psi-k Network. They have consisted of a short summary, a programme, list of participants and abstracts of presented papers. Unfortunately, as the number of yearly events has increased with time, the reports have become longer, leading to newsletters often approaching 200 A4 pages.

With the introduction of the Psi-k Portal, we have opted for shorter reports (without abstracts) published in the newsletters, while asking the events' organizers to upload the complete reports (including abstracts), in the pdf-format, to the Psi-k Portal.

Hereby, we would like to remind all the organizers of the events supported by the Psi-k Network to submit short reports (consisting of short summary, programme and list of participants), in the latex format, by e-mail to

psik-coord@dl.ac.uk,

to be published in the Psi-k newsletter, subsequent to the event, and to upload complete reports (with abstracts of presented papers), in the pdf-format, to the 'Psi-k Repository' on the Psi-k Portal.

All the reports are stored in the Repository for an easy access if anybody is interested to read also the abstracts of papers presented at a given event.

The Psi-k Portal is accessed from the Psi-k Network webpage

http://www.psi-k.org

by choosing the option **'Login to Psi-k Portal'**.

3 Psi-k Activities

”Towards Atomistic Materials Design”

3.1 Psi-k Workshop Announcements

3.1.1 Workshop on Catalysis from First-principles

Wien, May 25-28, 2009

The Ψ_k-Working Group ”Catalysis and Surface Science” organizes a biannual series devoted to the discussion of recent progress and methodological advances in first-principles methods applied to catalysis, co-organized by Jürgen Hafner, Jens Norskøv and Matthias Scheffler. The next workshop will be held on May 25 to May 28, 2009 at the Erwin Schrödinger Institute (ESI) for Mathematical Physics in Wien.

Topical sessions will discuss
(A) Recent progress in density functional theory of solids - and beyond (invited speakers J.P. Perdew, B. Lundqvist. S. Grimme, G. Kresse, M. Fuchs)
(B) Ab-initio calculations of free-energy barriers and reaction rates (C. Dellago, M. Parrinello, H. Metiu, T. Bucko, T. Bligaard)
(C) Materials design (D. Morgan, M. Mavrikakis, F. Studt)
(D) Catalysis by metals and metal-support interactions (G. Pacchioni, S. Piccinin, R. Grybos, P. Raybaud, A. Michaelides, A. Gross)
(E) Electrocatalysis (M. Koper, J. Rossmeisl, S. Sugino)
(F) Acid-based catalysis in zeolites and related materials (J. Sauer, L. Benco, R. Catlow, S. Bordiga)
(G) Catalysis by oxides (R. Schlögl, F. Mittendorfer, C. Noguera, J. van Bokhoven, K. Reuter)

Contributions to these topics are sollicited (oral contributions will be 15 min incl discussion). Abstracts of contributions (LATEX format, 12pt, double-spaced, max. 1 page) should be sent until March 15 per email to J. Hafner (juergen.hafner@univie.ac.at). Notification of acceptance will be given until March 30, registration form will be mailed with the acceptance notification. Attendance to the meting is limited due to the capacity of the lecture hall. There will be no conference fee.

Jürgen Hafner
Faculty of Physics, Universität Wien
and Center for Computational Materials Science

3.2 Workshop on Magnetism in complex systems - Spin density theory and beyond

TU-Vienna, Austria

April, 16-19, 2009

Psi-k, TU-Wien, University Vienna, BMWF, CMS

Peter Mohn and Jürgen Hafner

http://www.cms.tuwien.ac.at/

Topics:

Magnetism in strongly correlated materials (or Magnetism and electronic correlation)

Magnetism in nano-structures

Multiferroics

Magnetism in intermetallic compounds

Magnetic Semiconductors

Magnetic anisotropy

Magnetism in bio-relevant materials

Energy Loss Magnetic Chiral Dichroism, experiment and theory

3.2.1 Workshop QTS-5: Quantum Theory of Solids

Århus University

May 18-20, 2009

Sponsored by: Psi-k, CTN-Århus, IFA-Århus

Organizers: N. E. Chrsitensen and A. Svane

Web page: http://www.phys.au.dk/qts5/

The fifth Århus workshop on Quantum Theory of Solids is held at the Department of Physics and Astronomy, University of Århus. The main theme of the workshop will be new development in correlation physics of solids including electron-electron as well as electron-hole correlations, in semiconductors, transition metal oxides and f-electron systems. New developments and applications of GW, DMFT, SIC, TDDFT and BSE methodology will be discussed. Also some other aspects of the quantum theory of electrons in the solid state will be treated, including recent progress in the theory of diluted magnetic semiconductors and reactions at surfaces.

Invited speakers: R. C. Albers, M. Alouani, C. Ambrosch-Draxl, V. Antonov, O. K. Andersen, S. Biermann, A. N. Chantis, O. Eriksson, L. Errico, M. Gatti, E. K. U. Gross, O. Gunnarsson, B. Hammer, P. Hyldgaard, E. Kotomin, K. Köpernik, J. Kudrnovsky, W. R. L. Lambrecht, R. Laskowski, M. Lüders, G. K. H. Madsen, R. Nieminen, L. Nordström, P. M. Oppeneer, L. Petit, A. Postnikov, S. Satpathy, S. Savrasov, W. Temmerman, M. van Schilfgaarde, G. Zwicknagl

Attendance fee: 150 Euro (lunches and coffee, conference dinner).

Register by email: nec@phys.au.dk no later than April 15th 2009.

3.3 6th Nanoquanta-ETSF Young Researchers Meeting (YRM09)

Berlin

2 - 6 June, 2009

DFG, Psi-K

NQ-ETSF node at the Free University Berlin

http://www.nanoquanta.de/yrm2009

The Sixth International Young Researchers NQ-ETSF (Nanoquanta-European Theoretical Spectroscopy Facility) conference will take place in the cosmopolitan city of Berlin during June 2009. This conference is organized by the ETSF young researchers working at the Theoretical Physics Department of the Free University Berlin.

The YRM09 aims to bring together young researchers, comprising of PhD students and postdocs, working on applications and code development in the field of theoretical spectroscopy.

The conference facilitates an open exchange of ideas and a better understanding in the field of spectroscopy, with the help of ab-initio calculations.

Recent advances in the field of Density Functional Theory, the GW method and the Bethe-Salpeter Equation will be discussed. These represent state-of-the-art methods for determining the electronic spectra of, among others, bio-molecules, nano-devices and quantum dots. Extensions of the basic formalisms to cover the most diverse situations, such as magnetic systems, superconductors and non-equilibrium phenomena will be the subject of posters and oral presentations.

Registration is open until March 22, 2009.

More details can be found at http://www.nanoquanta.de/yrm2009

3.4 Reports on Psi-k Workshops

3.4.1 Report on Nanoferronics Workshop

International Workshop on Nanoferronics: "Novel multifunctional metal-oxide tunnel-junctions relevant for future devices"

Aachen, October 9-10, 2008

Scientific Coordinators:

Marjana Ležaić (Forschungszentrum Jülich, Germany)

Silvia Picozzi (CNR-INFM, L`Aquila, Italy)

Stefan Blügel(Forschungszentrum Jülich, Germany)

Hermann Kohlstedt (Forschungszentrum Jülich, Germany)

Summary

The acronym *nanoferronics* stands for spin transport electronics through multifunctional (multiferroic) tunnel junctions. The motivation for the workshop was to discuss, explore and trigger the next steps in this rapidly developing field.

Last December, the prestigious scientific journal *Science*, classified recent advances on multiferroics and oxide interfaces as one of the 10 breakthroughs of the year! It is easy to see why the oxide junctions attract so much attention by considering just one example. In the past year, in several experiments conducted on the interface between two insulators, $SrTiO_3$ (STO) and $LaAlO_3$ (LAO), this interface was found to exhibit a whole spectrum of different behaviors, ranging from magnetism to superconductivity or to metal-insulator transition. The mentioned investigations at LAO/STO interface are just an example, and they result from sustained progress in the growth of complex oxides thin films using advanced deposition techniques during the past two decades. Combined with sophisticated real time in-situ monitoring of surface and structural properties, this opened new avenues to engineer complex oxides interfaces, heterostructures and devices at the atomic scale level. Such interfaces and the variety of different physical phenomena that are observed at them were one of the main topics of the workshop.

During the invited talks and the poster session the discussions went along several directions. These include:

1. The theoretical tools and the results of the Density Functional Theory applied on oxides and their junctions
2. The discussion of observed phenomena at the interfaces of perovskite materials
3. The development of experimental tools relevant for the characterization of oxide films and interfaces
4. The control and manipulation of the spin-dependent quantum transport through the tunnel junctions e.g. by external magnetic or electrical fields
5. The switching of the magnetization and the ferroelectric polarization as relevant for reading and writing of information.

PROGRAM

Thursday, October 9

Welcome

09.00 - 10.40 Session 1 : Current status and trends
Discussion leader: Wolfgang Kleemann

9:00 **Hans Schmid, Universite de Genèva, Switzerland**
The trail from Pierre Curie to maximal single phase multiferroic complexity

9:50 **Nicola Spaldin, University of California, Santa Barbara, USA**
Recent progress in single phase multiferroics

10.40 Coffee break

11:00 - 13:00 Session 2 : Ferroelectricity and magnetism
Discussion leader: Marjana Ležaić

11:00 **Philippe Ghosez, University of Liege, Belgium**
Engineering exotic phenomena at ferroelectric oxide interfaces : a first-principles perspective

11:40 **Gustav Bihlmayer, Forschungszentrum Jülich, Germany**
Describing complex magnetism from first principles

12:20 **Claude Ederer, Trinity College Dublin, Ireland**
Toroidal moments and magneto-electric coupling: the case of BiFeO versus FeTiO$_3$

13:00 - 14:30 Lunch Break

14:30 - 16:30 Session 3 : Oxides and interfaces
Discussion leader: Liu-Hao Tjeng

14:30 **Yasuyuki Hikita, University of Tokyo, Japan**
Controlling Band Offsets in Manganite-Titanate Heterojunctions

15:10 Alexander Brinkman, University of Twente, Enschede, Netherlands
Magnetoresistance oscillations and relaxation effects at the $SrTiO_3$-$LaAlO_3$

15:50 Andrea Caviglia, University of Geneva, Switzerland
Electric Field Control of the $LaAlO_3/SrTiO_3$ Interface Ground State

16:30 - 16:50 Coffee break

16:50 - 18:10 Session 4 : Correlations at interfaces I
Discussion leader: Silvia Picozzi

16:50 Ansgar Liebsch, Forschungszentrum Jülich, Germany
Coulomb correlations at surfaces and interfaces

17:30 Warren E. Pickett, University of California Davis, USA
Surface-Interface Coupling of $LaAlO_3$ overlayers on $SrTiO_3$: Domestication of the Polar Catastrophe

18:40 Poster session / Dinner

Friday, October 10

09:00 - 11:00 Session 5 : Advanced Analytics
Discussion leader: Uwe Klemradt

09:00 Salia Cherifi, Institut Néel, CNRS, Grenoble, Fance
Imaging submicron ferroelectric domains with slow electrons

09:40 Chunlin Jia, Forschungszentrum Jülich, Germany
Atomic-scale study of electric dipoles near 180^0 domain walls in ferroelectric thin films

10:20 Bernhard Keimer, MPI for Solid State Research, Stuttgart, Germany
Spectroscopy of electronic reconstructions at oxide interfaces

11:00 - 11:30 Coffee break

11:30 - 13:30 Session 6 : Correlations at interfaces II
Discussion leader: Stefan Blügel

11:30 Kiyoyuki Terakura, JAIST, Ishikawa, Japan
Screening mechanism for polar discontinuity for $LaAlO_3/SrTiO_3$ thin films

12:10 Zhicheng Zhong, University of Twente, Netherlands
Electronic structure induced reconstruction and magnetic ordering at the $LaAlO_3/SrTiO_3$ interface

12:50 Evgeny Tsymbal, University of Nebraska-Lincoln, Lincoln, USA
Modeling of Magnetoelectric Interfaces

13:30 - 15:00 Lunch Break

15.00 - 17:00 Session 7 : Strain-assisted phenomena

Discussion leader: Thomas Brückel

15:00 Nikolay A. Pertsev, Physico-Technical Institute, St. Petersburg, Russian Federation

Strain-mediated electric effects in ferroic heterostructures and tunnel junctions

15:40 Darrell G. Schlom, Cornell University, USA

The effect of strain on thin ferroelectric and multiferroic layers

16:20 Sebastian Gönnenwein, Bayrische Akademie der Wissenschaft, Garching, Germany

Magnetoelastic magnetization manipulation in ferromagnet/ferroelectric hybrids

17:00 - 17:30 Coffee break

17:30 - 19:30 Session 8 : Towards Oxide Electronics

Discussion leader: Hermann H. Kohlstedt

17:30 Angès Barthélémy, Unité Mixte de Physique CNRS/Thales, Palaiseau, France

Oxide based heterostructures for spintronics

18:10 Andreas Schmehl, University Augsburg, Germany

EuO_{1-x} -A Half-Metallic Ferromagnetic Semiconductor with High Potential for Application Driven Science

18:50 Regina Dittmann, Forschungszentrum Jülich, Germany

Influence of strain relaxation and interface configuration on the dielectric response of ferroelectric BST thin film capacitors

20:00 Closing & Dinner

Poster contributions

Con-01 Theo A. Costi

Kondo Proximity Effect: How Does a Metal Penetrate Into a Mott Insulator?

Con-02 Bruce A. Davidson

Ferromagnetic correlations at atomically-engineered manganite interfaces

Con-03 Mario Disch

Probing ferroelectricity in ultrathin wedged epitaxial $BaTiO_3$films

Con-04 **Michael Fechner**
Magnetic phase transition in two-phase multiferroics predicted from first principles

Con-05 **Christoph Friedrich**
All-Electron *GW*Calculations for Strontium and Barium Titanate

Con-06 **Vincent Garcia**
Magnetic tunnel junctions with ferroelectric tunnel barriers : electroresistance and tunneling magnetoresistance

Con-07 **Fumiyuki Ishii**
Noncollinear Magnetism in the Perovskite Manganite Superlattice

Con-08 **Hermann Kohlstedt**
A novel total electron yield set-up for interface studies under soft x-ray radiation and a simultaneously applied bias field

Con-09 **Alexey Melnikov**
Non-equilibrium surface and bulk spin-dynamics at Gd(0001)

Con-10 **Frederico D. Novaes**
Tunneling across a ferroelectric barrier : a first-principles study

Con-11 **Kourosh Rahmanizadeh**
First-principles investigation of thin $ATiO_3$films with stacking faults

Con-12 **Hasan Sadat Nabi**
Microscopic origin of magnetism in hematite - ilmenite heterostructures

Con-13 **Marco Salluzzo**
XAS and XMCD spectroscopy on $Nd_1Ba_2Cu_3O_7$/STO interface

Con-14 **Keisuke Shibuya**
Correlation between stacking defect and resistive switching in Sr_2TiO_4thin films

Con-15 **Kunihiko Yamauchi**
Theoretical study of $La_{1-x}Sr_xMnO_3/BiFeO_3$heterojunction: Exchange bias and magnetoelectric coupling

Con-16 **Wolfgang Kleemann**
$(Sr,Mn)TiO_3$- a magnetoelectric multiglass

Con-17 **Marjana Ležaić**
Double perovskite multiferroics: the room temperature challenge

Con-18 **Mohammed Bouhassoune**
Electronic structure and effective masses in strained Silicon

Con-19 **Ersoy Sasioglu**
Ab initio many-body calculation of magnetic excitations in 3d transition metals

PARTICIPANTS

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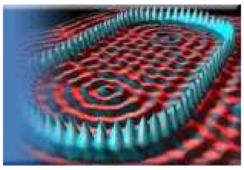
4 News from UK's CCP9 Programme



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

4.1 Reports on UK CCP9's Meetings

4.1.1 Report on AIMPRO'08 Meeting

10-12th December 2008

Institute of Materials, Nantes, France

AIMPRO'08 is the latest in the successful series of meetings, organised on a roughly annual basis to allow users of the AIMPRO[1] DFT code to exchange latest results, techniques and information, learn about the latest code developments and discuss possible developments for the coming year. This year was the first time it was not held in the UK, but instead in Nantes on the West coast of France, at the "Institute of Materials Jean Rouxel"[2], an Institute jointly run by the CNRS and the University of Nantes. It was the largest meeting yet with 40 attendees, and 27 lectures spread over 3 days. Attendees came from 13 different institutions covering 7 different European countries with the majority from UK-based institutions. The meeting was covered in the most popular regional newspaper 'Ouest France'.

Financial support from CCP9, the C'Nano nanotechnology network from the west of France, and the "nano2hybrids" European project[3] meant that conference attendance and meals were free for attending delegates, and we are most grateful to our sponsors for facilitating attendance in this way.

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[1] http://aimpro.ncl.ac.uk

[2] http://www.cnrs-imn.fr

[3] http://www.nano2hybrids.net/

Programme

The programme was as follows:

Wednesday 10th December

13:00-13:50	Lunch University Restaurant
13:50-14:10	Chris Ewels, Jean-Luc Duvail - Welcome
14:10-14:30	Jose Coutinho "Surface segregation of phosphorus and boron in nanocrystalline silicon"
14:30-14:50	Calvin Davidson "Adsorbates on oxidised copper surfaces"
14:50-15:10	Alexandra Carvalho "Intrinsic defects in CdTe"
15:10-15:15	Malcolm Heggie "Introduction to the Graphite Project"
15:15-15:45	Chris Latham "Behaviour of interstitials in graphite"
15:45-16:05	Coffee
16:05-16:35	Gemma Haffenden "Thermal Properties of Graphite from first principles"
16:35-16:45	Glen Sheehan "Modelling Carbon"
16:45-16:55	Jean-Jo Adjizian "Modelling Carbon Part 2"
16:55-17:05	James Boone "Modelling Carbon Part 3"
17:05-17:20	Vincent Guiot "Magnetic Molecules in carbon nanotubes"
17:20-17:30	Alberto Zobelli "Using ROCKS to administer computing clusters"
20:00	"Restaurant"

Thursday 11th December

09:00-10:30	Patrick Briddon
	"AIMPRO++ : What's new, what's coming"
10:30-11:00	Discussion
11:00-11:20	Coffee + Journalist
11:20-12:20	Mark Rayson
	"Progress in techniques for large-scale *ab initio* calculations : A quantum of speed-up"
12:20-12:40	Ben Hourahine
	"Methods for handling dispersion forces in DFT and DFTB"
12:40-13:00	Discussion
13:00-14:00	Lunch University Restaurant
14:00-14:30	Ben Hourahine
	"Latest updates in DFTB"
14:30-14:50	Sylvain Latil
	"Integrating transport calculations in DFT"
14:50-15:20	Alberto Zobelli
	"Electron irradiation damage in carbon and BN nanosystems"
15:20-15:40	Emmanuel Fritsch
	"Oxygen in diamond: The strange case of CO_2 diamonds"
15:40-16:00	Coffee
16:00-16:30	Elena Bichoutskaia
	"Motional Freedom in Carbon Nanotubes and its applications"
16:30-17:00	Irene Suarez-Martinez
	"Metals and Carbon Nanotubes : The Dream, The Nightmare (s)"
17:00-17:20	Estelina Silva
	"Zn, Cu and Ni metal impurities in Ge"
17:20-17:30	Discussion and Close

Friday 12th December

9:15-9:45	Vika Ivanovskaya "Ab initio studies of bilateral doping within the MoS_2-NbS_2 systems"
9:45-10:15	Philippe Moreau "Contribution of Electron Energy-Loss Spectroscopy in a Transmission Electron Microscope to the study of lithium battery materials"
10:15-10:40	Chris Ewels "Modelling realistic nanotubes: Surface deposition, tube filling and cones"
10:40-11:00	Coffee
11:00-11:10	Jens Ryden "Manganese in graphite
11:10-11:30	Jon Goss "Hyperfine calculations using AIMPRO: the success of defects in diamond"
11:30-11:50	Natalia Martsinovich "Theoretical studies of hydrogen bonded supra-molecular structures"
11:50-12:00	Ngoc Bich Nguyen "Atomic and electronic structure of silicon nanocrystals embedded in a silica matrix"
12:00-12:15	Chris Ewels COST Project and networking discussion
12:15-13:00	Discussion General Discussion, Meeting close

Presentations

Jose Coutinho opened the conference with the following presentation:

Surface segregation of phosphorus and boron in nanocrystalline silicon: density-functional studies, Jose Coutinho, Vitor Torres

The possibility of tailoring the electronic properties of atomic nanostructures is a well known issue that stands as a fundamental step for the reach of a whole next generation of materials. Doping nanosized structures presents a remarkable task although its feasibility has been demonstrated already. Here we present a study of the energetics and electronic structure details of phosphorus and boron dopants in large silicon atomic clusters (1000 Si atoms). Contrary to other systems, it is found that a size-driven self-purification mechanism has a low impact on doping deactivation of nSi:P and nSi:B. On the other hand, surface segregation is suggested as a dominant sink dopants, especially for P impurities. Besides stabilizing these impurities, segregation proceeds via formation of electrically inert P and B atoms.

Other topics

The talks covered a surprisingly wide variety of material types and problematics. The first morning was an 'open floor' to allow free debate, which ranged over problems of compilation for different architectures (as well as several proposed solutions), different visualisation tools and comparison of approaches between laboratories. It was also an excellent opportunity for new PhD students from the collection of laboratories to meet each other and form contacts.

While AIMPRO was traditionally primarily used to study defects in Group-IV semiconductors it was clear from the talks given at AIMPRO'08 that it has now significantly surpassed this original remit. The diversity of subjects covered is reflected in the Wednesday afternoon session, which started with defect segregation in silicon nanoparticles, moved on to self-organisation of organic molecules on copper oxide, then different point defect symmetry in CdTe, before discussing in detail a range of short- and long-ranged defect species in graphite. The final talk covered structural and electronic studies of large high-spin molecular magnets and their interaction with carbon nanotubes.

The second morning was devoted to code developments from Patrick Briddon and Mark Rayson, either recently completed or under development. In particular we were lucky to have present code developers from both DFT (AIMPRO) and DFTB (DFTB+), and a wide ranging discussion covered topics such as inclusion of dispersion forces (Ben Hourahine), transport calculations (Sylvain Latil) and screened exchange, and ways to move beyond traditional basis set descriptions. This was followed by more application talks. Finally on Friday the meeting covered more current applications such as modelling of hyperfine interactions for defects in diamond, and bilateral doping studies in MoS_2-NbS_2. There was then open discussions on the future for the network, in particular possibilities for future network funding.

I think it is fair to say that the general feeling was that the meeting was extremely interesting and stimulating, with fascinating talks spanning a wide range of scientific areas, and great promise for the future of AIMPRO, both in terms of code developments, and areas of application. The discussion was open and lively, extending well beyond the sessions into the evening banquet and beyond. The IMN, and Nantes itself, provided an excellent backdrop, with many delegates visiting our local mechanised elephant on the Friday afternoon (type 'nantes elephant' into youTube to see it in action).

Attendees

Sylvain Latil	CEA Saclay, Paris, France
Alexandra Carvalho	EPFL, Lausanne, Switzerland
Vika Ivanosvka	Laboratoire de Physique des Solides, Paris
Alberto Zobelli	Laboratoire de Physique des Solides, Paris
Sven Öberg	LuleåInstitute of Technology, Sweden

Mark Rayson	Max-Planck-Institut, Dusseldorf, Germany
Elena Bichoutskaia	Nottingham University, UK
Jose Coutinho	University of Aveiro, Portugal
Estelina Silva	University of Aveiro, Portugal
Vitor Torres	University of Aveiro, Portugal
Bob Jones	University of Exeter, UK
Hugo Pinto	University of Exeter, UK
Mark Taylforth	University of Newcastle, UK
Mariam Ahmed	University of Newcastle, UK
Patrick Briddon	University of Newcastle, UK
Khaled Etmimi	University of Newcastle, UK
Jonathan Goss	University of Newcastle, UK
Abdusalam Gsiea	University of Newcastle, UK
Rob MacLeod	University of Newcastle, UK
Ben Hourahine	University of Strathclyde, Glasgow, Scotland
Simon Kraeusel	University of Strathclyde, Glasgow, Scotland
Jean-Jo Adjizian	University of Sussex, Brighton, UK
James Boone	University of Sussex, Brighton, UK
Calvin Davidson	University of Sussex, Brighton, UK
Gemma Haffenden	University of Sussex, Brighton, UK
Malcolm Heggie	University of Sussex, Brighton, UK
Chris Latham	University of Sussex, Brighton, UK
Jens Ryden	University of Sussex, Brighton, UK
Glen Sheehan	University of Sussex, Brighton, UK
Natalia Martsinovich	Warwick University, UK
Sebastien Petit	Universite de Caen, France
Ngoc Bich Nguyen	Universite de Caen, France
Emmanuel Fritsch	Institut des Materiaux, Nantes
Philippe Moreau	Institut des Materiaux, Nantes
Chris Ewels	Institute of Materials, Nantes, France
Vincent Guiot	Institute of Materials, Nantes, France
Irene Suarez Martinez	Institute of Materials, Nantes, France
Abu Yaya Sulley	Institute of Materials, Nantes, France

5 General Workshop/Conference Announcements

5.1 WIEN2009: Hands on Workshop on the WIEN2k package

Penn State University, University Park, PA, USA

June 23-26, 2009

J.O. Sofo and the WIEN2k developers team

http://www.msc.psu.edu

The forth US workshop on the WIEN code (16th in the history of the WIEN code) is a hands-on activity dedicated to teach the use of the WIEN2k Density Functional Theory Package (http://www.wien2k.at). WIEN2k is one of the most popular electronic structure codes used to perform calculations with the Full Potential LAPW method. The workshop is a unique opportunity to learn the use, power and limitations of the package with the tutoring of the authors and developers of the code. The activities will be aimed at graduate students and researchers from industry and academia. The only pre-requisite is to have a basic knowledge of solid state physics, and chemistry. It is planned as a four-day activity with lectures on the scientific aspects of the method, applications, hand-on activities on selected examples, and the opportunity to receive a head start on a personal project.

This year the participation is limited to 40 people.

For more information or to register go to http://www.msc.psu.edu

The tentative list of invited speakers includes:

- Prof. C. Ambrosch-Draxl (Univ. Leoben, Austria)
- Prof. P. Blaha (TU Vienna, Austria)
- Dr. G. Madsen (Univ. Aarhus, Denmark)
- Prof. K. Schwarz (TU Vienna, Austria)
- Dr. F. Tran (TU Vienna, Austria)

Chair: Prof. J. O. Sofo (Penn State Univ, USA)

6 General Job Announcements

Post-Doc position in theoretical heterogeneous catalysis

École Normale Supérieure de Lyon, Lyons, France

A post-doctoral position is available at École Normale Supérieure de Lyon (ENS-Lyon, France). The position is now open, and funded for 12 months from starting date. The net salary will be between 2300 and 2500 eur net/month depending on the candidate experience.

The successful candidate will develop and test methods to realize hybrid quantum method/classical force fields (QM/MM) or quantum method high level/quantum method lower level (QM/QM') calculations. This project is focused on calculations in heterogeneous catalysis. Ab initio methods will be coupled to standard quantum chemistry packages as well as molecular dynamic codes. Besides simple test reactions, applications will include realistic models of complex systems used in heterogeneous catalysis.

Applicants should hold a PhD in theoretical chemistry/physics, applied computer science, or other related areas with a competitive track record. Candidates are required to have experience in numerical scientific computing, with either VASP or CPMD knowledge. Fluency in a high-level programming language, such as FORTRAN90 or/and C/C++ is a requirement. Experience with parallel computing libraries, such as MPI, and extensive experience in a unix/linux environment is a definite advantage.

Scientific meetings and stays in Saudi Arabia at KAUST will take place. The aim of KAUST is to become one of the top leading world class university within 10 years (see www.kaust.edu.sa). To reach this objective, world class scientists and research institutes (among which ENS-Lyon) are associated with the education and research buildup of KAUST. Several challenging scientific problems have been identified and human and material resources have been gathered to solve them.

Motivated candidates are invited to send their CV, including a short motivation for carrying out this project, list of publications, abstract of research results (1 page) and two recommendation letters by e-mail (preferred format pdf or plain text) to

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or

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Postdoctoral Position
Ecole Polytechnique, Palaiseau (southern Paris area), France

We have an opening for a postdoctoral fellow starting Sept. 2009 or earlier in the field of electronic structure calculations for correlated materials, in a collaboration between B. Amadon (CEA Bruyeres-le-Chatel) and S. Biermann (Ecole Polytechnique). The postdoctoral researcher will use dynamical mean field theory combined with band structure techniques ("LDA+DMFT") to investigate the electronic structure of oxide and f-electron materials. We are seeking a fellow who is interested in both, methodological developments and applications to materials. Applicants should be familiar with first principles electronic structure calculations. Previous experience with many-body techniques will be a very positive point. Please send your CV, a brief description of your research interests, and the names of at least two referees to silke.biermann@polytechnique.edu

Doctoral Training Centre in Theory and Simulation of Materials
Imperial College London, UK

Applications are invited for **ten** four-year studentships leading to both MSc and PhD degrees in the newly-established Doctoral Training Centre (DTC) in Theory and Simulation of Materials at Imperial College London. Students resident in an EU country for the last three years are eligible for funding to cover their fees. Students resident in the UK for the last three years are also eligible for a stipend to cover living expenses.

The DTC aims to provide a cutting-edge educational and research environment in the theory and simulation of materials across length and time scales, spanning the disciplines of physics, materials, chemistry and mechanical engineering to enable students to learn how to look at materials problems from different perspectives.

PhD study within the DTC will differ significantly from the traditional approach in the UK. The first year will provide a rigorous training in the required theoretical methods and simulation techniques through a new MSc course. The PhD research project, which will occupy years 2–4, will have two supervisors (one of whom may be in industry or at another university) whose combined expertise will bridge multiple length and time scales. A key emphasis of research projects will be on the development and implementation of new theory and code for materials simulation. The research of the DTC will be carried out in the Thomas Young Centre, the London Centre for the Theory and Simulation of Materials involving University College London and King's College London as well as Imperial.

One of the special features of this DTC is that each intake of students will have strong sense of cohort identity. This will be fostered through the cohort itself being responsible for organising activities such as a monthly journal club, seminars, and conferences both for themselves and other year groups. They will also attend award-winning residential transferable skills courses and networking activities together. Each cohort will have a dedicated cohort mentor, who will hold weekly meetings throughout the duration of the programme to take feedback and to discuss all aspects of the DTC with students.

Prospective applicants are encouraged to make informal enquiries by contacting the Admissions Tutor Dr Peter Haynes: `p.haynes@imperial.ac.uk`. Applicants should normally have, or expect to achieve, a first class (or equivalent) Bachelor's or Master's degree in the physical sciences or engineering. The selection procedure will include an interview with members of the Research Board of the DTC. Applications will be considered as they are received, with the expectation that all funded positions will be filled by 31st March 2009.

Further information is available at `www.cmth.ph.ic.ac.uk/dtc/`

7 Abstracts

Giant magnetic anisotropy of the bulk antiferromagnets IrMn and $IrMn_3$ from first principles

L. Szunyogh[1], B. Lazarovits[1,2], L. Udvardi[1], J. Jackson[3],
and U. Nowak[4]

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[4]*Fachbereich Physik, Universität Konstanz, Germany*

Abstract

We perform an ab-initio study of the ordered phases of IrMn and $IrMn_3$, the most widely used industrial antiferromagnets. Calculation of the form and the strength of the magnetic anisotropy allows the construction of an effective spin model, which is tested against experimental measurements regarding the magnetic ground state and the Néel temperature. Our most challenging result is the extremely strong second order anisotropy for $IrMn_3$ appearing in its frustrated triangular magnetic ground state, which is surprising since the ordered $L1_2$ phase has a cubic symmetry. We explain this large anisotropy by the fact that cubic symmetry is locally broken for each of the three Mn sublattices.

Phys. Rev.B 79, 020403(R) 2009
Contact: szunyogh@phy.bme.hu

Chiral asymmetry of the spin-wave spectra in ultrathin magnetic films

L. Udvardi and L. Szunyogh

Budapest University of Technology and Economics, Hungary

Abstract

We raise the possibility that the chiral degeneracy of the magnons in ultrathin films can be lifted due to the presence of Dzyaloshinskii-Moriya interactions. By using simple symmetry arguments, we discuss under which conditions such a chiral asymmetry occurs. We then perform relativistic first principles calculations for an Fe monolayer on W(110) and explicitly reveal the asymmetry of the spin-wave spectrum in case of wave-vectors parallel to the (001) direction. Furthermore, we quantitatively interpret our results in terms of a simplified spin-model by using calculated Dzyaloshinskii-Moriya vectors. Our theoretical prediction should inspire experiments to explore the asymmetry of spin-waves, with a particular emphasis on the possibility to measure the Dzyaloshinskii-Moriya interactions in ultrathin films.

arXiv:0901.2671v1

Contact: szunyogh@phy.bme.hu

Density-functional description of superconducting and magnetic proximity effects across a tunneling barrier

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Harwell Science and Innovation Campus, Didcot OX11 0QX, United Kingdom

[2] *Departamento de Física e Informática, Instituto de Física de São Carlos,*
Universidade de São Paulo, 13560-970 São Carlos, SP, Brazil

Abstract

A density-functional formalism for superconductivity and magnetism is presented.The resulting relations unify previously derived Kohn-Sham equations for superconductors and for noncollinear magnetism. The formalism, which discriminates Cooper-pair singlets from triplets, is applied to two quantum liquids coupled by tunneling through a barrier. An exact expression is derived, relating the eigenstates and eigenvalues of the Kohn-Sham equations, unperturbed by tunneling, on one side of the barrier to the proximity-induced ordering potential on the other.

(Phys. Rev. B 78, p. 205426 (2008))
Contact person: Klaus Capelle (capelle@ifsc.usp.br)

Contribution of the second Landau level to the exchange energy of the three-dimensional electron gas in a high magnetic field

J. Morbec and K. Capelle

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Abstract

We derive a closed analytical expression for the exchange energy of the three-dimensional interacting electron gas in strong magnetic fields, which goes beyond the quantum limit (L=0) by explicitly including the effect of the second, L=1, Landau level and arbitrary spin polarization. The inclusion of the L=1 level brings the fields to which the formula applies closer to the laboratory range, as compared to previous expressions, valid only for L=0 and complete spin polarization. We identify and explain two distinct regimes separated by a critical density n_c. Below n_c, the per particle exchange energy is lowered by the contribution of L=1, whereas above n_c it is increased. As special cases of our general equation we recover various known more limited results for higher fields, and we identify and correct a few inconsistencies in some of these earlier expressions.

(Phys. Rev. B 78, p. 085107 (2008))
Contact person: Klaus Capelle (capelle@ifsc.usp.br)

Universal and nonuniversal contributions to block-block entanglement in many-fermion systems

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Abstract

We calculate the entanglement entropy of blocks of size x embedded in a larger system of size L, by means of a combination of analytical and numerical techniques. The complete entanglement entropy in this case is a sum of three terms. One is a universal x- and L-dependent term, first predicted by Calabrese and Cardy, the second is a nonuniversal term arising from the thermodynamic limit, and the third is a finite size correction. We give an explicit expression for the second, nonuniversal, term for the one-dimensional Hubbard model, and numerically assess the importance of all three contributions by comparing to the entropy obtained from fully numerical diagonalization of the many-body Hamiltonian. We find that finite-size corrections are very small. The universal Calabrese-Cardy term is equally small for small blocks, but becomes larger for $x > 1$. In all investigated situations, however, the by far dominating contribution is the nonuniversal term stemming from the thermodynamic lim

(Phys. Rev. A 77, p. 062324 (2008))
Contact person: Klaus Capelle (capelle@ifsc.usp.br)

Orbital-polarization terms: from a phenomenological to a first-principles description of orbital magnetism in density-functional theory

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Universidade de São Paulo, 13560-970 São Carlos, SP, Brazil

Abstract

Phenomenological orbital-polarization (OP) terms have been repeatedly introduced in the single-particle equations of spin-density-functional theory, in order to improve the description of orbital magnetic moments in systems containing transition metal ions. Here we show that these *ad hoc* corrections can be interpreted as approximations to the exchange-correlation vector potential $\mathbf{A}_{xc}$ of current-density-functional theory (CDFT). This connection provides additional information on both approaches: Phenomenological OP terms are connected to first-principles theory, leading to a rationale for their empirical success and a reassessment of their limitations and the approximations made in their derivation. Conversely, the connection of OP terms with CDFT leads to a set of simple approximations to the CDFT potential $\mathbf{A}_{xc}$, with a number of desirable features that are absent from electron-gas-based functionals.

(Int. J. Quantum Chem. 108, p. 2433 (2008))
Contact person: Klaus Capelle (capelle@ifsc.usp.br)

Empirical analysis of the Lieb-Oxford bound in ions and molecules

M. M. Odashima and K. Capelle

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Abstract

Universal properties of the Coulomb interaction energy apply to all many-electron systems. Bounds on the exchange-correlation energy, in particular, are important for the construction of improved density functionals. Here we investigate one such universal property — the Lieb-Oxford lower bound — for ionic and molecular systems. In recent work [J. Chem. Phys. **127**, 054106 (2007)], we observed that for atoms and electron liquids this bound may be substantially tightened. Calculations for a few ions and molecules suggested the same tendency, but were not conclusive due to the small number of systems considered. Here we extend that analysis to many different families of ions and molecules, and find that for these, too, the bound can be empirically tightened by a similar margin as for atoms and electron liquids. Tightening the Lieb-Oxford bound will have consequences for the performance of various approximate exchange-correlation functionals.

(Int. J. Quantum Chem. 108, p. 2428 (2008))

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

Energy of bond defects in quantum spin chains obtained from local approximations and from exact diagonalization

V. L. Libero, K. Capelle, F. C. Souza, A. P. Favaro

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Abstract

We study the influence of ferromagnetic and antiferromagnetic bond defects on the ground-state energy of antiferromagnetic spin chains. In the absence of translational invariance, the energy spectrum of the full Hamiltonian is obtained numerically, by an iterative modification of the power algorithm. In parallel, approximate analytical energies are obtained from a local-bond approximation, proposed here. This approximation results in significant improvement upon the mean-field approximation, at negligible extra computational effort.

(J. Magn. Magn. Mater 320, p. E418-E420 (2008), proceedings of LMMM conference)
Contact person: Klaus Capelle (capelle@ifsc.usp.br)

Friedel oscillations in one-dimensional metals: from Luttinger's theorem to the Luttinger liquid

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Abstract

Charge density and magnetization density profiles of one-dimensional metals are investigated by two complementary many-body methods: numerically exact (Lanczos) diagonalization, and the Bethe-Ansatz local-density approximation with and without a simple self-interaction correction. Depending on the magnetization of the system, local approximations reproduce different Fourier components of the exact Friedel oscillations.

(J. Magn. Magn. Mater. 320, p. E421-E424 (2008), proceedings of LMMM conference)
Contact person: Klaus Capelle (capelle@ifsc.usp.br)

Efficient *O(N)* Integration For All-Electron Electronic Structure Calculation Using Numeric Basis Functions

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Abstract

We consider the problem of developing $O(N)$ scaling grid based operations needed in many central operations when performing electronic structure calculations with numeric atom-centered orbitals as basis functions. We outline the overall formulation of localized algorithms, and specifically the creation of localized grid batches. The choice of the grid partitioning scheme plays an important role in the performance and memory consumption of the grid based operations. Three different top-down partitioning methods are investigated, and compared with formally more rigorous yet much more expensive bottom-up algorithms. We show that a conceptually simple top-down grid partitioning scheme achieves essentially the same efficiency as the more rigorous bottom-up approaches.

(submitted to: Journal of Computational Physics)

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Assessing the efficiency of first-principles basin-hopping sampling

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Abstract

We present a systematic performance analysis of first-principles basin-hopping (BH) runs, with the target to identify all low-energy isomers of small Si and Cu clusters described within density-functional theory. As representative and widely employed move classes we focus on single-particle and collective moves, in which one or all atoms in the cluster at once are displaced in a random direction by some prescribed move distance, respectively. The analysis provides detailed insights into the bottlenecks and governing factors for the sampling efficiency, as well as simple rules-of-thumb for near-optimum move settings, that are intriguingly independent of the distinctly different chemistry of Si and Cu. At corresponding settings, the observed performance of the BH algorithm employing two simple, general-purpose move classes is already very good, and for the small systems studied essentially limited by frequent revisits to a few dominant isomers.

(submitted to: Phys. Rev. B)
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Nature of Ar bonding to small Co_n^+ clusters and its effect on the structure determination by far-infrared absorption spectroscopy

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Abstract

Far-infrared vibrational spectroscopy by multiple photon dissociation has proven to be a very useful technique for the structural fingerprinting of small metal clusters. Contrary to previous studies on cationic V, Nb and Ta clusters, measured vibrational spectra of small cationic cobalt clusters show a strong dependence on the number of adsorbed Ar probe atoms, which increases with decreasing cluster size. Focusing on the series Co_4^+ to Co_8^+ we therefore use density-functional theory to analyze the nature of the Ar-Co_n^+ bond and its role for the vibrational spectra. In a first step, energetically low-lying isomer structures are identified through first-principles basin-hopping sampling runs and their vibrational spectra computed for a varying number of adsorbed Ar atoms. A comparison of these fingerprints with the experimental data enables in some cases a unique assignment of the cluster structure. Independent of the specific low-lying isomer, we obtain a pronounced increase of the Ar binding energy for the smallest cluster sizes, which correlates nicely with the observed increased influence of the Ar probe atoms on the IR spectra. Further analysis of the electronic structure motivates a simple electrostatic picture that not only explains this binding energy trend, but also rationalizes the stronger influence of the rare-gas atom compared to the preceding studies by the small atomic radius of Co.

(submitted to: J. Chem. Phys.)
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First principles elaboration of low band gap ladder-type polymers

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Abstract

Ladder-type polymers, obtained by small modifications of the atomic structure of ladder-type polythiophene, are studied using density- functional theory calculations. Within the local-density (LDA) and GW approximations it is found that upon a simple substitution of the sulfur atoms by nitrogen and boron atoms, the band structure of the resulting polymer exhibits bands overlap between the occupied and the unoccupied states. However, the three-parameter Becke hybrid functional (B3LYP) predicts these polymers to be small band gap semiconductors. Finally, results of time-dependent density-functional theory (TDDFT) are reported on increasing length oligomers indicating that the polymers would have very low excitation energies.

(Accepted to Journal of Chemical Physics)
Contact person: Michel Côté (Michel.Cote@umontreal.ca)

Exchange coupling in transition metal monoxides

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[3] *ORNL, Oak Ridge, TN, USA*
[4] *European Synchrotron Radiation Facility, Grenoble, France*
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Abstract

An *ab initio* study of magnetic exchange interactions in antiferromagnetic and strongly correlated $3d$ transition metal monoxides is presented. Their electronic structure is calculated using the local self-interaction correction approach, implemented within the Korringa-Kohn-Rostoker band structure method, which is based on multiple scattering theory. The Heisenberg exchange constants are evaluated with the magnetic force theorem. Based on these the corresponding Néel temperatures T_N and spin wave dispersions are calculated. The Néel temperatures are obtained using mean field approximation, random phase approximation and Monte Carlo simulations. The pressure dependence of T_N is investigated using exchange constants calculated for different lattice constants. All the calculated results are compared to experimental data.

(Submitted to Physical Review B)
Contact person: guntram.fischer@physik.uni-halle.de

8 Presenting Other Initiatives: Atomistix ToolKit (ATK)

This is just to inform all who know about or are interested in Atomistix ToolKit that since December 2008 it is being developed and distributed by a new company called QuantumWise.

For more information see

http://quantumwise.com/component/content/article/6-announcement-from-the-ceo.

At Atomistix we could clearly see how appreciated the Psi-k network was, and we got a lot of referrals from the link list the Psi-k provides. We would naturally like that people also in the future could find their way to us and the latest versions of ATK via the Psi-k network.

The new link for "Atomistix ToolKit" is its new home page:

http://www.quantumwise.com.

Anders Blom, Ph.D.
Sales, Marketing and Support Manager
QuantumWise A/S
Gyvelvej 20, 2680 Solrød Strand, Denmark
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9 SCIENTIFIC HIGHLIGHT OF THE MONTH

Using Chebyshev-Filtered Subspace Iteration Methods to Solve the Kohn-Sham Problem

James R. Chelikowsky[1] and Yousef Saad[2]

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Abstract

The ground state electronic properties of a material can be obtained using density functional theory as embodied by the Kohn-Sham equation. Typically, one employs eigensolver-based approaches to solve this equation. These approaches can be computationally demanding and have largely limited the applicability of the Kohn-Sham framework to systems of no more than a few hundred atoms. Here we discuss a different approach based on a nonlinear Chebyshev-filtered subspace iteration, which avoids computing explicit eigenvectors except to initiate the process. Our method centers on solving the original nonlinear Kohn-Sham equation by a nonlinear form of the subspace iteration technique, without emphasizing the intermediate linearized Kohn-Sham eigenvalue problems. The method achieves self-consistency within a similar number of self-consistent field iterations as eigensolver-based approaches. *However, replacing the standard diagonalization at each self-consistent iteration by a Chebyshev subspace filtering step results in a significant speedup over methods based on standard dagonalization, often by more than an order of magnitude.* Algorithmic details of a parallel implementation of this method are discussed. Numerical results are presented to show that the method enables one to perform a class of highly challenging applications that heretofore were not feasible.

1 Introduction

Electronic structure calculations based on first principles use often employ a very successful combination of *density functional theory* (DFT) [1, 2] and *pseudopotential theory* [3–6]. DFT reduces the original multi-electron Schrödinger equation into an effective one-electron Kohn-Sham equation, where the non-classical electronic interactions are replaced by a functional of the charge density. Pseudopotential theory further simplifies the problem by replacing the “all electron” atomic potential with an effective "pseudopotential" that is smoother, but takes into account the effect of core electrons. Combining pseudopotential with DFT greatly reduces the number of one-electron wave-functions to be computed, but more importantly the energy and length scales are set solely by the valence states. As such, species such as a carbon and lead can be treated on equal footing. However, even with these simplifications, solving the Kohn-Sham equation remains computationally challenging when the systems of interest contain a large number, *e.g.*, more than a few hundred, atoms.

Several approaches have been advocated for solving the Kohn-Sham equations. They can be classified in two major groups: basis-free or basis-dependent approaches, according to whether they use an explicit basis set for electronic orbitals or not. Among the basis-dependent approaches, plane wave methods are frequently used in applications of DFT to periodic systems where plane waves can easily accommodate the boundary conditions [7, 8]. In contrast, localized basis sets such as Gaussian orbitals are very popular in quantum-chemistry applications [6, 9]. Special basis sets have also been designed for all-electron DFT calculations, which do not make use of pseudopotentials. These basis sets include: linearized augmented plane waves, muffin-tin orbitals, projector-augmented waves. A survey of advantages and disadvantages of these explicit-basis methods can be found in [6, 10].

Here we will focus on a different approach based on *real space* methods, which are "basis free." Real space methods have gained ground in recent years [11–14] owing in great part to their simplicity and ease of implementation. In particular, these methods are readily implemented in parallel environments. A second advantage is that, in contrast with a plane wave approach, real space methods do not impose artificial periodicity in non-periodic systems. In contrast, plane wave basis techniques can be applied to clusters (or molecules) by placing the system of interest in a large supercell. Provided the supercell is sufficiently large so that the cluster of interest is removed from neighboring replicants, the electronic structure solution will correspond to that of the isolated cluster. However, the potentials from neighboring cells can be an issue. This makes supercell solutions converge slowly with the size of the cell [15]. A related, and perhaps more significant issue, is that supercells complicate the handling of systems that are not electronically neutral. Charged systems can be handled within plane wave methods by including a compensating uniform charge [15]. Real space methods need not address such complications. A third advantage is that the application of the Hamiltonian to electron wave-functions is performed directly in real-space. Although the Hamiltonian matrix in real space methods is typically much larger than with plane waves, the Hamiltonians are *highly sparse* and never stored or computed explicitly. Only matrix-vector products that represent the application of the Hamiltonians on wave-functions need to be computed.

As in plane wave methods, the chief impediment to solving the Kohn-Sham problem is "diagonalizing" the Hamiltonian and obtaining a self-consistent field (SCF) solution. We present examples of a recently developed nonlinear Chebyshev-filtered subspace iteration (CheFSI) method, implemented in our own DFT solution package called PARSEC (Pseudopotential Algorithm for Real-Space Electronic Calculations) [11, 12]. Although described in the framework of real-space DFT, CheFSI can be employed to other SCF iterations. The subspace filtering method takes advantage of the fact that intermediate SCF iterations do not require accurate eigenvalues and eigenvectors of the Kohn-Sham equation.

The “standard” SCF iteration framework is used in CheFSI, and a self-consistent solution is obtained as with previous work, which means that CheFSI has the *same* accuracy as other standard DFT approaches. Unlike, some so-called “order-N” methods [16, 17] CheFSI is equally applicable to metals and insulators. One can view CheFSI as a technique to tackle directly the original nonlinear Kohn-Sham eigenvalue problems by a form of nonlinear subspace iteration, without emphasizing the intermediate linearized Kohn-Sham eigenvalue problems. In fact, within CheFSI, explicit eigenvectors are computed only at the first SCF iteration, in order to provide a suitable initial subspace. After the first SCF step, the explicit computation of eigenvectors at each SCF iteration is replaced by a single subspace filtering step. The method reaches self-consistency within a number of SCF iterations that is close to that of eigenvector-based approaches. However, since eigenvectors are not explicitly computed after the first step, a significant gain in execution time results when compared with methods based on explicit diagonalization.

When compared with calculations based on efficient eigenvalue packages such as ARPACK [18] and TRLan [19, 20] an order of magnitude speed-up is usually observed.

CheFSI enabled us to perform a class of highly challenging DFT calculations, including clusters with over ten thousand atoms, which were not feasible before without invoking additional approximations in the Kohn-Sham problem [21–24].

2 Eigenvalue problems in density functional calculations

The Kohn-Sham equation as defined in density functional theory is given by

$$\left[-\frac{\hbar^2}{2m}\nabla^2 + V_{total}(\rho(r), r)\right] \Psi_i(r) = E_i \Psi_i(r), \tag{1}$$

where $\Psi_i(r)$ is a wave function, E_i is a Kohn-Sham eigenvalue, $\hbar$ is the Planck constant, and m is the electron mass. (We will often use atomic units: $\hbar = m = e = 1$ in the following discussion.)

The *total potential* V_{total}, is the sum of three terms,

$$V_{total}(\rho(r), r) = V_{ion}(r) + V_H(\rho(r), r) + V_{xc}(\rho(r), r), \tag{2}$$

where V_{ion} is the ionic potential, V_H is the Hartree potential, and V_{xc} is the exchange-correlation potential. The Hartree and exchange-correlation potentials depend on the *charge density* $\rho(r)$, which is defined as

$$\rho(r) = 2 \sum_{i=1}^{n_{occ}} |\Psi_i(r)|^2. \tag{3}$$

Here n_{occ} is the number of occupied states, which is equal to half the number of valence electrons in the system. The factor of two comes from spin multiplicity, if the system is non-magnetic. Eq. (3) can be easily generalized to situations where the highest occupied states have fractional occupancy or when there is an imbalance in the number of electrons for each spin component.

The most computationally expensive step of DFT is in solving the Kohn-Sham Eq. (1). Since V_{total} depends on the charge density $\rho(r)$, which in turn depends on the wave functions Ψ_i, Eq. (1), can be viewed as a *nonlinear eigenvalue problem*. The SCF iteration is a general technique used to solve this nonlinear eigenvalue problem. The iteration process begins with an initial guess of the charge density usually constructed from a superposition of free atomic charge densities, then obtains the initial V_{total} and solves Eq. (1) for $\Psi_i(r)$'s to update $\rho(r)$ and V_{total}. Then the Kohn-Sham (Eq. (1)) is solved again for the new $\Psi_i(r)$'s and the process is iterated until V_{total} (and also the wave functions) becomes stationary. The standard SCF process is described in Algorithm 2.1 and illustrated in Fig. 1

Algorithm 2.1 *Self-consistent-field iteration:*

```
1. Provide initial guess for $\rho(r)$, get $V_{total}(\rho(r), r)$.
2. Solve for $\Psi_i(r)$, $i = 1, 2, ...$, from
       $$\left[-\frac{1}{2}\nabla^2 + V_{total}(\rho(r), r)\right]\Psi_i(r) = E_i\Psi_i(r).   (4)$$
3. Compute the new charge density $\rho(r) = 2\sum_{i=1}^{n_{occ}} |\Psi_i(r)|^2$.
4. Obtain new Hartree potential $V_H$ by solving: $\nabla^2 V_H(r) = -4\pi\rho(r)$.
5. Update $V_{xc}$; get new $\tilde{V}_{total}(\rho, r) = V_{ion}(r) + V_H(\rho, r) + V_{xc}(\rho, r)$ with a potential-mixing step.
6. If $\|\tilde{V}_{total} - V_{total}\| < tol$, stop; Else, $V_{total} \leftarrow \tilde{V}_{total}$, goto step 2.
```

The number of eigenvectors needed in *Step 2* of Algorithm 2.1 is just the number of occupied states. In practice, a few more eigenvectors are usually computed. For complex systems, *i.e.*, when the number of valence electrons is large, each of the linearized eigenvalue problems can be computationally demanding. This is compounded by the fact that Hamiltonian matrices can be of very large size.

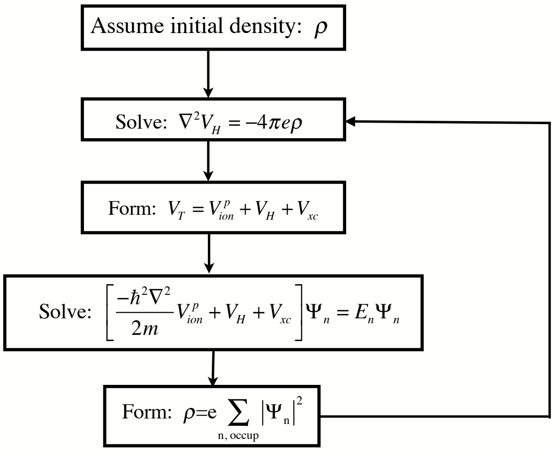

Figure 1: Flow diagram for obtaining a self-consistent solution of the Kohn-Sham equation.

For this reason, one hopes to lessen the burden of solving Eq. 4 in the SCF iteration. There are several options here. One could use some physical arguments to reduce the matrix size or zero some existing elements. Or, one could attempt to avoid diagonalization altogether, as is done in work represented by linear-scaling or order-N methods (see e.g. [16,17]). This approach, however, has other limitations. In particular, the approximations involved rely heavily on some decay properties of the density matrix in certiain function bases. In particular, they can be difficult to implement in real-space discretizations or for systems where the decay properties are not optimal, *e.g.*, in metals. Another option is to use better (faster) diagonalization routines. However, this approach is limited as most diagonalization software is quite mature.

Our approach *avoids standard diagonalizations*, but otherwise makes no new approximations to the Hamiltonian. We take advantage of the fact that accurate eigenvectors are unnecessary at each SCF iteration, since Hamiltonians are only approximate in the intermediate SCF steps, and exploit the nonlinear nature of the problem. The main point of the new algorithm is that once we have a good starting point for the Hamiltonian, it suffices to *filter* each basis vector at each iteration. In the intermediate SCF steps, these vectors are no longer eigenvectors but together they represent a good basis of the desired invariant subspace.

3 Numerical methods for parallel platforms

The motivation and original ideas behind our real space method (PARSEC) go back to the early 1990s, see [11, 12]. Within PARSEC, an uniform Cartesian grid in real-space is placed on the region of interest, and the Kohn-Sham equation is discretized by a high order finite-difference method [25] on this grid. Wave functions are expressed as values on grid positions. Outside a specified sphere boundary that encloses the physical system, wave functions are set to zero for non-periodic systems. In addition to the advantages mentioned in the introduction, another advantage of the real-space approach is that periodic boundary conditions are also reasonably simple to implement [26].

The latest version of PARSEC is written in Fortran 90/95. PARSEC has now evolved into a mature, massively parallel package, which includes most of the functionality of comparable DFT codes [27]. The reader is referred to [28, 29] for details and the rationale of the parallel implementation. The PARSEC software can be obtained from

http://parsec.ices.utexas.edu/

The following is a brief summary of the most important points. PARSEC allows for either parallel or sequential excecutions. When run in the parallel mode, PARSEC uses the standard Message Passing Interface (MPI) library for communication. Parallelization is achieved by partitioning the physical domain which can have various shapes depending on boundary conditions and symmetry operations. Fig. 2 illustrates four cube-shaped neighboring sub-domains. For a generic, confined system without symmetry, the physical domain is a sphere which contains all atoms plus some additional space (owing to delocalization of electron charge).

In recent years, PARSEC has been enhanced to take advantage of physical symmetry. If the system is invariant upon certain symmetry operations, the physical domain is replaced with an irreducible wedge constructed according to those operations. For example, if the system has mirror symmetry

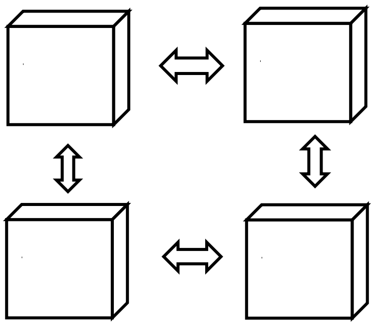

Figure 2: Sample decomposition of a physical domain used in the PARSEC package.

on the xy plane, the irreducible wedge covers only one hemisphere, either above or below the mirror plane. For periodic systems, the physical domain is the periodic cell, or an irreducible wedge of it if symmetry operations are present. In any circumstance, the physical domain is partitioned in compact regions, each assigned to one processor only. Good load balance is ensured by enforcing that the compact regions have approximately the same number of grid points.

Once the physical domain is partitioned, the physical problem is mapped onto the processors in a data-parallel way: each processor is in charge of a block of rows of the Hamiltonian corresponding to the block of grid points assigned to it. The eigenvector and potential vector arrays are row-wise distributed in the same fashion. The program only requires an index function $indx(i, j, k)$ which returns the number of the processor in which the grid point (i, j, k) resides.

Because the Hamiltonian matrix is never stored, we need an explicit reordering scheme which renumbers rows consecutively from one processor to the next one. For this purpose we use a list of pointers that gives for each processor, the row with which it starts.

Since finite difference discretizetion is used, when performing an operation such as a matrix-vector product, communication will be required between nearest neighbor processors. For communication we use two index arrays, one to count how many and which rows are needed from neighbors, the other to count the number of local rows needed by neighbors. With this decomposition and mapping, the data required by the program is completely distributed. In other words, the code runs in the so-called "Single Program Multiple Data" approach. For large problems it is quite important to be able to distribute memory loads among processors on high performance computers. For example, certain large jobs can simply not be run on a small number of processors on good-size distributed memory machines.

Parallelizing subspace methods for the linearized eigenvalue problems (represented as Eq. 4) becomes quite straightforward with the above mentioned decomposition and mapping. Note that the subspace basis vectors contain approximations to eigenvectors, therefore the rows of the basis vectors are distributed in the same way as the rows of the Hamiltonian. In this way, all vector updates (e.g., linear combinations of vectors), can be executed locally (i.e., without communication). Matrix-vector products, and matrix-matrix products, can be easily executed in parallel but may require some communication with a few neighbors. Reduction operations, e.g., computing inner products and making the result available in each processor, are efficiently handled by the MPI reduction function

`MPI_ALLREDUCE()`.

4 The nonlinear Chebyshev-filtered subspace iteration

Since the Hamiltonians of the intermediate SCF steps are approximate, there is no need to compute eigenvectors of the intermediate Hamiltonians to a high accuracy. Moreover, as observed in Refs. [13, 17, 22, 30–32], the (discretized) charge density is the diagonal of the "functional" charge density matrix defined as $P = \Phi\Phi^T$, where the columns of the matrix Φ are discretized wave functions corresponding to occupied states. Notice that for any orthonormal matrix Q of a suitable dimension, $P = (\Phi Q)(\Phi Q)^T$. Therefore, explicit eigenvectors are not needed to calculate the charge density. Any orthonormal basis of the eigensubspace corresponding to occupied states can give the desired intermediate charge density.

The proposed method combines the outer SCF iteration and the inner iteration required for diagonalization at each SCF step into one nonlinear subspace iteration. In this approach an initial subspace is progressively refined by a low degree Chebyshev polynomials filtering. This means that each basis vector u_i is processed as follows:

$$u_{i,new} := p_m(H)u_i$$

where p_m is some shifted and scaled Chebyshev poynomial whose goal is to enhance eigencomponents of u_i associated with the occupied states. Throughout the article the integer m denotes the degree of the polynomial p_m which is used for filtering.

If it were not for the nonlinear nature of the SCF loop, i.e., if H were a fixed operator, this approach would be equivalent to the well-known Chebyshev accelerated subspace iteration proposed by Bauer [33], and later refined by Rutishauser [34, 35][4].

Chebyshev polynomial filtering has long been utilized in electronic structure calculations (see e.g. [30, 36–40]), focussing primarily on approximating the Fermi-Dirac operator.

Chebyshev polynomials of rather high degree were necessary and additional techniques were required to suppress the Gibbs phenomena. In contrast, the polynomials used in our approach are of relatively low degree (say < 20). They exploit the fast growth property of Chebyshev polynomials outside the interval $[-1, 1]$ to filter out undesired eigencomponents.

The main idea of CheFSI is to start with a good initial subspace V corresponding to occupied states of the initial Hamiltonian, this initial V is usually obtained by a diagonalization step. No diagonalizations are necessary after the first SCF step. Instead, the subspace from the previous iteration is filtered by a degree-m polynomial, $p_m(t)$, constructed for the current Hamiltonian H. The polynomial differs at each SCF step since H changes. Note that the goal of the filter is to make the subspace spanned by $p_m(H)V$ approximate the eigensubspace corresponding to the occupied states of the final H. At the intermediate SCF steps, the basis need not be an accurate eigenbasis since the intermediate

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[4] Rutishauser published an Algol routine called *ritzit* in the volume: "Handbook for automatic computations: linear algebra", see [35]. This volume was largely at the origin of the EISPACK package (which later became a part of LAPACK), but Rutishauser's *ritzit* Algol routine was not translated into EISPACK.

Hamiltonians are not exact. The filtering is designed so that the resulting sequence of subspaces will progressively approximate the desired eigensubspace of the final Hamiltonian when self-consistency is reached. At each SCF step, only two parameters are required to construct an efficient Chebyshev filter, namely, a lower bound and an upper bound of the higher portion of the spectrum of the current Hamiltonian H in which we want $p_m(t)$ to be small. These bounds can be obtained with little additional cost, as will be seen in Section 4.2.

After self-consistency is reached, the Chebyshev filtered subspace includes the eigensubspace corresponding to occupied states. Explicit eigenvectors can be readily obtained by a *Rayleigh-Ritz refinement* [41] (also called *subspace rotation*) step.

4.1 Chebyshev-filtered subspace iteration

The main structure of CheFSI, which is given in Algorithm 4.1, is quite similar to that of the standard SCF iteration (Algorithm 2.1). One major difference is that the inner iteration for diagonalization at *Step 2* is now performed only at the first SCF step. Thereafter, diagonalization is replaced by a single Chebyshev subspace filtering step, performed by calling Algorithm 4.2.

Although the charge density (Eq. (3)) requires only the lowest n_{occ} states, the number of computed states, which is the integer s in Algorithm 4.1, is typically set to a value larger than n_{occ}, in order to avoid missing any occupied states. In practice we fix an integer n_{state} which is slightly larger than n_{occ}, and set $s = n_{state} + n_{add}$ with $n_{add} \leq 10$.

The parallel implementations of Algorithms 4.1 and 4.2 are quite straightforward with the parallel paradigm discussed in Section 3. We only mention that the matrix-vector products related to filtering, computing upper bounds, and Rayleigh-Ritz refinement, can easily execute in parallel. The re-orthogonalization at *Step 4* of Algorithm 4.2 uses a parallel version of the iterated Gram-Schmidt DGKS method [42], which scales better than the standard modified Gram-Schmidt algorithm. This process is illustrated in Fig. 3.

The estimated complexity of the algorithm is similar to that of the sequential CheFSI method in [22]. For parallel computation it suffices to estimate the complexity on a single processor. Assume that p processors are used, i.e., each processor shares N/p rows of the full Hamiltonian. The estimated cost of Algorithm 4.2 on each processor with respect to the dimension of the Hamiltonian denoted by N, and the number of computed states s, is as follows:

- The Chebyshev filtering in *Step 3* costs $O(s * N/p)$ flops. The discretized Hamiltonian is sparse and each matrix-vector product on one processor costs $O(N/p)$ flops. *Step 3* requires $m * s$ matrix-vector products, at a total cost of $O(s * m * N/p)$ where the degree m of the polynomial is small (typically between 8 and 20).
- The ortho-normalization in *Step 4* costs $O(s^2 * N/p)$ flops. There are additional communication costs because of the global reductions.
- The eigen-decomposition at *Step 5* costs $O(s^3)$ flops.
- The final basis refinement step ($\Phi := \Phi Q$) costs $O(s^2 * N/p)$.

If a standard iterative diagonalization method is used to solve the linearized eigenproblem (Eq. 4) at each SCF step, then it also requires (i) the orthonormalization of a (typically larger) basis; (ii) the eigen-decomposition of the projected Rayleigh-quotient matrix; and (iii) the basis refinement (rotation). These operations need to be performed several times within this single diagonalization. But Algorithm 4.2 performs each of these operations only once per SCF step. Therefore, although Algorithm 4.2 scales in a similar way to standard diagonalization-based methods, the scaling constant is much smaller. For large problems, CheFS can achieve a tenfold or more speedup per SCF step, over using the well-know efficient eigenvalue packages such as ARPACK [18] and TRLan [19, 20].

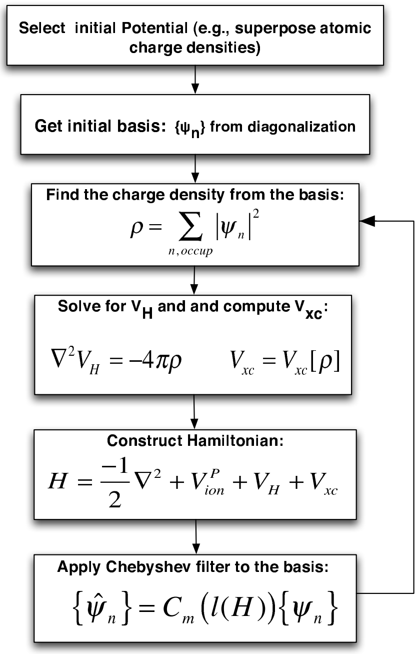

Figure 3: Flow diagram for obtaining a self-consistent solution of the Kohn-Sham equation using damped Chebyshev subspace filtering.

In summary, a standard SCF method has an outer SCF loop—the usual nonlinear SCF loop, and an inner diagonalization loop, which iterates until eigenvectors are within specified accuracy. Algorithm 4.1 essentially bypasses the second loop, or rather it merges it into a single outer loop, which can be considered as a *nonlinear subspace iteration algorithm*. The inner diagonalization loop is replaced by a single Chebyshev subspace filtering step.

4.2 Chebyshev filters and estimation of bounds

Chebyshev polynomials of the first kind are defined, for $k = 0, 1, \cdots$, by (see e.g., [41, p.371], or [43, p.142]):

$$C_k(t) = \begin{cases} \cos(k \ \cos^{-1}(t)), & -1 \leq t \leq 1, \\ \cosh(k \ \cosh^{-1}(t)), & |t| > 1. \end{cases}$$

Algorithm 4.1 *CheFSI for SCF calculation:*

```
1. Start from an initial guess of $\rho(r)$, get $V_{total}(\rho(r), r)$.
2. Solve $\left[-\frac{1}{2}\nabla^2 + V_{total}(\rho(r), r)\right] \Psi_i(r) = E_i \Psi_i(r)$ for $\Psi_i(r),\ i = 1, 2, ..., s$.
3. Compute new charge density $\rho(r) = 2\sum_{i=1}^{n_{occ}} |\Psi_i(r)|^2$.
4. Solve for new Hartree potential $V_H$ from $\nabla^2 V_H(r) = -4\pi\rho(r)$.
5. Update $V_{xc}$; get new $\tilde{V}_{total}(\rho, r) = V_{ion}(r) + V_H(\rho, r) + V_{xc}(\rho, r)$ with a potential-mixing step.
6. If $\|\tilde{V}_{total} - V_{total}\| < tol$, stop; Else, $V_{total} \leftarrow \tilde{V}_{total}$ (update $H$ implicitly),
   call the Chebyshev-filtered subspace method (Algorithm 4.2) to get $s$ approximate wave functions; goto step 3.
```

Algorithm 4.2 *Chebyshev-filtered Subspace (CheFS) method:*

```
1. Get the lower bounds $b_{low}$ and $\gamma$ from previous Ritz values (use the largest one and the smallest one, respectively).
2. Compute the upper bound $b_{up}$ of the spectrum of the current discretized
   Hamiltonian $H$ (call Algorithm 4.4 in Section 4.2).
3. Perform Chebyshev filtering (call Algorithm 4.3 in Section 4.2) on the previous basis $\Phi$,
   where $\Phi$ contains the discretized wave functions of $\Psi_i(r),\ i = 1, ..., s$:
   $\Phi = \texttt{Chebyshev\_filter}(\Phi,\ m,\ b_{low},\ b_{up},\ \gamma)$.
4. Ortho-normalize the basis $\Phi$ by iterated Gram-Schmidt.
5. Perform the Rayleigh-Ritz step:
   (a) Compute $\hat{H} = \Phi^T H \Phi$;
   (b) Compute the eigendecomposition of $\hat{H}$: $\hat{H}Q = QD$,
       where $D$ contains non-increasingly ordered eigenvalues of $\hat{H}$, and $Q$ contains the corresponding eigenvectors;
   (c) 'Rotate' the basis as $\Phi := \Phi Q$; return $\Phi$ and $D$.
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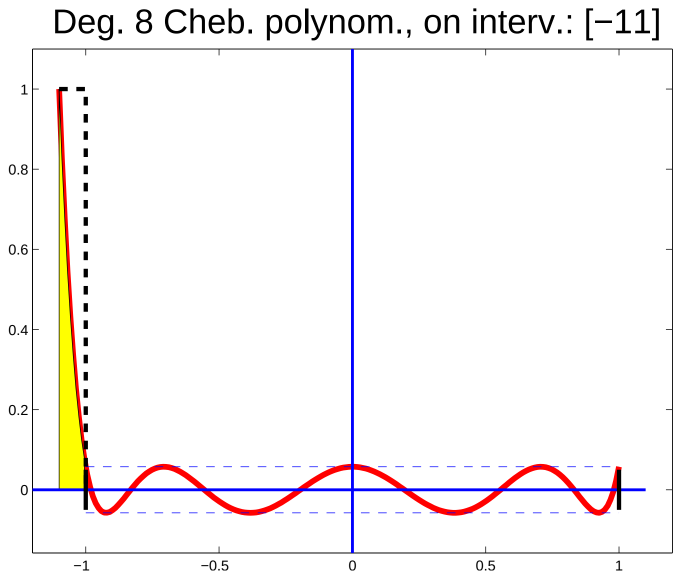

Figure 4: Degree 8 Chebyshev polynomial on the interval [-1, 1] scaled to one at $\gamma = -0.2$. The shaded area corresponds to eigen-components that will be amplified relative to the other eigencomponents, those corresponding to the interval $[-1, 1]$, which will be dampened.

Note that $C_0(t) = 1, C_1(t) = t$. The following important 3-term recurrence is easy to derive from properties of the cosine function,

$$C_{k+1}(t) = 2t\ C_k(t) - C_{k-1}(t), \quad t \in \mathbb{R}. \tag{5}$$

By filtering we mean a process applied to a vector that has the effect of magnifiant desired eigen-components of this vector relative to other, undesirable, components. If the process is repeated indefinitely, the resulting vector will have zero components in the undesirable part of the spectrum. In our context, we need to filter out all components associated with the non-occupied states, or, equivalently to enhance the components associated with occupied states, relative to other components.

Filtering can be readily achieved by exploiting well-known properties of Chebyshev polynomials. It is known that among all polynomials of degree k, which have value one at a certain point $|\gamma| > 1$, the polynomial $C_k(t)/C_k(\gamma)$ is the one whose maximum absolute value in the interval $[-1, 1]$ is minimal. Thus, $C_k(t)/C_k(\gamma)$ can be viewed as an optimal polynomial if one wishes to dampen values of the polynomial in $[-1, 1]$ among all polynomials p of degree k, scaled so that $p(\gamma) = 1$. The 8th degree Chebyshev polynomial scaled at $\gamma = -0.2$ is shown in Figure 4.

Assume that the full spectrum of H (denoted by $\Lambda(H)$) is contained in $[\gamma, b]$. Then, in order to approximate the eigensubspace associated with the lower end of the spectrum, say $[\gamma, a]$ with $\gamma < a < b$, it is necessary to map $[a, b]$ into $[-1, 1]$ before applying the Chebyshev polynomnial. This can be easily realized by an affine mapping defined as

$$\mathcal{L}(t) := \frac{t-c}{e}; \quad c = \frac{a+b}{2}, \quad e = \frac{b-a}{2}$$

where c denotes the center and e the half-width of the interval $[a, b]$. The Chebyshev iteration utilizing the three-term recurrence (5) to dampen values on the interval $[a, b]$ is listed in Algorithm 4.3, see also [22]. The algorithm computes

$$Y = p_m(H)X \qquad \text{where} \qquad p_m(t) = C_m\left[\mathcal{L}(t)\right]. \tag{6}$$

This yields the iteration

$$X_{j+1} = \frac{2}{e}(H - cI)X_j - X_{j-1}, \quad j = 1, 2, ..., m-1.$$

with X_0 given and $X_1 = (H - cI)X_0$.

The above iteration is without any scaling. In the case of the interval $[-1, 1]$ we scaled the polynomial by $C_k(\gamma)$ in order to ensure that the value of the polynomial at γ equals one. For general intervals, this leads to the scaled sequence of polynomials [43]

$$\tilde{X}_j = \frac{C_j[\frac{2}{e}(H - cI)]}{C_j[\frac{2}{e}(\gamma - cI)]}X_0.$$

Thus, the scaling factor is $\rho_j = C_j[\frac{2}{e}(\gamma - cI)]$. Clearly this requires an estimate for γ which, in our case, is the smallest eigenvalue of the Hamiltonian. However, since this is used for scaling, for the purpose of avoiding overflow, only a rough value is needed. For the first SCF iteration, we can use the smallest Ritz value of T from the same Lanczos run (Algorithm 4.4 below) as used to obtain the upper bound b for γ. For the latter SCF steps, the smallest Ritz value from the previous SCF step can be used. Clearly, the vector sequence is not computed as shown above because ρ_j itself can be large and this would defeat the purpose of scaling. Instead, each $\tilde{X}_{j+1}$ is updated using the scaled vectors $\tilde{X}_j$ and $\tilde{X}_{j-1}$. The corresponding algorithm, discussed in [43] is shown in Algorithm 4.3 (the tildes and vector subscripts are omitted).

The eigen-components associated with eigenvalues in $[a, b]$ will be transformed to small values while those to the left of $[a, b]$ will be around unity owing to the properties of the Chebyshev polynomials. This is the desired filtering property when computing an approximation to the eigensubspace associated with the lower end of $\Lambda(H)$. As seen in Algorithm 4.3, a desired filter can be easily controlled by adjusting two endpoints that bound the higher portion of $\Lambda(H)$.

The wanted lower bound can be any value which is larger than the Fermi-level but smaller than the upper bound. It can also be a value slightly smaller than the Fermi-level; thanks to the monotonicity of the shifted and scaled Chebyshev polynomial on the spectrum of H, and the fact that we compute $s > n_{occ}$ number of Ritz values, the desired lowered end of the spectrum will still be magnified properly with this choice of lower bound.

Since the previous SCF iteration performs a Rayleigh-Ritz refinement step, it provides naturally an approximation for the lower bound a. Indeed, we can simply take the largest Rayleigh-quotient from the previous SCF iteration step as an approximation to the lower bound for the current Hamiltonian. In other words, a is taken to be the largest eigenvalue computed in step 5-(b) of Algorithm 4.2 from the previous SCF iteration, with no extra computation.

The upper bound for the spectrum (denoted by b) can be estimated by a k-step standard Lanczos method. As pointed out in [23], the higher endpoint b must be a bound for the full spectrum of H. This is because the Chebyshev polynomial also grows fast to the right of $[-1, 1]$. So if $[a, b]$

Algorithm 4.3 $[Y] =$ `Chebyshev_filter`(X, m, a, b, γ).

Purpose: Filter column vectors of X by an m degree Chebyshev polynomial in H that dampens on the interval $[a, b]$. Output the filtered vectors in Y.

```
1.  $e = (b - a)/2$;     $c = (b + a)/2$;
2.  $\sigma = e/(\gamma - c)$;     $\sigma_1 = \sigma$;     $\gamma = 2/\sigma_1$.
3.  $Y = \frac{\sigma_1}{e}(HX - cX)$;
4.  For $i = 2 : m$
5.      $\sigma_2 = 1/(\gamma - \sigma)$;
6.      $Y_{new} = \frac{2\sigma_2}{e}(HY - cY) - \sigma\sigma_2 X$;
7.      $X = Y$;
8.      $Y = Y_{new}$;
9.      $\sigma = \sigma_2$;
10. End For
```

---

with $b < \lambda_{max}(H)$ is mapped into $[-1, 1]$, then the $[b, \lambda_{max}(H)]$ portion of the spectrum will also be magnified, which will cause the procedure to fail. Therefore, it is imperative that the bound b be larger than $\lambda_{max}(H)$. On the other hand it should not be too large as this would result in slow convergence. The simplest strategy which can be used for this is to use Gerschgorin's Circle Theorem. Bounds obtained this way can, however, overestimate $\lambda_{max}(H)$.

An inexpensive way to estimate an upper bound of $\Lambda(H)$ by the standard Lanczos [44] method is described in Algorithm 4.4, to which a safeguard step is added. The largest eigenvalue $\tilde{\lambda}$ of the tridiagonal matrix T is known to be below the largest eigenvalue λ of the Hamiltonian. If $\tilde{u}$ is the corresponding Ritz vector and $r = (H - \tilde{\lambda}I)\tilde{u}$ then there is an eigenvalue of H in the interval $[\tilde{\lambda} - \|r\|, \tilde{\lambda} + \|r\|]$ (see e.g. [41]). Algorithm 4.4 estimates λ_{max} by $max(\tilde{\lambda}) + \|f\|$, since it is known that $\|r\| \leq \|f\|$. This is not theoretically guaranteed to return an upper bound for λ_{max} - but it is generally observed to yield an effective upper bound. The algorithm for estimating b is presented in Algorithm 4.4 below. Note that the algorithm is easily parallelizable as it relies mostly on matrix-vector products. In practice, we found that $k = 4$ or 5 is sufficient to yield an effective upper bound of $\Lambda(H)$. Larger k values (e.g., $k > 10$) are not necessary in general.

In the end we can see that the extra work associated with computing bounds for constructing the Chebyshev polynomials is negligible. The major cost of filtering is in the three-term recurrences in Algorithm 4.3, which involve matrix-vector products. The polynomial degree m is left as a free parameter. Our experience indicates that an m between 8 and 20 is good enough to achieve overall fast convergence in the SCF loop.

Algorithm 4.4 *Estimating an upper bound of $\Lambda(H)$ by k-step Lanczos:*

```
1.  Generate a random vector $v$, set $v \leftarrow v/\|v_2\|$;
2.  Compute $f = Hv$;  $\alpha = f^T v$;  $f \leftarrow f - \alpha v$;  $T(1,1) = \alpha$;
3.  Do $j = 2$ to $min(k, 10)$
4.      $\beta = \|f_2\|$;
5.      $v_0 \leftarrow v$;  $v \leftarrow f/\beta$;
6.      $f = Hv$;  $f \leftarrow f - \beta v_0$;
7.      $\alpha = f^T v$;  $f \leftarrow f - \alpha v$;
8.      $T(j, j-1) = \beta$;  $T(j-1, j) = \beta$;  $T(j, j) = \alpha$;
9.  End Do
10. Return $\|T_2\| + \|f_2\|$ as the upper bound.
```

5 Diagonalization in the first SCF iteration

Within CheFSI, the most expensive SCF step is the first one, as it involves a diagonalization in order to compute a good subspace to initiate the nonlinear SCF loop. This section discusses options available for this task.

In principle, any effective eigenvalue algorithms can be used for the first SCF step. PARSEC originally had three diagonalization methods: Diagla, which is a preconditioned Davidson method [28, 29]; the symmetric eigensolver in ARPACK [18, 45]; and the Thick-Restart Lanczos algorithm called TRLan [19, 20]. For systems of moderate sizes, Diagla works well, and then becomes less competitive relative to ARPACK or TRLan for larger systems when a large number of eigenvalues are required. TRLan is about twice as fast as the symmetric eigensolver in ARPACK, because of its reduced need for re-orthogonalization. In [22], TRLan was used for the diagonalization at the first SCF step.

Another option suggested and tested in [32] but not implemented in PARSEC, is to resort to the Lanczos algorithm with partial reorthogonalization. Partial reorthogonalization Lanczos would run the Lanczos algorithm without restarting, reorthogonalizing the vectors only when needed, see [41]. This is a very effective procedure, some would even say optimal in some sense, except that it typically requires an enormous amount of memory. As illustrated in [32] the method can be 5 to 7 times faster than ARPACK for moderate size problems. It is possible to address the memory problem by resorting to secondary storage, though parallel implementations would be tedious.

At the other extreme when considering memory usage, one can use the Chebyshev filtered subspace iteration *in its linear implementation*. This means that we will now add an outer loop to the procedure described by Algorithm 4.2 and test convergence for the same Hamiltonian (the initial one) without updating potential from one outer loop to the next. Practically, this is simply as a variant of

Algorithm 4.1, whereby step 2 is replaced by as many filtering steps of Algorithm 4.2 as are required for the subspace to converge. This procedure is the most economical in terms of memory, so it is recommended if memory is an issue. However, it is well-known that subspace iteration methods (linear) are not as effective as the Lanczos algorithm, and other Krylov-based methods, see, e.g., [41, Chap. 14].

Even with standard restart methods such as ARPACK and TRLan, the memory demand can still remain too high in some cases. Hence, it is important to develop a diagonalization method that is less memory demanding but whose efficiency is comparable to ARPACK and TRLan. The Chebyshev-Davidson method [23, 24] was developed with these two goals in mind. Details can be found in [23, 24]. The principle of the method is to simply build a subspace by a procedure based on a form of Block-Davidson approach. The Block-Davidson approach builds a subspace by adding a 'window' of preconditioned vectors. In the Chebyshev-Davidson approach, these vectors are built by exploiting Chebyshev polynomials.

The first step diagonalization by the block Chebyshev-Davidson method, together with the Chebyshev-filtered subspace method (Algorithm 4.2), enabled us to perform SCF calculations for a class of large systems, including the silicon cluster $Si_{9041}H_{1860}$ for which over 19,000 eigenvectors of a Hamiltonian with dimension around 3 million were to be computed. These systems are practically infeasible with the other three eigensolvers (ARPACK, TRLan and Diagla) in PARSEC, using the current supercomputer resources available to us at the Minnesota Supercomputing Institute (MSI).

Though results obtained with the Chebyshev-Davidson method in the first step diagonalization are satisfactory, there is still much work to be done in this area. We do not know for example how accurate the subspace must be in order to be a good initial guess to ensure convergence. It may possible to further reduce execution times by changing the stopping criterion needed in the first SCF step. It may be also possible to exploit well-known "global convergence" strategies utilized for non-linear iterations (such as continuation, or damping) to avoid completely the first step diagonalization.

6 Numerical Results

PARSEC has been applied to study a wide range of material systems ($e.g.$ [12, 26, 27]). The focus of this section is on large systems where relatively few numerical results exist because of the infeasibility of eigenvector-based methods. We mention that Ref. [46] contains very interesting studies on clusters containing up to 1100 silicon atoms, using the well-known efficient plane wave DFT package VASP [8, 47]; however, it is stated in Ref. [46] that a cluster with 1201 silicon atoms is "too computationally intensive." As a comparison, PARSEC using CheFSI, together with the currently developed symmetric operations of real-space pseudopotential methods [48], can now routinely solve silicon clusters with several thousands of atoms.

The hardware used for the computations is the SGI Altix cluster at MSI, it consists of 256 Intel Itanium processors at CPU rates of 1.6 GHz, sharing 512 GB of memory (but a single job is allowed to request at most 250 GB memory).

The goal of the computations is not to study the parallel scalability of PARSEC, but rather to use

PARSEC to do SCF calculation for large systems that were not studied before. Therefore, we do not use different processor numbers to solve the same problem. Scalability is studied in [29] for the preconditioned Davidson method, we mentioned that the scalability of CheFSI is better than eigenvector-based methods because of the reduced reorthogonalizations.

In the reported numerical results, the `total_eV/atom` is the total energy per atom in electron-volts, this value can be used to assess accuracy of the final result; the `#SCF` is the iteration steps needed to reach self-consistency; and the `#MVp` counts the number of matrix-vector products. Clearly `#MVp` is not the only factor that determines CPU time, the orthogonalization cost can also be a significant component.

For all of the reported results for CheFSI, the first step diagonalization used the Chebyshev-Davidson method. In Tables 4–11, the `1st CPU` denotes the CPU time spent on the first step diagonalization by Chebyshev-Davidson; the `total CPU` counts the total CPU time spent to reach self-consistency by CheFSI.

dim. of H	n_{state}	`#MVp`	`#SCF`	`total_eV/atom`	`1st CPU`	`total CPU`
1074080	5843	1400187	14	-86.16790	7.83 hrs.	19.56 hrs.

Table 4: $Si_{2713}H_{828}$, using 16 processors. $m = 17$ for Chebyshev-Davidson; $m = 10$ for CheFS. (First step diagonalization by TRLan cost 8.65 hours, projecting it into a 14-steps SCF iteration cost around 121.1 hours.)

The first example (Table 5) is a relatively small silicon cluster $Si_{525}H_{276}$, which is used to compare the performance of CheFSI with two eigenvector-based methods. All methods use the same symmetry operations [48] in PARSEC.

method	`#MVp`	`#SCF` steps	`total_eV/atom`	CPU(secs)
CheFSI	189755	11	-77.316873	542.43
TRLan	149418	10	-77.316873	2755.49
Diagla	493612	10	-77.316873	8751.24

Table 5: $Si_{525}H_{276}$, using 16 processors. The Hamiltonian dimension is 292584, where 1194 states need to be computed at each SCF step. The first step diagonalization by Chebyshev-Davidson cost 79755 #MVp and 221.05 CPU seconds; so the total #MVp spent on CheFS in CheFSI is 110000. The polynomial degree used is $m = 17$ for Chebyshev-Davidson and $m = 8$ for CheFS. The fist step diagonalization by TRLan requires 14909 #MVp and 265.75 CPU seconds.

For larger clusters $Si_{2713}H_{828}$ (Table 4) and $Si_{4001}H_{1012}$ (Table 6), Diagla became too slow to be practical. However, we could still apply TRLan for the first step diagonalization for comparison, but we did not iterate until self-consistency was reached since that would cost a significant amount of our CPU quota. Note that with the problem size increasing, Chebyshev-Davidson compares more favorably over TRLan. This is because we employed an additional trick in Chebyshev-Davidson, which corresponds to allowing the last few eigenvectors not to converge to the required accuracy. The number of the non fully converged eigenvectors is bounded above by act_{max}, which is the maximum dimension of the active subspace. Typically $30 \leq act_{max} \leq 300$ for Hamiltonian size over a million where several thousand eigenvectors are to be computed. The implementation of this trick is rather straightforward since it corresponds to applying the CheFS method to the subspace spanned by the last few vectors in the basis that have not converged to required accuracy.

dim. of H	n_{state}	`#MVp`	`#SCF`	`total_eV/atom`	`1st CPU`	`total CPU`
1472440	8511	1652243	12	-89.12338	18.63 hrs.	38.17 hrs.

Table 6: $Si_{4001}H_{1012}$, using 16 processors. $m = 17$ for Chebyshev-Davidson; $m = 8$ for CheFS. (First step diagonalization by TRLan cost 34.99 hours, projecting it into a 12-steps SCF iteration cost around 419.88 hours.)

For even larger clusters $Si_{6047}H_{1308}$ (Table 8) and $Si_{9041}H_{1860}$ (Table 7), it became impractical to apply TRLan for the first step diagonalization because of too large memory requirements. For these large systems, using an eigenvector-based method for each SCF step is clearly not feasible. We note that the cost for the first step diagonalization by Chebyshev-Davidson is still rather high, it took close to 50% of the total CPU. In comparison, the CheFS method (Algorithm 4.2) saves a significant amount of CPU for SCF calculations over diagonalization-based methods, even if very efficient eigenvalue algorithms are used.

dim. of H	n_{state}	`#MVp`	`#SCF`	`total_eV/atom`	`1st CPU`	`total CPU`
2992832	19015	4804488	18	-92.00412	102.12 hrs.	294.36 hrs

Table 7: $Si_{9041}H_{1860}$, using 48 processors. $m = 17$ for Chebyshev-Davidson; $m = 8$ for CheFS.

dim. of H	n_{state}	`#MVp`	`#SCF`	`total_eV/atom`	`1st CPU`	`total CPU`
2144432	12751	2682749	14	-91.34809	45.11 hrs.	101.02 hrs.

Table 8: $Si_{6047}H_{1308}$, using 32 processors. $m = 17$ for Chebyshev-Davidson; $m = 8$ for CheFS.

Once the DFT problem, Eq. (1), is solved, we have access to several physical quantities. One of them is the ionization potential (IP) of the nanocrystal, defined as the energy required to remove one electron from the system. Numerically, we use a ΔSCF method: perform two separate calculations, one for the neutral cluster and another for the ionized one, and observe the variation in total energy between these calculations. Fig. 5 shows the IP of several clusters, ranging from the smallest possible (SiH_4) to $Si_{9041}H_{1860}$. For comparison, we also show the eigenvalue of the highest occupied Kohn-Sham orbital, E_{HOMO}. A known fact of DFT-LDA is that the negative of the E_{HOMO} energy is lower than the IP in clusters [6], which is confirmed in Figure 5. In addition, the figure shows that the IP and $-E_{HOMO}$ approach each other in the limit of extremely large clusters.

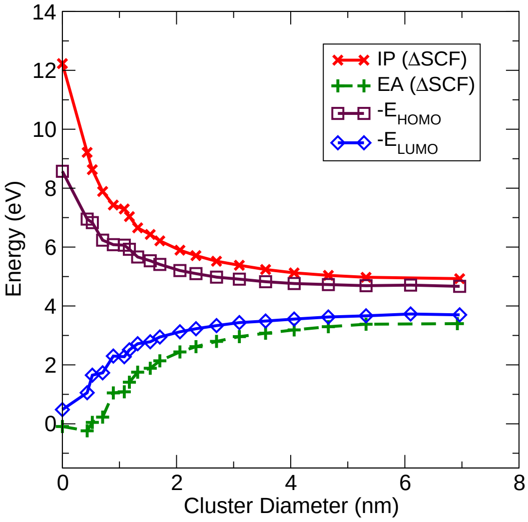

Figure 5: Ionization potential, IP, (crosses) and electron affinity, EA, (“plus” signs), for various clusters with diameters ranging from 0 nm (SiH_4) to 7 nm ($Si_{9041}H_{1860}$). “Squares” denote the negative of the highest occupied molecular orbital ($-E_{HOMO}$) eigenvalue energy of the neutral cluster. “Diamonds” denote the negative of the lowest unoccupied molecular orbitaleigenvalue energy ($-E_{LUMO}$).

Fig. 5 also shows the electron affinity (EA) of the various clusters. The EA is defined as the energy released by the system when one electron is added to it. Again, we calculate it by performing SCF calculations for the neutral and the ionized systems (negatively charged instead of positively charged now). In PARSEC, this sequence of SCF calculations can be done very easily by reusing previous information: The initial diagonalization in the second SCF calculation is waived if we reuse eigenvectors and eigenvalues from a previous calculation as initial guesses for the ChebFSI method. Fig. 5 shows that, as the cluster grows in size, the EA approaches the negative of the lowest-unoccupied eigenvalue energy. A power-law analysis in Fig. 5 indicates that both the ionization potential and the electron affinity approach their bulk values according to a power-law decay R^n with $n \approx 1$. The numerical fits are:

$$\mathrm{IP} = \mathrm{IP}_0 + A/D^{\alpha} \tag{7}$$

$$\mathrm{EA} = \mathrm{EA}_0 - B/D^{\beta} \tag{8}$$

with $\mathrm{IP}_0 =$ 4.50 eV, $\mathrm{EA}_0 =$ 3.87 eV, $\alpha =$ 1.16, $\beta =$ 1.09, $A =$ 3.21 eV, $B =$ 3.13 eV. These values for A and B assume a cluster diameter D given in nanometers. The difference between ionization potential and electron affinity is the electronic gap of the nanocrystal. As expected, the value of the gap extrapolated to bulk, $\mathrm{IP}_0 - \mathrm{EA}_0 =$ 0.63 eV, is very close to the energy gap predicted in various DFT calculations for silicon, which range from 0.6 eV to 0.7 eV [6,49]. Owing to the slow power-law decay, the gap at the largest crystal studied is still 0.7 eV larger than the extrapolated value.

Other properties of large silicon clusters are also expected to be similar to the ones of bulk silicon, which is equivalent to a nanocrystal of “infinite size”. Fig. 6 shows that the density of states already assumes a bulk-like profile in clusters with around ten thousand atoms. The presence of hydrogen atoms on the surface is responsible for subtle features in the DOS at around -8 eV and -3 eV. Because of the discreteness of eigenvalues in clusters, the DOS is calculated by adding up normalized Gaussian distributions located at each calculated energy eigenvalue. In Fig. 6, we used Gaussian functions with dispersion of 0.05 eV. More details are discussed in [50].

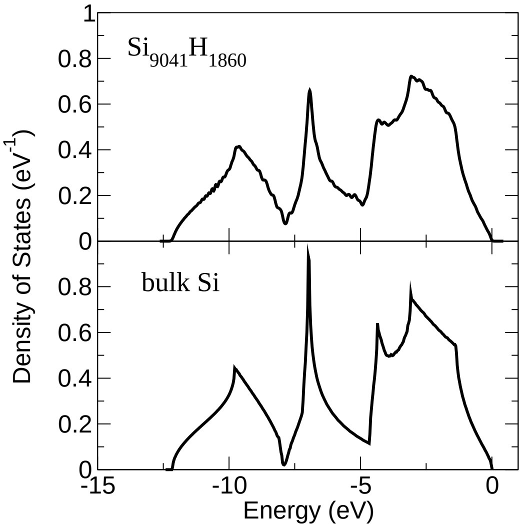

Figure 6: Density of states (DOS) of the cluster $Si_{9041}H_{1860}$ (upper panel) compared with periodic crystalline silicon (lower panel). As a consequence of the large size, the DOS of the $Si_{9041}H_{1860}$ cluster is very close to that of bulk silicon (the inÃđnite-size limit).

H size	n_{state}	`#MVp`	`#SCF`	`total_eV/atom`	`1st CPU`	`total CPU`
2790688	1812×2	9377435	110	-795.18064	16.16 hrs.	112.44 hrs.

Table 9: Fe_{302}, using 16 processors. $m = 20$ for Chebyshev-Davidson; $m = 19$ for CheFS.

H size	n_{state}	`#MVp`	`#SCF`	`total_eV/atom`	`1st CPU`	`total CPU`
2985992	1956×2	10241385	119	-795.19898	11.62 hrs.	93.15 hrs.

Table 10: Fe_{326}, using 24 processors. $m = 20$ for Chebyshev-Davidson; $m = 19$ for CheFS.

We also applied PARSEC to some large iron clusters. Tables 9–11 contain three clusters with more than 300 iron atoms. The number of states, n_{state}, is multiplied by two because these clusters are magnetized and spin degeneracy is broken. These metallic systems are well-known to be very difficult for DFT calculations, because of the "charge sloshing" [7, 8]. The LDA approximation used to get exchange-correlation potential V_{xc} is also known not to work well for iron atoms. However, PARSEC was able to reach self-consistency for these large metallic clusters within reasonable time length. Physical significance of the computed data will be discussed in [51]. It took more than 100 SCF steps

H size	n_{state}	`#MVp`	`#SCF`	`total_eV/atom`	`1st CPU`	`total CPU`
3262312	2160×2	12989799	146	-795.22329	16.55 hrs.	140.68 hrs.

Table 11: Fe_{360}, using 24 processors. $m = 20$ for Chebyshev-Davidson; $m = 17$ for CheFS.

to reach self-consistency, which is generally considered too high for SCF calculations, but we observed (from calculations performed on smaller iron clusters) that eigenvector-based methods also required a similar number of SCF steps to converge, thus the slow convergence is associated with the difficulty of DFT for metallic systems. Without CheFS, and under the same hardware conditions as listed in Tables 9–11, over 100 SCF steps using eigenvector-based methods would have required months to complete for each of these clusters.

7 Concluding Remarks

We developed and implemented the parallel CheFSI method for DFT SCF calculations. Within CheFSI, only the first SCF step requires a true diagonalization, and we perform this step by the block Chebyshev-Davidson method. No diagonalization is required after the first step; instead, Chebyshev filters are adaptively constructed to filter the subspace from previous SCF steps so that the filtered subspace progressively approximates the eigensubspace corresponding to occupied states of the final Hamiltonian. The method can be viewed as a nonlinear subspace iteration method which combines the SCF iteration and diagonalization, with the diagonalization simplified into a single step Chebyshev subspace filtering.

Additional tests not reported here, have also shown that the subspace filtering method is robust with respect to the initial subspace. Besides self-consistency, it can be used together with molecular dynamics or structural optimization, provided that atoms move by a small amount. Even after atomic displacements of a fraction of the Bohr radius, the CheFSI method was able to bring the initial subspace to the subspace of self-consistent Kohn-Sham eigenvectors for the current position of atoms, with no substantial increase in the number of self-consistent cycles needed.

CheFSI significantly accelerates the SCF calculations, and this enabled us to perform a class of large DFT calculations that were not feasible before by eigenvector-based methods. As an example of physical applications, we discuss the energetics of silicon clusters containing up to several thousand atoms.

8 Acknowledgments

We thank the staff members at the Minnesota Supercomputing Institute, especially Gabe Turner, for the technical support. There were several occasions where our large jobs required that the technical support staff change certain default system settings to suit our needs. The calculations would not have been possible without the computer resource and the excellent technical support at MSI. This work was supported by the MSI, by the National Science Foundation under grants ITR-0551195, ITR-0428774, DMR-013095 and DMR-0551195 and by the U.S. Department of Energy under grants DE-FG02-03ER25585, DE-FG02-89ER45391, and DE-FG02-03ER15491.

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