Ψ_k Newsletter

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

Number 65 October 2004

Editor: Z. (Dzidka) Szotek
E-mail: psik-coord@dl.ac.uk

Contents

1 Editorial **4**

2 General News **5**

2.1 Psi-k2005 Conference 5

2.2 Towards a European Strategy for Nanotechnology 6

3 News from the ESF Programme **7**

3.1 Reports on the ESF Workshops/Conferences 7

3.1.1 Report on the Workshop "Electronic structure beyond density functional theory" 7

3.1.2 Report on International TDDFT Workshop and School 13

3.1.3 Report on CECAM - Psi-k Tutorial 44

3.1.4 Report on ESSN-2004 and the Workshop of WG7 54

3.2 ESF Workshop/Conference Announcements 60

3.2.1 WORKSHOP ON AB INITIO PHONON CALCULATIONS 60

3.2.2 Mini-workshop on FLAPW development 61

4 News from UK's CCP9 Programme **62**

4.1 CCP9 Conference Announcements 62

4.1.1 CCP9 Conference 62

5 General Workshop/Conference Announcements **64**

5.1 Computational Materials Science Workshop 64

5.2 ICTP - INFM/Democritos - ISMO - IUT School 66

6 General Job Announcements **68**

7 Abstracts **84**

8 Release of FPLO-4 Code **104**

9 SCIENTIFIC HIGHLIGHT OF THE MONTH **105**

1 **Introduction** **105**

2 **Formalism** **107**

3 **Real-space (multigrid) methods** **108**

3.1 RQMG method 110

4 **Technical enhancements** **112**

4.1 Double grid technique 112

4.2 Mixing schemes (traditional) 115

4.3 Response iteration methods 116

4.4 Higher-order compact discretizations 117

4.5 RQMG with Galerkin conditions 117

4.6 Alternative eigenproblem solvers 118

5 **Status of `MIKA/rspace`** **119**

6 **Quantum dots in 2DEG** **120**

6.1 Introduction and the model 120

6.2 Computational aspects 121

6.3 Zero-field results 121

6.4 Magnetic fields and the vortex clusters 122

6.5 Impurities in quantum dots 124

7 **Nanophysics in axial symmetry** **124**

7.1 Ultimate jellium model for a breaking nanowire 125

7.2 Adsorbed Na quantum dots on Cu(111) 127

8 **Positron calculations** **128**

9 **Summary and outlook** **130**

10 **Acknowledgements** **131**

1 Editorial

We start this newsletter with some details on the Psi-k 2005 Conference, providing the conference web-page where the suggestion form for symposia and speakers can be found. The suggestions need to be submitted by the end of October. Then we have some information concerning European Strategy for Nanotechnology. In the section of the **ESF Programme** readers can find four reports on various workshops sponsored by the Programme of which some contain also the abstracts of presented papers. In the same section we also advertise two future workshops of this Programme. In the **UK's CCP9** section we announce the CCP9 Conference which will take place in Daresbury Laboratory, UK, in November 2004. At this conference Professor Matthias Scheffler (FHI Berlin), the winner of the Institute of Physics Max Born Medal and Prize for 2004, will deliver the Max Born lecture. We encourage our readers to register for this conference which promises to be a very stimulating scientific event. Note that the number of places is limited to about 80, so do not leave it too late to register. Two further workshop/school announcements can be found in the **General Workshop/Conference Announcements**, followed by a number of announcements of available positions. Abstracts of newly submitted papers are in their usual section, and just before the scientific highlight one can find a short note on the release of the Dresden FPLO-4 code. The scientific highlight is by T. Torsti (*Helsinki and Espoo, Finland*), V. Lindberg (*Växjö, Sweden*), I. Makkonen (*Helsinki, Finland*), E. Ogando (*Donostia, Spain*), E. Räsänen, H. Saarikoski, M. J. Puska and R. M. Nieminen (*Helsinki, Finland*) on **"MIKA - a multigrid-based program package for electronic structure calculations"**. Please check the table of content for further details.

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

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

The above contains information on the Psi-k 2004 workshops and hands-on courses (subject to funding). In these pages you can also find information on how to apply for funding to make collaborative visits.

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

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

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

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

2 General News

2.1 Psi-k2005 Conference

Towards atomistic materials design"

September 17-21, 2005

Schwäbisch Gmünd, Germany

The conference website is now open at

http://www.fyslab.hut.fi/psik2005/

As the two previous Psi-k meetings (1996, 2000), Psik-2005 will cover theoretical and computational research of electronic structure and properties of matter, ranging from new materials to systems of biological interest. The conference carries the motto "Towards atomistic materials design", and is supported by the Psi-k Programme and Network of the European Science Foundation. Details concerning the programme, participation, accommodation and funding will be available in due course (see the provisional organisational timetable).

The programme of the conference is now being planned. We would like to have your suggestions for plenary and invited speakers and symposia topics. The conference website contains suggestion forms for plenary and other invited speakers as well as symposia topics and organisers.

Please fill out the suggestion form by the end of October. We are looking forward to a wide selection of suggestions from the worldwide electronic structure community.

Risto Nieminen
Conference Chairman

2.2 Towards a European Strategy for Nanotechnology

To Psi-k Network

You might be interested to know that we have launched an open consultation on the Communication "Towards a European Strategy for Nanotechnology"

(http://www.cordis.lu/nanotechnology/src/communication.htm)

that was published earlier this year.

In order to take part, Nanoforum (http://www.nanoforum.org) have created an online questionnaire that should take around 15 minutes to complete and we would encourage all interested persons to participate by the 30th September. The outcome of this survey will be published in the form of a freely available report and will help shape future European initiatives in nanoscience and nanotechnologies.

Kind regards

Raymond Monk
Programme Officer
Nanosciences and Nanotechnology
European Commission - DG Research
MO75 00/51, B-1049 Brussels
tel.: +32-2-29.84493
fax: +32-2-29.86150
e-mail: Raymond.Monk@cec.eu.int
http://www.cordis.lu/nanotechnology

Assistant: Olivia Palimeris
tel.: +32-2-29.66454
e-mail: Olivia.Palimeris@cec.eu.int

3 News from the ESF Programme

”Towards Atomistic Materials Design”

3.1 Reports on the ESF Workshops/Conferences

3.1.1 Report on the Workshop “Electronic structure beyond density functional theory”

Electronic structure beyond density functional theory

Lorentz Center, Leiden, 12-16 July 2004

Organisers

Claudia Filippi, Universiteit Leiden, Instituut-Lorentz, Leiden, The Netherlands

Matthew Foulkes, Imperial College, Condensed Matter Theory Group, London, UK

Shiwei Zhang, College of William and Mary, Department of Physics, Williamsburg, USA

Summary

The focus of the workshop was on electronic structure beyond density functional theory, in particular, quantum Monte Carlo methods. The primary objective of the workshop was to spur and facilitate rapid growth of the field by bringing together scientists from different communities with a common interest in ab-initio many-body calculations, and by reaching out to junior researchers and researchers doing quantum Monte Carlo in smaller or isolated groups. A total of 53 participants from 9 countries attended the workshop, with research focus on quantum Monte Carlo, quantum chemistry, lattice models, computational diagrammatic approaches such as the GW, dynamical mean-field theory, etc. The participation was substantially larger than anticipated, and essentially at peak capacity of the Lorentz Center venue.

The format of the workshop was chosen to allow ample time for interactions. The number of talks per day was typically three or four, and a total of six focused discussions on outstanding issues were also scheduled. Each discussion had a leader who gave introductory presentations on the topic and was in charge of organising the session. This formula was very successful in creating lively sessions and a relaxed atmosphere where participants felt comfortable to openly discuss problems encountered in calculations, partial solutions or preliminary results, and new avenues for further investigation.

Within quantum Monte Carlo for electronic strucure, the workshop covered recent methodological developments and efforts to push the frontier of applications to ever more complex systems. The main topics, each followed by a partial list of speakers/discussion-leaders, were: Geometry optimisation and incorporation of molecular dynamics in quantum Monte Carlo (Ceperley, Grossman, Rappe), general and robust ways to obtain variational many-body wave functions (Fahy, Filippi, Sorella), new algorithms and insight for the fermionic problem in quantum Monte Carlo (Bressanini, Kalos, Sorella, Zhang), pseudopotential in many-body calculations (Bachelet, Dolg), computation of observables (Ceperley, Reynolds), and applications to large realistic systems (Williamson, Mitas, Moroni, Needs, Wood).

Topics and the respective key participants in related fields included: Coupled cluster calculations (Dolg, Schütz), quantum Monte Carlo for lattice models of strongly correlated systems (Sorella, Troyer, Zhang), GW calculations (Godby), dynamical mean-field theory calculations (Lichtenstein).

The meeting reached the intended goal to create an opportunity to discuss recent progress as well as current limitations of quantum Monte Carlo approaches. The presence of researchers from a broader many-body community had a significant impact on the workshop. Practitioners were able to compare and discuss in some detail different techniques for treating electron correlations in materials, and found the experience mutually stimulating.

The participants clearly enjoyed the workshop both for its scientific content as well as for the logistical aspects, which were very smoothly taken care of by the management of the Lorentz Center. The workshop was funded by the Lorentz Center and the Psi-k ESF Programme, with additional support for US junior participants from the US NSF.

List of participants

Roland Assaraf	(Paris, France)
Claudio Attaccalite	(Trieste, Italy)
Giovanni Bachelet	(Roma, Italy)
Bastiaan Braams	(Atlanta, GA, United States)
Benoit Braida	(Paris, France)
Dario Bressanini	(Como, Italy)
Michele Casula	(Trieste, Italy)
David Ceperley	(Urbana, IL, United States)
Michael Dolg	(Köln, Germany)
Dominik Domin	(Berkeley, United States)
Stephen Fahy	(Cork, Ireland)
Martin Feldbacher	(Stuttgart, Germany)
Claudia Filippi	(Leiden, Netherlands)
Matthew Foulkes	(London, United Kingdom)

Martin Fuchs	(Berlin, Germany)
Gianluca Giovannetti	(Rome, Italy)
Rex Godby	(York, United Kingdom)
Jeffrey Grossman	(Livermore, United States)
Richard Hennig	(Columbus, Ohio, United States)
Markus Holzmann	(Paris, France)
Malvin Kalos	(Livermore, CA, United States)
Diemo Koedderitzsch	(Halle, Germany)
Henry Krakauer	(Williamsburg, United States)
Alexander Landa	(Livermore, CA, United States)
Alexander Lichtenstein	(Hamburg, Germany)
Martin Lueders	(Warrington, United Kingdom)
Andrea Ma	(Cambridge, United Kingdom)
Burkhard Militzer	(Washington, DC, United States)
Lubos Mitas	(Raleigh, United States)
Saverio Moroni	(Rome, Italy)
Richard Needs	(Cambridge, United Kingdom)
Carlo Pierleoni	(L'Aquila, Italy)
Victor Popa	(Enschede, Netherlands)
Zoltan Radnai	(Cambridge, United Kingdom)
Tapio Rantala	(Tampere, Finland)
Andrew Rappe	(Philadelphia, United States)
Peter Reinhardt	(Paris, France)
Peter Reynolds	(Durham, NC, United States)
Romelia Salomon	(Berkeley, CA, United States)
Anthony Scemama	(Leiden, Netherlands)
Kevin Schmidt	(Tempe, United States)
Martin Schuetz	(Stuttgart, Germany)
Sandro Sorella	(Trieste, Italy)
Arash Sorouri Khorashad	(London, United Kingdom)
Mike Towler	(Cambridge, United Kingdom)
John Trail	(Cambridge, United Kingdom)
Matthias Troyer	(Zürich, Switzerland)
Cyrus Umrigar	(Ithaca, United States)
Lucas Wagner	(Raleigh, NC, United States)
Andrew Williamson	(Livermore, United States)
Ben Wood	(London, United Kingdom)
Maurizio Zaccheddu	(Leiden, Netherlands)
Shiwei Zhang	(Williamsburg, United States)

Programme

Monday, July 12

09:15-09:20	Introduction
	Chairman: Foulkes (London)
09:20-10:10	Ceperley (Urbana-Champaign) *Coupled Electron-Ion Monte Carlo*
09:10-11:00	Bressanini (Como) *Much ado about .... zeroes (of trial functions)*
11:00-11:30	Coffee/tea
11:30-12:00	Free discussion
12:00-13:30	Lunch
	Chairman: Needs (Cambridge)
13:30-14:20	Mitas (North Carolina) *Topology of fermion nodes and local current conservation for accurate QMC wave functions*
14:20-15:10	Zhang (Williamsburg) *Electronic structure by Slater determinant random walks*
15:10-15:40	Coffee/tea
15:40-17:00	*Discussion on fermion sign problem* Leader: M. Kalos (Livermore)
17:00	Posters with wine cheese

Tuesday, July 13

	Chairman: Mitas (North Carolina)
09:20-10:10	Troyer (Zurich) *Overcoming free energy barriers in quantum Monte Carlo simulations*
10:10-11:00	Grossman (Livermore) *Coupled quantum Monte Carlo and ab initio molecular dynamics simulations*
11:00-11:30	Coffee/tea
11:30-12:30	*Discussion on MD in QMC* Leader: Mitas (North Carolina)
12:30-15:00	Lunch and informal discussions
	Chairman: Towler (Cambridge)
15:00-15:50	Sorella (Trieste) *Antisymmetrized Jastrow geminal product: an efficient Resonating Valence Bond approach to quantum chemistry*
15:50-16:40	Fahy (Cork) *Energy minimization methods for Jastrow-Slater wave functions*
16:40-17:00	Coffee/tea
17:00-18:30	*Discussion on wave function optimization for ground and excited states* Leader: C. Filippi (Leiden)

Wednesday, July 14

	Chairman: Ceperley (Urbana-Champaign)
09:20-10:10	Williamson (Livermore) *Linear scaling QMC of the optical properties of nanoclusters*
10:10-11:00	Schuetz (Stuttgart) *Local correlation methods with density fitting*
11:00-11:30	Coffee/tea
11:30-12:30	*Discussion on linear scaling* Leader: Williamson (Livermore)
12:30-15:00	Lunch and informal discussions
	Chairman: Krakauer (Williamsburg)
15:00-15:50	Godby (York) *Spectral, ground-state and transport properties of many-electron systems from a GW approach*
15:50-16:40	Dolg (Köln) *Ab initio correlated calculations for periodic systems*
16:40-17:00	Coffee/tea
17:00-18:30	*Discussion on Pseudopotential/PseudoHamiltonian* Leader: G. Bachelet (Roma)

Thursday, July 15

	Chairman: Godby (York)
09:20-10:10	Umrigar (Cornell) *Quantum Monte Carlo study of planar quantum dots*
10:10-11:00	Lichtenstein (Hamburg) *Multiband QMC for local DMFT problems*
11:00-11:30	Coffee/tea
11:30-12:30	*Discussion on Computing observables* Leader: Reynolds (Durham)
12:30-15:00	Lunch and informal discussions
	Chairman: Pierleoni (L'Aquila)
15:00-15:50	Moroni (Roma) *Susceptibility of the electron gas*
15:50-16:20	Wood (London) *Improving the accuracy of surface simulations*
17:30	Conference dinner

Friday, July 16

	Chairman: Kalos (Livermore)
09:00- 9:50	Schmidt (Tempe) *Pairing Wave Functions in Quantum Monte Carlo*
09:50-10:40	Rappe (Philadelphia) *Electronic parameter updates and atomic forces in quantum Monte Carlo*
10:40-11:10	Coffee/tea
11:10-12:00	Needs (Cambridge) *Is DMC any good?*
12:00-14:00	Lunch and informal discussions
14:00-15:30	*Discussion and summary* Leader: Foulkes

3.1.2 Report on International TDDFT Workshop and School

Report on: "TIME DEPENDENT DENSITY FUNCTIONAL THEORY: PROSPECTS AND APPLICATIONS"

International Workshop and School

2004, August 28 – September 12

A. Rubio (Universidad del País Vasco, Centro Mixto CSIC-UPV/EHU and DIPC),
E. K. U. Gross (Freie Universität Berlin),
M. A. L. Marques (Universidad del País Vasco, Centro Mixto CSIC-UPV/EHU and DIPC),
F. Nogueira (Universidad de Coimbra and Centro de Física Computacional)

SPONSORED BY:
CECAM
ESF Psi_k Programme
Spanish Ministry of Science and Technology
Benasque Center for Science
NANOQUANTA Network of Excellence
Universities of the Basque Country and Coimbra

The School and workshop was hosted by the Benasque Center for Science, located at the heart of the Pirinees. The aim of the school was to introduce theoretical, practical, and numerical aspects of Time-dependent-density functional theory (TDDFT) to young graduate students, post-docs and even older scientists that are envisaging a project for which TDDFT would be the tool of choice. During the school we incentivated a close and informal contact between the students and the teachers. Furthermore, the students presented their current research activities and future interests (six of those presentations were selected as oral contributions to the international workshop). We felt that this was an important point, since young scientists should be involved in the building up of a strong community. The number of applications (above 150) surpassed all expectations and, of course, the limit of 45 places that we had to satisfy in order for the students to get the maximum benefit from the school, and also due to space and computer resource limitations. The students (graduate and postgraduate) also did participate in the workshop held just after the 10 days of school. The total number of participants was 91 from all over the world (including 16 females; three as invited speakers/lectures). The distribution was:

Italy (11,8)	UK (10,3)	USA (10,4)
Spain (10,3)	Sweden (6,2)	Belgium (4,3)
Germany (10,5)	Japan (2,1)	Portugal (2,1)
France (10,6)	Switzerland (5,3)	The Netherlands (3,2)
Russia (1,1)	Austria (1,1)	Finland (2,0)
Argentina (1,0)	Israel (2,1)	Poland (1,1)

in parenthesis it is indicated the total number of participants for each country and also the number of student (graduate and post-graduated) that have participated in the school and workshop.

The aim of the Workshop was to assess the present status of TDDFT approaches to the study of spectroscopic properties of real materials, and explore their capability for applications in further systems with technological and biological interest. The recent developments of TDDFT covered during the workshop include TDDFT versus current-DFT, van der Waals interactions, applications to biological systems, new functionals, transport phenomena, optical spectra of solids , etc. Due to the different methods used to tackle this problem (Many-Body Theory, Density Functional Theory, Configuration Interaction, semi-empirical approaches), this Workshop was intended as a way to promote links among scientists coming from different communities working or interested in electron excited states. Also it was intended as a follow-up event for the students attending the school as it was a good opportunity for them to see the real implications of the school lectures and get the new theoretical advances in the the development of exchange-correlation functionals as well as applications to complex systems (nanostructures, bio-molecules, interstellar molecular analysis, solids, etc.) Our goal was to bring together scientists working on foundations and different applications of TDDFT and many-body theory, trying to assess the capability of current approximations to be applied to real systems of increasing complexity. The invited and contributed talks covered:

I) Fundamental topics on TDDFT, Many-Body Theory, and electron transport theory.

II) New approximations and techniques.

III) Ab-initio calculations of spectroscopic properties of complex materials.

As a consequence, there was a broad variety of participants which helped to get an interdisciplinary vision of the field. Thus, although some of the more specific topics were far from the research interest of many participants, the meeting was an excellent opportunity to see how the same techniques are used by members of other communities.

School Program

time	29/8	30/8	31/8	1/9	2/9	3/9	4/9	5/9	6/9	7/9
10-11.30	DFT1	NUM	PP	free	PROP1+DP	APP1	free	APP2	BIO1	ALT1
12-13.30	VXC	TDDFT1	TDDFT2	free	TDDFT3	PROP2	free	RT	BIO2	ALT2
Lunch										
15.30-17	OCT1	OCT3	QD2	free	OCT4	PW1	free	PW3	QD5	ALT2
17.30-19	OCT2	QD1	QD3	free	QD4	PW2	free	PW4	PROJ	free
21h				School Dinner						

Theoretical Sessions

DFT1	U. von Barth	An Introduction to DFT
VXC	U. von Barth	XC functionals
NUM	X. Gonze	Numerical methods: plane waves real space methods, etc.
TDDFT	E.K.U. Gross	Time dependent density functional theory
PP	X. Gonze	Pseudopotentials
PROP	A. Castro	Propagation schemes (1h45 + 45m)
APP	A. Rubio	Applications of TDDFT for finite and infinite systems
DP	V. Olevano	Implementation of TDDFT for solids (45 m.)
RT		Round table - the past and future of TDDFT
BIO	X. López	Biological systems
ALT1	L. Reining	TDDFT vs BSE
ALT2	G. Vignale	TDDFT vs CDFT

Practical Sessions

OCT	F. Nogueira	Finite systems using octopus
QD	A. Castro	Development of a TDDFT program for quantum dots
PW	S. Botti, X. Gonze	Periodic systems with ABINIT+DP
PROJ		Project

Propagators for the time-dependent Kohn-Sham equations

Alberto Castro

Institut für Theoretische Physik, Freie Universität Berlin, Arnimallee 14, D-14195 Berlin, Germany

In this lesson we address the problem of the numerical integration of the time- dependent Schrödinger equation $\mathrm{i}\partial_t\varphi = \hat{H}\varphi$. In particular, we are concerned with the important case where $\hat{H}$ is the selfconsistent Kohn-Sham Hamiltonian that stems from time-dependent functional theory. As the Kohn-Sham potential depends parametrically on the time-dependent density, $\hat{H}$ is in general time-dependent, even in the absence of an external time-dependent field. The present analysis also holds for the description of the excited state dynamics of a many-electron system under the influence of arbitraty external time-dependent electromagnetic fields. Our discussion is separated in two parts: i) First, we look at several algorithms to approximate $\exp(\hat{A})$, where $\hat{A}$ is a *time-independent* operator [e.g. $\hat{A} = -\mathrm{i}\Delta t\hat{H}(\tau)$ for some given time τ]. In particular, polynomial expansions, projection in Krylov subspaces, and split-operator methods are investigated. ii) We then discuss different approximations for the time-evolution operator, li ke the mid-point and implicit rules, and Magnus expansions. Split-operator techniques can also be modified to approximate the full time-dependent propagator. As the Hamiltonian i s time-dependent, problem ii) is not equivalent to i). All these techniques have been implemented and tested in our computer code `octopus`, but can be of general use in other frameworks and implementations.

Numerical methods (I and II)

Xavier Gonze

Louvain la Neuve

We take as starting point the equations of Density-Functional Theory and examine the basic ideas leading to actual computer programs.

In this respect, one encounters two kinds of high-level problems : (1) mathematical quantities (like the electronic density or wavefunctions) must be represented by finite sets of numbers ; (2) mathematical equations must be solved. Supposing a representation, with some inevitable numerical inaccuracies, algorithms for solving equations will lead to computer predictions, also with a finite numerical precision. In both cases, the size of the numerical errors must be weighted against the inherent error present in any approximation to the "true" DFT. They can be reduced, at the expense of more memory space or more CPU time. In order to use properly the different computer programs, the user must be aware of this trade-off.

First, we will focus on the algorithms needed to find the optimized geometry for molecules, clusters or solids, including the resolution of the Kohn-Sham equations (in order for the electrons to be in their ground state). The similarities between geometry optimization, Kohn-Sham self-consistency, and iterative resolution of the Kohn-Sham (or Schroedinger) equation will be highlighted. Basic iterative methods will be described, as well as more advanced methods like conjugate gradients, Broyden, and damped dynamics algorithms.

Then, we examine the concept of pseudopotential, a crucial ingredient for several representation methodologies. Pseudopotentials allow to avoid treating explicitely core electrons. They introduce quite small errors, compared to the inherent (in)accuracy of present day exchange-correlation functionals. The freezing of the core electrons will be distinguished from the actual pseudopotential construction. The historical Kleinman approach will be described, followed by the discussion of more recent norm-conserving pseudopotentials, and a brief introduction to ultrasoft pseudopotentials, and projector augmentation.

We will then focus on a particular representation, based on planewaves, well-adapted to the case of crystalline solids : Bloch theorem, set of planewave coefficients in reciprocal space, Brillouin zone, computation of the density from wavefunctions, computation of the electrostatic and exchange-correlation potential, treatment of metals.

Finally, we present the ABINIT software : availability, structure, features, and present status of development.

Chromophores in biological environments

Xabier López

Kimika Fakultatea; Euskal Herriko Unibertsitatea

An introduction of chromophores in biological environments will be given. Biochromophores that absorb in the visible lighth mainly consist of phrostehtic groups or cofactors covalently bound to proteins. In this lecture, we will see some basic examples of these phrostethic organic molecules and how the absorption of light is coupled with their complex biological functions. In addition, and since the optical response of these phrosthetic groups is often modulated by their proteic environment, an introduction to protein structure and its modelization will be given. Finaly, we discuss some illustrative examples of chromophores emdebbed in proteins and how their optical absorption is a consequence of both chromophore chemical nature and interaction (structural and electrostatic) with its proteic surroundings.

How to describe exchange and correlation effects in the response properties of valence electrons? Answers from TDDFT and Many-Boby Perturbation Theory

Lucia Reining

Laboratoire des Solides Irradiés, UMR 7642 CNRS/CEA, École Polytechnique, F-91128 Palaiseau, France

Today, one of the big challenges of theoretical condensed matter physics is to find ways for describing accurately and efficiently the response of electrons to an external perturbation. In fact, the knowledge of response functions allows one to directly derive spectra (such as absorption or electron energy loss); moreover, response functions enter the description of correlation effects, for example through the screened Coulomb interaction W in Hedin's GW approximation to the electron self-energy. Two main developments for the *ab initio* calculation of response functions of both finite and infinite systems are, on one side, the solution of the Bethe-Salpeter equation (BSE), and, on the other hand, Time-Dependent Density Functional Theory (TDDFT). Both approaches are promising, but suffer from different shortcomings: the solution of the Bethe-Salpeter equation is numerically very demanding, whereas for TDDFT, despite recent progress a generally reliable but at the same time very efficient description of exchange-correlation effects has still to be developed. Therefore, one would ideally like to combine the advantages of both pictures.

In this lesson, we will show that both approaches can be interpreted as containing the same physics, but in a different world. We focus on their comparison by putting them on the same footing. The meaning and importance of different contributions to the induced potentials will be analyzed. The similarities will allow us to propose combinations of TDDFT and the BSE approach that are leading to a class of exchange-correlation kernels which yield excellent spectra and are potentially very efficient in numerical calculations.

Applications of TDDFT: optical absorption and electron energy loss spectroscopy of nanostructures and extended systems

Angel Rubio

Departamento de Física de Materiales, Facultad de Química s, UPV/EHU, and Centro Mixto CSIC-UPV/EHU, 20018 San Sebastián, Spain

In this set of lectures we will present a comparison between TDDFT and other approaches for the description of the response properties of many electron systems [1]. We will provide a short review of the computational isssues related to the practical implementation of TDDFT for finite and extended systems (within the octopus project [2]). This general scheme allows to treat on the same footing arbitrary external electromagnetic fields. As application we will show results for the optical absorption and photoinduced fragmentation of small clusters as well as the photoresponse of biomolecules (Green-Fluorescent protein and azobencene) [3]. At the end we will discuss some of the deficiencies of the standard DFT-based approaches to cope with the response function of extended systems (one, two and three-dimensional) [1]. The problem is traced back to the lack of long-range interaction in the exchange-correlation kernel. We will show how this can be incorporated in TDDFT by deriving a formally exact exchange-correlation kernel based on many-body-perturbation theory [4] in connection with Lucia Reining lectures. Also we will present an alternative, nonperturbative way to treat the electric response of extended systems by a time-propagation scheme in the same spirit done for nanostructures[2].

Work done in collaboration with M.A.L. Marques, A. Castro, X. Lopez, E.K.U. Gross, D. Varsano, G. Bertsch, L. Reining, A. Marini, R. Del Sole and G. Onida. We acknowledge support from the European Community Research Training Network NANOPHASE (HPRN-CT-2000-00167), Network of Excellence NANOQUANTA (NOE 500198-2), Spanish MCyT(MAT2001-0946) and the University of the Basque Country (9/UPV 00206.215-13639/2001). The computer time was granted by DIPC and CEPBA (Barcelona).

[1] G. Onida, L. Reining and A. Rubio, Rev. Mod. Phys. **74**, 601 (2002).

[2] M. A. L. Marques, A. Castro, G. F. Bertsch and A. Rubio, Computer Phys. Commun. 151, 60 (2003). The code OCTOPUS is available at http://www.tddft.org/programs/octopus. A. Castro, M.A.L. Marques, J.A. Alonso and A. Rubio Journal of Computational and Theoretical Nanoscience (in press 2004)

[3] M.A.L Marques, X. López, D. Varsano, A. Castro, and A. Rubio, Phys. Rev. Lett. 90, 258101 (2003); and work to be published for azobencene and DNA basis.

[4]A. Marini, R. Del Sole, and A. Rubio, Phys. Rev. Lett. **91**, 256402 (2003); F. Sottile, V. Olevano and L. Reining, Phys. Rev. Lett. **91**, 056402 (2003); L. Reining, V. Olevano, A. Rubio, and G. Onida, Phys. Rev. Lett. **88**, 066404 (2002); R.D. Sole, G. Adragna, V. Olevano and L. Reining, Phys. Rev. B **67**, 045207 (2003).

Lectures on TDDFT vs CDFT

G. Vignale

Univ. Missouri, USA

1. THE ELASTICITY OF THE ELECTRON LIQUID

In this lecture I review the two classical macroscopic theories of collective dynamics, hydrodynamics and elasticity, and I show that the usual description of the macroscopic dynamics of an electron liquid in terms of exchange-correlation fields can be viewed as a combination of these two theories, where the frequency-dependent visco-elastic coefficients are determined by the quantum excitation spectrum. Exact results and approximate expressions f or the visco-elastic coefficients are presented.

2. TIME-DEPENDENT CURRENT DENSITY FUNCTIONAL THEORY

Here I show how the results obtained for the homogeneous electron liquid can be used to construct a local approximation for the exchange-correlation potential for non-homogeneous electronic systems. Such a construction must be done within the framework of the current-density functional theory (CDFT), in which the basic variable is the current density, an d the exchange-correlation effects are described in terms of a vector potential. The explicit form of the exchange correlation potential beyond the adiabatic local density approximation is then discussed.

Workshop

Day I: Wednesday 8th

09h00 - 09h10	Angel Rubio	Opening remarks
09h10 - 10h00	Robert van Leeuwen	An overview of basic concepts in TDDFT and some new extensions
10h00 - 10h50	Ilya Tokatly	Quantum many-body dynamics in Lagrangian frame: Geometric formulation of TDDFT
10h50 - 11h20		Caffeine break
11h20 - 12h10	Neepa Maitra	Aspects of non-adiabaticity in TDDFT
12h10 - 13h00	Shaul Mukamel	Spontaneous Density Fluctuations, Intermolecular Forces and Nonlinear TDDFT Response; Superoperator Approach
13h00 - 15h00		Lunch break
15h00 - 15h50	Juerg Hutter	Plane-wave TDDFT calculations of molecules in solution
15h50 - 16h40	Michiel Sprik	Car-Parrinello TDDFT computation of electronic spectra of some transition metal aqua ions in solution
16h40 - 17h10		Beer break
17h10 - 18h00	Yoshiyuki Miyamoto	Excited State Molecular Dynamics with use of the code FPSEID: First Principles Simulation tool for Electron Ion Dynamics
18h00 - 19h00		Poster Session

Day II: Thursday 9th

09h10 - 10h00	Giovanni Vignale	Advances in time-dependent spin density functional theory
10h00 - 10h50	Roi Baer	Time dependent density functional theory: new functionals and applications
10h50 - 11h20		Caffeine break
11h20 - 12h10	Tuomas Torsti	Real-space multigrid methods for DFT and TDDFT
12h10 - 13h00	M. Marques	Octopus: present, past, and future
13h00 - 15h00		Lunch break
15h00 - 15h50	Raffaele Resta	Localization and polarization in the insulating state of matter
15h50 - 16h40	I. Tavernelli	Excited state ab initio MD of photochemical processes in model compounds
16h40 - 17h10		Beer break
17h10 - 18h00	Giacomo Mulas	Using ab initio tools to solve the astrophysical puzzle of interstellar PAHs

Day III: Friday 10th

09h10 - 10h00	Kieron Burke	Rigorous DFT treatment of transport through single molecules
10h00 - 10h50	Roberto Car	Electron transport and dissipation in nanoscale devices
10h50 - 11h20		Caffeine break
11h20 - 12h10	Carl-Olof Almblahd	Time-dependent quantum transport by means of TDDFT
12h10 - 13h00	Rex Godby	Self-Energy Approaches for Excited and Ground States: Lessons for and from DFT
13h00 - 15h00		Lunch break
15h00 - 15h50	Martin Fuchs	Use of the the adiabatic-connection fluctuation-dissipation approach to exchange-correlation in the ground state
15h50 - 16h40	P. Garcia Gonzalez	TDDFT as an useful tool to calcute accurate correlation energies
16h40 - 17h10		Beer break
17h10 - 18h00		Presentations from the best posters.

Day IV: Saturday 11th

09h10 - 10h00	Andreas Goerling	Exact-exchange TDDFT methods for molecules and solids
10h00 - 10h50	P. de Boeij	The time-dependent current-functional approach for the response of solids and polymers
10h50 - 11h20		Caffeine break
11h20 - 12h10	Lucia Reining	TDDFT and Many-Boby Perturbation Theory: comparisons and combinations
12h10 - 15h00		Lunch break
15h00 - 17h30		Discussions
17h30 - 17h45	E.K.U. Gross	Closing remarks

Time-dependent quantum transport by means of TDDFT

Gianluca Stefanucci and Carl-Olof Almbladh

Department of Theoretical Physics, University of Lund, Lund, Sweden

An exact theoretical framework based on Time Dependent Density Functional Theory (TDDFT) is proposed in order to deal with the time-dependent quantum transport in fully interacting systems. We use a partition-free approach by Cini in which the whole system is in equilibrium before an external electric field is switched on. Our theory includes the interactions between the leads and between the leads and the device. It is well suited for calculating measurable transient phenomena as well as a.c. and other time-dependent responses and is valid for finite as well as macroscopic electrodes. We show that the steady-state current results from a *dephasing mechanism* provided the leads are macroscopic and the device is finite. In the d.c. case, we obtain a Landauer-like formula when the effective potential of TDDFT is uniform deep inside the electrodes.

The time-dependent current-functional approach for the response of solids and polymers'

Paul L. de Boeij

Groningen, The Netherlands

The first-principles description of the response of crystalline systems to external fields relies heavily on the use of periodic boundary conditions. This treatment has important implications for the time-dependent density functional framework. I will show how intrinsic, i.e. material properties can be obtained and how extrinsic, i.e. size and shape dependent effects can effectively be removed from the computational scheme. The result of this analysis is that a uniform component of the current-density appears as an extra degree of freedom, which is not uniquely fixed by the lattice periodic density. A natural way to treat the periodic systems is now obtained by changing the basic dynamical variable from the time-dependent density to the induced current-density. Observable quantities, like for instance the induced macroscopic polarization can then be given in closed form as current functionals. The response to both longitudinal and transverse fields can be treated in this unified approach. I will give the linear response and excitation formulation for the resulting time-dependent Kohn-Sham system, and show how (non)-adiabatic density and current-density dependent exchange-correlation functionals are included. The approach is equally well suitable to treat finite systems as infinite metallic or insulating systems. I apply the time-dependent current-density functional approach to the response properties of periodic systems and finite systems. The periodic structures include several (semi)metallic and semiconducting crystals and polymers. The finite systems cover several pi-conjugated and non-conjugated oligomers and small molecules. In these systems some failures of the ALDA are discussed and results are presented for the current-density dependent exchange-correlation functional derived by Vignale and Kohn. The influence of this functional on the linear response and excitation energies is discussed. For the oligomer polarizabilities the asymptotic relation to the polymer susceptibilities is discussed.

Rigorous DFT treatment of transport through single molecules

Kieron Burke

Dept of Chemistry and Chemical Biology, Rutgers University

Transport through single molecules has become a hot topic since the first experiments several years ago. But it is unclear if the present methodology (Landauer formalism plus ground-state

DFT) is the correct approach for calculating conductance in these devices. I'll discuss the problems, and show some recent results in the weak bias limit, derived using TDDFT. I'll also discuss a new methodology for handling dissipation in electronic systems using a Kohn-Sham master equation.

Electron transport and dissipation in nanoscale devices

Roberto Car

Princeton University, Princeton, NJ08544, USA

We present a quantum-kinetic scheme for the calculation of non-equilibrium transport properties in nanoscale systems. Our approach is based on a time-dependent Kohn-Sham master equation for the reduced electronic density operator and represents a generalization of the well-known Boltzmann kinetic equation. The approach allows us, in particular, to model transport situations under high applied fields by adopting periodic boundary conditions. Applications to nanoscale devices and molecular structures are discussed

The time-dependent current-functional approach for the response of solids and polymers

Paul L. de Boeij

Groningen, The Netherlands

The first-principles description of the response of crystalline systems to external fields relies heavily on the use of periodic boundary conditions. This treatment has important implications for the time-dependent density functional framework. I will show how intrinsic, i.e. material properties can be obtained and how extrinsic, i.e. size and shape dependent effects can effectively be removed from the computational scheme. The result of this analysis is that a uniform component of the current-density appears as an extra degree of freedom, which is not uniquely fixed by the lattice periodic density. A natural way to treat the periodic systems is now obtained by changing the basic dynamical variable from the time-dependent density to the induced current-density. Observable quantities, like for instance the induced macroscopic polarization can then be given in closed form as current functionals. The response to both longitudinal and transverse fields can be treated in this unified approach. I will give the linear response and excitation formulation for the resulting time-dependent Kohn-Sham system, and show how (non)-adiabatic density and current-density dependent exchange-correlation functionals are included. The approach is equally well suitable to treat finite systems as infinite metallic or insulating systems. I apply the time-dependent current-density functional approach to the response properties of periodic systems and finite systems. The periodic structures include several (semi)metallic and semiconducting crystals and polymers. The finite systems cover several pi-conjugated and non-conjugated oligomers and small molecules. In these systems some failures of the ALDA are discussed and results are presented for the current-density dependent exchange-correlation functional derived by Vignale and Kohn. The influence of this functional on the linear response and excitation energies is discussed. For the oligomer polarizabilities the asymptotic relation to the polymer susceptibilities is discussed.

Use of the adiabatic-connection fluctuation-dissipation approach to exchange-correlation in the ground state

Martin Fuchs

Fritz-Haber-Institut der Max-Planck-Gesellschaft, Berlin, Germany

The adiabatic-connection fluctuation-dissipation theorem (ACFDT) provides an exact formula for the exchange-correlation (XC) energy in terms of the dynamical linear density-density response function, a quantity given by time-dependent density-functional theory. Approximate "ACFDT" XC functionals may be generated from suitable response functions, opening the way for improvements beyond present functionals such as the LDA, GGA, or hybrids: (i) proper treatment of van der Waals interactions, and (ii) systematically higher accuracy for the bond energetics of molecules and solids.

Here we consider ACFDT XC functionals based on the random phase approximation (RPA) alone and the RPA augmented by an (approximate) exchange kernel (RPA+X), which we have recently implemented in a pseudopotential plane-wave framework [1,2]. Calculating the groundstate potential energy curves for H_2 and Be_2, we find that the RPA gives excellent results for the binding energy, equilibrium bond length and fundamental vibrational frequency. Considering stretched H_2, we show that the RPA largely overcomes the long-standing symmetry dilemma of DFT: the molecule dissociates properly into two atoms without taking recourse to artificial symmetry breaking as in the usually applied spin-unrestricted Kohn-Sham schemes. The RPA thus captures the strong static (left-right) correlations when the bond breaks, as is apparent from the corresponding adiabatic connection curves. At intermediate bond lengths, the RPA as well as the RPA+X potential energy curves remain too repulsive however. We discuss implications of this finding on the construction TDDFT XC kernels for ACFDT XC functionals beyond the RPA.

[1] M. Fuchs and X. Gonze, Phys. Rev. B 65, 235109 (2002); M. Fuchs, K. Burke, Y.-M. Niquet, and X. Gonze, Phys. Rev. Lett. 90, 189701 (2003).

[2] X. Gonze et al., Comput. Materials Science 24, 478 (2002).

work performed with Yann-Michel Niquet (SP2M/L_Sim, CEA Grenoble, France), Kieron Burke (Dept. of Chemistry and Chemical Biology, Rutgers Univ., U.S.), and Xavier Gonze (Unite PCPM, Univ. Catholique de Louvain, Belgium).

Exact-exchange TDDFT methods for molecules and solids

Andreas Goerling

Bonn University

The Kohn-Sham formalism is reconsidered in order to introduce the concept of orbital-dependent functionals for exchange-correlation energies, potentials, and kernels. Adiabatic connection perturbation theory for a systematic construction of functionals in the static as well as in the time-dependent case is discussed. Response properties (excitation energies, NMR chemical shifts) of molecules based on effective exact-exchange KS orbitals and eigenvalues are presented. An exact-exchange TDDFT approach for solids is presented and compared to methods based on the Bethe-Salpeter equation.

TDDFT as an useful tool to calcute accurate correlation energies

P. Garcia-Gonzalez (1), J. Jung (1), A. Marini (2), J. Dobson (3), R.W. Godby (4), and A. Rubio (2)

(1) Departamento de Fisica Fundamental, UNED, Apartado 60.149, E-28080 Madrid, Spain

(2) Donostia International Physics Center, Apartado 1072, E-20018 San Sebastian, Spain

(3) School of Science, Griffith University, Nathan, Queensland 4111, Australia

(4) Department of Physics, University of York, Heslington, York YO10 5DD, United Kingdom

The adiabatic-connection fluctuation-dissipation theorem (ACFDT) in the framework of Time Dependent Density Functional Theory (TDDFT) has emerged as a promising alterative to standard implementations of Kohn-Sham (KS) theory to calculate correlation energies. In this approach, the correlation energy is calculated from the knowledge of the interacting density response, without resorting to mean-field-like approximations. Thus, using the ACFDT scheme we can easily describe many-body effects that are absent in the KS-LDA or KS-GGA without the numerical expense of diffusion quantum Monte Carlo calculations.

If we neglect local-field corrections in the construction of the density response, it is well known that the absolute correlation energies so obtained are not accurate at all. Nonetheless, it is believed that even at this RPA level, the "binding" correlation energies are very accurate. To confirm this trend, we have calculated the RPA energies of model jellium-like systems as well as the structural properties of simple solids (Si, NaCl), where the KS-LDA performs quite well. As expected, there are minor differences between the KS-LDA and the RPA results. However, in model layered systems, where layer-layer interactions are very weak, there are evident discrepancies between the KS and the TDDFT binding energies. This is due to the presence of long-ranged correlations that cannot be described at all by mean-field approximations.

In the ACFDT framework, local-field corrections mainly account for short-ranged electron-electron correlations. They can be built in either through LDA/GGA functionals or by including non-local XC kernels in the evaluation of the density response. Since we are interested on correlation energies, both corrections are constructed by imposing the reproduction of the exact homogeneous electron gas energies. We will see that these procedures are very robust, since the corrected correlation energies are rather insensitive to the details of the method used to implement the local-field corrections. The comparison with the corresponding RPA energies suggests that the RPA slightly overcorrects the KS-LDA results.

Self-Energy Approaches for Excited and Ground States: Lessons for and from DFT

Rex Godby

Department of Physics, University of York, Heslington, York YO10 5DD, United Kingdom

Density-functional theory was originally a theory for the ground-state total energy which more recently, through TDDFT, has been applied to calculations of certain excited-state properties. On the other hand, self-energy approaches (within the framework of many-body perturbation theory) are theories of the one-electron Green's function which is most directly related to spectral properties such as quasiparticle energies and lifetimes for added electrons or holes, but can also be applied to the calculation of ground-state properties such as the total energy.

In situations where both methods are applicable, each has advantages and disadvantages. (TD)DFT is typically inexpensive, but in systems where electronic exchange and correlation has more than a peripheral role, the uncontrolled (and sometimes quite pathological) errors in the usual density-based exchange-correlation functionals (such as the LDA and GGA) limit its applicability. *Ab initio* many-body perturbation theory provides, in principle, a convergable series of successive approximations to the exact answer, but the numerical complexity in practice restricts its application to relatively low-order approximations such as the GW approximation, which is the first-order term in an expansion of the self-energy operator Σ in powers of the dynamically screened electron-electron interaction, W. It may be thought of as exact exchange (the Hartree-Fock exchange operator), together with an partial inclusion of correlation diagrams through dynamical screening of the Coulomb interaction. From Σ, the one-electron Green's function G may be calculated, from which various spectral and ground-state properties are available. For transport properties (as well as certain other excited-state properties), the two-electron Green's function is required, which may also be formulated at the same level of approximation as GW.

By way of introduction to GW, I shall give a brief review of key applications to spectral properties such as quasiparticle energies and lifetimes for added electrons or holes.

In applying GW to the ground-state total energy, the choice of whether G and/or W are made to be consistent with the Green's function that arises *from* Σ is particularly important: G_0W_0, GW_0 and fully self-consistent GW, where G_0 generally indicates the LDA Green's function. I shall present results for finite and infinite systems at all three levels of self-consistency. These include converged results resulting from the incorporation of self-consistency and GW total-energy techniques into our general-purpose GWST "space-time" supercell code suite [1], which interfaces with pseudopotential plane-wave DFT calculations as its input. This allows the extension of the GW total-energy approach from high-symmetry test systems [2] to general systems, and opens the possibility of applications to systems whose energetics is not described sufficiently reliably within the usual DFT-based approaches.

I shall also describe our recent formulation [3] of the conductance of a junction between two nanowires in a form which permits the inclusion of electronic correlation effects in a GW-like framework.

[1] “Space-time method for *ab initio* calculations of self-energies and dielectric response functions of s olids”, H. N. Rojas, R. W. Godby and R. J. Needs, Phys. Rev. Lett. **74** 1827 (1995)

[2] “Many-body GW calculations of ground-state properties: quasi-2D electron systems and van der Waals fo rces”, P. García-González and R. W. Godby, Phys. Rev. Lett. **88** 056406 (2002)

[3] “Conductance and polarization in quantum junctions”, P. Bokes and R.W. Godby, Phys. Rev. B **69** 245420 (2004)

Further details at http://www-users.york.ac.uk/∼rwg3/.

Plane-wave TDDFT calculations of molecules in solution

Juerg Hutter

Physical Chemistry Institute, University of Zurich

A formulation of time dependent linear response density functional theory within the plane-wave pseudopotential framework has recently been introduced [J. Hutter, J. Chem. Phys., 118, 3928 (2003)]. This implementation allows for efficient calculations of excitation spectra, excited state properties and coupling to classical force fields in QM/MM approaches. The scheme has been applied in combination with Car-Parrinello molecular dynamics to study the solvent shift and intensity enhancement effects of the first electronic transition in acetone-water systems [L. Bernasconi et al., J. Chem. Phys., 119, 12417 (2003)]. In agreement with experiment a general increase in the mean oscillator strength and a blue shift of 0.19 eV of the transition was found. However, this analysis was severely hampered by shortcomings of traditional density functionals. Both, the poor eigenvalues of occupied and virtual Kohn-Sham orbitals and the lack of a correct representation of charge transfer (CT) in the response kernel result in many unphysical solute-solvent and solute-solute CT states overlapping with the acetone n-¿π^* transition. These problems are partially solved using hybrid functional, although only with drastically increased computational costs [L. Bernasconi et al., Chem. Phys. Lett., 394, 141 (2004)]. Another approach combines standard DFT calculations with TDDFT using the statistical average of orbital model exchange-correlation potentials. The improved representation of orbital energies helps to isolate low-lying local transitions and is a first step towards an accurate description of CT states.

Aspects of non-adiabaticity in TDDFT

Neepa Maitra

Department of Physics and Astronomy Hunter College and City University of New York

Memory is a feature of time-dependent density functionals that is well-known to exist but little understood. Indeed, the vast majority of TDDFT calculations utilise adiabatic approximations, where memory is entirely neglected. In this talk, I review some formal aspects of memory in TDDFT, and point out its significance in quantum control problems. I shall discuss some applications in linear response where non-adiabaticity plays a prominent role; these include the description of states of significant double excitation character and long-range charge transfer states.

Octopus: present, past, and future

M. A. L. Marques

Departamento de Física de Materiales, Facultad de Químicas, Universidad del País Vasco, Centro Mixto CSIC-UPV/EHU and Donostia International Physics Center (DIPC), 20080 San Sebastián, Spain

We present a computer package aimed at the simulation of the electron-ion dynamics of finite systems, both in one and three dimensions, under the influence of time-dependent electromagnetic fields. The electronic degrees of freedom are treated quantum mechanically within the time-dependent Kohn-Sham formalism, while the ions are handled classically. All quantities are expanded in a regular mesh in real space, and the simulations are performed in real time. Although not optimized for that purpose, the program is also able to obtain static properties like ground-state geometries, or static polarizabilities. The method employed proved quite reliable and general, and has been successfully used to calculate linear and non-linear absorption spectra, harmonic spectra, laser induced fragmentation, etc. of a variety of systems, from small clusters to medium sized quantum dots.

*Excited State Molecular Dynamics with use of the code FPSEID: First Principles Simulation tool for Electron Ion Dynamics

Yoshiyuki Miyamoto* and Osamu Sugino†

†Fundamental and Environmental Research Labs. NEC

Institute for Solid State Physics, University of Tokyo

In this talk, I will give molecular dynamics (MD) simulations on the adiabatic potential energy surfaces of electronic excited states. In these MD simulations, adiabatic approximation for the exchange-correlation potential is adopted, and the excitation is simply mimicked by manually promoted electronic occupations. Even with this simplified approximation, the time-dependent treatment for the Kohn-Sham equation is necessary to follow the right potential energy surface. Numerical stability for simulation-time beyond hundreds femtoseconds and difficulty in treating non-adiabatic (nonradiative) decay of excitation will be discussed. The applications are MD simulations on photo-excited carbon nanotubes, which will be related to nanotube engineering.

This work has been done in collaborations with Profs. Angel Rubio and David Tománek. Part of present works were supported by the Earth Simulator Center and by NAREGI Nanoscience Project, Ministry of Education, Culture, Sports, Science and Technology, Japan.

Spontaneous Density Fluctuations, Intermolecular Forces and Nonlinear TDDFT Response; Superoperator Approach

Shaul Mukamel

University of California, Irvine, CA 92697-2025

Dispersive long-range forces are ubiquitous in nature and have been the subject of intense experimental and theoretical attention [1-3]. van der Waals (vdW), non-bonded interactions between neutral, polarizable molecules that play an important role in many chemical and biological dynamical processes. vdW forces may be computed using the nonlocal linear polarizabilities or charge response functions of the individual molecules [4]. By formulating quantum dynamics in terms of superoperators in Liouville space [3] intermolecular forces may be expressed to all orders in terms of both the charge density response and the spontaneous charge fluctuations of individual molecules. The building blocks of the p'th order response are 2p, (p + 1)- point correlation functions of the charge density which differ by permutations of their time arguments. Each correlation function represents a Liouville Space pathway for the density matrix [5]. A complete description of intermolecular forces requires a set of p+1 combinations of these pathways denoted generalized response functions (GRF) [6]. The p'th order polarizability is only one member of that family. Using a superoperator formulation of TDDFT [7,8,9], we calculate the GRFs of individual molecule which,in turn, are evaluated using the collective electronic oscillator (CEO) eigenmodes of the linearized TDDFT .These GRFs are used to compute the intermolecular energy in terms of CEO modes[10]. The "causality" paradox" [11] of the TDDFT response is naturally reolved by the non-retarded supreroperator formalism. In Liouville space all physical observables can be expressed in terms of positively ordered products of superoperators avoiding the negative time ordering required for ordinary operators in Hilbert space (the Keldysh loop). Non-equlibrium Greens functions may thus be evaluated in real (physical) time.

[1] W. Kohn, Y. Meir and D. E. Makarov, Phys. Rev. Lett. 80, 4153 (1998).

[2] M. Lein, J. F. Dobson and E. K. U. Gross, J. Computational Chem. 20, 12(1999).

[3] S. Tsuzuki, K. Honda, T. Uchimaru, M. Mikami and K. Tanabe, J. Am. Chem. Soc. 124, 104 (2002).

[4] A. D. McLachlan, Proc. R. Soc. London A 271, 387 (1963); 274, 80 (1963).

[5] S. Mukamel “Principles of Nonlinear Optical Spectroscopy”, (Oxford Univ. Press, New York, 1995).

[6] A. E. Cohen and S. Mukamel, Phys. Rev. Lett. 91, 233202 (2003).

[7] O. Berman and S. Mukamel, Phys. Rev. A 67, 042503 (2003).

[8] V. Chernyak and S. Mukamel, J. Chem. Phys. 104, 444 (1996).

[9] S. Tretiak and S. Mukamel, Chem.. Rev. 102, 3171 (2002).

[10] U. Harbola and S. Mukamel, “Intermolecular Forces and Non-Bonded Interactions: Superoperator Nonlinear TDDFT Response Approach”, Phys. Rev. A (In press) (2004).

[11] E. K. U. Gross, J. F. Dobson and M. Petersilka, Density Functional Theory, edited by R. F. Nalewajski (Springer, New York, 1996).

[12] S. Mukamel, “Generalized TDDFT Response Functions for Spontaneous Density Fluctuations and Nonlinear Response: Resolving the Causality Paradox in Real Time” (in preparation) (2004).

Using ab initio tools to solve the astrophysical puzzle of interstellar PAHs

Giacomo Mulas and Giuliano Malloci

Cagliari, Italy

The presence of a large amount of gas-phase Polycyclic Aromatic Hydrocarbons (PAHs) in the InterStellar Medium (ISM) of our galaxy was suggested about twenty years ago (Léger & Puget, 1984; Allamandola et al., 1985), to account for the ubiquitous infrared emission bands near 3.3, 6.2, 7.7, 8.6, 11.3 and 12.7 micrometers seen wherever dusty environments are excited by UV photons. In the last two decades this ”PAH hypothesis” was the subject of intensive study, and these molecules and their derivatives were speculated to also give rise to other unidentified interstellar spectral features: the Diffuse Interstellar Bands (a set of 300 absorption features throughout the visible) and the far-UV rise of the interstellar extinction curve, just to name two of the most outstanding puzzles in the spectroscopy of the interstellar medium. Nonetheless, no single PAH has been identified to date in astronomical spectra.

Since a large scale, systematic experimental study of the whole family of PAHs and derivatives in conditions comparable to those in the ISM would be a hopelessly demanding task, we are using (TD)DFT techniques, together with a Monte Carlo model of the photophysics of interstellar PAHs, to prepare an atlas of their computed interstellar spectra, for direct comparison with astronomical data and as a guide for targeted experimental measures on specific molecules, which would say the final word. We here present some preliminary results of this ongoing effort.

Localization and polarization in the insulating state of matter

Raffaele Resta

INFM DEMOCRITOS National Simulation Center, Trieste, and Dipartimento di Fisica Teorica, University of Trieste

At variance with what happens in metals, the electronic charge in insulators cannot flow freely under an applied dc field, and undergoes instead static polarization. Both these features owe to the different nature of the excitation spectrum, but also to a different organization of the electrons in their ground state: electrons are localized in insulators and delocalized in metals. Such localization feature, however, is hidden in a rather subtle way into the many-body wavefunction. There have been recent advances in the theory of the insulating state, which in turn are deeply rooted into the modern theory of polarization, based on a Berry phase. Localization and polarization can be regarded as two aspects of the same phenomenon, and stem from essentially the same formalism.

The theory is very general, and applies on the same footing to either correlated wavefunctions or independent electrons, and to either disordered or crystalline systems. Its implications for a Kohn-Sham crystal can be stated as follows. In insulators, a set of well localized orbitals (the Wannier functions) spans the same Hilbert space as do the Bloch orbitals of the occupied bands. The first moment (dipole) of these orbitals defines macroscopic polarization, while their spherical second moment (spread) can be made finite. In metals macroscopic polarization is ill-defined, while it is impossible to span the Hilbert space of the occupied Bloch states using localized orbitals whose spread is finite.

Car-Parrinello TDDFT computation of electronic spectra of some transition metal aqua ions in solution

Leonardo Bernasconi, Michiel Sprik, and Jürg Hutter

Department of Chemistry, University of Cambridge, UK

Department of Chemistry, University of Zurich, Switzerland

Transition metal complexes show a variety of electronic excitations often observable as absorption of light in the visible range. These transitions can be broadly divided into $d \rightarrow d$ excitations (largely metal → metal), charge transfers between ligands and metal and $d \rightarrow s$ transitions. Using the time dependent density functional response theory method as implemented in the CPMD code[1,2], we have studied the electronic absorption spectrum of $\mathrm{Ru}^{2+}\,(\mathrm{H_2O})_6$, as an example of $d \rightarrow d$ transitions and Ag^+ and Cu^+ as examples of $d \rightarrow s$ transitions. The result of the finite temperature $t_{2g}^6 \rightarrow t_{2g}^5 e_g^1$ (visible) absorption spectrum of $\mathrm{Ru}^{2+}\,(\mathrm{H_2O})_6$ at the BLYP level of theory was found in good agreement with experiment including the splitting between the ${}^1T_{2g}$ and ${}^1T_{1g}$ terms due to electronic repulsion. Apart from minor changes in intensities we found little difference between the vacuum spectrum of the hexahydrate and the spectrum in bulk aqueous solution. The computed UV spectrum of Ag^+, while red shifted w.r.t to experiment by 2 eV, shows a line shape in fair agreement with experiment. Our calculations suggest that the observed three peak structure is consistent with a dihedrally distorted fourfold coordination[3]. Similar to our previous calculation of the spectrum of aqueous acetone[2,4], the $Ru^{2+}\,(H_2O)_6$ spectrum shows spurious solvent → solute and solute → solvent charge transfer excitations, which can be eliminated by switching over (at considerable computational cost) to a density functional which includes a fraction of exact exchange (PBE0). This also essentially cures the 2 eV redshift of the position of the Ag^+ absorption band, which because of the highly delocalized nature of the $5s$ state in solution can be considered as a manifestation of the well known underestimation of band gaps in DFT. Our calculations seem to confirm therefore the importance of exact exchange for the computation of excitation spectra in condensed molecular systems. Finally we will present our first results on the emission spectrum of $Ru^{2+}\,(H_2O)_6$ obtained by a molecular dynamics simulation on the energy surface associated with the lowest $t_{2g}^6 \rightarrow t_{2g}^5 e_g^1$ excitation with special attention to solvent effects on the Stokes shift.

Excited state ab initio MD of photochemical processes in model compounds

Ivano Tavernelli, Enrico Tapavicza, Ute Röhrig, Ursula Röthlisberger

Swiss Federal Institute of Technology, EPFL, CH-1015 Lausanne, Switzerland

This talk will focus on two photochemical processes of chemical and biological relevance, namely photo-isomerisation and photoinduced electron transfer. Our computational approach is based on the implementation of time-dependent density functional theory [1] (TDDFT) in the *ab initio* MD code CPMD [2]. Recently, the possibility to compute excited state properties within a mixed quantum-classical (QM/MM) [3] scheme was included. This gives us the opportunity to study for the first time ET processes in large molecular systems in different complex environments.

Photo-isomerisation. Photoinduced *cis-trans* isomerisations of C=C, C=N and N=N double bonds are investigated in three model compounds, namely the 2,4-pentadiene-1-iminium cation (PSB), formaldimine, and diimide. For formaldimine and diimide, the results obtained using TDDFT are in agreement with experimental data and previously reported theoretical results. The molecular dynamics simulations yield new insights into the relaxation pathways in the excited state. For PSB, which is a model system for the retinal protonated Schiff base involved in the visual process, the forces computed from the LR-TDDFT S_1 surface do not lead to double bond isomerisation but to single bond rotation [4]. The same reaction was also observed for the case of photoexcited retinal in its protein environment.

Phoinduced electron transfer. Electron transfer is an important chemical process with applications in physics, chemistry and biology. ET in molecular systems is characterized by a spontaneous charge redistribution between an initially prepared reactant state and a well defined product state. It is usually described as the transport of a single electron from a donor (D) molecular orbital (MO) to an acceptor (A) MO even though all MO of the system are modified during the transition. Because of its intrinsic properties, namely charge separation and orbital reorganization, ET processes constitute a major challenge for modern DFT studies.

In the case of intramolecular photoinduced ET, the reactant state is obtained after optical excitation of an electron from the ground state into one of its excited states. The ET process proceeds then through a rearrangement of the nuclear coordinates together with the relaxation of the excited electron into the LUMO (lowest unoccupied molecular orbital) on the acceptor site. In the present work we investigate using *ab initio* molecular dynamics (MD) methods the orbital and nuclear rearrangements that follow the electronic vertical photo-excitation of small organic molecules. Of particular interest is the analysis of the dependence of electronic and nuclear rearrangements on the spacing between donor and acceptor moieties (obtained by adding a number of bridge units) and on the screening effects induced by solvents with different polarity.

[1] E. Runge and E.K.U. Gross, *Rhys. Rev. Lett.* **52**, 997 (1984),
J. Hutter, *J. Chem. Phys.* **118**, 3928 (2003)

[2] Car-Parrinello Molecular Dynamics code, `http://www.cpmd.org`

[3] A. Laio, J. VandeVondele and U. Röthlisberger, *J. Chem. Phys.* **116**, 6941 (2002)

[4] I. Tavernelli, U.Röhrig and U. Röthlisberger, submitted to *J.Mol.Phys.*

Quantum many-body dynamics in Lagrangian frame: Geometric formulation of TDDFT

I.V. Tokatly

Lerhrstuhl für Theoretische Festkörperphysik, Universität Erlangen-Nürnberg, Staudtstrasse 7/B2, 91058 Erlangen, Germany

In this talk I formulate equations of time-dependent density functional theory (TDDFT) in the co-moving Lagrangian reference frame. The main advantage of Lagrangian description of many-body dynamics is that in the co-moving frame both the density of particles and the current density become the exact integrals of motion. The current density is exactly zero in every point of Lagrangian space, while the density of particles preserves its initial form. In other words, a local co-moving observer will see no currents in the system, and a stationary density distribution – the picture, which is very similar to that, seen in the equilibrium system from the laboratory frame. Reformulation of the theory in Lagrangian frame shows that the most natural complete set of basic variables in TDDFT consists of Lagrangian coordinate, $\boldsymbol{\xi}$, a symmetric deformation tensor $g_{\mu\nu}$, and a skew-symmetric vorticity tensor, $F_{\mu\nu}$. These three quantities, one vector, one symmetric tensor, and one skew-symmetric tensor, contain twelve independent numbers, which are required for the complete local characterization of a deformed state of any continuum media. Namely, $\boldsymbol{\xi}$, $g_{\mu\nu}$ and $F_{\mu\nu}$ respectively describe the translation, deformation and rotation of an infinitesimal fluid element. On the other hand, tensors $g_{\mu\nu}$ and $F_{\mu\nu}$ have a clear geometric meaning: $g_{\mu\nu}$ is a metric tensor in Lagrangian space, while $F_{\mu\nu}$ determines a local angular velocity of the co-moving frame. All above quantities are functionals of the fluid velocity in accordance with Runge-Gross mapping theorem. Formulation of TDDFT in terms of new basic variables allows to regularly derive a local nonadiabatic approximation for the xc potential. Stationarity of the density in the co-moving frame makes the derivation to a large extent similar to that of the static LDA. In the last part of the talk I will show a few explicit examples of nonlinear nonadiabatic xc functionals.

Real-space multigrid methods for DFT and TDDFT

T. Torsti[1,2] J. Ignatius[1], M. J. Puska[2], and R. M. Nieminen[2]

[1] CSC - Scientific Computing Ltd., P.O. Box 405, FIN-02101 Espoo, Finland
[2] Laboratory of Physics, Helsinki University of Technology, P.O. Box 1100, FIN-02015 HUT, Finland

MIKA (Multigrid Instead of the K-spAce) [1] is a program package for electronic structure calculations based on density-functional theory. The central numerical technique in MIKA is the Rayleigh-quotient multigrid method (RQMG) [2] for the eigenproblem. Multigrid methods significantly speed up the solution of the ground state in the case of large-scale real-space calculations.

The main applications of the MIKA-package have been made in research of the properties of quantum dots in two-dimensional electron gas [3,4] and computationally two-dimensional axially symmetric model systems for nanostructures containing up to thousands of electrons [5]. The MIKA-code can also be used for simulations of finite as well as periodic three-dimensional systems described by norm-conserving pseudopotentials [2].

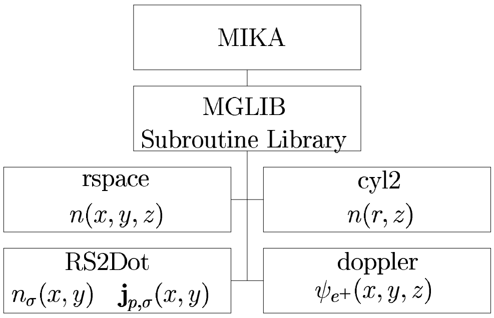

Fig. 1: Schematic of the most important components of the MIKA-package.

We are looking forward to extend the MIKA-code to perform real-time TDDFT calculations. We will benefit greatly from the pioneering work already done in the Octopus-project [6]. The public availability of the source code for both MIKA and Octopus should also help us, or anyone else, willing to develop real-space real-time schemes for large scale TDDFT calculations.

[1] T. Torsti *et al.*, Int. J. Quantum Chem **91**, 171 (2003);
`http://www.csc.fi/physics/mika/`

[2] M. Heiskanen *et al.*, Phys. Rev. B 63, 245106 (2001).

[3] H. Saarikoski, Ph. D. -thesis (2003); http://lib.hut.fi/Diss.

[4] E. Räsänen, Ph. D. -thesis (2004); http://lib.hut.fi/Diss.

[5] T. Torsti, Ph. D. -thesis (2003); http://lib.hut.fi/Diss.

[6] M. Marques *et al.*, Comp. Phys. Comm. 151 60 (2003);
`http://www.tddft.org/programs/octopus/`

An overview of basic concepts in TDDFT and some new extensions

Robert van Leeuwen

Groningen, The Netherlands

We give an overview of the underlying concepts of time-dependent density-functional theory (TDDFT). This includes an extension of the Runge-Gross theorem, the question of the invertibility of the density-density reponse function, and a discussion of the subtleties related to the action principle. We will further discuss a way to construct density-functionals that incorporate memory effects and satisfy basic conservation laws. We finally discuss a multi-component extension of TDDFT in order to treat coupled electronic and nuclear motion. This will provide a TDDFT formalism that can be applied to a treatment of the electron-phonon interaction and to molecules in strong laser fields.

Advances in time-dependent spin density functional theory

G. Vignale

Univ. Missouri, USA

Time-dependent density functional generally suffers from an ultra-nonlocality problem, namely the local density approximation for the exchange-correlation potential always fails, no matter how slowly varying is the density. I show that this problem is particularly severe in time-dependent spin density functional theory, but can be cured by switching to a formulation in which the spin currents are the basic variables. I discuss the physical significance of the new terms that appear in the spin-current dependent functional, and review the progress that has been made in providing explicit expressions for the latter.

Poster Session

Ground state and excited state calculations of GeTe

Wojciech Wełnic[a,b], Silvana Botti[b], Matthias Wuttig[a] and Lucia Reining[b]

[a]I. Physikalisches Institut, RWTH Aachen, 52056 Aachen, Germany

[b]Laboratoire des Solides Irradiés, École Polytechnique, 91128 Palaiseau cedex - France

Chalcogenide alloys, which show a significant change of optical reflectivity and electric conductivity under phase transformation from the amorphous to the crystalline structure are widely used for optical data storage today (e.g. DVD-RW). As they can also be used as non volatile memories (Phase-Change-RAM), they are furthermore promising candidates for future electronic data storage techniques. In this work ground state and excited state calculations are presented for GeTe, the basic phase-change-material. It is reported to crystallize in a cubic rocksalt phase and in a trigonal phase, which can be described as a distorted cubic structure. From literature relatively little is known about the amorphous structure, but the available data hints towards a tetragonal, diamond-like local coordination. The focus of the project is on the relation between optical properties and geometrical structure in different phases of GeTe, ranging from the two crystalline phases, defect structures and the amorphous phase. The origin for the difference of the optical and electronic properties in these different states is examined. The problem of obtaining a realistic amorphous structure is approached in two different ways: on one side we employ ab initio molecular dynamics within a 64-atom supercell and on the other side we use a simple model structure which reproduces the local configuration reported in earlier experimental work. The electronic structure is presented in the GW-correction and the theoretical spectra are calculated within TDDFT and GW-RPA. They are compared with experimental data of thin film GeTe-samples. Differences between theory and experiment are discussed as well as the changes in the optical and electronic properties upon phase transition from the crystalline to the amorphous state.

Real time dynamics of photoinduced deformation of benzene by TDDFT

Yoshitaka Tateyama, Yoshiyuki Miyamoto, Norihisa Oyama, Takahisa Ohno

Coupled dynamics of ions and electrons in the excited states of molecular and solid benzene is investigated on the femtosecond scale by TDDFT with the Suzuki-Trotter decomposition for the propagation. Within the π - π^* excitations, any out-of-plane motion of the ions is not induced in the molecular system, as expected from the symmetry consideration. In the solid, however, we found that large swing of the C-H bonds and subsequent twist of the carbon ring take place, leading to $sp3$-like bonding of carbon ions. This swing-to-twist motion presents a plausible mechanism underlying the photoinduced ring opening in solid benzene experimentally observed under pressure.

Linear response at the 4-component relativistic DFT level: Application to the frequency-dependent dipole polarizability of the mercury atom and dimer

Trond Saue

UMR 7551 CNRS/UniversitÃ© Louis Pasteur, Laboratoire de Chimie Quantique et de ModÃ©lisation MolÃ©culaire, 4 rue Blaise Pascal, F-67000 Strasbourg, France

We report the implementation and application of DFT linear response theory based on the 4-component relativistic Dirac-Coulomb Hamiltonian in the DIRAC code [1,2]. Due to the separability of Hamiltonians and methods, the theory can be developed with little reference to relativity. We have based the theory on the quasienergy formalism or Floquet theory (see [3,4] and references therein), which can be applied quite generally to both variational and non-variational wave-function methods as well as DFT using variational perturbation theory. In quasienergy DFT, the dependence of the initial state in the Runge-Gross theorem is replaced by periodic boundary conditions. Contradictions in causality and time-symmetry arguments are thereby avoided and the exchange-correlation potential and kernel can be expressed as functional derivatives of the quasienergy.

We apply the method to the calculation of the frequency-dependent polarizability of the mercury atom, which show very large effects of both relativity and correlation. We furthermore calculate the polarizability anisotropy of the mercury dimer and simulate the depolarized collision induced Raman spectrum and compare with a recent experimental study [5].

[1] DIRAC, a relativistic ab initio electronic structure program, Release 3.2 (2000), written by T. Saue, V. Bakken, T. Enevoldsen, T. Helgaker, H. J. Aa. Jensen, J. K. Laerdahl, K. Ruud, J. Thyssen, and L. Visscher (`http://dirac.chem.sdu.dk`).

[2] P.Salek, T.Helgaker, and T.Saue.,Chem. Phys., in press.

[3] O.Christiansen, P.Jorgensen, and C.Hättig, Int. J. Quant.Chem., 68(1998) 1

[4] F. Aiga, T. Tada, and R. Yoshimura, J. Chem. Phys. 111(1999) 2878

[5] N. Gaston, P. Schwerdtfeger, J. Greif and T. Saue, in preparation

Density functional for bosons in the path integral approach

Anna Okopinska

Institute of Physics, Swietokrzyska Academy, Kielce, Poland

The density functional for a system of interacting bosons is defined as the effective action for composite operators. The functional depends on both the condensate density and the total density, the physical values of which are determined by variational principle. An expansion in powers of the Planck constant generates a systematic approximation scheme being an extension of the Kohn-Sham approach to bosonic systems.

Time-dependent exchange-correlation current density functionals with memory

Yair Kurzweil and Roi Baer

Department of Physical Chemistry and the Lise Meitner Minerva-Center for Computational
Quantum Chemistry, the Hebrew University of Jerusalem, Jerusalem 91904 Israel.

Most present applications of time-dependent density functional theory use adiaba tic functionals, i.e. the effective potential at time t is determined solely by the density at the same time. Our work discusses a method that aims to go beyond this approximation, by incorporating "memory" effects: the potential will depend also on the history. We add to the adiabatic approximation an additional part that includes memory and yields a functional that is totally consistent with known dynamical properties of the homogeneous electron gas (in the linear response limit). In order to achieve this, we write down an action principle from which Kohn-Sham equations are derived for description of the time-dependent electron density and fluid velocity field. We construct the action on Lagrangian coordinate s system and pseudo time domain (Keldysh contour). Therefore, action principle is built in such a way that it is Galilean invariant and yields causal equations.

Ultrafast dissociation of adenine-water hydrogen bonds by photoexcitation.

Myrta Grüning*, Alberto Castro$^{\bullet}$, Angel Rubio*,‡

* Donostia International Physics Center;
$^{\bullet}$ Departamento de Física Teórica, Universidad de Valladolid;
‡ Departamento de Física de Materiales, Facultad de Químicas, Universidad del País Vasco

Recent molecular-beam studies of hydrated cluster of adenines show the anomalous loss of the solvent molecules after excitation by a nanosecond laser pulse at 262 nm[1,2].

The goal of this work is to provide the molecular mechanism behind this phenomenon working within the time-dependent density functional theory (DFT) framework.

The dissociation of the hydrogen bonds has been attributed to the dissociative character of the potential energy surface in the excited state: we investigate this hypothesys calculating the evolution of the system after the interaction with the laser pulse with real-space real-time time dependent DFT.

Preliminary ground state and linear response time dependent DFT calculations indicate that the potential energy surface in the excited state is not dissociative, but the excitation provides the complex with enough energy to dissociate.

[1] Kim et al. J. Phys. Chem. A (2000) **104**, 6552. [2] Kang et al. Chem. Phys. Lett. (2002) **359**, 213.

Scattering amplitudes from time-dependent density functional theory

Adam Wasserman, Neepa T. Maitra, and Kieron Burke

Rutgers University

The linear response formalism of time-dependent density functional theory is adapted to study low-lying electronic continuum states of atoms. Exact formulas to extract transmission amplitudes from the susceptibility are derived for one dimensional scattering, and exemplified on a simple model. Continuum states of the ground-state Kohn-Sham potential of an N-electron system can provide a good approximation to scattering from the corresponding (N-1)-electron system, as shown here for the case of electron-He+ scattering.

Valence electronic structure and TDDFT study on RuO_4 and OsO_4

Giuseppina Menconi and Nikolas Kaltsoyannis

Department of Chemistry, University College London, 20 Gordon Street, London WC1H 0AJ, UK

We present a study of the valence electronic structures of RuO_4 and OsO_4, incorporating both scalar and spin-orbit relativistic corrections. Extensive comparison is made with previous experimental data on vibrational frequencies and ionization energies.

Excitation energies are also calculated using Time-Dependent Density Functional Theory. Large basis-set were used together with a range of functionals, including the LB94 potential. Comparison is made with results obtained from earlier experiments and from extended HÃ¼ckel type calculations [J. Chem. Phys. 60, 3166 (1974)]

Hartree Fock exchange in Time Dependent Density Functional Theory

Leonardo Bernasconi*, Michiel Sprik*, and Jürg Hutter†

*Department of Chemistry, University of Cambridge, Lensfield Road, Cambridge CB2 1EW, U.K.

†Physical Chemistry Institute, University of Zurich, Winterthurerstrasse, 190, CH-8057 Zurich, Switzerland

The absorption spectrum of acetone in aqueous solution at finite temperature is computed using Time Dependent Density Functional Theory and Car Parrinello Molecular Dynamics at the BLYP, B3LYP and PBE0 level of theory. The role of the exchange-correlation functional in separating spectral features originating from localised (intra-molecular) and charge-transfer or collective electronic excitations is analysed. In the limit of local and frequency independent exchange-correlation kernels, admixture of Hartree Fock exchange in the density functional is proved to be a necessary requirement in order to remove the unphysical degeneracy between

the intra-molecular n→ π^* and solvent→solvent transitions. Results for the n→ π^* transition energy, oscillator strength and solvatochromic shift are computed in excellent agreement with experiment.

1. J. Hutter, *J. Chem. Phys.* **118**, 3928 (2003).
2. L. Bernasconi, M. Sprik, and J. Hutter, *J. Chem. Phys.* **119**, 12417 (2003).
4. L. Bernasconi, M. Sprik, and J. Hutter, *Chem. Phys. Lett.* (2004, to be published).

An iterative GW approach for the (111) surface of diamond

Margherita Marsili

Università di Roma Tor Vergata

The Pandey Chain model seems to be the most stable reconstruction for the (111) surface of diamond, being the atoms on the chain neither buckled nor dimerized. Experimental data confirm the absence of dimerization but cannot exclude the presence of buckling. Within DFT the electronic band structure related to the fully relaxed structure appears semimetallic in contrast with experiments which show a gap of at least 0.5 eV. This could be due to a wrong equilibrium geometry in the calculations or to the usual DFT band gap problem. Introducing quasiparticle corrections within a self-consistent GW scheme, using an iterative procedure for updating the quasiparticle energies, we found for this surface an electronic gap close to 1 eV. Preliminary results on the optical properties are also presented and discussed.

Photoionisation using DFT wave functions

Michael Walter and Hannu Häkkinen

University of Jyväskylä, Finland

The determination of photoionisation cross sections using the Kohn-Sham wave functions from accurate DFT calculations. The continuum electron is described by an analytical wave function and the matrix elements are calculated in both in length and velocity form of the dipole operator.

The test case of water shows excellent agreement between the calculations and experiment in the ionisation energies if a vertical transition is considered. The cross sections agree well with the experiment in particular in case of the velocity form results. Differences to the length from indicate the limitations in an analytical description of the continuum.

Beyond Ehrenfest dynamics

Cristian G. Sanchez[‡], and Tchavdar N. Todorov[‡] Andrew P. Horsfield[⋆], D. R. Bowler[⋆†], A. J. Fisher[⋆†]

[⋆]Department of Physics and Astronomy, University College London, Gower Street, London WC1E 6BT, United Kingdom

[†]London Centre for Nanotechnology, University College London, Gower St, London WC1E 6BT

[‡]School of Mathematics and Physics, Queen's University of Belfast, Belfast BT7 1NN, United Kingdom

Here we present a method to introduce electron-ion correlations into Ehrenfest dynamics which is computationally affordable. Assuming that the ionic wavefunctions are narrow a moment expansion of the full density matrix is made. The many-electron problem is then reduced to a single-electron problem by tracing over all electrons but one. Using the first moment approximation, we carry out tight binding simulations of the effect of an electric current on a mobile atom. The classical (Ehrenfest) contribution to the ionic heating is negative (cooling) and independent of the bias. The quantum contributions shows strong heating, with a rate proportional to the bias.

Failure of time-dependent density functional theory for long-range charge-transfer excited states

Andreas Dreuw and Martin Head-Gordon

Departement of Chemistry, University of California, Berkeley, and Chemical Science Division, Lawrence Berkeley National Laboratory, Berkeley, California 94720-1470, USA

Over the last few years, time-dependent density-functional theory (TDDFT) has advanced to one of the most popular theoretical approaches to calculate excited state properties of medium-sized and large molecules up to about 200 second-row atoms. Recently, it has been pointed out that TDDFT yields substantial errors for charge-transfer (CT) excited states. Here, we focus on the failures of TDDFT to predict the excitation energies of charge-transfer states correctly and to give the correct long-range $1/R$ dependence on donor-acceptor distance. The CT states of a ethylene-tetrafluorethylene model system are investigates and the dependence of their $1/R$ asymptotic behavior on the exact exchange part in hybrid functionals is explored. While the wrong excitation energies can be related to missing discontinuities in the approximate xc-potentials, the wrong asymptote of CT excited states is due to the local character of the approximate xc-functionals leading to a so-called electron-transfer self-interaction error. Future perspectives how this failure of TDDFT might be cured are discussed.

Furthermore, a hybrid approach of TDDFT and configuration interaction singles (CIS) is suggested to yield reasonable estimates for long-range CT states of large molecular systems. This approach combines the benefits of TDDFT and CIS in yielding accurate results for valence-excited states in the one hand and correctly shaped potential energy surfaces for CT states

on the other. Within this approach, the CIS curves are gauged with a electron-transfer self-interaction free ΔDFT calculation. This approach is applied to large molecular systems of biological interest.

Excited-state density functionals?

Rene Gaudoin (POSTER)

Rutgers University, USA

For a given excited state there exist densities that arise from more than one external local one-body potential. This is due to a qualitatively different energy-density relationship from that of the ground state and is related to positive eigenvalues in the non-local susceptibility for excited states. Consequences for the adiabatic connection method and time-dependent density functional theory are discussed.

Understanding the dissociation of diatomic molecules in the DFT-ACFD formalism : ground-state and excited-state studies

Y. Pouillon*, F. Tournus, Y.-M. Niquet, and X. Gonze (POSTER)

Unitè de Physico-Chimie et Physique des Matériaux (PCPM) Université Catholique de Louvain 1348 Louvain-la-Neuve (Belgium)

There is a growing need for exchange-correlation (XC) functionals going beyond the Local-Density and Generalized-Gradient Approximations (LDA and GGA), as these do not account for long-range correlations occuring for instance in weakly-bonded compounds and biomolecules. In such systems van der Waals (vdW) interactions play a crucial role and can only be taken into account by means of fully non-local XC functionals. Contrary to the LDA and GGA cases, most of the latter depend on the Kohn-Sham orbitals and their energies. One way to build such a functional is to resort to the Adiabatic-Connection Fluctuation-Dissipation (ACFD) theorem [1, 2] in conjunction with the Random-Phase Approximation (RPA). The RPA captures the physics of the vdW interactions and has been tested non self-consistently on some atoms, diatomic molecules, and solids.

However, a spurious maximum in the dissociation curve was evidenced for the N2 [3] and H2 [4] molecules. It may result from either (a) the RPA being insufficient to describe the dissociation regime, or (b) the lack of self-consistency, as well as (c) H2 and N2 being pathological cases, without forgetting (d) a possible bug in the implementation.

In parallel with studies concerning points (a), (b) and (d), we are tackling point (c) by examining the dissociation of several diatomic molecules within the ACFD-RPA framework as well as their excitation energies through Time-Dependent DFT (TDDFT) and SCF calculations. We compare some of their ground-state properties with the results obtained from LDA/GGA approximations too. In addition of being heteroatomic, and composed of low Z atoms, the LiH molecule presents very peculiar properties and is often used as a test case for new computational methods. That is why we have decided to put a particular emphasis on it. To further enhance our understanding of weakly-bonded systems we are also considering the van der Waals molecules Be2 and Mg2 . In particular, it is known that the vdW interaction is quite larger in the latter than in all those previously tried.

[1] W. Kohn, Y. Meir, and D. Makarov, Phys. Rev. Lett. 80, 4153 (1998).

[2] M. Fuchs and X. Gonze, Phys. Rev. B 65, 235109 (2002).

[3] F. Furche, Phys. Rev. B 64, 195120 (2001).

[4] M. Fuchs, K. Burke, Y.-M. Niquet, and X. Gonze, Phys. Rev. Lett. 90, 189701 (2003).

*Electronic address: pouillon@pcpm.ucl.ac.be

Non-additive nature of van der Waals dispersion energy in layered model-systems.

Jeil Jung

Dept. de Fisica Fundamental, Facultad de Ciencias UNED, Spain

---

Optimization of Effective Atom Centered Potentials for Molecular Properties

O.A.v. Lilienfeld-Toal

Swiss Federal Institute of Technology EPFL, Lausanne, Switzerland

3.1.3 Report on CECAM - Psi-k Tutorial

on "Linear Scaling Density Functional Calculations with Local Orbitals"

December 9-13, 2003

Organizers:
Emilio Artacho
Department of Earth Sciences,
University of Cambridge, United Kingdom
emilio@esc.cam.ac.uk
Pablo Ordejón
Instituto de Ciencia de Materiales de Barcelona, CSIC, Spain
ordejon@icmab.es

Motivation

Electronic structure methods have become mature enough to be used by scientists not trained in the development of the methods themselves. There is an increasing demand for training in the sensible use of these methods (by *sensible* we mean that the user understands the physical and main technical approximations behind a method and can assess its reliability).

The possibility of addressing large system sizes has opened up opportunities in many disciplines (bio, geo, nano, to name a few) and more scientific communities are now interested in this training. Because of this, the SIESTA method has become very popular in the last few years given its large-size capabilities, efficiency, accessibility and documentation (see documentation and references in http://www.uam.es/siesta). Previous SIESTA schools (addressing specific communities in Barcelona 99, Lyon 99, Rio de Janeiro 00, and Cambridge 02) were always quite popular as well. This international CECAM school represented a good opportunity for many interested young scientists. We also considered it very timely and interesting to the same audience to introduce them into CONQUEST, a linear-scaling density-functional method which is on one hand very similar to SIESTA in many aspects, but on the other represents an ideally complementary method: its not relying on atomic orbitals allows a much cleaner systematics in the achievement of convergence, albeit with larger computational effort. The student would thus obtain a more complete picture of the possibilities at hand nowadays with linear-scaling DFT.

Aims

A first aim of the course was to show the students the thread between fundamental laws of physics and properties of condensed matter, and, in so doing, transmit the difficulty of the problem and the essence of the approximations along that thread. The main take-home knowledge was: (i) what can be computed, (ii) how to do it, (iii) how good the results can be, and (iv) how bad they can be if things are not done critically and carefully (even if *ab initio*). This part was common to other courses in *ab initio* methods. We had decided not to assume previous *ab initio* experience of the students, since most prospective users prefer self-contained courses.

The school balanced the more traditional aspects of standard electronic structure first principles methods with the more modern aspect of linear scaling. Even if the lectures dedicated to linear-scaling solvers appeared only in the third day, the linear scaling character of both methods was present in other parts like the basis sets (numerical atomic orbitals of finite support or blips, for linear scaling) and the way matrix elements are calculated within SIESTA and CONQUEST.

It was not the purpose of this school to train new method developers (even if this is a possible first step for it), but to train future users of these methods. It is always very important to educate future *ab initio* users in the critical use of these methods. We taught them to control and assess the main approximations involved (LDA/GGA, pseudopotentials, basis sets, localisation for linear scaling) as well as the more technical ones.

Audience

It was addressed to young people wanting to use electronic structures methods in their research. Some fundamental knowledge of quantum mechanics and was assumed, as well as statistical mechanics for the molecular dynamics part. Basic solid state physics background was not strictly required (even if considered helpful). The basics of these areas was quickly covered to establish the language. Experts in other electronic structure methods could still profit from most of the lectures, even if the course was less intense for them.

The course was very successful from the point of view of the interest raised: in spite of the not too convenient dates there were many more applicants than places available. The final number of attendees was of 25, with a waiting list with 12 other names. We could not expand the numbers because of limitations in the practical sessions (most students practised in pairs, even if some teams were of three students).

The origin of the students was also very varied, both geographical and in terms of the scientific field.

A list of attendees follows is given in the corresponding Section below.

Format

The main scheme adopted was that of morning lectures followed by afternoon practical sessions. The lectures were on fundamental aspects of the physics and/or methodology, but tended towards more practical issues in the lecture before lunch, preparing for the afternoon session. Some topics (like pseudopotentials) rendered themselves nicely to a formal lecture before coffee, and a how-to lecture before lunch. Other topics, however, were better explained with both aspects kept together.

The Tutorial was thus organized using this general scheme: (1) Formal Lectures in the early morning, giving the theoretical background of the different aspects of linear-scaling calculations based on local orbitals; (2) Practical Lectures, in the late morning, with the practicalities, and in particular the description of the use of the SIESTA code and fundamentas of the CONQUEST code, and (3) Hands-on Sessions, in the afternoon.

Documentation and bibliography

The materials related to the course (talks and exercises) can be found in the Documentation section of the SIESTA web site (http://www.uam.es/siesta).

Documentation and user guides can be found in http://www.uam.es/siesta and http://www.cmmp,uck.ac.uk/conquest, including basic references.

Program of the Tutorial

Tuesday, December 9

9:30 PABLO ORDEJON
Introduction: Ab initio simulations

10:00 DANIEL SANCHEZ-PORTAL
Fundamentals: the quantum-mechanical
many-electron problem and the DFT approach.

11:30 PABLO ORDEJON
Relaxations

12:00 ALBERTO GARCIA
Introduction to running siesta (input, output,
tools, k-points, SCF)

14:30 Practical session: First run on simple examples

Wednesday, December 10

9:00 ALBERTO GARCIA
Pseudopotentials

10:00 DANIEL SANCHEZ-PORTAL
Calculating matrix elements of H and S.
Finite grid and pseudpotential hardness

11:30 ALBERTO GARCIA
How to generate Pseudos. Partial core corrections
and semicore states

12:15 EDUARDO ANGLADA
Converging with Mesh-cutoff. The eggbox and
gridcellsampling

14:30 Practical session: Generating pseudopotentials and
testing their hardness with {\sc Siesta}

Thursday, December 11

9:00 DANIEL SANCHEZ-PORTAL
Atomic orbitals of finite range as basis sets

10:00 DAVID BOWLER
Basis sets as in Finite-elements calculations: Blips

11:30 EDUARDO ANGLADA
How to generate and test basis sets

12:15 ALBERTO GARCIA
Systematic convergence for reallistic projects

14:30 Practical session: Generating and testing basis sets

Friday, December 12

9:00 DAVID BOWLER
Linear-scaling solvers: Fundamentals and solvers
based on the density matrix

10:00 PABLO ORDEJON
Linear-scaling solvers based on Wannier-like functions

10:30 PABLO ORDEJON

Basics about Molecular Dynamics

11:30 PABLO ORDEJON
Practicalities about using Molecular Dynamics

12:15 PABLO ORDEJON
How to run with linear scaling solvers

14:30 Practical session Linear-scaling runs and tests; MD

Saturday, December 13

9:00 DAVID BOWLER
The parallelisation of Conquest

10:00 DANIEL SANCHEZ-PORTAL
The parallelisation of {\sc Siesta}

11:30 EDUARDO ANGLADA
Compiling and running in parallel

12:15 DANIEL SANCHEZ-PORTAL
Questions and Concluding Remarks

Conclusions and perspectives

The tutorial was very successful both in attendance and satisfaction of the attendees. There is still considerable interest in learning the basic of *ab initio* methods *for their use* (this is a relatively new trend), and size-efficient methods are still very sought-after options. We do not see indications of decline of the interest of young scientists in these methods, which allows us to suggest some form of continuity. The success of this and previous courses is quite evident in view of the over 350 papers published using SIESTA in the last few years. We think that CONQUEST will take a similar route once it is ready for use by non-developers.

Acknowledgements

We acknowledge the financial support of the ESF Programme Psi-k and CECAM. We are indebted to Emmanuelle Crespeau for her invaluable help in managing the Tutorial. We thank Frederic Barmes for his help with the computers setup.

List of Lecturers

List of Lecturers in Theory Presentations

Pablo Ordejón
Instituto de Ciencia de Materiales de Barcelona
CSIC
Campus de la UAB, Bellaterra
08193 Barcelona
España ordejon@icmab.es+34 93 5801853+34 93 5805729

Alberto García
Departamento de Fisica de la Materia Condensada
Facultad de Ciencias
Universidad del Pais Vasco
Apartado 644
E-48080 Bilbao
Spain wdpgaara@lg.ehu.es+34-946.012.490+34-946.013.500

Daniel Sánchez-Portal
Departamento de Física de Materiales
Facultad de Química
Universidad del País Vasco
Apdo. 1072, E-20080 San Sebastián
Spain sqbsapod@scsx03.sc.ehu.es(34) 943 01 5368(34) 943 01 5600

Eduardo Anglada
Dep. Física de la Materia Condensada
Univ. Autónoma de Madrid
E-28049 Madrid
Spain eduardo.anglada@uam.es(34) 91 497 3803(34) 91 497 3961

David Bowler
Department of Physics and Astromomy
University College, London
Gower Street, London WC1E 6BT
U.K. david.bowler@ucl.ac.uk44 20 7679 722944 20 7679 1360

List of Assistants in Practical Sessions

Natalia Bedoya
Instituto de Ciencia de Materiales de Barcelona
CSIC
Campus de la UAB, Bellaterra
08193 Barcelona
España natalia@icmab.es+34 93 5801853+34 93 5805729

Eduardo Machado
Instituto de Ciencia de Materiales de Barcelona
CSIC
Campus de la UAB, Bellaterra
08193 Barcelona
España ordejon@icmab.es+34 93 5801853+34 93 5805729

List of Participants

Jordi Cirera Fernandez
Estructura Electronica
Department of Inorganic Chemistry
University of Barcelona
Diagonal 647
08028 Barcelona
Espagne jordi.cirera@qi.ub.es

Fadwa El-Mellouhi
Departement de Physique
Université de Montreal
CP 6128, succ. Centre Ville
Montreal (Quebec) H3C 3J7
Canada f.el.mellouhi@umontreal.ca

Thomas Cauchy
Estructura Electronica
Department of Inorganic Chemistry
University of Barcelona
Diagonal 647
08028 Barcelona
Espagne thomas.Cauchy@wanadoo.fr

Lorenz Romaner
School of Biochemistry and Chemistry
Georgia Institute of Technology
1127 A McMillan St.
Atlanta, GA, 30318
USA lr95@mail.chemistry.gatech.edu

Layla Martin-Samos
Service de Recherche de Me'tallurgie-Physique
DEN/DMN/SRMP
CEA-Saclay
91191 Gif-sur-Yvette Ce'dex
France lmartinsamos@cea.fr01 69 08 37 6901 69 08 68 67

Guido Roma
CEA-Saclay,
91191 Gif sur Yvette
France roma@cea.fr

Neeti Kapur
Department of Chemical Engineering
University of Virginia
102 Engineer's way
P.O.BOX 400741
Charlottesville, VA, 22904-4741
USA nk2j@cms.mail.virginia.edu

Lê Thiên-Nga
Laboratoire de Mécanique des Solides
Ecole Polytechnique
LMS - Ecole Polytechnique
91128 Palaiseau cedex
France tnle@lms.polytechnique.fr

Chu Chun Fu
Service de Recherches de Métallurgie Physique
CEA/Saclay
91191 Gif-sur-Yvette
France chuchun@cea.fr01.69.08.43.4901.69.08.68.67

Dimas Suarez Rodriguez
Departamento de Quimica Fisica y Analitica
Universidad de Oviedo
Julian Claveria 8. 33006.
Oviedo
Spain dimas@correo.uniovi.es+34-9851822686 +34-985103125

Natalia Diaz Fernandez
Institut de Biologie Structurale Jean-Pierre Ebel
41 rue Jules Horowitz
38027 - Grenoble
France diaz-fer@ibs.fr

Juan Carlos Samcho-Garcia
Laboratory for Chemistry of Novel Materials
Materia Nova R&D Center
B-7000 Mons
Belgium jc.sancho@averell.umh.ac.be+ 32 065 37 38 65+ 32 065 37 38 61

Prof. Dietrich Foester
Laboratory CPMOH
Universite de Bordeaux

Avenue de la Liberation
Talence
France d.foerster@cpmoh.u-bordeaux1.fr+33 (0)5 4000 2507 +33 (0)5 40 00 25 01

Leandro Liborio
Atomistic Simulation Group - Physics Building
School of Maths and Physics
Queen's University Belfast
University Road
Belfast, Northern Ireland
BT7 1NN
UK l.liborio@qub.ac.uk++44(2890)273557 ++44(2890)241958

Juan Marí García Lastra
Group of Computational Physics of Materials
Departamento CITIMAC
Facultad de Ciencias
Universidad de Cantabria
39005 Santander
Spain garcialjm@unican.es 34-942 201505 34-942 201402

Chaitanya das Pemmaraju
Computational Spintronics Group
Department of Physics
Trinity College Dublin 2
Ireland pemmaras@tcd.ie

Ivan Degtyarenko
Laboratory of Physics
Helsinki University of Technology
P.O.Box 1100
02015 Espoo
Finland imd@fyslab.hut.fi+358-9-451 3103+358-9-451 3116

Jean Nicola
Trinity College
Dublin
Ireland jeann@tcd.ie

Juan Ignacio Beltrán Fínez
Instituto de Ciencias de los Materiales de Madrid (ICMM)
C.S.I.C.
Cantoblanco 28049
Madrid
Spain jbeltran@icmm.csic.es +34 913349000 (ext 366) +34 913720623

Mariusz Sokol
Institute of Physiscs

University of Silesia
Poland msokol@us.edu.pl(+48) 323591832(+48) 322588431

Przemyslaw Raczynski
Institute of Physiscs
University of Silesia
Poland praczyns@us.edu.pl(+48) 323591832(+48) 322588431

Mario Gabriel Del Popolo
Atomistic Simulation Group
Physics Building
School of Maths and Physics
Queen's University Belfast
University Road
Belfast, Northern Ireland
BT7 1NN
U.K. m.del-popolo@qub.ac.uk ++44(2890)273557 ++44(2890)241958

Mr. Tsogbadrakh Namsrai (M. Sc.)
Room 416A, Institute for Materials Research
The University of Salford
Salford, M5 4WT
U.K. T.Namsrai@pgr.salford.ac.uk Tsogbadrakh@num.edu.mn+ 44 - (0)161 - 295 4988

Francis Marinelli
Physique des interactions ioniques et moleculaires (PIIM)
Université de Marseille
France francis@piimsdm11.univ-mrs.fr +33 4 91 28 27 11

Dr. Slawomir Lepkowski
High Pressure Research Center "Unipress"
Polish Academy of Sciences
ul. Sokolowska 29/37 01-142 Warszawa
Poland slawek@unipress.waw.pl +4822 6325010 (ext. 329)

3.1.4 Report on ESSN-2004 and the Workshop of WG7

ELECTRONIC STRUCTURE SIMULATIONS OF NANOSTRUCTURES: TOWARDS AN UNDERSTANDING OF PHYSICAL, CHEMICAL AND BIOLOGICAL PROCESSES (ESSN-2004)

and

PSI-K WORKING GROUP 7 (SEMICONDUCTORS AND NANOTECHNOLOGY)

UNIVERSITY OF JYVäSKYLä, FINLAND

JUNE 18-21, 2004

ORGANIZING COMMITTEE:

Hannu Häkkinen, Chair (Jyväskylä, Finland)
Ulrich Heiz (Ulm, Germany)
Matti Manninen (Jyväskylä, Finland)
Gianfranco Pacchioni (Milan, Italy)
Annabella Selloni (Princeton, USA)

WORKING GROUP 7 SPOKESPERSON:
Risto Nieminen (Helsinki, Finland)

GENERAL

The scope of this workshop was to explore the current status of the research in the broad area of electronic structure simulations of nanoclusters, nanoparticles and nanostructures in various fields of physics, chemistry and biology. A number of experimental talks were added in the program to promote exchange of ideas and interdisciplinary collaborative efforts between simulations and experiments. The program consisted of invited lectures, short "hot topic" presentations, poster sessions, and a tutorial session on modern electronic structure theory. This workshop was one of the first activities organized by the new University Nanoscience Center in Jyväskylä, Finland, and it was also a part of a series of international meetings in connection with a yearlong celebration of the University's 70 years of operation. Embedded in the ESSN-2004, Prof. Risto Nieminen (Helsinki University of Technology) organized the Psi-K WG-7 workgroup meeting. All scientific sessions were open to both ESSN-2004 and WG-7 participants. The combined number of participants of the two meetings was 69, of which more than 50researchers at the postgraduate or post-doctoral level.

SCIENTIFIC PROGRAM

The scientific program consisted of 23 invited talks, 8 "hot topic" talks selected from the contributed abstracts, and 36 posters. In addition, Dr. Tuomas Torsti from CSC (The Finnish IT Center for Science) held a two-hour tutorial session on the GNU-licensed electronic structure calculation code MIKA (”Multigrid Instead of the K-spAce, see www.csc.fi/physics/mika). The tutorial session was well-attended by the younger participants. The scientific program was closed by a round-table discussion on the current prospects and challenges in modeling nanosctructures, mediated by Prof. Risto Nieminen. The invited talks, hot topic talks and posters are listed given below.

INVITED TALKS

Wanda Andreoni (Switzerland):
Towards the design of novel materials on the basis of electronic structure calculations

Thorsten Bernhardt (Germany):
Size effects in noble metal cluster reactivity and catalysis

Jussi Eloranta (Finland):
Theory of electronic spectroscopy in helium nanodroplets

Ralph Gebauer (Italy):
Kinetic theory of quantum transport at the nanoscale

Francesco Gervasio (Italy):
Charge transfer and oxidative damage in DNA fibers

Bjork Hammer (Denmark):
Catalysis by nano-sized gold particles on oxide support - a DFT study

Ulrich Heiz (Germany):
Cooler cluster catalysis

Olli Ikkala (Finland):
Self-assembly at different length scales: Concepts for structural hierarchy and functional matter

Peter Kratzer (Germany):
Growth-related Structural and Electronic Properties of InAs Quantum Dots on GaAs

Uzi Landman (USA):
Small is different: Emergent phenomena in classical and quantum fluid systems

Nicola Marzari (USA):

Dynamics and thermodynamics of nanoparticles under pressure

Elisa Molinari (Italy):
Excitations in carbon nanotubes

Michael Moseler (Germany):
Symmetry breaking by relativistic effects

Atsu Nakajima (Japan):
Size-selective electronic properties of isolated and supported binary clusters

Gianfranco Pacchioni (Italy):
Supported metal atoms and clusters on MgO, SiO_2 and TiO_2 thin films

Jean-Yves Raty (Belgium):
Ab initio simulations of carbon nanostructures: from nanodiamonds to nanotube growth

Karsten Reuter (Germany):
Towards a predictive modelling of the mesoscale: matching density-functional theory with statistics

Angel Rubio (Spain):
Applications of TDDFT to the optical response of nanostructures and biomolecules

Kurt Schroeder (Germany):
Clusters and steps on Si(111): surfacant effect due to As and Sb

Annabella Selloni (USA):
Organic-inorganic interfaces

Massimiliano Di Ventra (USA):
Understanding transport at the nanoscale: Physical issues and open questions

Robert Wolkow (Canada):
Controlled molecular adsorption on Si: laying a foundation for molecular devices

Ludger Wöste (Germany):
Coherent control of cluster dynamics

HOT TOPIC TALKS

Lars Ismer:
First principles vibrational and themodynamic analysis of the infinite poly-alanine alpha-helix

Andrey Gal:
Towards molecular manipulation on insulating surfaces by local force application

Cristiana Di Valentin:
Electron rich surfaces: from solvated electrons in ionic oxides to inorganc electrides

Henrik Gronbeck:
CO induced modification of the metal/metal oxide nnteraction

Paula Havu:
Electron transport through quantum wires and point contacts

Elizabeth Lupton:
Mechanical manipulation of siloxane elastomers: a first-principles molecular dynamics study

Mikael Johansson:
Au_{32}: a 24-carat golden fullerene

Zeljko Sljivancanin:
Ammonia synthesis on a supported iron nanocluster

POSTERS

Nicolae Atodiresei:
The bonding of carboxylate functional group to metal surfaces: ab initio calculations of electronic and geometrical structure of formate, 3-thiophene carboxylate and glycinate molecules on the Cu(110) surface

Luis Carlos Balbás:
Trends in the structure and bonding of pure and doped noble metal clusters

Peter Broqvist:
CO oxidation over supported au nanoparticles: promoting and poisonous effects of coadsorbates

Giorgos Fagas:
Complex-band structure and conductance properties of oligomer junctions

Jan-Ole Joswig:

A genetic-algorithms search and electronic structure calculations for Ti_2 to Ti_100

Adam Kiejna:
Layered surface-oxide structures on Mg(0001)

Katri Laaksonen:
Computational study of the structure and properties of $GaAs_{1-x}N_x$

Markku Leino:
Temperature effects on electron correlations in coupled quantum dots

Philip Lindan:
The hallmark of hexagonal order in sp^2-bonded carbon

Andrey Lyalin:
Fission and fragmentation of Na, Mg and Sr clusters

Yuchen Ma:
Magnetic properties of vacancies in graphene and single-walled carbon nanotubes

Francesco Mercuri:
A theoretical approach to the study of mechanicalmotion in molecular machines and devices

Julián Milano:
Magnetotransport properties in transition metals nanostructures

Indu Bhusan Mishra:
Nanometallic clusters as catalysts

Luis M. Molina:
Structures and reactivities of small Au clusters supported on MgO(001) – a DFT study

Nassira Keghouche:
Magnetic properties of Ni-Pt/SiO_2 nanoaggregates

Sven Neukermans:
Electronic and geometric structure of stable endohedral doped clusters

Olli Pakarinen:
Ab initio modeling of Au clusters on the KBr surface

Nicolas Papanicolaou:
Diffusion of platinum dimers on Pt(111) surface by molecular-dynamics simulation

Martti Puska:
Vortex clusters in quantum dots

Esa Räsänen:
Regular behavior of irregular quantum dots in high magnetic fields

Lavanya Ramaniah:
A first-principles study of the structural, energetic and dynamical properties of C60 Ta_n(n=1,3) clusters

Kurt Schroeder:
Clusters and steps on Si(111): surfactant effect due to As and Sb

Michelle Thomas:
Theoretical study of quasi 1D crystals in carbon nanotubes

Shalva Tsiklauri:
Persistent current in two-dimensional (2D) four-electron quantum dot

Hua Wu:
First-principles study of thin magnetic transition-metal alloy films on Si(001)

BUDGET

ESSN-2004 and WG-7 had a combined budget totaling 28809.46 EUR. The meetings were sponsored by the Academy of Finland, the European Science Foundation through the Psi-k Programme and the Finnish Cultural Foundation.

3.2 ESF Workshop/Conference Announcements

3.2.1 WORKSHOP ON AB INITIO PHONON CALCULATIONS

Cracow, 2-4 December, 2004

Sponsored by
ESF Psi-k Programme

We would like to announce that the above workshop is organized by the Institute of Nuclear Physics, PAN and Pedagogical University in Cracow under support of the European Science Fundation Programme PSI-k.

This workshop is aimed at anyone who wants to learn how phonon calculations within the density functional theory approach can be done for solids.

You can find detailed information on the Workshop at:

http://wolf.ifj.edu.pl/workshop/

Phonons are the fundamental description of vibrations in solid state materials, and to large extent they define the finite temperature properties of solids. They play an important role for quite a number of microscopic and bulk phenomena. A deep understanding of the phonon behavior, especially that of new materials, is a necessary condition for future technological developments.

Prof. dr hab. Krzysztof Parlinski
Head of the Department of Materials Research by Computers
Institute of Nuclear Physics
Polish Academy of Sciences
ul.Radzikowskiego 152
31-342 Cracow
Poland

E-mail: b8parlin@cyf-kr.edu.pl
krzysztof.parlinski@ifj.edu.pl

Tel. (+48)-(12)-662-8209, 8408
Fax. (+48)-(12)-662-8458

`WWW institute: http://www.ifj.edu.pl/`
`WWW personal:  http://wolf.ifj.edu.pl/~parlinsk/cv/index.html`
`WWW "Phonon":  http://wolf.ifj.edu.pl/phonon/`

3.2.2 Mini-workshop on FLAPW development

Sponsored by the Ψ_k Network: Electronic Structure Calculations of Solids and Surfaces
Venue: Forschungszentrum Jülich, D-52425 Jülich, Germany
Date: 10.Dec.04 – 11.Dec.04
Organized by: Stefan Blügel (email: s.bluegel@fz-juelich.de)
Peter Blaha (email: pblaha@theochem.tuwien.ac.at)

Aim: We would like to invite graduate students, postdocs and scientists active in developing the FLAPW method to a two-days mini-workshop. The workshop is in the spirit of two previous workshops of this type in Jülich focussing on recent highlights, developments and current state of the art of the different groups. An important issue is also future directions of the method. In order keep the meeting efficent we plan to restrict the number of participants to about 30.

For further information and application please

Contact: Stefan Blügel (email: s.bluegel@fz-juelich.de)
(http://www/fz-juelich.de/iff/staff/Bluegel_S)

4 News from UK's CCP9 Programme

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

4.1 CCP9 Conference Announcements

4.1.1 CCP9 Conference

Daresbury Laboratory, UK

29-30 November 2004

http://www.ccp9.ac.uk

Organizers:

James Annett and Walter Temmerman

Scope: All ab-initio and materials specific calculations of the electronic properties of condensed matter systems such as metals, semiconductors, magnets, superconductors, biological systems, minerals, surfaces etc.

Topical areas: Magneto-electronics, catalysis, nanotechnology, high temperature superconductors, novel wide band gap semiconductors, etc.

Techniques: DFT, GW, TD-DFT, DMFT, QMC, SIC-LSDA, LSDA+U.

All contributions dealing with the solution of the Schrödinger/Dirac equation in condensed matter systems are welcome.

Register on http://www.ccp9.ac.uk or by e-mail to S.Miller@dl.ac.uk.

Programme of the CCP9 Conference 2004

Monday, 29th November

09.30 - 10.30		Registration and coffee
10.30 - 11.30	**Richard Martin**	Building on the successes of Electronic Structure Theory

11.30 - 11.55	Mike Towler	Recent progress in quantum Monte Carlo
12.00 - 12.25	Dzidka Szotek	Self-interaction corrected Local Spin Density calculations for spintronics materials
12.30 - 14.30		Buffet Lunch and Posters
14.30 - 15.30	**Rex Godby**	The GW approach to spectral, ground-state and transport properties
15.30 - 15.55	Bob Jones	Density functional treatment of extended interstitial defects in Si
16.00 - 16.25	Martin Lüders	Ab-initio theory of superconductivity: Density functional formalism, approximate functionals and first applications
16.30 - 17.00		Coffee
17.00 - 18.00	**Born Prize Presented to Matthias Scheffler**	Statistical Mechanics from First Principles
20.00		Conference Dinner

Tuesday, 30th November

08.45		Coffee and Pastries
09.00 - 10.00	**Mike Payne**	Next Generation Simulation Techniques
10.00 - 10.25	Chris-Kriton Skylaris	Introducing ONETEP: Linear-Scaling Density Functional Theory with Plane Waves
10.30 - 10.55	David Pettifor	Recent Developments in analytic bond-order potentials
11.00 - 11.30		Coffee
11.30 - 11.55	Derwyn Rowlands	First-principles description of disordered metallic systems with short-range order
12.00 - 12.25	Chris Pickard	Interpreting magnetic resonance experiments from first principles
12.30 - 14.55		Lunch and posters
15.00 - 16.00	**Mikhail Katsnelson**	Non-quasiparticle states in half-metallic ferromagnets
16.00 - 17.00	**Takao Kotani**	Quasiparticle self-consistent GW method

5 General Workshop/Conference Announcements

5.1 Computational Materials Science Workshop

Hands-on-FLEUR
12-16 October 2004
Buenos Aires

Abstract

FLEUR is a FLAPW-Code developed by the Theory I group of the Institute of Solid State Research of the Research Centre Jülich in collaboration with other theoretical groups of the Psi-k Network.

The FLAPW-Method (Full Potential Linearized Augmented Plane Wave Method) is an all-electron method which within density functional theory is universally applicable to all atoms of the periodic table and to systems with compact as well as open structures such as surfaces, chains, clusters or molecules. Due to the all-electron nature of the method, collinear and non-collinear magnetism is included rigorously, and nuclear quantities e.g. isomer shift, hyperfine field, electric field gradient (EFG), and core level shift are calculated routinely. The capability of calculating the forces exerted on the atoms within the LAPW method opens the gate to structure optimization.

For more information on FLEUR see: http://www.flapw.de

PURPOSE OF THE HANDS-ON:

The purpose is to offer an introduction to the fundamentals of ab-initio density functional theory and to the handling with the FLEUR code. The hands-on training will be based on a LINUX platform.

The speakers will be mostly members of the organizing team, plus current FLEUR users presenting selected applications.

ORGANIZERS:

- Gustav Bihlmayer, IFF-Jülich, Germany
- Stefan Blügel, IFF-Jülich, Germany
- Ana Maria Llois, CNEA and FCEyN-UBA, Buenos Aires, Argentina

PARTICIPANTS:

Those interested in getting acquainted with the use of LAPW codes, in particular with FLEUR are invited to participate. Due to limitations in the number of available terminals and tutors for the sessions we are forced to restrict the number of participants to about 20.

The workshop should enable the participants to use FLEUR, to interpret its outputs and to be aware of problems arising when running simple cases.

SITE OF THE WORKSHOP:

The workshop is going to take place at Centro Atomico Constituyentes, which lies by the city of Buenos Aires.

CONTACT: Ana Maria Llois: llois@cnea.gov.ar

5.2 ICTP - INFM/Democritos - ISMO - IUT School

on "Electronic-structure calculations and their applications in materials science"

25 April - 6 May 2005

Isfahan, Iran

A School on Electronic-structure calculations and their applications in materials science will be held at the Isfahan University of Technology (IUT) in Iran from 25 April to 6 May 2005. The School will be jointly sponsored by the Abdus Salam International Center for Theoretical Physics (ICTP, http://www.ictp.trieste.it), the Italian INFM/Democritos National Simulation Center (http://www.democritos.it), the Center for International Research & Collaboration (ISMO, http://www.ismo.ir), and organized in collaboration with the Isfahan University of Technology

(IUT, http://www.iut.ac.ir).

The directors are: Hadi Akbarzadeh (IUT), local organizer, Stefano Baroni (Scuola Internazionale Superiore di Studi Avanzati-SISSA and Democritos, Trieste, Italy), Maria Peressi (Universita di Trieste and Democritos, Trieste, Italy), and Abdallah Qteish (Yarmouk University, Irbid, Jordan).

The School will cover the fundamentals of modern electronic structure theory based on density functional theory, with strong emphasis on the pseudopotential/plane wave approach, together with some of the most relevant recent developments and applications. The School will consist of a three-day international workshop devoted to some of the recent advances in the field, followed by a full-immersion one-week hands-on tutorial course on the use of the Pwscf/DEMOCRITOS suite of computer codes

(http://www.pwscf.org, http://www.democritos.it/scientific.php).

A tentative list of speakers and lecturers includes:

Hadi Akbarzadeh (Isfahan University of Technology, Isfahan - Iran)
Stefano Baroni (SISSA, Trieste - Italy)
Keyvan Esfarjani (Sharif University of Technology, Tehran - Iran)
Paolo Giannozzi (Scuola Normale Superiore, Pisa - Italy)
Stefano de Gironcoli (SISSA, Trieste - Italy)
Oguz Gulseren (Bilkent University, Ankara - Turkey)
Volker Heine (Cambridge University, Cambridge - UK)
Nicola Marzari (Massachussetts Institute of Techology, Cambridge - USA)
Noureddine Meskini (Universite de Tunis, Tunis - Tunisia)

Maria Peressi (Universita degli Studi di Trieste, Trieste - Italy)
Abdallah Qteish (Yarmouk University, Irbid - Jordan)
Lucia Reining (Ecole Polytechnique, Palaiseau - France)
Carlo Sbraccia (*) (International School for Advanced Studies, Trieste - Italy)
Sandro Scandolo (ICTP, Trieste - Italy)
Nacir Tit (United Arab Emirates University, Al-Ain - United Arab Emirates)
Erio Tosatti (SISSA and ICTP, Trieste - Italy)
Renata Wentzcovitch (University of Minnesota, Minneapolis - USA)

(* = to be confirmed)

PARTICIPATION

Scientists and students from all countries which are members of the United Nations, UNESCO or IAEA may attend the School. As it will be conducted in English, participants should have an adequate working knowledge of this language. All participants are also required to have an adequate working knowledge of Linux and Fortran. Although the main purpose of the School is to help research workers from developing countries, through a programme of training within a framework of international cooperation, a limited number of students and post-doctoral scientists from developed countries are also welcome to attend. As a rule, travel and subsistence expenses of the participants should be borne by the home institution. Every effort should be made by candidates to secure support for their fare (or at least half-fare). However, limited funds are available for some participants who are nationals of, and working in, a developing country, and who are not more than 45 years old. Such support is available only for those who attend the entire duration of the School. There is no registration fee.

The Application Form is obtainable from the ICTP WWW server:

`http://agenda.ictp.trieste.it/agenda/current/fullAgenda.php?email=0&ida=a04223`

(which will be constantly up-dated) or from the activity Secretariats (address below). It should be completed and a hard copy returned (no applications via e-mail will be considered) before 15 December 2004 as follows:

For applicants from Iran: to Mrs. Shams, International & Scientific Cooperation Office (ISCO), Isfahan University of Technology, Electronic Structure School In Iran (Ref. smr. 1690)- 84154 Isfahan, Iran (phone: +98- 311 ?3912505 or 2506; fax: +98-311- 391 2511 isco@cc.iut.ac.ir).

For applicants from all other countries: to The Abdus Salam I.C.T.P. - Electronic Structure School In Iran (Ref. smr. 1690)- Strada Costiera, 11 - 34014 Trieste, Italy (tel. +39-040-2240540 - fax +39-040-224163 - cm@ictp.trieste.it).

Activity Home Page:

`http://agenda.ictp.trieste.it/agenda/current/fullAgenda.php?email=0&ida=a04223`

6 General Job Announcements

IFP Post-doctoral Position (Rueil-Malmaison, France) DFT Study of the Reactivity on Co(Ni)MoS Sulfides Catalysts

One postdoctoral position is available in the Department of Thermodynamics and Molecular Modeling at the French Institute of Petroleum (IFP). The general topic of the project is the "DFT study of the reactivity on Co(Ni)MoS sulfides catalysts". These important catalysts are industrially used in hydrodesulfurization (HDS) for producing cleaner fuels in refineries. Density Functional Theory (DFT) results obtained in our group (see the list below) have been proven to be very successful for the atomic scale characterization of Co(Ni)MoS active phase. The present project aims at investigating well defined key reaction mechanisms on Co(Ni)MoS including the adsorption and transition states calculations at the DFT level, for a better prediction of the reactivity of such catalysts.

The work will be carried out in collaboration with the Direction of Catalysis and Separation for relevant comparisons with available experimental catalytic tests.

List of publications in the field (non exhaustive)

H. Toulhoat and P. Raybaud, J. Catal. 216 (2003) 63.

P. Raybaud et H. Toulhoat, Fuel Chem. Div. Prep. 48(1) (2003) 78.

H. Schweiger, P. Raybaud, and H. Toulhoat, J. Catal. 212 (2002) 33.

H. Schweiger, P. Raybaud, G. Kresse, and H. Toulhoat, J. Catal. 207 (2002) 76.

P. Raybaud, J. Hafner, G. Kresse, S. Kasztelan, and H. Toulhoat, J.Catal. 189 (2000) 129; ibid. 190 (2000) 128.

P. Raybaud, J. Hafner, G. Kresse, and H. Toulhoat, Stud. Surf. Sci. Catal. 127 (1999) 309.

P. Raybaud, J. Hafner, G. Kresse, and H. Toulhoat, Phys. Rev. Lett. 80 (1998) 1481.

Location: Rueil-Malmaison, very close to Paris (France) in the Department of Thermodynamics and Molecular Modeling - Direction of Applied Chemistry and Physical Chemistry - IFP

http://www.ifp.fr

Eligibility: The preference will be given to non-french candidates, having defended their PhD in the past three years.

Qualification: Candidates should have a PhD and a background in the theoretical and computational methods of condensed matter physics. Experience of density functional calculations is desirable.

Duration: Up to 18 months, with an initial contract of 12 months.

Application: Candidates should send, preferably by e-mail, their CV, list of publications and coordinates of a few reference persons to:

Pascal Raybaud
Departement Thermodynamique et Modelisation Moleculaire
Direction Chimie et Physico-chimie Appliquees
Institut Francais du Petrole (IFP)
1 & 4 Avenue de Bois Preau
92852 Rueil-Malmaison, FRANCE
Phone : +33 1.47.52.71.84
Fax : +33 1.47.52.70.58
email: pascal.raybaud@ifp.fr

Ph.D. Studentship: "Theoretical modelling of unconventional superconductors"

Laboratory of Solid State Physics and Magnetism Interfaces and Wetting group

Institute of Nuclear and Radiation Physics Nuclear Condensed Matter group

Katholieke Universiteit Leuven, Belgium

A Ph.D. position is available at the Department of Physics and Astronomy of the University of Leuven (Belgium). The goal of the project is to use ab initio and phenomological modelling tools in order to understand the behaviour of unconventional superconductors (Sr2RuO4 etc.).

Supervisor of this Ph.D. project will be Prof. Dr. Joseph Indekeu. The project is part of the Concerted Research Action on "Magnetism and Superconductivity in Hybrid Nanosystems". A proper training in ab initio methods and Ginzburg-Landau modelling will be provided. As the successful applicant will act as a go-between between the different research groups that are involved, a reasonable degree of independence and communicative skills are required. Acquaintance with the field of superconductivity would be helpful (although not an absolute prerequisite).

Inquiries should be addressed to Stefaan.Cottenier@fys.kuleuven.ac.be. Add a CV, the e-mail addresses of at least 2 referees, and a to-the- point motivation why you are suitable for this position.

Starting date is October 1, 2004, or any later date that would be mutually agreed upon. Applications will be considered as long as the position is open, but preferably before September 15.

More details about the involved research groups and the university can be found on the following web pages:

Laboratory of Solid State Physics and Magnetism:

http://www.fys.kuleuven.ac.be/vsm/

Interfaces and Wetting group:

http://www.fys.kuleuven.ac.be/vsm/joi/joi.html

Institute of Nuclear and Radiation Physics:

http://www.fys.kuleuven.ac.be/iks/

Nuclear Condensed Matter group:

http://www.fys.kuleuven.ac.be/iks/nvsf/nvsf.html

both at Katholieke Universiteit Leuven, Belgium:

http://www.kuleuven.ac.be/english/

Dr. Stefaan Cottenier
Instituut voor Kern- en Stralingsfysica
K.U.Leuven
Celestijnenlaan 200 D
B-3001 Leuven (Belgium)

tel: + 32 16 32 71 45
fax: + 32 16 32 79 85
e-mail: stefaan.cottenier@fys.kuleuven.ac.be

Computational Materials Scientist/Physicist Position
Silicon Valley, California, USA

Position open for a Computational Materials Scientist in a nanotechnology start-up company focusing on multiscale modeling and simulations of new composite nanoparticle material in the catalyst application area. We are a fast growing nanotechnology company located in Silicon Valley, California, USA

We are searching for a Ph.D. in Physics, Materials Science, Chemistry or associated disciplines with solid foundation and demonstrated extensive experience of density-functional theory methods and molecular dynamics simulations as well as C++ programming is required. It is highly desirable for a candidate to have working experience in simulation of transition-metal nanoparticles. A prior knowledge of automobile catalytic converter or fuel cell applications will be useful. Good communication skills and ability to work well in a team of scientists are essential.

Salary will be commensurate with experience. The position is immediately available and applications will be considered until it is filled. Please submit a formatted resume (Word or PDF), list of publications and references to jobs@nanostellar.com

Jonathan Woo
jwoo@nanostellar.com

Postdoc Position in Theory of Laser Induced Phase Transitions
Institute of Physics, Universitaet Kassel, Germany

In the framework of the european research training program FLASH a postdoc position in theoretical physics/computational physics is available at the Institute of Physics, Universitaet Kassel, Germany. In collaboration with the group of Prof. U. von Barth (Lund, Sweden) we plan to develop a theoretical method to describe ultrafast structural changes induced by femtosecond laser pulses. The method will be based on Density Functional Theory.

A large variety of problems involving many-body physics and nonequilibrium processes are related to this subject, like excitation of coherent phonons, laser induced Peierls-transitions, laser manipulation of nanostrutures and macromolecules, nonthermal melting, and magnetic-non-magnetic transitions.

The selected candidate is expected to work on the description of these phenomena in close collaboration with other theoretical groups and experimental groups in Europe and the USA.

The position is for one year with an optional second year. If the work is progressing very well an even longer employment is possibile. Several trips to Lund University in Sweden are envisaged as well as participation in yearly network conferences.

A background in computational physics, solid state physics and Density Functional Theory will be considered favourably.

Applicants should submit a CV (as a PDF-file) and arrange to have at least two letters of recomendation sent to:

Prof. Dr. Martin E. Garcia
Theoretical Physics
Fachbereich Naturwissenschaften
Universitaet Kassel
Heinrich-Plett-Str. 40,
34132 Kassel, Germany
e-mail: garcia@physik.uni-kassel.de

TENURE TRACK ASSISTANT PROFESSOR

Theoretical Condensed Matter and Materials Physics at the Nanoscale

THE UNIVERSITY OF NEBRASKA-LINCOLN, USA

The Department of Physics and Astronomy at the University of Nebraska-Lincoln is seeking a tenure-track Assistant Professor in theoretical condensed matter and materials physics (CMMP). The successful candidate will join a current group of 9 experimental and 2 theoretical CMMP faculty studying bulk, surface and nanoscale properties of electronic, ferroelectric, magnetic and magneto-optical materials, structures, and devices. While applicants will be considered from any area of CMMP, preference will be given to candidates whose research interests strengthen the areas currently represented in the Department. Candidates who can also contribute to on-campus interdisciplinary programs including the Center for Materials Research and Analysis, the Program of Excellence in Nanoscale Science and Technology, and the NSF-funded Materials Research Science and Engineering Center in Quantum and Spin Phenomena in Nanomagnetic Structures are especially encouraged to apply.

Applicants should have a Ph.D. in physics or related area, with two years of postdoctoral experience being highly desirable. The successful candidate will have a strong research record, the potential for establishing a significant, externally-funded research program, and a strong interest in undergraduate and graduate teaching. Start-up funds are available. Candidates should send a letter of application, curriculum vitae, publication list, statement of research interests, and the names and addresses of at least three references to:

Professor Evgeny Tsymbal,
CMMP Search Committee Chair,
Department of Physics and Astronomy,
116 Brace Lab,
The University of Nebraska-Lincoln,
Lincoln, NE 68588-0111

e-mail: tsymbal@unl.edu
web: `http://physics.unl.edu/~tsymbal/tsymbal.html`

Screening of applicants will begin on 15 November 2004, but the search will continue until a suitable candidate is found. The University of Nebraska is committed to a pluralistic campus community through Affirmative Action and Equal Opportunity and is responsive to the needs of dual career couples. We assure reasonable accommodation under the Americans with Disabilities Act. Contact Jennifer Becic at (402) 472-9223 for assistance.

Research Associate

“Relativistic Optimized Potential Method for Magnetic Solids”

Department of Chemistry and Pharmacy (AK Ebert)
University of Munich, Germany

Applications are invited for a research associate (PostDoc) position to work on development of the “Relativistic Optimized Potential Method for Magnetic Solids” which is part of the DFG Priority Program 1145: MODERN AND UNIVERSAL FIRST-PRINCIPLES METHODS FOR MANY-ELECTRON SYSTEMS IN CHEMISTRY AND PHYSICS (http://www.uni-koeln.de/spp1145/).

The position is available for one year with a possible extension up to 5 years.

Applicants need to have a PhD or equivalent in physics, material science, chemistry, or related field. Demonstrated experience in research and development in electronic structure methods as well as fluency in FORTRAN programming language are required. An acquaintance with relativistic theory, KKR method would be a great plus.

The candidate is supposed to develop and implement relativistic optimized potential method in the framework of spin-polarized relativistic Korringa-Kohn-Rostoker (SPR-KKR) method

(http://olymp.cup.uni-muenchen.de/ak/ebert/SPRKKR).

The salary is according to BAT-IIa, which is about 50 kEuro p.a. depending on age.

Applications including curriculum vitae, list of publications, and contact details of three references should be sent as soon as possible in electronic form to:

Diana.Benea@cup.uni-muenchen.de

H. Ebert

LMU München

Postdoc Position in Theory of Laser Induced Phase Transitions

Institute of Physics, Universitaet Kassel, Germany

In the framework of the european research training program FLASH a postdoc position in theoretical physics/computational physics is available at the Institute of Physics, Universitaet Kassel, Germany. In collaboration with the group of Prof. U. von Barth (Lund, Sweden) we plan to develop a theoretical method to describe ultrafast structural changes induced by femtosecond laser pulses. The method will be based on Density Functional Theory.

A large variety of problems involving many-body physics and nonequilibrium processes are related to this subject, like excitation of coherent phonons, laser induced Peierls-transitions, laser manipulation of nanostrutures and macromolecules, nonthermal melting, and magnetic-non-magnetic transitions.

The selected candidate is expected to work on the description of these phenomena in close collaboration with other theoretical groups and experimental groups in Europe and the USA.

The position is for one year with an optional second year. If the work is progressing very well an even longer employment is possibile. Several trips to Lund University in Sweden are envisaged as well as participation in yearly network conferences.

A background in computational physics, solid state physics and Density Functional Theory will be considered favourably.

Applicants should submit a CV (as a PDF-file) and arrange to have at least two letters of recomendation sent to:

Prof. Dr. Martin E. Garcia
Theoretical Physics
Fachbereich Naturwissenschaften
Universitaet Kassel
Heinrich-Plett-Str. 40
34132 Kassel, Germany
e-mail: garcia@physik.uni-kassel.de

Research Associate:

Developing Multiscale Techniques to Connect the Quantum to the Mesoscopic Level

Theoretical Chemistry, Ruhr-Universitaet Bochum, Germany

Applications are invited for a research associate position. Subject to funding the preferred starting date would be fall/winter 2004.

The ideal candiate would have significant experience in electronic structure theory, mixed quantum/classical simulation, and dynamical multiscale simulation. She or he would work primarily on developing and implementing novel techniques to connect a quantum description (Car-Parrinello) via a microscopic level to a coarse-grain treatment. Although the ultimate goal is to predict properties of soft materials under irradiation, the project focuses heavily on code development in close collaboration with an outstanding partner group. In addition, he/she can also be involved in other challenging research projects including both method development and large-scale applications.

Information on the techniques used and developed are accessible via

http://www.theochem.rub.de/go/cprev.html.

The Center of Theoretical Chemistry at RUB offers an exciting interdisciplinary environment with excellent working conditions (including several parallel platforms and a 500 GFlop/s SCI machine in house).

Candidates should send a detailed resume including an outline of their research achievements and interests as well as contact information for academic references as one pdf file to

office@theochem.rub.de.

Consideration of candidates will begin immediately and continue until the position is filled. The University particularly welcomes applications from women.

`Professor Dominik Marx`
`Lehrstuhl fuer Theoretische Chemie`
`Ruhr-Universitaet Bochum`
`44780 Bochum, Germany`
`Email: office@theochem.rub.de`
`Fax: ++49 234 32 14045`
`URL: http://www.theochem.rub.de/`

PhD Position: Proton Transfer in Biosystems
Theoretical Chemistry, Ruhr-Universitaet Bochum, Germany

Applications are invited for a PhD position embedded in an international doctorate study program. The preferred starting date would be fall/winter 2004.

The ideal candiate would have previous experience in electronic structure theory, ab initio MD and mixed quantum/classical simulation. She or he would work primarily with dynamical QM/MM (Car-Parrinello) simulation techniques, including some code development, in order to understand proton transfer along hydrogen bonded networks in complex biomatrices.

Information on the techniques used and developed are accessible

via http://www.theochem.rub.de/go/cprev.html.

The Theoretical Chemistry Center at RUB offers an exciting interdisciplinary environment with excellent working conditions (including several parallel platforms and a 500 GFlop/s SCI machine in house).

Candidates should send a detailed resume including an outline of their achievements and interests as well as contact information for academic references as one pdf file to

office@theochem.rub.de.

Consideration of candidates will begin immediately and continue until the position is filled. The University particularly welcomes applications from women.

Professor Dominik Marx
Lehrstuhl fuer Theoretische Chemie
Ruhr-Universitaet Bochum
44780 Bochum, Germany
Email: office@theochem.rub.de
Fax: ++49 234 32 14045
URL: http://www.theochem.rub.de/

Ph.D Position

Theory of Ultra-Fast Spin-Dynamics of Magnetic Systems

Research Centre Jülich, Germany

Magnetic and magneto-optical data storage and data processing are key technologies of the information age. Their rapid progress stems from a close link between basic research and commercial product development. The Giant Magnetoresistance (GMR) effect, for example, became the state-of-the-art of modern hard disks within a few years of its discovery at the Research Centre Jülich in 1988. Since then, the Research Centre Jülich (www.fz-juelich.de), with its wide spectrum of theoretical expertise and experimental facilities, has continued to play a leading role in unravelling complex magnetic phenomena and exploiting their effects in novel applications.

The department Theory I (www.fz-juelich.de/iff/e_th1) at the Institute of Solid State Research now seeks a motived Ph.D. student to strengthen its research activities in the field of magnetoelectronics and spintronics. The goal of the project is to understand the principles of ultrafast spin-dynamics on the femto-second time scale, one of the greatest challenges of magnetism. An emphasis is on the theory of excitation, relaxation and magnetic depolarization and the role of the spin-orbit interaction. The work involves the solution of the time-dependent Schrodinger equation of an embedded magnetic cluster.

Candidates should have a Master or Diplom degree in physics, chemistry or a related subject, excellent academic background and good computational skills. The position is funded through the Priority Programm SPP-1133 Ultrafast Magnetization Processes (www.spindynamik.de) of the German Research Foundation (www.dfg.de).

Applications for this position and further inquiries should be addressed to

Dr. Andreas Bringer (a.bringer@fz-juelich.de)
– or –
Prof. Stefan Blügel (s.bluegel@fz-juelich.de)
Institut für Festkörperforschung
Forschungszentrum Jülich
Germany

Applications may be submitted electronically and should include a curriculum vitae, a statement of relevant academic experience and addresses of potential referees. The position is available from 1.October.2004, with the exact starting date open to negotiation.

Ph.D Position

Ab-initio investigation of spin-dependent transport through magnetic tunneljunctions

Research Centre Jülich, Germany

Magnetic and magneto-optical data storage and data processing are key technologies of the information age. Their rapid progress stems from a close link between basic research and commercial product development. The Giant Magnetoresistance (GMR) effect, for example, became the state-of-the-art of modern hard disks within a few years of its discovery at the Research Centre Jülich in 1988. Since then, the Research Centre Jülich (www.fz-juelich.de), with its wide spectrum of theoretical expertise and experimental facilities, has continued to play a leading role in unravelling complex magnetic phenomena and exploiting their effects in novel applications.

The department Theory I (www.fz-juelich.de/iff/e_th1) at the Institute of Solid State Research now seeks a motived Ph.D. student to strengthen its research activities in the field of magnetoelectronics and spintronics. The goal of the project is to understand the principles of spin-dependent transport through magnetic tunneljunctions. The transport is described by the Landauer-Büttiker theory which is combined with the full-potential linearized augmented plane wave method (FLAPW) using an embedded Green-function approach (for details see: Wortmann etal, PRB 65, 165103 (2002); Wortmann etal, PRB 66, 075113 (2002)). We plan to investigate junctions of the type Fe/MgO/Fe. A particular challenge is the extention of the method to noncollinear magnetism, spin-orbit interaction and non-equilibrium transport.

Candidates should have a Master or Diplom degree in physics or a related subject, excellent academic background and excellent computational skills. The position is funded by the FZJ typically for a period of 3 years.

Further inquiries for this position should be addressed to

Dr. Jussi Enkovaara (j.enkovaara@fz-juelich.de)
– or –
Dr. Daniel Wortmann (d.wortmann@fz-juelich.de)

Applications for this position should be addressed to

Prof. Stefan Blügel (s.bluegel@fz-juelich.de)
Institut für Festkörperforschung
Forschungszentrum Jülich
Germany

Applications may be submitted electronically and should include a curriculum vitae, a statement of relevant academic experience and addresses of potential referees. The position is available from 1.November.2004, with the exact starting date open to negotiation.

Lecturer in Condensed Matter Physics (Maitre de Conferences-MCF),

University Montpellier 2, France

The University Montpellier 2 is susceptible to opening a permanent position for a lecturer in Condensed Matter Physics (Maitre de Conferences (MCF) in the 28th section of the CNU "Milieu denses et continus") with the profile along the lines given below. The final decision on the post will be given by the Ministry of Education. Starting date would be September 2005. The successful candidate will teach in the Physics Department and will work in the theory group of the Laboratoire des Verres (LdV).

Scientific profile:

For the MdC position the candidate should possess a PhD in Condensed Matter Physics or Theoretical Chemistry. Postdoctoral experience are highly appreciated. The theory group of the LdV studies the structure and dynamics of disordered systems such as oxide and polymer glasses, spin glasses, as well as simple models for disordered materials. Most of these investigations are done by means of computer simulations (ab initio, molecular dynamics, Monte Carlo). Therefore the candidate is expected to have a strong background in ab initio Molecular Dynamics calculations, and to know, or to be willing to learn, first-principles methods reproducing experimental spectra (Raman, Infra-Red, NMR, etc..). He/she will collaborate with experimental groups from the LdV who are developping new experimental techniques for the study of the structure and dynamics of glasses. He/she is expected to work also on the properties of hybrid materials studied at LdV, as well as on nanostructured materials developped by the Groupe de Dynamique des Phases Condensées (GDPC).

Teaching profile:

It is essential for the candidate to be sufficiently proficient in the French language to be able to teach in French. Furthermore it would be a considerable advantage for the candidate to have already had a teaching experience in physics. The teaching will be in the domain of numerical techniques in physics.

- IMPORTANT NOTE: In order to be eligible for this position, it is necessary to have the "qualification" accorded by the national CNU commission.This administrative procedure has to be initiated by deposing a "lettre d'intention" BEFORE OCTOBER 19, 2004, 5 pm Paris time. More information on this can be found on

`http://www.education.gouv.fr/personnel/enseignant_superieur/enseignant_chercheur/antares.`

and click on the "ANTARES" link.
- Check particularly on the limiting dates for obtaining the thesis.
- A "qualification" already obtained in any commission of the CNU over the previous three years is still valid.

Interested applicants should sent a CV and statement of research to

Dr. Estelle PITARD
e-mail: estelle.pitard@ldv.univ-montp2.fr
Laboratoire des Verres, cc 069
Universite Montpellier 2
Place Eugene Bataillon
34095 Montpellier Cedex, France

PhD Studentship: Computer Modelling of "Clean Energy" Oxide Materials

University of Surrey, UK

Applications are invited for a PhD Studentship on multi-scale computer modelling of oxide materials within the materials chemistry group of Dr M. Saiful Islam. The project will involve atomistic/MD modelling of the ion diffusion and surface properties of ceramic oxides for potential applications in "clean energy" fuel cells and sensors. This is part of a major project funded by the EPSRC (with collaborative links with Morgan Matroc Ltd and the School of Engineering).

You should have a degree in Chemistry, Physics, Materials Engineering or related discipline. Some background in computer simulation techniques would be useful. The studentship award provides a maintenance grant at EPSRC rates (tax-free) and payment of tuition fees (and is open to UK/EU students).

Applications, with a covering letter, a detailed CV and the names and addresses of two referees, should be posted to

Dr Saiful Islam
Chemistry Division (C4), SBMS,
University of Surrey,
Guildford GU2 7XH, UK.

who can be contacted for an informal discussion (tel: 01483-686844; email: m.islam@surrey.ac.uk).

Further information on Chemistry can be found at:

http://www.surrey.ac.uk/Chemistry.

Closing date for applications: 25 October 2004.

7 Abstracts

Crystal structure and vibrational spectra of $AlVO_4$. A DFT study

Veronika Brázdová, M. Verónica Ganduglia-Pirovano and Joachim Sauer
Humboldt Universität zu Berlin, Institut für Chemie,
Unter den Linden 6, D-10099 Berlin, Germany

Abstract

We present periodic density functional calculations within the generalised gradient approximation (Perdew-Wang 91) on structure and vibrational properties of bulk $AlVO_4$. The optimised structure agrees well with crystallographic data obtained by Rietveld refinement (the RMS deviation of bond distances is 0.032 Å), but the positions of the lighter oxygen atoms may not have been experimentally determined as accurately as those of the heavier Al and V atoms. All observed bands in the Raman and IR spectrum have been assigned to calculated harmonic frequencies. Bands in the 1020 – 900 cm^{-1} region have been assigned to V–$O^{(2)}$ stretches in V–$O^{(2)}$–Al bonds. The individual bands do not arise from vibrations of only one bond, not even from vibrations of several bonds of one VO_4 tetrahedron. The results confirm that vibrations around 940 cm^{-1} observed for vanadia particles supported on thin alumina film are V–O–Al interface modes with two-fold coordinated oxygen atoms in the V–$O^{(2)}$–Al interface bonds.

(submitted to: Inorg. Chem.)
Contact person: Joachim Sauer (js@chemie.hu-berlin.de)

Applicability of the Spin-Orbit Sum Rule for the Actinide $5f$ States

G. van der Laan
Magnetic Spectroscopy, Daresbury Laboratory, Warrington WA4 4AD, UK
K.T. Moore, J.G. Tobin, B.W. Chung, M. A.Wall, and A.J. Schwartz
Lawrence Livermore National Laboratory, Livermore, California 94550, USA

Abstract

The branching ratio of core-valence transitions in electron energy-loss spectroscopy and x-ray absorption spectroscopy is linearly related to the expectation value of the spin-orbit operator of the valence states. Here, we analyze the branching ratio of the $N_{4,5}$ edges in the actinides and find that the spin-orbit sum rule gives an accurate result without the need to include the core-valence interactions. The branching ratio is not only useful to study the variations in the $5f$ spin-orbit interaction, it also allows us to constrain the $5f$ count for given angular-momentum coupling conditions.

Published in Physical Review Letters **93**, 097401 (2004).
Manuscript available from g.van_der_laan@dl.ac.uk

The interdependence of defects, electronic structure and surface chemistry

Philip Lindan, Elizabeth Duplock, Changjun Zhang, Michelle Thomas,
Ryan Chatten, and Alan Chadwick
School of Physical Sciences, University of Kent,
Canterbury CT2 7NR, UK

Abstract

In this article we present three diverse applications of first-principles simulations to problems of materials chemistry and chemical physics. Their common characteristic is that they are essentially problems of the relationships among atomic structures and the properties they promote in real materials and real applications. The studies are on transition-metal oxide surface chemistry, the reactivity and electronic structure of sp^2- bonded carbon systems, and defects and electrochromic properties in WO_3. In these demanding applications we must have concern for how realistic our model systems are and how well current implementations of DFT perform, and we comment on both.

(Dalton Trans. 19, 3076 (2004))
Contact person: p.lindan@kent.ac.uk

On the controversy surrounding water dissociation on TiO_2 (110)

Philip J. D. Lindan, Changjun Zhang
School of Physical Sciences, University of Kent,
Canterbury CT2 7NR, UK

Abstract

There has been a long-running debate among theorists and experimentalists on the precise nature of water adsorption at the TiO_2 (110) surface. Some experimentalists argue that dissociative adsorption occurs only at defect sites and therefore at low coverages. Although there is no doubt that defect sites are strongly reactive, until now there has been no firm understanding of adsorption on the perfect surface with which to contrast behavior. Here we report benchmark calculations that demonstrate unequivocally that dissociation of a molecule is exothermic. Experimental findings are rationalized by the existence of a metastable molecular state separated from the dissociated state by a substantial barrier. We show that the barrier varies in height with coverage and with the presence of neighboring adsorbates, and we detail mechanisms for both phenomena. Finally, we reassess photoelectron spectroscopy results, showing their consistency with our predictions.

(Submitted to Phys. Rev. B.)
Contact person: p.lindan@kent.ac.uk

TEMPERATURE DEPENDENT MAGNETIC ANISOTROPY IN METALLIC MAGNETS FROM AN AB-INITIO ELECTRONIC STRUCTURE THEORY: $L1_0$-ORDERED FePt

J.B.Staunton^A, S.Ostanin^B, S.S.A.Razee^C, B.L.Gyorffy^D, L.Szunyogh^E,
B.Ginatempo^F and Ezio Bruno^F
^{A} *Department of Physics,University of Warwick,*
Coventry CV4 7AL, U.K.
^{B} *Department of Earth Sciences, University College London,*
Gower Street, London WC1E 6BT, U.K.
^{C} *Department of Physics, Kuwait University, P.O. Box 5969,*
SAFAT 13060, Kuwait
^{D} *H.H.Wills Physics Laboratory, University of Bristol,*
Tyndall Avenue, Bristol BS8 1TL, U.K.
^{E} *Department of Theoretical Physics,*
Budapest University of Technology and Economics, Budapest, Hungary
^{F} *Dipartimento di Fisica and Unita INFM, Universita di Messina,*
Sicily, Italy

Abstract

On the basis of a first-principles, relativistic electronic structure theory of finite temperature metallic magnetism, we investigate the variation of magnetic anisotropy, K, with magnetisation,M, in metallic ferromagnets. We apply the theory to the high magnetic anisotropy material, $L1_0$-ordered FePt, and find its uniaxial K consistent with a magnetic easy axis perpendicular to the Fe/Pt layering for all M and to be proportional to M^2 for a broad range of values of M. For small M, near the Curie temperature, the calculations pick out the easy axis for the onset of magnetic order. Our results are in good agreement with recent experimental measurements on this important magnetic material.

(Submitted to Phys. Rev. Lett.)
A preprint is available on cond-mat/0407774.
Further information about the work can be obtained via email to **j.b.staunton@warwick.ac.uk**.

Evidence for large configuration-induced band-gap fluctuations in GaAsN alloys

G. Bentoumi, V. Timoshevskii, N. Madini, M. Côté, R. Leonelli
Département de Physique and Regroupement Québécois sur
les Matériaux de Pointe (RQMP), Université de Montréal,
Case Postale 6128, Succursale Centre-ville,
Montréal, Québec, H3C 3J7 Canada
J.-N. Beaudry, P. Desjardins, and R. A. Masut
Département de Génie Physique and Regroupement Québécois sur
les Matériaux de Pointe (RQMP), École Polytechnique, Case Postale 6079,
Succursale Centre-ville, Montréal, Québec, H3C 3A7 Canada

Abstract

We have measured the near band-gap absorption of $\mathrm{GaAs}_{1-x}\mathrm{N}_x$ thin films with $x < 0.012$. The spectra were analyzed with a model which allows a precise determination of the band gap and of the width of the optical transitions; the latter is found to increase, for $x > 0.002$, well beyond what is expected in a III-V alloy. *Ab-initio* calculations were performed within the generalized gradient approximation with the exchange-correlation functional of Engel and Vosko [Phys. Rev. B **47**, 13164 (1993)]. They reveal that the band gap depends markedly on nitrogen atomic configuration. The anomalous broadening of the intrinsic optical transitions thus gives strong evidence for configuration-induced band-gap fluctuations.

(Phys. Rev. B. **70**, 035315 (2004))
Contact person: Michel.Cote@umontreal.ca

First principles study of the rotational transitions of H_2 physisorbed over benzene

Sébastien Hamel and Michel Côté
Département de Physique, Université de Montréal,
Case Postale 6128, Succursale Centre-ville, Montréal,
Québec H3C 3J7, CANADA
Regroupement Québécois sur les Matériaux de Pointe (RQMP)

Abstract

In the ongoing search for promising compounds for hydrogen storage, novel porous metal-organic frameworks (MOF) have been discovered recently. Binding sites in these MOF were deduced from inelastic neutron scattering (INS) spectroscopy of the rotational transitions of the adsorbed molecular hydrogen. In light of this discovery, it is important to have a fundamental understanding of hydrogen adsorption at different sites in this class of MOF materials. As a first step, here we study the case of H_2 adsorbed on benzene as a model of the organic linkers in the microporous crystal. We access the DFT results by comparing with correlated *ab initio* methods, e.g. second-order Møller-Plesset (MP2) and coupled cluster (CCSD(T)). Different approximations for the exchange-correlation potentials were accessed for a set of relevant properties (binding energy, energetically favored configuration, distance between the adsorbents and adsorbates). In particular, theoretical rotational spectra of the adsorbed H_2 were obtained that could be compared to the experimental INS spectra.

(Accepted for publication in *Journal of Chemical Physics*).

Contact person: Michel.Cote@umontreal.ca

Electronic Structure of Sm and Eu Chalcogenides

A. Svane, G. Santi,
Department of Physics and Astronomy, University of Aarhus,
DK-8000 Aarhus C, Denmark,
Z. Szotek, W. M. Temmerman,
Daresbury Laboratory, Warrington WA4 4AD,
United Kingdom
P. Strange, M. Horne,
Department of Physics, Keele University,
ST5 5DY, United Kingdom
G. Vaitheeswaran, V. Kanchana,
Max-Planck-Institut für Festkörperforschung,
D-70569 Stuttgart, Germany
L. Petit,
Computer Science and Mathematics Division,
and Center for Computational Sciences,
Oak Ridge National Laboratory,
Oak Ridge, TN 37831, USA

Abstract

The ground state configuration of the monochalcogenides of Sm and Eu is determined from total energy calculations using the self-interaction corrected local-spin-density approximation. The Sm chalcogenides, with the exception of SmO, are characterized by divalent f^6 Sm ions, while all the Eu chalcogenides have divalent f^7 Eu ions in the ground state. With pressure, the Eu and Sm chalcogenides exhibit isostructural transitions into an intermediate valent state, which in the total energy calculations is represented by localized f^5 configurations on the Sm ions (f^6 on Eu ions) together with a partly occupied f-band at the Fermi level. The energy of the fundamental $f \rightarrow d$ transition, which determines the value of the semiconducting gap, is determined by total energy calculations of the charged rare earth ion (Eu$^+$ or Sm$^+$) in a supercell approach with one f-electron removed. The pressure coefficients are in excellent agreement with experiment, and the occurrence of isostructural transitions is intimately related to the closure of the band gap.

(Phys. Stat. Sol. (b): accepted)
Manuscripts available from: svane@phys.au.dk

Electronic structure and volume magnetostriction of rare-earth metals and compounds

I. Turek[1,2], J. Rusz[2] and M. Diviš[2]
[1] *Institute of Physics of Materials, ASCR, Brno, Czech Republic*
[2] *Department of Electronic Structures, Charles University in Prague, Czech Republic*

Abstract

A first-principle theory of spontaneous volume magnetostriction is presented. It is based on selfconsistent electronic structure calculations for a magnetically ordered ground state and a disordered local moment state. The effect of highly localized $4f$ orbitals of rare-earth atoms is taken into account by an open-core treatment within the local spin-density approximation. The theory is applied to hexagonal gadolinium and to selected intermetallic compounds with the cubic C15 Laves structure: RCo$_2$ (R = Gd, Dy, Er) and GdAl$_2$. The results are compared to experiment and discussed in terms of: (i) magnitudes of the local moments and (ii) volume-dependent exchange interactions.

Submitted to: J. Magn. Magn. Mater.
Contact person: Ilja Turek (turek@ipm.cz)

An elementary derivation of Lloyd's formula valid for full-potential multiple-scattering theory

Rudolf Zeller
Institut für Festkörperforschung, Forschungszentrum Jülich GmbH,
D-52425 Jülich, Germany

Abstract

Lloyd's formula is an elegant tool in multiple-scattering theory. It implicitly provides an analytical integration over energy and over all space and directly gives the number of states as function energy. The usual derivations of Lloyd's formula are involved and the range of their applicability is not obvious. It is purpose of this paper to give a derivation, which requires only elementary mathematical manipulations. The result is valid for potentials of general shape and for arbitrary complex energies.

Published in J. Phys.: Condens. Matter, 16, 6453 (2004)
Contact person: ru.zeller@fz-juelich.de

Oscillatory behavior of $5d$ magnetic moments in Fe/W multilayers

N. Jaouen
European Synchrotron Radiation Facility, B.P. 220,
F-38043 Grenoble Cédex, France
G. van der Laan
Magnetic Spectroscopy, Daresbury Laboratory, Warrington, WA4 4AD, UK
T. K. Johal
Magnetic Spectroscopy, Daresbury Laboratory, Warrington, WA4 4AD, UK
F. Wilhelm and A. Rogalev
European Synchrotron Radiation Facility, B.P. 220,
F-38043 Grenoble Cédex, France
S. Mylonas
Laboratoire de Métallurgie Physique, Université de Poitiers,
86962 Futuroscope Chasseneuil, France
L. Ortega
Laboratoire de Cristallographie, CNRS Grenoble, France

Abstract

We used x-ray resonant magnetic scattering (XRMS) across the W L_3 absorption edge in combination with x-ray magnetic circular dichroism and anomalous x-ray reflectivity to obtain the magnetic polarization profile in a Fe(30 Å)/W(11 Å) multilayer. This extends the use of XRMS to the $5d$ transition metals for the study of induced magnetization. Analysis of our experimental results shows that there is a strong oscillatory behavior of the magnetization in the W layer. This tendency is in good agreement with the recent theoretical predictions by Tyer *et al.* [Phys. Rev. B **67**, 104409 (2003)].

Published in Physical Review B **70**, 094417, 2004.
Manuscript available from g.van_der_laan@dl.ac.uk

Half-metallicity in the Heusler alloy $Co_2MnSi(001)$ surface - a density-functional theory study

S. Javad Hashemifar[1,2], P. Kratzer[1] and M. Scheffler[1]
[1] Fritz-Haber-Institut der Max-Planck-Gesellschaft,
Faradayweg 4–6, D-14195 Berlin, Germany
[2] Department of Physics, Isfahan University of Technology,
84156 Isfahan, Iran

Abstract

We have studied the stability, the electronic and magnetic properties of $Co_2MnSi(001)$ thin films for 15 different terminations using density-functional theory (DFT) calculations. The phase diagram obtained by *ab initio* atomistic thermodynamics shows that in practice the MnSi, pure Mn, or pure Si terminated surfaces can be stabilized under suitable conditions. Analyzing the surface band structure, we find that the pure Mn termination, due to its strong surface-subsurface coupling, preserves the half-metallicity of the system, while surface states appear for the other terminations.

(submitted to: Phys. Rev. Lett.)
Contact person: Peter Kratzer (kratzer@fhi-berlin.mpg.de)

Atomic structure of the GaAs(001)-$c(4 \times 4)$ surface: first-principles evidence for diversity of heterodimer motifs

E. Penev, P. Kratzer and M. Scheffler
Fritz-Haber-Institut der Max-Planck-Gesellschaft,
Faradayweg 4–6, D-14195 Berlin, Germany

Abstract

The GaAs(001)-$c(4 \times 4)$ surface was studied using *ab initio* atomistic thermodynamics based on density-functional theory calculations. We demonstrate that in a range of stoichiometries, between those of the conventional three As-dimer and the new three Ga-As dimer model, there exists a diversity of atomic structures featuring Ga-As heterodimers. These results fully explain the experimental scanning tunneling microscopy images and are likely to be relevant also to the $c(4 \times 4)$-reconstructed (001) surfaces of other III-V semiconductors.

(submitted to: Phys. Rev. Lett.)
Contact person: Peter Kratzer (kratzer@fhi-berlin.mpg.de)

Ab initio DFT studies of oxygen K edge NEXAFS spectra for the V_2O_3(0001) Surface

C. Kolczewski and K. Hermann
Fritz-Haber-Institut der Max-Planck-Gesellschaft,
Faradayweg 4-6, D-14195 Berlin, Germany

Abstract

Theoretical near edge X-ray absorption fine structure (NEXAFS) spectra describing oxygen 1s core excitation have been evaluated for the differently coordinated oxygen species appearing near the V_2O_3(0001) surface with half metal layer VOV termination. Adsorption of oxygen above vanadium centers of the VOV terminated surface (O$-t$VO termination) results in very strongly bound vanadyl oxygen which has also been considered for core excitation in this study. The angle-resolved spectra are based on electronic structure calculations using ab initio density-functional theory (DFT) together with model clusters. Experimental NEXAFS spectra for V_2O_3(0001) show a rather strong dependence of peak positions and relative intensities on the photon polarization direction. This dependence is well described by the present theoretical spectra and allows us to assign spectral details in the experiment to specific O 1s core excitations where final state orbitals are determined by the local binding environments of the differently coordinated oxygen centers. As a result, a combination of the present theoretical spectra with experimental NEXAFS data enables an identification of differently coordinated surface oxygen species at the V_2O_3(0001) surface.

(submitted to: Theoretical Chemical Accounts)
Contact person: Christine Kolczewski (kolczew@fhi-berlin.mpg.de)

First-Principles Study of Low-Index Surfaces of Lead

Dengke Yu and Matthias Scheffler
Fritz-Haber-Institut der Max-Planck-Gesellschaft,
Faradayweg 4–6, D-14195, Berlin-Dahlem, Germany

Abstract

We report a density-functional theory (DFT) study for Pb(111), Pb(100), and Pb(110) surfaces using *ab initio* pseudopotentials and a plane-wave basis set. Creating the pseudopotential with the $6s$, $6p$, and $6d$ states in the valence shell is found to yield good results for the bulk lattice constant, bulk modulus, and cohesive energy. Convergence of the surface energies with plane-wave cutoff, **k**-mesh, vacuum and slab thickness was carefully checked, as was the affect of the non-linearity of the core-valence exchange-correlation interaction. Employing the local-density approximation (LDA) of the exchange-correlation functional we obtain excellent agreement of the calculated surface energies and surface-energy anisotropies with recent experimental results. However, with the generalized gradient approximation (GGA) the calculated surface energies are about 30% too low. For all three studied surfaces, the calculations give interlayer relaxations that are in reasonable agreement with low-energy electron diffraction analysis. The relaxations exhibit a damped oscillatory behavior away from the surface, which is typical for a metal surface.

(Accepted for publication in Phys. Rev. B)

Contact person: Dengke Yu (yu_d@fhi-berlin.mpg.de)

Role of semicore states in the bandgaps of group-III-nitrides: An exact-exchange study

A. Qteish and A. I. Al-Sharif
Department of Physics, Yarmouk University, 21163-Irbid, Jordan

M. Fuchs and M. Scheffler
Fritz-Haber-Institut der Max-Planck-Gesellschaft,
Faradayweg 4–6, D-14195, Berlin-Dahlem, Germany

S. Boeck and J. Neugebauer
Department of Theoretical Physics, University of Paderborn
D-33095 Paderborn, Germany

Abstract

The bandstructure of group-III-nitride semiconductors (AlN, GaN, InN) has been calculated employing exact-exchange (EXX) Kohn-Sham density-functionl theory. In contrast to previous EXX calculations the cation semicore states have been explicitly treated as valence. For AlN and GaN excellent agreement with valence only and all-electron *GW* calculations has been found. For InN, where the application of *GW* is problematic due to the negative LDA bandgap, the EXX approach allows a fully consistent treatment.

(submitted to Phys. Rev. B)

Contact person: Abdallah Qteish (aqteish@fhi-berlin.mpg.de)

Comment on "Band-Gap Problem in Semiconductors Revisited: Effects of Core States and Many-Body Self-Consistency

Kris Delaney[1], P. García-González[2], Angel Rubio[3], Patrick Rinke[4] and R. W. Godby[1]
[1] *Department of Physics, University of York,*
Heslington, York YO10 5DD, U.K.
[2] *Dpto. de Física de la Materia Condensada,*
Universidad Autónoma de Madrid, 28049 Madrid, Spain
[3] *Dpto. de Física Materiales, UPV, Centro Mixto CSIC-UPV,*
and DIPC, San Sebastián, Spain
[4] *Fritz-Haber-Institut der Max-Planck-Gesellschaft,*
Faradayweg 4–6, D-14195, Berlin-Dahlem, Germany

Abstract

In absence of an abstract for comments the 1st paragraph is listed: In a recent Letter [1], Ku and Eguiluz concluded that deep-core states and many-body self-consistency have an important effect on obtaining a good description of the band gap in semiconductors, based on their calculations for bulk Si and Ge. Their conclusions question the validity of pseudopotentials in *GW* calculations, claiming that this approach is successful due to a previously unknown error cancellation. We would like to address two points rasied by the Letter: First, which approximation for the self-energy operator is best used for electronic-structure calculations, and second, the validity of pseudopotentials.

(accepted by Phys. Rev. Lett.)

Contact person: Kris Delaney (kdelaney@uiuc.edu)

Diffusion of Fe atoms on W surfaces and Fe/W films and along surface steps

D. Spišák and J. Hafner
Institut für Materialphysik and Center for Computational
Materials Science, Universität Wien, Wien, Austria

Abstract

The diffusion of Fe atoms on clean W(100) and W(110) surfaces and along surface steps, and the diffusion of Fe adatoms and vacancies on Fe/W(100) and Fe/W(110) films has been investigated using ab-initio DFT methods. Our results demonstrate that even a single Fe adatom on the W(100) surface induces locally a partial dereconstruction of the surface, leading to the activation energy for hopping diffusion of 1.2 eV which is lower on the reconstructed than on the ideal surface. On W(110) diffusion occurs by elementary jumps along close-packed directions, the calculated activation energies of 0.7 eV are in quantitative agreement with experimental estimates. Exchange diffusion of Fe is unfavorable on both surfaces. The investigations of adatom diffusion on 1-ML Fe films reveal a delicate interplay between structural and magnetic effects. For nonmagnetic Fe/W(100) films, at low coverages (below 0.4 ML) adatoms do not propagate the pseudomorphic structure, but occupy bridge instead of hollow sites. The site preference switches to the hollow at higher coverages. Correspondingly, the potential energy surface is rather smooth, leading to low activation energies for hopping diffusion of 0.4 eV and 0.5 eV for jumps to nearest and next-nearest neighbor sites, respectively. Exchange diffusion requires a larger activation energy of 0.7 eV. Antiferromagnetic ordering of the film completely changes the picture. The magnetic interactions around the adsorbate are necessarily frustrated, the adatom induces the formation of a ferromagnetic defect. As a consequence of the frustration, the potential energy is even flatter than for the nonmagnetic case with an activation energy of only 0.3 eV, leading to the prediction of faster diffusion below the Néel temperature of the film. Fe adatoms on Fe/W(110) induce a local transition from a pseudomorphic to a close-packed arrangement, the adatom is incorporated in the film forming a Fe–Fe dumbbell occupying a lattice site. Our studies are completed by the investigation of vacancy diffusion in Fe/W films and adatom diffusion along step edges. Vacancy diffusion requires a higher activation energy than adatom hopping, in particular in Fe/W(100) films. Diffusion along steps has been studied on a vicinal (110) surface with ⟨100⟩-type steps. The minimal activation energy is with 1.3 eV considerably higher than for diffusion on the terraces. Decoration of the steps with a row of Fe atoms lowers all activation energies, so that diffusion rates on terraces and along Fe-decorated steps are comparable. The implication of our results on the kinetics of film growth are discussed.

Accepted in: Phys. Rev. B
Preprint available from: http://cms.mpi.univie.ac.at/spisak/

Magnetic Properties of Co Nanowires on the Cu(001) Surfaces

A. B. Klautau[1], S. Frota-Pessôa[2]
[1]*Departamento de Física, Universidade Federal do Pará,*
Belém, PA, Brazil
[2]*Instituto de Física, Universidade de São Paulo,*
CP 66318, São Paulo, SP, Brazil

Abstract

We present *ab initio* calculations for spin and orbital moments of finite Co_n ($n = 1, 3, 5, 7, 9$) nanowires on Cu(001) surfaces, performed using the linear muffin tin orbital atomic sphere approximation method implemented directly in real space (RS-LMTO-ASA), in which the spin-orbit coupling and the orbital-polarization term have been included. For Co as an adatom on Cu(001) we predict an extremely large orbital moment, which is comparable to the spin moment. Our investigations for Co nanowires on Cu(001) address the persistence and extent of this large orbital moment in the wires as a function of their size. We find that the average orbital moment (M_{orb}) per Co atom decreases as the size of the wire is increased, and this behavior is strongly correlated with the coordination number of the Co atoms. The magnetic moments per atom of very long nanowires inferred from the present finite nanowire calculations are in good agreement with the those given in the literature for ideal infinite wires on Cu(001).

(Accepted, Phys. Rev. B)
Contact person: aklautau@usp.br

Ab-initio theory of superconductivity - I: Density functional formalism and approximate functionals

M. Lüders[1,2], M. A. L. Marques[3,2], N. N. Lathiotakis[3,2], A. Floris[3,4], G. Profeta[5],
L. Fast[6,2], A. Continenza[5], S. Massidda[4], E. K. U. Gross[3,2]
[1]*Daresbury Laboratory, Warrington WA4 4AD, United Kingdom*
[2]*Institut für Theoretische Physik, Universität Würzburg,*
Am Hubland, D-97074 Würzburg, Germany
[3]*Institut für Theoretische Physik, Freie Universität Berlin,*
Arnimallee 14, D-14195 Berlin, Germany
[4]*INFM SLACS, Sardinian Laboratory for Computational Materials Science and*
Dipartimento di Scienze Fisiche, Università degli Studi di Cagliari,
S.P. Monserrato-Sestu km 0.700, I–09124 Monserrato (Cagliari), Italy
[5]*C.A.S.T.I. - Istituto Nazionale Fisica della Materia (INFM) and*
Dipartimento di Fisica, Università degli studi dell'Aquila,
I-67010 Coppito (L'Aquila) Italy
[6]*SP Swedish National Testing and Research Institute, P.O.B. 857,*
S-501 15 Borås, Sweden

Abstract

A novel approach to the description of superconductors in thermal equilibrium is developed within a formally exact density-functional framework. The theory is formulated in terms of three "densities": the ordinary electron density, the superconducting order parameter, and the diagonal of the nuclear N-body density matrix. The electron density and the order parameter are determined by Kohn-Sham equations that resemble the Bogoliubov-de Gennes equations. The nuclear density matrix follows from a Schrödinger equation with an effective N-body interaction. These equations are coupled to each other via exchange-correlation potentials which are universal functionals of the three densities. Approximations of these exchange-correlation functionals are derived using the diagrammatic techniques of many-body perturbation theory. The bare Coulomb repulsion between the electrons and the electron-phonon interaction enter this perturbative treatment on the same footing. In this way, a truly ab-initio description is achieved which does not contain any empirical parameters.

(submitted to: Phys. Rev. B; cond-mat/0408685)
Preprints available from M.Lueders@dl.ac.uk

Ab-initio theory of superconductivity - II: Application to elemental metals

M. A. L. Marques[1,2], M. Lüders[3,2], N. N. Lathiotakis[1,2], G. Profeta[4], A. Floris[1,5],
L. Fast[6,2], A. Continenza[4], E. K. U. Gross[1,2], S. Massidda[5]
[1]*Institut für Theoretische Physik, Freie Universität Berlin,*
Arnimallee 14, D-14195 Berlin, Germany
[2]*Institut für Theoretische Physik, Universität Würzburg,*
Am Hubland, D-97074 Würzburg, Germany
[3]*Daresbury Laboratory, Warrington WA4 4AD, United Kingdom*
[4]*C.A.S.T.I. - Istituto Nazionale Fisica della Materia (INFM) and*
Dipartimento di Fisica, Università degli studi dell'Aquila,
I-67010 Coppito (L'Aquila) Italy
[5]*INFM SLACS, Sardinian Laboratory for Computational Materials Science and*
Dipartimento di Scienze Fisiche, Università degli Studi di Cagliari,
S.P. Monserrato-Sestu km 0.700, I–09124 Monserrato (Cagliari), Italy
[6]*SP Swedish National Testing and Research Institute, P.O.B. 857,*
S-501 15 Borås, Sweden

Abstract

The density functional theory for superconductors developed in the preceding article is applied to the calculation of superconducting properties of several elemental metals. In particular, we present results for the transition temperature, for the gap at zero temperature, and for thermodynamic properties like the specific heat. We obtain an unprecedented agreement with experimental results. Superconductors both with strong and weak electron-phonon coupling are equally well described. This demonstrates that, as far as conventional superconductivity is concerned, the first-principles prediction of superconducting properties is feasible.

(submitted to: Phys. Rev. B; cond-mat/0408686)
Preprints available from M.Lueders@dl.ac.uk

Superconducting properties of MgB_2 from first principles

A. Floris[1,2], G. Profeta[3], N. N. Lathiotakis[1], M. Lüders[4], M. A. L. Marques[1],
C. Franchini[3], E. K. U. Gross[1], A. Continenza[3], S. Massidda[2]
[1] *Institut für Theoretische Physik, Freie Universität Berlin,*
Arnimallee 14, D-14195 Berlin, Germany
[2] *INFM SLACS, Sardinian Laboratory for Computational Materials Science and*
Dipartimento di Scienze Fisiche, Università degli Studi di Cagliari,
S.P. Monserrato-Sestu km 0.700, I–09124 Monserrato (Cagliari), Italy
[3] *C.A.S.T.I. - Istituto Nazionale Fisica della Materia (INFM) and*
Dipartimento di Fisica, Università degli studi dell'Aquila,
I-67010 Coppito (L'Aquila) Italy
[4] *Daresbury Laboratory, Warrington WA4 4AD, United Kingdom*

Abstract

Solid MgB_2 has rather interesting and technologically important properties, such as a very high superconducting transition temperature. Focusing on this compound, we report the first non-trivial application of a novel density-functional-type theory for superconductors, recently proposed by the authors. Without invoking any adjustable parameters, we obtain the transition temperature, the gaps, and the specific heat of MgB_2 in very good agreement with experiment. Moreover, our calculations show how the Coulomb interaction acts differently on σ and π states, thereby stabilizing the observed superconducting phase.

(submitted to: Phys. Rev. Lett.; cond-mat/0408688)
Preprints available from afloris@physik.fu-berlin.de

Pressure Induced Charge Disproportionation in $LaMnO_3$

G. Banach and W.M. Temmerman
Daresbury Laboratory, Daresbury, Warrington WA4 4AD, UK

Abstract

We present a total energy study as a function of volume in the cubic phase of $LaMnO_3$. A charge disproportionated state into planes of $Mn^{3+}O_2/Mn^{4+}O_2$ was found. It is argued that the pressure driven localisation/delocalisation transition might go smoothly through a region of Mn^{3+} and Mn^{4+} coexistence.

(Accepted, J. Phys. Condens. Matter, cond-mat/0407069)
Contact person: W.M.Temmerman@dl.ac.uk

Electronic and magnetic properties of the (001) surface of hole-doped manganites

H. Zenia
Department of Physics and Astronomy, University of Sheffield,
Sheffield, S3 7RH, UK
G. Banach and W.M. Temmerman
Daresbury Laboratory, Daresbury, Warrington WA4 4AD, UK
G.A. Gehring
Department of Physics and Astronomy, University of Sheffield,
Sheffield, S3 7RH, UK

Abstract

The electronic and magnetic properties of ferromagnetic doped manganites are investigated by means of model tight-binding and *ab initio* self-interaction corrected local spin density approximation calculations. It is found that the surface alone by breaking the cubic symmetry induces a difference in the occupation of the two e_g orbitals at the surface. With *ab initio* calculations we found surface localisation of one orbital and hence a change in the Mn valency from four in the bulk to three at the sub-surface. Different surface or disordered interface induced localisation of the orbitals are considered too with respect to the nature and the strength of the magnetic exchange coupling between the surface/interface and the bulk-like region.

(Submitted to Phys. Rev. B, cond-mat/0407558)
Contact person: W.M.Temmerman@dl.ac.uk

8 Release of FPLO-4 Code

This is just to inform you that a new edition of the FPLO code has been released as FPLO-4.

This full-potential local-orbital scheme (FPLO) is designed to solve the Kohn-Sham-equations on regular lattices in a most efficient and accurate way.

Included are:

- scalar relativistic and 4-component fully relativistic solvers
- coherent potential approximation for partial chemical disorder
- LSDA + U method in different variants
- getting-started script
- user's manual

Elementary cells of up to 100 atoms can be treated on single-processor machines.

Please find details at the following url:

http://www.FPLO.de

Manuel Richter

9 SCIENTIFIC HIGHLIGHT OF THE MONTH

MIKA - a multigrid-based program package for electronic structure calculations

T. Torsti[1,2], V. Lindberg[3], I. Makkonen[1], E. Ogando[4],
E. Räsänen[1], H. Saarikoski[1], M. J. Puska[1] and R. M. Nieminen[1]

[1]*Laboratory of Physics, Helsinki University of Technology,*
P.O. Box 1100, FIN-02015 HUT, Finland,
[2]*CSC – Scientific Computing Ltd., P.O. Box 405, FIN-20101 Espoo, Finland,*
[3]*Department of Physics, Växjö University, SE-351 95 Växjö, Sweden,*
[4]*Donostia International Physics Center (DIPC),*
1072 Posta Kutxa, 20080 Donostia, Spain

Abstract

We give an introduction to the real-space, multigrid-based progam package MIKA (Multigrid Instead of the K-spAce). We give a short account of the history of real-space methods, introduce the idea of multigrid acceleration techniques, and present a generalisation of the Rayleigh-quotient minimization multigrid method. We also describe recent technical improvements of the numerical methods, and give examples of the most recent applications of the program package. The software developed in the MIKA-project is freely available in the hope that it will be useful for the researchers in the electronic structure community in general.

1 Introduction

In this article, we give an overview of the real-space, multigrid-based program package called MIKA. It consists of several different modules for solving the Kohn-Sham equations of the density-functional theory in different geometries. The program package is visualized in Fig. 1. It is emphasized in this figure that all the four application codes `rspace`, `cyl2`, `doppler` and `rs2dot` share common numerical multigrid routines implemented in the subroutine library `MGLIB`. This,

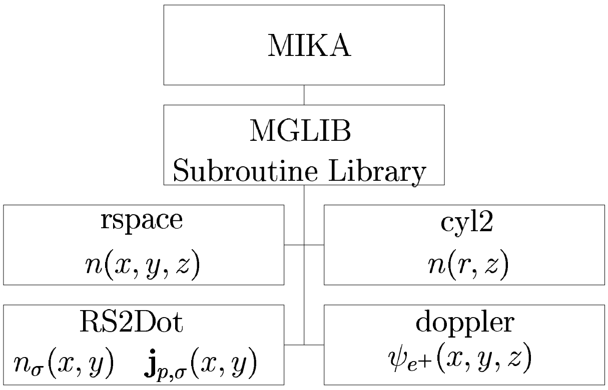

Figure 1: Schematic illutration of the software comprising the MIKA-package. Each of the four applications comes with a version of the numerical multigrid subroutine library `MGLIB`. Examples of applications of each of these codes are given in the text.

however, is in practice not true. There is a common ancestor to the multigrid subroutines, but in practice each code comes with its own version of the subroutine library. Some version of each of the codes is available from the MIKA-webpage [1]. The full source code is available, and the source code is licensed with the GNU general public license (GPL)[1]. Therefore, it is fully acceptable, and even recommended, for other researchers to take a piece of software that he/she considers useful, make further improvements, and start distributing the derived product on his/her own web-page. We believe that such a distributed mode of development, based on voluntary work of researchers, should in the long run be more efficient than a centralized mode. Of course, some form of centralized effort may be necessary to coordinate such activity.

The outline of this article is as follows. In section 2 we give, for the sake of completeness, the Kohn-Sham equations, the numerical solution of which is the subject of the rest of this article. In section 3 we give first some motivation for using grid-based real-space methods as opposed to plane-wave schemes and techniques based on the use of atom-centered basis functions. We use the standard and well-known multigrid solver for the Poisson equation to illustrate the basic ideas of the multigrid methodology. We then give a classification of three different types of multigrid techniques appearing in the litterature for the eigenvalue problem. Without making any conclusions about the relative efficiency of the three approaches, we proceed to describe in detail our own approach, the Rayleigh-quotient minimization multigrid (RQMG) method [5]. In section 4 we outline various technical improvements related to the RQMG method, to efficient methods for reaching self consistency, and to the computationally inexpensive use of auxiliary finer grids to improve the numerical accuracy of real-space grid-based calculations in general. Sections 5-8 contain brief introductions to the applications of our MIKA-package in general three-dimensional pseudopotential calculations for both finite and periodic systems, quantum dots in two-dimensional electron gas, axially symmetric jellium models for nanostructures and for the calculation of positron states in solids, respectively. In addition to these, a modification of the RQMG method for one-dimensional problems has been applied by Ogando et al. to treat thin metallic films on solid surfaces [6, 7].

---

[1] This seems to be a general trend in our community, advocated by the `fsatom` project [2], and followed e.g. by the `abinit` [3] and `octopus` [4] -projects.

2 Formalism

In the Kohn-Sham method for electronic structure calculations one solves for a set of equations self-consistently [8]. In the following, for the sake of completeness and simplicity, we present the equations and do so in the spin-compensated form, respectively. In practice, where needed (i.e. thus far for the `rs2dot` and `cyl2` -codes), we have made the straightforward generalization using the spin-density functional theory. The set of equations reads as (atomic units with $\hbar = m_e = e = 1$ are used):

$$\left(-\frac{1}{2}\nabla^2 + V_{\mathrm{eff}}(\mathbf{r})\right)\Psi_i = \epsilon_i \Psi_i, \tag{1}$$

$$n(\mathbf{r}) = \sum_i^N |\Psi_i(\mathbf{r})|^2, \tag{2}$$

$$V_{\mathrm{eff}}(\mathbf{r}) = V_{\mathrm{ion}}(\mathbf{r}) + V_{\mathrm{H}}(\mathbf{r}) + V_{\mathrm{xc}}(\mathbf{r}), \tag{3}$$

$$V_{\mathrm{H}}(\mathbf{r}) = \int \frac{n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} d\mathbf{r}', \tag{4}$$

$$V_{\mathrm{xc}}(\mathbf{r}) = \frac{\delta E_{\mathrm{xc}}[n(\mathbf{r})]}{\delta n(\mathbf{r})}. \tag{5}$$

The first equation (1) is a Schrödinger equation for non-interacting particles in an effective potential $V_{\mathrm{eff}}(\mathbf{r})$. For finite systems the wave functions are required to vanish at the boundaries of the computation volume. In the case of infinite periodic systems the complex wave functions have to obey the Bloch theorem at the cell boundaries. The electron density $n(\mathbf{r})$ is obtained from a sum over the N occupied states. The effective potential consists of an external potential $V_{\mathrm{ion}}(\mathbf{r})$ due to ions (or nuclei in all-electron calculations), the Hartree potential $V_{\mathrm{H}}(\mathbf{r})$ calculated from the electron density distribution, and the exchange-correlation potential $V_{\mathrm{xc}}(\mathbf{r})$. In the examples of the present article we use the local-density approximation (LDA) for the exchange-correlation energy

$$E_{\mathrm{xc}}[n(\mathbf{r})] = \int \epsilon_{\mathrm{xc}}(n(\mathbf{r}))n(\mathbf{r})d\mathbf{r}, \tag{6}$$

and for the exchange-correlation potential

$$V_{\mathrm{xc}}(\mathbf{r}) = \epsilon_{\mathrm{xc}}(n(\mathbf{r})) + n(\mathbf{r}) \left.\frac{d\epsilon_{\mathrm{xc}}}{dn}\right|_{n=n(\mathbf{r})}. \tag{7}$$

The Hartree potential is solved from the Poisson equation

$$\nabla^2 V_{\mathrm{H}}(\mathbf{r}) = -4\pi n(\mathbf{r}). \tag{8}$$

In practice, the electron density $n(\mathbf{r})$ is substituted by the total charge density $\rho(\mathbf{r})$, which includes a positive charge neutralizing the system. This positive charge is composed of Gaussian charge (with charge Z_I) distributions centered at the ions I. Once Eq. 8 is numerically solved, the analytically known potential caused by the Gaussians is replaced by the local part of the pseudopotential. Obviously, this correction has finite range, since both potentials have the asumptotic behaviour $Z_I/|\mathbf{r}-\mathbf{r}_I|$. In the case of finite systems, Dirichlet boundary conditions are used with the Coulomb potential values calculated using a multipole expansion. For periodic systems we fix the average Coulomb potential to zero – this is equivalent to setting $V_C(G =$

0) = 0 in the plane-wave approach – and allow the periodic boundary conditions to result in the corresponding converged potential.

The self-consistent solution of the above Kohn-Sham equations leads to the ground state electronic structure minimizing the total energy

$$\begin{aligned} E_{\mathrm{tot}} &= \sum_i \int \Psi_i^*(\mathbf{r}) \left(-\frac{1}{2}\nabla^2 \right) \Psi_i(\mathbf{r}) d\mathbf{r} + \frac{1}{2} \int V_{\mathrm{H}}(\mathbf{r}) n(\mathbf{r}) d\mathbf{r} \\ &+ \int V_{\mathrm{ion}}(\mathbf{r}) n(\mathbf{r}) d\mathbf{r} + E_{\mathrm{xc}} + E_{\mathrm{ion-ion}} \ , \end{aligned} \tag{9}$$

where $E_{\mathrm{ion-ion}}$ is the repulsive interaction between the ions (nuclei) of the system. Instead of the self-consistency iterations the solution of the Kohn-Sham problem can be found by minimizing directly the total energy with respect to the wave function parameters, *e.g.* plane-wave coefficients [9]. However, Kresse and Furthmüller [10, 11] have found this scheme less efficient than the self-consistency iterations.

3 Real-space (multigrid) methods

The plane-wave pseudopotential method has proven to be an excellent computational tool for solving large-scale electronic structure problems in condensed matter physics [12, 9]. Notable strengths of the method are the ability to use the fast Fourier transform for updating the Kohn-Sham equations, lack of dependence of the basis on atom positions, and the clear control of convergence with the cutoff energy determined by the shortest-wavelength mode. However, the method encounters difficulties in treating widely varying length scales. This issue is relevant for all-electron calculations, surfaces, clusters, and the hard pseudopotentials of first-row elements or transition metals. It is not necessary to use the supercell approximation, when treating clusters or molecules with real-space methods. However, it should be noted that this is not necessary in the plane-wave methodology either [13].

Approaches, where the basis functions are atom-centered or floating Gaussians or atomic orbitals, are very well established, and are used by the majority of the quantum-chemistry community as well as by an increasing number of condensed-matter physicists. A wide selection of well-established codes based on atom-centered basis functions is available, including e.g. DMOL [14], ADF [15], TURBOMOLE [16], NWCHEM [17] and SIESTA [18], among others. The basis sets used in these methods are at least an order of magnitude smaller than in the plane-wave methods, but the magnitude of the related basis-set truncation error is difficult to estimate.

Considerable effort has recently been focused also on developing “fully numerical” real-space methods [19], which permit systematic studies of convergence in the spirit of the plane-wave methods. These methods are based on finite elements [20, 21, 22, 23, 24], finite-difference discretizations [25, 26, 27, 28, 29, 30, 31] or wavelets [32]. Advantages of these approaches include the free choice of boundary conditions, allowing e.g. the treatment of finite and periodic systems with equal effort. Near-locality of the kinetic energy operator in real-space representations leads to simplicity in developing domain-decomposition parallel algorithms. In addition, it is possible to implement adaptive grid-refinement strategies to focus effort in spatial regions with large variations in the computed functions, for example near the nuclei. In finite-difference methods, the available strategies for mesh refinement include composite grids [33, 34, 35] and adaptive coordinates [36, 31]. In finite-element methods, on the other hand, there is in principle complete freedom in the choice of the computational mesh. However, generating an optimal finite element mesh (or finite-difference composite grid) for a given problem is a nontrivial task [37, 38, 39], which either requires *a priori* knowledge of the spatial dependence of the required density of the mesh, or involves a repeated sequence of solving the problem in a given mesh, making an *a posteriori* error estimation and then remeshing. Representations on real space grids allow also the use of multigrid (MG) algorithms with their excellent convergence characteristics and scaling properties [40, 41]. A real-space formulation is also often used in efficient implementations of $O(N)$ electronic structure methods, in which the computational work required scales linearly with the number of atoms [42, 43].

Among the pioneers of real-space methods for molecular systems were A. D. Becke [44, 45] and Pyykkö *et al.* [46, 47, 48], who made highly accurate fully numerical all-electron real-space calculations for diatomic molecules, employing the prolate spheroidal coordinate system. In the axial symmetry of diatomic molecules, the azimuthal dependence of the single-particle functions can be treated analytically and the ensuing numerical problem is two-dimensional. Their approach for diatomic molecules is very similar to our more general method for axially symmetric systems, described in Sec. 7. Besides the density-functional theory, Pyykkö *et al.* applied their fully numerical approach to other quantum chemical models such as Hartree-Fock, MCSCF, and Relativistic DFT [46].

Several approaches employing the multigrid idea within electronic structure calculations have appeared during the last decade [5, 49, 27, 28, 43, 30, 29]. The main idea of multigrid methods is that they avoid the critical slowing-down (CSD) phenomenon occuring when a partial differential equation discretized on a real space grid is solved with a simple relaxation method such as the Gauss-Seidel method. The discretized operators use information from a rather localized region of the grid at a time. Therefore the high-frequency error of the length scale of the grid spacing is reduced very rapidly in the relaxation. However, once the high-frequency error has effectively been removed, the slow convergence of the low-frequency components dominates the overall error reduction rate [40], i.e. CSD occurs. In multigrid methods one stops the relaxation on a given (fine) grid before CSD sets in and transfers the equation to a coarser grid (the so-called *restriction* operation) where the low-frequency components can be solved more efficiently. On the coarsest grid the problem is solved exactly or as accurately as possible, after which one interpolates (the so-called *prolongation* operation) the correction to finer grids, performing simultaneously relaxations in order to remove the high-frequency errors introduced in the interpolation.

It is best to illustrate these ideas in the case of the simple Poisson problem $\nabla^2 V = f$. After a few relaxation sweeps on the fine grid f the rapidly varying components of the residual $R_f = f - \nabla^2 V_f$ have been efficiently damped. A smooth correction V_c (approximately satisfying $V = V_f + I_c^f V_c$) is solved from another Poisson equation $\nabla^2 V_c = I_f^c R_f$. The transfer operators I_f^c and I_c^f are referred to as *restrictor* and *prolongator*, respectively.

Refs. [50, 51] are classical textbooks on multigrid methods. Introductory material can be found in the recently appeared second edition of the Multigrid tutorial by W. L. Briggs [52].

The full-approximation storage method [40] (FAS) is a standard recipe for nonlinear problems.

Beck *et al.* [30, 53] have applied the FAS eigensolver of Brandt *et al.* [41] for electronic structure calculations of small molecules. Costiner and Ta'asan [54, 55] have made several technical improvements to overcome various obstacles related to the application of the FAS-method in electronic structure calculations. It has also been noted [55, 56] that the FAS-scheme, applicable to nonlinear systems of equations, can be directly applied to the nonlinear Kohn-Sham problem, bypassing the self-consistency iterations. However, according to the authors' knowledge, none of these methods are yet routinely applied in large-scale electronic structure calculations. When many eigenfunctions are solved simultaneously, the FAS methods may suffer from problems with representing the eigenfunctions accurately on the coarse levels, limiting the number of levels that can be used.

Briggs *et al.* [49, 27] apply a steepest descent method, with a special preconditioner. In the preconditioning step, the Hamiltonian is approximated by the kinetic energy term only – thus they end up solving a Poisson equation in the preconditioning step. The same preconditioner is applied also in the (almost) linear scaling method by Fattebert *et al.* [43]. Mortensen *et al.* [57] apply this preconditioning technique in connection with the DIIS-method (direct inversion in the iterative subspace) in their real-space implementation of the projector augmented wave method.

There are efficient solvers for the matrix eigenproblems arising from the finite-difference or finite-element discretization of the Kohn-Sham equations involve that do not involve the multigrid concept. Chelikowsky *et al.* [58, 25, 59, 60] have succesfully applied iterative diagonalization schemes based on preconditioned Krylov techniques, such as the Lanczos method [61]. Their current implementation uses a preconditioned generalized Davidson algorithm [62]. Some form of a multigrid technique should probably play a role in the optimal preconditioning step of Krylov subspace techniques as well. There exists interesting recent development in the field of preconditioned eigensolvers by A. Knyazev and K. Neymeyr [63, 64].

3.1 RQMG method

We have developed a generalization of the so-called Rayleigh quotient multigrid method (RQMG) introduced by Mandel and McCormick [65]. Our generalization is presented in Ref. [5]. In this method the coarse grid relaxation passes are performed so that the Rayleigh quotient calculated on the *fine* grid will be minimized. In this way there is no requirement for the solution to be well represented on a coarse grid and the coarse grid representation problem is avoided. Mandel and McCormick [65] introduced the method for the solution of the eigenpair corresponding to the lowest eigenvalue. We have generalized it to the simultaneous solution of a desired number of lowest eigenenergy states by developing a scheme which keeps the eigenstates separated by the use of a penalty functional, Gram-Schmidt orthogonalization, and subspace rotations.

A basic ingredient of the scheme is a very simple relaxation method called *coordinate relaxation* [66]. Coordinate relaxation is a method of solving the discretized eigenproblem

$$Hu = \lambda Bu \tag{10}$$

by minimizing the Rayleigh quotient

$$\frac{\langle u|H|u\rangle}{\langle u|B|u\rangle}. \tag{11}$$

Above, H and B are matrix operators chosen so that the Schrödinger equation discretized on a real-space point grid with spacing h is satisfied to a chosen order $O(h^n)$. In Eq. (11) u is a vector, containing the values of the Kohn-Sham orbitals at the grid points. In the relaxation method, the current estimate u is replaced by $u' = u + \alpha d$, where the search vector d is simply chosen to be unity in one grid point and to vanish in all other points, and α is chosen to minimize the Rayleigh quotient. This leads to a simple quadratic equation for α. For complex eigenfunctions it is possible to either solve a remarkably complicated coupled pair of quadratic equations for the real and imaginary parts of α, or to sequentially apply separate coordinate relaxation steps for the real and imaginary parts. A complete coordinate relaxation pass is then obtained by performing the minimization at each point in turn and these passes can be repeated until the lowest state is found with desired accuracy.

Naturally, also the coordinate relaxation suffers from CSD because of the use of local information only in updating u in a certain point. In order to avoid it one applies the multigrid idea. In the multigrid scheme by Mandel and McCormick [65] the crucial point is that *coarse* grid coordinate relaxation passes are performed so that the Rayleigh quotient calculated on the *fine* grid will be minimized. In this way there is no requirement for the solution to be well represented on a coarse grid. In practice, a coarse grid search substitutes the fine grid solution by

$$u'_f = u_f + \alpha I_c^f e_c, \tag{12}$$

where the subscripts f and c stand for the fine and coarse grids, respectively, and I_c^f a prolongation operator interpolating the coarse grid vector to the fine grid. The Rayleigh quotient to be minimized is then

$$\frac{\langle u_f + \alpha I_c^f d_c | H_f | u_f + \alpha I_c^f d_c \rangle}{\langle u_f + \alpha I_c^f d_c | B_f | u_f + \alpha I_c^f d_c \rangle} = \frac{\langle u_f | H_f u_f \rangle + 2\alpha \langle I_f^c H_f u_f | d_c \rangle + \alpha^2 \langle d_c | H_c d_c \rangle}{\langle u_f | B_f u_f \rangle + 2\alpha \langle I_f^c B_f u_f | d_c \rangle + \alpha^2 \langle d_c | B_c d_c \rangle}. \tag{13}$$

The second form is obtained by relating the coarse grid operators, H_c and B_c, with the fine grid ones, H_f and B_f, by the Galerkin condition

$$H_c = I_f^c H_f I_c^f; \quad B_c = I_f^c B_f I_c^f; \quad I_f^c = \left(I_c^f \right)^T. \tag{14}$$

Note, however, that the Galerkin condition was not satisfied in our original implementation - instead we discretized the original equation separately on each grid to obtain H_c and B_c [discretization coarse grid approximation (DCA)].

The key point to note is that when $H_f u_f$ and $B_f u_f$ are provided from the fine grid to the coarse grid, the remaining integrals can be calculated on the coarse grid itself. Thus one really applies coordinate relaxation on the coarse grids to minimize the *fine level* Rayleigh quotient. This is a major departure from the earlier methods, which to some extent rely on the ability to represent the solution of some coarse grid equation on the coarse grid itself. Here, on the other hand, one can calculate the *exact* change in the Rayleigh quotient due to *any* coarse grid change, no matter how coarse the grid itself is. There is no equation whose solution would have to be representable.

Next we consider the generalization of the RQMG method to the simultaneous solution of several (N) mutually orthogonal eigenpairs. The separation of the different states is divided into two or three subtasks. First, in order to make the coarse grid relaxations converge towards the desired state we apply a penalty functional scheme. Given the current approximations for the k lowest eigenfunctions, the next lowest, $(k+1)$'th state is updated by minimizing the functional

$$\frac{\langle u_{k+1}|H|u_{k+1}\rangle}{\langle u_{k+1}|B|u_{k+1}\rangle} + \sum_{i=1}^{k} q_i \frac{|\langle u_i|u_{k+1}\rangle|^2}{\langle u_i|u_i\rangle \cdot \langle u_{k+1}|u_{k+1}\rangle}. \tag{15}$$

The modulus of the overlap integral in the penalty term is squared to make the penalty positive definite. The denominator is required to make the functional independent of the norms of u_i, $i = 1 \ldots k+1$. The minimization of this functional is equivalent to imposing the orthonormality constraints against the lower k states, when $q_i \to \infty$. By increasing the shifts q_i any desired accuracy can be obtained, but in order to obtain a computationally efficient algorithm a reasonable finite value should be used, for example

$$q_i = (\lambda_{k+1} - \lambda_i) + \mathrm{Q}, \tag{16}$$

where Q is a sufficiently large positive constant. In our calculations we have used the value $Q = 2$ Ha.

The substitution (12) is introduced in the functional (15) and the minimization with respect to α leads again to a quadratic equation. This time the coefficients contain terms due to the penalty part.

While the penalty functional keeps the states separated on the coarse levels, we apply a simple relaxation method (Gauss-Seidel) on the finest level. The Gauss-Seidel method converges to the nearest eigenvalue, so ideally no additional orthogonalizations would be needed. In practice, however, we use Gram-Schmidt orthogonalizations and subspace rotations. However, the number of fine grid orthogonalizations remains small, for example, in comparison with the conjugate gradient search of eigenpairs employing only the finest grid [26].

4 Technical enhancements

4.1 Double grid technique

Representing functions with high frequency components on coarse grids has problems, sometimes referred to as *aliasing* (the high frequency components, not representable on the coarse grids, are aliased to lower frequency components), if one simply takes the pointwise values of the continuous functions at each grid point. The most direct way to see this in electronic structure calculations is to monitor the calculated total energy of an atom or a molecule as the system is moved with respect to the grid. Figure 6.16 on page 254 of [8] illustrates this *egg-box effect* in the case of CH_4 molecule when calculated with the real-space code `octopus`- the total energy varies with an amplitude of 70 meV when the central atom is moved from one grid point to another (the molecule rigidly following the movement). The first cure suggested to this problem was to simply Fourier filter away the high-frequency components of such a function [49, 27]. This, however, may not be the best solution to the problem.

A much more elegant solution was suggested by Ono and Hirose [67]. This scheme applies most directly to the evaluation of the inner products of the wave-function with the non-local projectors occuring in norm-conserving non-local pseudopotentials or the projector augmented wave (PAW)-method.

A careful and well-documented implementation of the Ono-Hirose scheme was recently made by Mortensen *et al.* in the context of the PAW method [57]. A key factor in this implementation was to use the scheme not only for the projector functions, but as a general recipe to transfer any function defined on a radial atom-centered mesh to the coarse grid where the wave-functions are computed.

In a grid presentation, integrals over space are turned into sums over grid points. In our implementation of the non-local norm-conserving pseudopotentials, we often need to calculate the integral of a localized function, centered on an atom, multiplied by the wavefunction extended over all space. The most obvious example is the projector function $\xi^a_{lm}(\mathbf{r}-\mathbf{R}^a)$ centered on atom a at position $\mathbf{R}^a$ multiplied by an extended wave-function $\psi_{nc}(\mathbf{r})$ defined by its values at the gridpoints of the computational grid (as indicated by the subscript c).

Using G to index the grid points used for the wave functions and transforming the integral to a sum over grid points with V_c being the volume per grid point we get

$$P^a_{lm} = V_c \sum_G \xi^a_{lmG}\psi_{nG} = \langle \xi^a_{lm,c} | \psi_{nc} \rangle \tag{17}$$

where $\psi_{nG} = \psi_n(\mathbf{r}_G)$, and $\mathbf{r}_G$ is the position of grid point G (only grid points in the localized region around atom a need to be summed over). For ξ^a_{lmG} we could use $\xi^a_{lm}(\mathbf{r}_G - \mathbf{R}_a)$. However, this is not accurate enough, unless we use a very fine grid, which would compromise efficiency. Instead we use the elegant double grid technique of Ono and Hirose [67]. Here we interpolate the wave function to a finer grid f, and evaluate the inner product there, using pointwise values of the projector function $\xi^a_{lm,f}$ on the finer grid. It is most convenient in the following discussion to use the prolongator (interpolation) operator I^f_c and its transpose, the restriction operator I^c_f.

$$P^a_{lm} = \langle \xi^a_{lm,f} | I^f_c \psi_{nc} \rangle = \langle I^c_f \xi^a_{lm,f} | \psi_{nc} \rangle. \tag{18}$$

Here the relation $I^f_c = (I^c_f)^T$ (Eq. 14) is used. We see, that the interpolation of the wave function needs not be done in practice. Comparing Eqs. (17) and (18) it is easy to see that

$$\xi^a_{lm,c} = I^c_f \xi^a_{lm,f}, \tag{19}$$

i.e. the projector is first evaluated on the auxiliary fine grid (this needs to be done only once in the beginning of the calculation), and then brought to the coarser grid used to represent the wave-functions by the restriction operator. The fine grid can, e.g. be a uniform grid with five times the density of the computation grid, as suggested in Ref. [67]. However, a more economic choice would be to select special integration points corresponding to a Gaussian quadrature for this finer grid, and properly account for the integration weights.

The projector functions are not the only localized atom-centered functions in our implementation of the pseudopotential method. In addition, we have atom centered Gaussian positive charge distributions, used to neutralize the charge density occuring in (Eq. 8), and associated local potential corrections $\Delta V_{loc} = V_{loc}(r) - Z\mathrm{erf}(r/r_c)/r$. In practice, we have used the same scheme of evaluating these functions on a fine grid and restricting them to the coarse computational grid, and found two orders of magnitude reduction in the egg-box effect, as reported also by Mortensen et al. in the case of the PAW scheme [57].

Note, however, that strictly speaking a nonlocal operator on the coarse grid should replace the local potential of the fine grid:

$$\langle I_c^f \psi_{nc} | (\Delta V_f) I_c^f \psi_{nc} \rangle = \langle \psi_{nc} | I_f^c (\Delta V_f) I_c^f \psi_{nc} \rangle. \tag{20}$$

The sparse matrix $I_f^c(\Delta V_f)I_c^f$ can be constructed in the same way as the Galerkin form H_c in Section 4.5. A similar accuracy – and similar nonlocal operator replacing the local potential – is obtained if the wave-functions are expanded in the nonorthogonal basis of piecewise polynomial functions associated with the grid points (the finite-element method), and the matrix-elements of the potential in this basis are properly evaluated.

In practice, the simple restriction may be justified, besides by the fact that it seems to work well in practice, also by the fact that we evaluate the density directly from the pointwise values of wave-functions on the coarse grid, and the related correction to the total energy satisfies (note that we use the notation $\langle f|g \rangle$ as a shorthand for $\int d\mathbf{r} f^\dagger g$)

$$\langle I_c^f n_c | \Delta V_f \rangle = \langle n_c | I_f^c (\Delta V_f) \rangle. \tag{21}$$

These relations seem to suggest, that in a numerically correct implementation, a local potential (obtained by simple restriction from the auxiliary fine grid in the double grid scheme) should operate on the density *e.g.* in expressions for the total energy, while the nonlocal form $I_f^c V I_c^f$ should be used in the eigenvalue problem when operating on the wave-functions. It could be the case that treating the local potential numerically properly, and also computing the density, exchange-correlation potential and electrostatic potential on a grid finer than that used for the wave functions, would allow the use of even coarser grids for the wave-functions, resulting in substantial memory and cpu savings. After all, plane-wave and grid presentations of the wave-functions should in principle be equivalent. Yet the conclusion made in *e.g.* in Ref. [57] is that an order of magnitude more memory is needed to represent the wave-functions on a real-space grid than by storing the plane-wave coefficients.

A possible improvement to the existing methodology would indeed be to evaluate the density on a finer grid (with grid spacing halved):

$$n_f = \sum_i |I_c^f \psi_{i,c}|^2. \tag{22}$$

The Hartree and exchange-correlation potentials would then be evaluated on this finer grid and returned to the coarse, wave-function grid through either the above described method yielding a short-range non-local potential operator, or by the simple restriction which may be accurate enough in practice (or, as suggested above, both of these operators would be needed for different purposes). Note that the use of Eq. (22) requires also a modification for the normalization condition for the wavefunctions, $(\psi, I_f^c I_c^f \psi) = 1$. This would be analogous to the plane-wave scheme, where the cutoff wave-vector for the density is twice the cutoff wave-vector for the wave-functions. Such a scheme is not yet implemented in `rspace` (or at least not properly tested), and not in any other real-space method either according to the authors knowledge. Note however that in the PAW-scheme by Mortensen *et al.*, such a finer mesh is used for the solution of the

Poisson equation. However, the relation (22) is not used – instead the density is first evaluated on the coarse grid and then interpolated to the fine grid.

Finally, it would be interesting to see, if the idea can be applied also to the kinetic energy stencil T_c (or $A_{\mathrm{mehr,c}}$ and $B_{\mathrm{mehr,c}}$ of section 4.4), by replacing it with $I_f^c T_f I_c^f$. Again this could be done using the same algorithm as explained for the B-stencil in Section 4.5.

We encourage the interested reader to obtain the source code of `rspace` from the web-page [1] (or use his/her own favourite implementation of real-space grid methods) and implement these ideas – there is no guarantee that we will have time to do so in the near future.

4.2 Mixing schemes (traditional)

Reaching self-consistency in the solution of the Kohn-Sham equations (1)-(5) can be a tricky task for systems where the Hartree and exchange-correlation potential dominate over the external potential (e.g. quantum dots described in Section 6), and/or when the system size is large (e.g. thousands of electrons as in the axially symmetric jellium model calculations described in Section 7). Defining the output density n_{out} as the density obtained from Eq. (2), when the orbitals are solved from Eq. (1) in the potential generated through Eqs. (3)-(5) by the input density n_{in}, the simplest stable iteration scheme results by choosing for the input density of the next iteration the linear combination

$$n_{\mathrm{in}}^{\mathrm{next}} = (1-\kappa)n_{\mathrm{in}} + \kappa n_{\mathrm{out}}. \tag{23}$$

Instead of the density n, the potential V_{eff} can equally well be mixed. In large systems, or quantum dots in low confinement, the mixing parameter κ may have to be chosen smaller than one percent. Clearly more sophisticated mixing schemes should be used.

We have recently implemented the standard Pulay mixing scheme [68, 69] and its several variants. An interesting new variant is the guaranteed reduction Pulay (GRPulay) method [70], where no mixing parameter needs to be given. The key idea of the GRPulay method is, that at the first iteration one computes also the residual of the output density. Then, in the two-dimensional space spanned by the input and output densities, the residual is minimized (assuming a linear dependence between input density and the residual), and the input and output densities for the next iteration are predicted, and the new residual of the output density computed.

A preconditioning to the Pulay scheme that damps the long wavelength changes of the density was proposed by Kerker [71][2]. Also the use of a special metric that weights long wavelength errors stronger than short wavelength errors was proposed by Kresse and Furthmüller in Refs [10, 11]. In these schemes, a Fourier decomposition of the density to components of different wavelengths is required. We have used the following multigrid-based method to make this decomposition. Here N denotes the coarsest grid used, so that n_N is the density component of the longest wavelength. $I_1^N = I_1^2 \dots I_{N-1}^N$ is the restriction operator from the finest grid 1 to the coarsest grid N.

$$n_N = I_N^1 I_1^N n \tag{24}$$

---

[2] Note, that the Kerker scheme was originally motivated by a real-space scheme [72, 73, 74], where, instead of the Poisson equation, a modified Helmholz equation is solved. We have implemented this idea as well, and found it very useful in some calculations.

$$n_{k-1} = I^1_{k-1} I^{k-1}_1 (n - \sum_{i=k}^{N} n_i). \tag{25}$$

It can be easily seen that this decomposition satisfies $\sum_{i=1}^{N} n_i = n$, and obviously each component n_i contains features with a wavelength characteristic for level i. Furthermore, it can be checked that the norm of n_N is equal to the number of electrons in the charge distribution n, while the norm of other components is zero.

4.3 Response iteration methods

While the mixing schemes referred to above use mainly mathematical tricks in accelerating the convergence towards self-consistency, Auer and Krotscheck [75, 76, 77] have suggested a "physical" method where the static dielectric function of the nonuniform electron gas is utilized to obtain a rapidly converging algorithm. They define the functional $F[n_{\rm in}](\mathbf{r}) = n_{\rm out}[n_{\rm in}](\mathbf{r}) - n_{\rm in}$ and obtain the following linear integral equation for the density correction $\delta n(\mathbf{r})$ to be added to $n_{\rm in}$:

$$F[n](\mathbf{r}) = \int d^3r' \epsilon(\mathbf{r}, \mathbf{r}'; 0) \delta n(\mathbf{r}'), \tag{26}$$

where

$$\epsilon(\mathbf{r}, \mathbf{r}'; 0) = \delta(\mathbf{r} - \mathbf{r}') - \int d^3\mathbf{r}'' \chi_0(\mathbf{r}, \mathbf{r}''; 0) V_{\rm p-h}(\mathbf{r}, \mathbf{r}') \tag{27}$$

is the static dielectric function of non-uniform electron gas, $\chi_0(\mathbf{r}, \mathbf{r}'; 0)$ is the zero-frequency Lindhard function of the noninteracting system (and can be expressed in terms of the occupied and unoccupied orbitals), and the particle-hole interaction (or hartree-exchange-correlation kernel) is defined as

$$V_{\rm p-h}(\mathbf{r}, \mathbf{r}') = \frac{e^2}{|\mathbf{r} - \mathbf{r}'|} + \frac{\delta V_{\rm xc}(\mathbf{r})}{\delta n(\mathbf{r}')} = K_{\rm hxc}(\mathbf{r}, \mathbf{r}'). \tag{28}$$

In a state-space formulation [76], they obtain the following form for this equation:

$$\begin{aligned} &u(\mathbf{r}) = F[n](\mathbf{r}) - \delta n(\mathbf{r}) = \\ &2 \sum_{p,h} \frac{\phi_p(\mathbf{r})\phi_h(\mathbf{r})}{\varepsilon_p - \varepsilon_h} \int d^3\mathbf{r}' d^3\mathbf{r}'' \phi_p(\mathbf{r}')\phi_h(\mathbf{r}') V_{p-h}(\mathbf{r}', \mathbf{r}'') \delta n(\mathbf{r}'') \equiv \sum_{h,p} u_{p,h} \phi_p(\mathbf{r}) \phi_h(\mathbf{r}), \end{aligned} \tag{29}$$

where the subscript p refers to "particle-states" (unoccupied states) and h refers to "hole-states" (occupied states). In practice, the number of unoccupied states needed for a calculation to converge is often no more than the number of occupied states. Nevertheless, a scheme were only occupied states are required is desirable, and was indeed derived [76] by making the *collective approximation* that the coefficients $u_{p,h}$ are matrix elements of a *local* function $\omega(\mathbf{r})$ i.e.

$$u_{p,h} = \int d^3\mathbf{r} \phi_p(\mathbf{r}) \phi_h(\mathbf{r}) \omega(\mathbf{r}). \tag{30}$$

After some manipulation one arrives at the following equation for $\tilde{\omega}(\mathbf{r}) = \sqrt{n(\mathbf{r})}\omega(\mathbf{r})$:

$$[H_0 + 2S_F * \tilde{V}_{\rm p-h} * S_F] * \tilde{\omega} = 2S_F * \tilde{V}_{\rm p-h} * \frac{\Delta n}{\sqrt{n}}, \tag{31}$$

where

$$H_0(\mathbf{r}) = \frac{1}{2}\left[-\nabla^2 + \frac{\nabla^2\sqrt{n(\mathbf{r})}}{\sqrt{n(\mathbf{r})}}\right], \tag{32}$$

$$\tilde{V}_{\mathrm{p-h}} = \sqrt{n(\mathbf{r})} V_{\mathrm{p-h}} \sqrt{n(\mathbf{r})} \tag{33}$$

and

$$S_F(\mathbf{r}, \mathbf{r}') = \delta(\mathbf{r} - \mathbf{r}') - \frac{1}{\nu} \frac{1}{\sqrt{n(\mathbf{r}) n(\mathbf{r}')}} \sum_{h,h'} \phi_h(\mathbf{r}) \phi_h(\mathbf{r}') \phi'_h(\mathbf{r}) \phi'_h(\mathbf{r}'), \tag{34}$$

where $\nu = 2$ for a spin-restricted calculation, and $\nu = 1$ otherwise. Finally, one obtains the density correction from

$$u(\mathbf{r}) = \sqrt{n(\mathbf{r})} [S_F * \tilde{\omega}](\mathbf{r}). \tag{35}$$

Above $[A * B](\mathbf{r}, \mathbf{r}')$ denotes the ordinary matrix product defined as $\int dr'' A(r, r'') B(r'', r')$, referred to as a *convolution* in Ref. [76]. In collaboration with M. Aichinger, we have implemented the response iteration schemes utilizing both the state-space formulation of the full-response method (Eq. 29) and the collective approximation (Eq. 31) in connection with the `rs2dot` and `cyl2` -programs. To solve the integral equations (29) and (31) we have used either the conjugate gradient or the generalized mimimum residual (GMRES)-method [78]. In the case of very large systems, a more efficient solver, maybe a multigrid scheme, for Eq. (31) could be useful.

4.4 Higher-order compact discretizations

The Mehrstellen discretized Schrödinger equation

$$H_{\mathrm{Mehr}} \psi_i = A_{\mathrm{Mehr}} \psi_i + B_{\mathrm{Mehr}} (V \psi_i) = \varepsilon_i \psi_i \tag{36}$$

was first introduced to electronic structure calculation by Briggs *et al.* [49, 27]. The matrices of this fourth order discretization only have elements corresponding to the nearest and second nearest neighbor grid points in three-dimensional space. This is in contrast to the traditional central finite difference (CDS) fourth order discretization, which is more nonlocal, and involves thirteen points in a starlike type constellation consisting of three orthogonal line segments of five grid points each. Going to higher order, the CDS stencils become more and more nonlocal [25]. It is argued in [49], that the fourth order Mehrstellen discretization has accuracy comparable to the sixth order CDS-stencil. In addition to the Mehrstellen discretization, we have derived and implemented a set of higher order compact, Mehrstellen type stencils for the Schrödinger and Poisson equations [79].

One immediately notes that although $B_{\mathrm{Mehr}}^{-1} H_{\mathrm{Mehr}}$ is Hermitian [27], H_{Mehr} itself is not. In the original implementation of the RQMG-method [5], Hermiticity of H and B is assumed, and this can degrade the performance of the RQMG method when used with Mehrstellen-type stencils. A generalization of the RQMG-method to non-hermitian discretizations is under construction.

4.5 RQMG with Galerkin conditions

As explained in Section 3.1, our original implementation of the RQMG method does not respect the Galerkin conditions of Eq. (14), but replaces the H and B matrices on the coarse levels by a rediscretization of the original problem (discretization coarse grid approximation, DCA). This can in some cases result in a limitation of the coarsest level that can be used during the multigrid V-cycle, and hinder the convergence of the higher, unoccupied levels, that are needed in, e.g., the linear-response calculations based on time-dependent DFT (TDDFT) or the full-response formulation of the response-iteration scheme (See Section 4.3). In practice, convergence for the required number of states can be obtained by selecting a grid dense enough and tuning the coarsest grid size, but in large three-dimensional calculations it is not desirable to have to use dense grids simply because of an improperly implemented numerical scheme.

We have recently implemented also the full Galerkin version of the RQMG method. Note that even for CDS-stencils, for which $B_f = I$ on the fine level, $B_c \neq I$ on the coarse level. We note that multiplying a coordinate vector e_G (which has the value 1 at a single grid point G and 0 in all other points) by a matrix A produces the column vector of A corresponding to the point G. Then, the column of H_c^T (the required row of H_c) corresponding to G is given by

$$H_c^T e_G^c = I_f^c H_f^T I_c^f e_G^c. \tag{37}$$

Here, e_G is first multiplied by I_c^f, and the (well-known) column vector of the prolongator is obtained. The result is multiplied by the transpose of H_f (given in stencil representation on the finest level, and compressed row storage (CRS)-format [80] on coarse levels). Finally multiplication with the restriction operator I_f^c gives the row of the Galerkin H_c. This vector will be nonzero only in the immediate vicinity of G, and thus we have obtained a row of the sparse matrix H_c, to be stored in CRS-format. This scheme is much faster than the more obvious alternative of representing each of the three matrices appearing above in Eq. 37 in CRS format and computing the two matrix products by standard methods. The matrix B_c is obtained in exactly the same way, but since B_f is independent of $\mathbf{r}$, so will B_c also be, and this can be stored in the simple stencil format, and is very fast to compute. The current implementation of this scheme is a bit slower than using the stencil representation, but results in guaranteed convergence even on very coarse grids. More speed may be obtained by using the Galerkin matrices only on the very coarse grids, while keeping the CDA on, e.g., the two finest levels. Also, more convenient formats than CRS could result in additional speed - in fact on each row of the matrix the nonzero elements have the same pattern, so that simple array could be a more convenient strorage format. Note that the kinetic energy operator still allows a simple stencil representation, as does B – it is the potential energy which requires the non-local non-stencil form in the Galerkin formulation.

4.6 Alternative eigenproblem solvers

It would be desirable to implement a few alternative eigenvalue solvers, in addition to RQMG, in connection with MIKA. For example, the approach chosen by Mortensen *et al.*, to follow as accurately as possible the plane-wave scheme of Kresse *et al.* [10, 11], based on the DIIS-method, only replacing the preconditioning operator by a multigrid V-cycle, seems promising. On the other hand, Krylov subspace methods such as Lanczos or block Davidson are well-known efficient schemes, and careful comparisons between them and the RQMG-method would be interesting. A parallel implementation of the generalized Davidson algorithm is used by Chelikowsky *et al.* [62] to treat three-dimensional systems of up to a thousand electrons. Recently, a new preconditioned, Krylov-space technique has been introduced by A. Knyazev [63, 64] - this method is claimed to be more efficient than its precursors. We have made some comparisons, according to which it seems not to be competitive with RQMG, but more work needs to be done before making

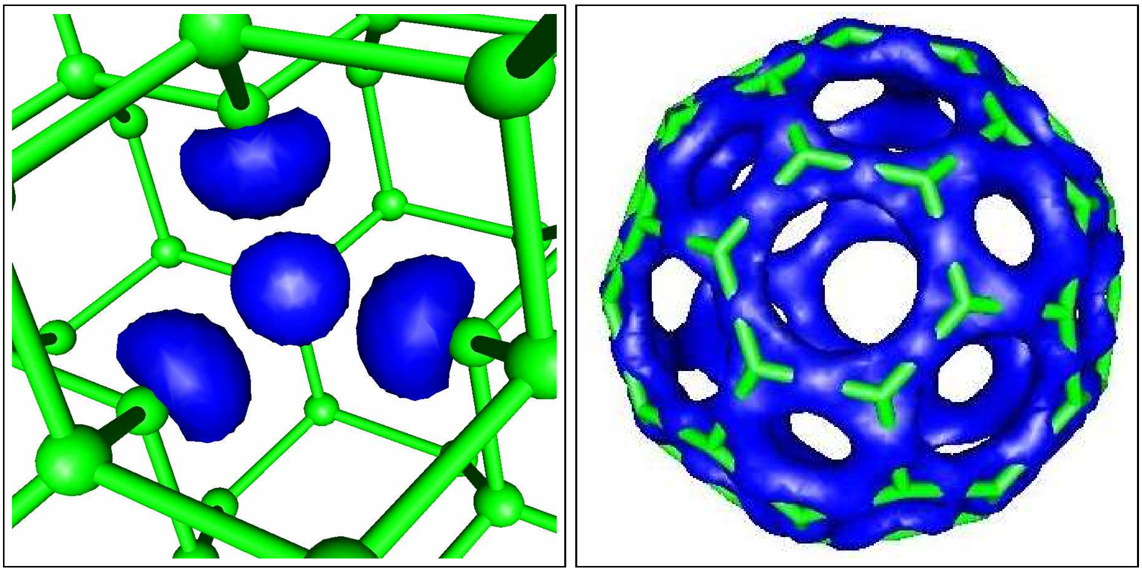

Figure 2: Archtypical applications of electronic structure calculations with periodic and cluster boundary conditions. Left panel: electron density isosurface corresponding to the deep states localized at the neutral, ideal (no ion relaxation) silicon vacancy in Si. Right panel: isosurface of the Kohn-Sham orbital corresponding to the lowest eigenvalue in the C_{60}-molecule.

a definite conclusion. Auer, Krotcheck and Aichinger [81, 77] have developed a surprisingly efficient scheme based on time evolution in imaginary time with fourth order factorization of the operator $\exp(-\epsilon H)$.

5 Status of `MIKA/rspace`

The development of `rspace` has been driven more by individual student projects, Masters projects and technical improvements as described in Section 4 and below than by actual research projects. In principle, nothing prevents the use of the code as it is today in many areas of research. Maybe the most topical field, where real-space grid methods are actively used, is in the applications of the real-time [82] as well as in the linear-response [83] formulations of time-dependent density-functional theory. This field also has a high priority as a future direction in the MIKA-project.

The `rspace` code allows both periodic and cluster boundary conditions. In the cluster case, the boundary values for the Coulomb potential in Eq. (8) are computed by a multipole expansion including terms up to the quadrupole term. In the periodic case, the average potential is set to zero. Boundary conditions for general **k**-points have been implemented. A simple generalization to a combination of cluster boundary conditions in one or two directions and periodic in the other directions would allow computations for surfaces or polymers, respectively, avoiding the periodic images problematic in plane-wave calculations. Even a special boundary condition for long polymers where a unit cell is invariant with respect to a combination of a translation and a rotation about the axis of translation can be implemented in the real-space grid context.

The code has been parallelized through domain decomposition in real-space, and also over the **k**-points. Forces and structural optimization have been implemented - in fact we have two implementations of structural optimization, one written in `Fortran90` and the other in `Python`. The `Fortran90` implementation has been tested by relaxing the structures of various defects in silicon [84], the results being in agreement with plane-wave calculations.

Recently, the Perdew-Burke-Ernzerhof (PBE) [85] generalized gradient approximation (GGA) has been included in this code - it was taken more or less directly from the other open-source real-space package `octopus` [4]. As a sequel to this small project, we will see if the numerical accuracy of this implementation can be improved by following the advice given by Mortensen *et al.* [57], and computing the potential $V_{\mathrm{xc}}(\mathbf{r}_G)$ exactly as the numerical derivative of the discretized E_{xc} (where the gradient of the density is evaluated via finite differences) with respect to the density at the grid point at $\mathbf{r}_G$ - a trick similar to that of White and Bird [86] used in the plane-wave context.

6 Quantum dots in 2DEG

6.1 Introduction and the model

In the rapidly expanding field of nanotechnology, semiconductor quantum dots (QD) represent basic elements of novel nanoelectronic components. They have dimensions from nanometers to a few microns and contain a controlled number of electrons, typically from one to several thousands. Semiconductor QD's are fabricated with several different methods [87]. The common objective between the techniques is to produce a lateral confinement of the two-dimensional electron gas (2DEG) at the interface of a semiconductor heterostructure, e.g. GaAs/AlGaAs, so that the transverse dimensions are considerably larger than the thickness of the dot. Hence, the corresponding model system is usually two-dimensional, and the shape of the lateral confining potential may be varied at will. The most common approximation is a parabolic confinement which has been shown to model the conventionally fabricated QD's with a reasonable accuracy [88]. In this report, however, we review our results for various geometries that have had manifestation in the experiments.

We define the quantum dot to be located on the xy plane and use the effective-mass approximation with the material parameters for GaAs, i.e., the effective mass m^*=0.067 m_e and the dielectric constant $\epsilon = 12.4 - 13$. The many-body Hamiltonian for this system in the presence of an external magnetic field can be written in SI units as

$$H = \frac{1}{2m^*}\sum_{i=1}^{N}\left[-i\hbar\nabla_i + e\mathbf{A}(\mathbf{r}_i)\right]^2 + \sum_{i<j}^{N}\frac{e^2}{4\pi\epsilon_0\epsilon|\mathbf{r}_i - \mathbf{r}_j|} + \sum_{i=1}^{N}\left[V_{\mathrm{ext}}(\mathbf{r}_i) + g^*\mu_B B s_{z,i}\right], \tag{38}$$

where the vector potential is chosen in the symmetric gauge, $\mathbf{A} = \frac{B}{2}(-y, x, 0)$. This determines the magnetic field perpendicular to the dot plane, i.e., $\mathbf{B} = \nabla \times \mathbf{A} = B\hat{z}$. The last term is the Zeeman energy, where g^* is the effective gyromagnetic ratio for GaAs (typically -0.44), μ_B is the Bohr magneton, and $s_z = \pm\frac{1}{2}$ for the electron spin $\sigma = \uparrow, \downarrow$, respectively. The spin-orbit interaction is excluded in the Hamiltonian, since it is supposed to be relatively small in a wide-gap material like GaAs.

6.2 Computational aspects

In the calculations we apply mostly the SDFT in the conventional self-consistent KS formulation. In high magnetic fields we have also employed the computationally more demanding current-spin-density-functional theory (CSDFT), which does not, however, represent a considerable qualitative improvement over the SDFT. A detailed comparison between these two methods for a six-electron quantum dot can be found in Ref. [89].

We have also tested different parametrizations for the exchange-correlation functionals in the LSDA [89]. Quantum Monte Carlo energies for a six-electron QD in zero and finite magnetic fields were taken as benchmark results. According to our calculations, the functional by Attaccalite and co-workers [90] generally gives more accurate results than the form by Tanatar and Ceperley [91]. However, the CSDFT suffers from the lack of accurate interpolation forms between the zero and high-field limits for a given spin polarization.

In our QD program `rs2dot`, the RQMG-method is used for solving the effective single-electron Schrödinger equation on a two-dimensional point grid. In practical calculations, the number of grid points is set between 80 and 128 in one direction. This gives ~ 1 nm for a typical grid spacing, which is sufficient for describing electrons in GaAs, and the discretizations are of the 4th order. The accuracy of the calculations has been checked with the Richardson extrapolation, leading to a typical error of less than $\sim 1\%$ in the total energy ($\lesssim 3\%$ in the low-density limit). A converged solution typically takes $100 \ldots 500$ self-consistency iterations, but that number could be remarkably reduced by using the density-response functions [75, 76, 77] which are currently implemented into the present method.

6.3 Zero-field results

As a symmetry-unrestricted method the real-space approach is suitable for treating QD's defined by a non-circular confining potential. In zero magnetic fields we have studied Wigner crystallization in polygonal systems [92], namely, how the electrons localize into a regular lattice at sufficiently low densities as the dot size is increased. The phenomenon is due to the different scalings of the potential and kinetic parts of the total energy. The former part becomes gradually dominant over the latter as the density decreases, and finally the kinetic energy remains in the zero-point motion of the vibrational modes.

For two-electron polygonal QD's, we find the Wigner-molecule formation as the density parameter $r_s = \sqrt{A/(N\pi)} \approx 3$, where A is the area of the polygonal potential well. This agrees well with the exact diagonalization (ED) results by Creffield *et al.* [93]. The qualitative behavior in the electron density is similar in both DFT and ED, leading to the localization to the corners of the QD as A increases (see Fig. 3). For $N > 2$, we find the formation of extra density peaks along the sides of the QD. In the case of a double number of electrons with respect to the number of corners in the dot, the enlargement of the dot area leads to N density peaks at $r_s \simeq 4.0$ in all polygonal QD's studied. This value is defined as the critical density parameter for the Wigner crystallization in those systems.

In Ref. [94] we have presented a detailed study on the electronic structure of rectangular QD's

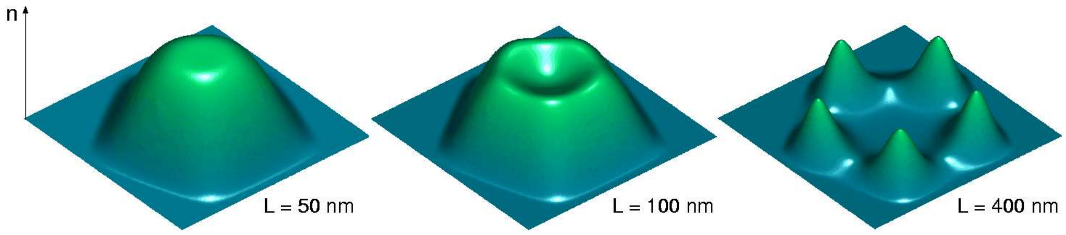

Figure 3: Electron densities for three different sizes of a pentagonal two-electron quantum dot. As the size of the dot increases, the electrons localize in the corners and form a Wigner molecule.

with a hard-wall confinement potential similar to the above presented polygonal system, i.e.,

$$V_{\text{ext}}(x,y) = \begin{cases} 0, & 0 \le x \le \beta L,\, 0 \le y \le L \\ \infty, & \text{elsewhere.} \end{cases} \tag{39}$$

The deformation parameter β thus determines the ratio between the side lengths of the rectangle, and the area of the rectangle is set to $\beta L^2 = \pi^2 {a_B^*}^2 \approx 1000\,\text{nm}^2$.

The chemical potentials and the addition energies are calculated as a function of β with both the SDFT and variational quantum Monte Carlo method. The agreement between the two methods is very precise. In addition, the comparison of our results with the experiments and previous simulations [95] shows that the hard-wall approximation is slightly more realistic than the elliptic one. However, more experimental data over a wider range of β would be needed.

As a result of Hund's rule, we find several partially spin-polarized states with $S = 1$ as β and N are varied. In the SDFT those states are bracketed by spin-density waves where the spin-up and spin-down densities are symmetrically coupled with each other. In Ref. [96], we have proven explicitly, that those states represent a wrong mixing of different spin states. The underlying problem is the fact that the SDFT can not properly describe ensemble–v-representable densities, i.e., systems with more than one major configuration in the ground-state wave function.

6.4 Magnetic fields and the vortex clusters

The solutions in high magnetic fields predict the existence of a completely spin-polarized finite structure called the maximum-density droplet (MDD). The MDD is related to the quantum Hall effect with one completely filled Landau level, i.e., the filling factor $\nu = 1$, and its existence has also been verified experimentally [97]. The MDD state can be found in various QD geometries. In the MDD state of a circular QD, electrons occupy successive angular momentum levels from $l = 0$ to $l = -N + 1$, where N is the number of electrons in the dot. The MDD state is stable for a rather wide range of the magnetic field, but at a certain field strength it reconstructs into a lower-density droplet (see below).

In Ref. [98] we study the MDD formation in non-circular hard-wall QD's defined as above. We identify the MDD window in the calculated chemical potentials $\mu(N)$. In addition, we predict the onset of the MDD from the number of flux quanta N_Φ penetrating through the QD and find a good agreement with the kinks in the chemical potentials (see Fig. 4). Due to the Coulomb interactions, the MDD electron density in a hard-wall dot is pronouncedly localized in

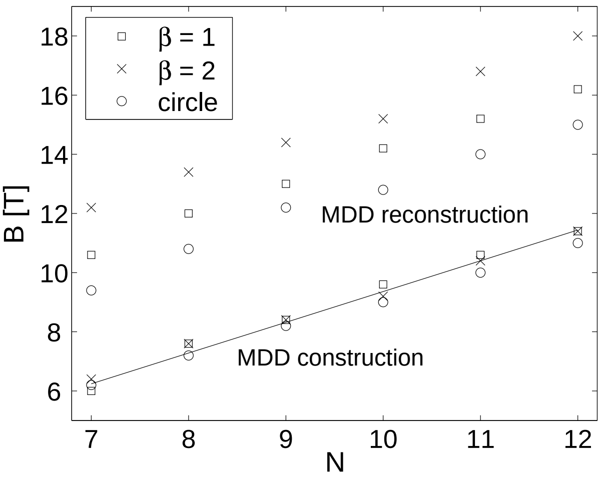

Figure 4: MDD-window limits obtained from the kinks in $\mu(N)$ as a function of N in different QD geometries. The line shows the prediction for the MDD formation, based on the number of flux quanta penetrating the dot.

the corners and on the edges, in contrast with the parabolic case that exhibits a smooth density distribution [99].

When the magnetic field is further increased the MDD-state breaks down to a lower density droplet. The mechanism of this breakdown has been a focus of much theoretical and experimental work. Recently, we have calculated beyond-MDD states of different QD's. SDFT predicts formation of vortex structures, i.e. holes in the charge density associated with rotating currents around them [100]. They can be seen directly in the total electron density obtained by our symmetry-unrestricted approach. However, these symmetry breaking solutions do not give the physical particle density in the laboratory frame of reference (since it must remain rotationally symmetric) but it may reveal electron-electron correlations in the true many-body wave function which is inaccessible in the density-functional approach. Detailed calculations using exact many-body methods lead to similar vortex structures, giving credence to the interpretation of the SDFT results [100].

Using different symmetry-breaking QD geometries it was found that the vortices are stable in high magnetic fields and they correspond to density minima also in the ED results [101]. The vortex formation is a considerable energetic effect and it could be observed in transport experiments similar to those of Oosterkamp *et al.* [97].

Vortex solutions were analyzed further using conditional wave functions in both the ED and the SDFT [102]. The results show that there are two types of vortices: vortices which are on top of an electron and additional vortices which are not bound to a particular electron (see Fig. 5). For the correct particle statistics (Fermion antisymmetry) the number of vortices on top of each electron must be odd. The off-electron vortices were found to give rise to charge minima associated with rotating currents around them. The vortex formation reduce the interaction energy and cause strong correlations between the electrons. Some of the solutions have much in common with the fractional quantum Hall states. For instance, the solution with three vortices near each electron was identified as a finite size precursor of the $\nu = 1/3$ fractional quantum Hall

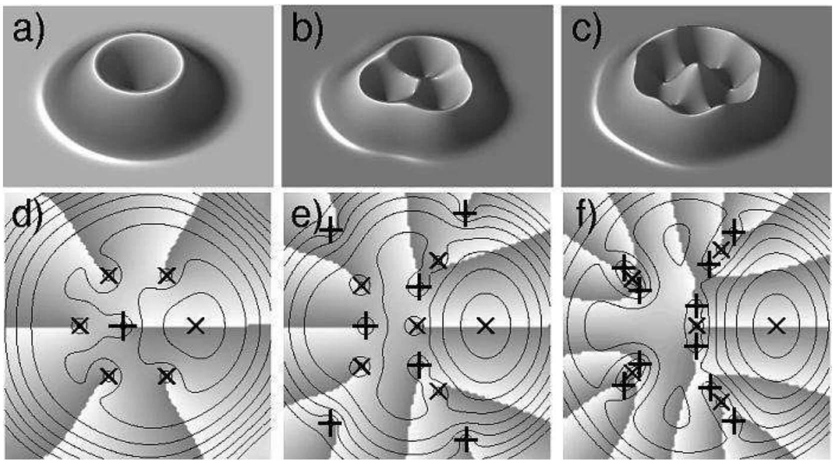

Figure 5: (a-c) Vortex holes in the density-functional electron density of six-electron quantum dots and (d-f) the corresponding conditional wave functions in the exact diagonalization. The fixed electrons are marked with crosses. The shading shows the wave-function phase which changes by 2π in a path around a vortex. There are vortices on top of each electron and additional vortices moving between the electrons (+ signs). The rightmost solution is related to the the $\nu = 1/3$ quantum Hall state with three vortices near each electron.

state [see Fig. 5(c) and (f)]. Moreover, there appear many similarities between vortex formation in bosonic and fermionic case, suggesting that the vortex formation is a universal phenomenon in 2D quantum systems [103].

6.5 Impurities in quantum dots

Theoretical modeling of quantum dots is usually based on the approximation of clean samples, although in real semiconductor devices the effects due to impurities or donor scattering centers may be remarkable. In Ref. [104], a measured transport spectrum of a vertical QD is shown to have clear deviations from the FD energies. We model the system with an external potential consisting of a parabolic confinement and a negatively charged Coulombic impurity placed in the vicinity of the QD. As demonstrated in Fig. 6, the model leads to a good agreement between the calculated single-electron eigenenergies and the experimental spectrum. We also show with the SDFT that in the high magnetic field regime the increasing electron number reduces the distortion induced by the impurity.

7 Nanophysics in axial symmetry

In Refs.[105, 106, 107], we have applied the RQMG-method in various nanostructure studies. We found it convenient in all these projects to use axially symmetric model systems instead of atomistic models. This approximation reduces the computational demands and allows us to study rather large systems encompassing hundreds (Refs. [105, 107]) and even thousands (Ref. [106]) of electrons. In addition, by restricting the geometry to the axial symmetry and resorting to jellium models, many random effects related to the detailed and sometimes unimportant

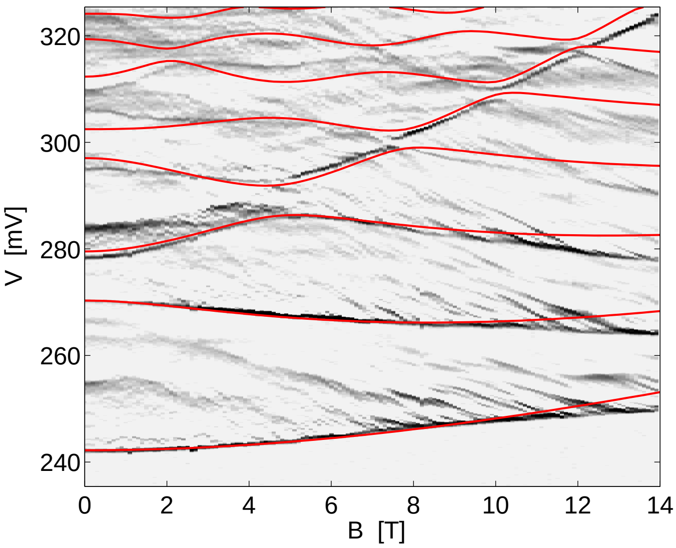

Figure 6: Measured transport spectrum (gray scale) of a GaAs/AlGaAs QD and the calculated single-electron energies (red lines) corresponding to the model potential given in Ref. [98].

atomic structure disappear, and the relevant physics is easier to extract from the simulations. In the axial symmetry, Eq. (1) for the Kohn-Sham orbital

$$\psi_{m\mathbf{k}n}(\mathbf{r}) = e^{im\phi}U_{m\mathbf{k}n}(r,z) \tag{40}$$

can be replaced by the following equation

$$-\frac{1}{2}\left(\frac{1}{r}\frac{\partial}{\partial r} + \frac{\partial^2}{\partial r^2} - \frac{m^2}{r^2} + \frac{\partial^2}{\partial z^2} + 2V_{\text{eff}}\right)U_{m\mathbf{k}n}(r,z) = \varepsilon_{m\mathbf{k}n}U_{m\mathbf{k}n}(r,z). \tag{41}$$

We denote the components of the **k**-vector by k_z and $k_{\|}$. The z-component k_z of the **k**-vector only has relevance in periodic systems, such as the nanowires studied in Ref. [107]. In the periodic case, the following Bloch boundary condition

$$U_{m\mathbf{k}n}(r, z + L_{\text{cell}}) = e^{ik_zL_{\text{cell}}}U_{m\mathbf{k}n}(r,z) \tag{42}$$

is satisfied. The radial component $k_{\|}$ enters in Ref. [106], where we approximate a planar system by a hexagonal lattice of circles. We see that the numerical problem is reduced to a two-dimensional one. Furthermore, the problem is conveniently split into a number of independent subproblems - a property which can be exploited in a massively parallel computer environment. The Kohn-Sham orbitals with different $(m,\mathbf{k})$ (or $(m,\mathbf{k},s)$, should we treat spin-polarized systems) are automatically orthogonal, and can be solved simultaneously.

7.1 Ultimate jellium model for a breaking nanowire

In Ref. [107], we have studied the stability of nanowires and the nanowire breaking process performing self-consistent calculations within the ultimate jellium model. In this model, electrons and positive background charge acquire the optimal density minimizing the total energy. The model enables thus studies of shape-dependent properties of nanoscopic systems such as

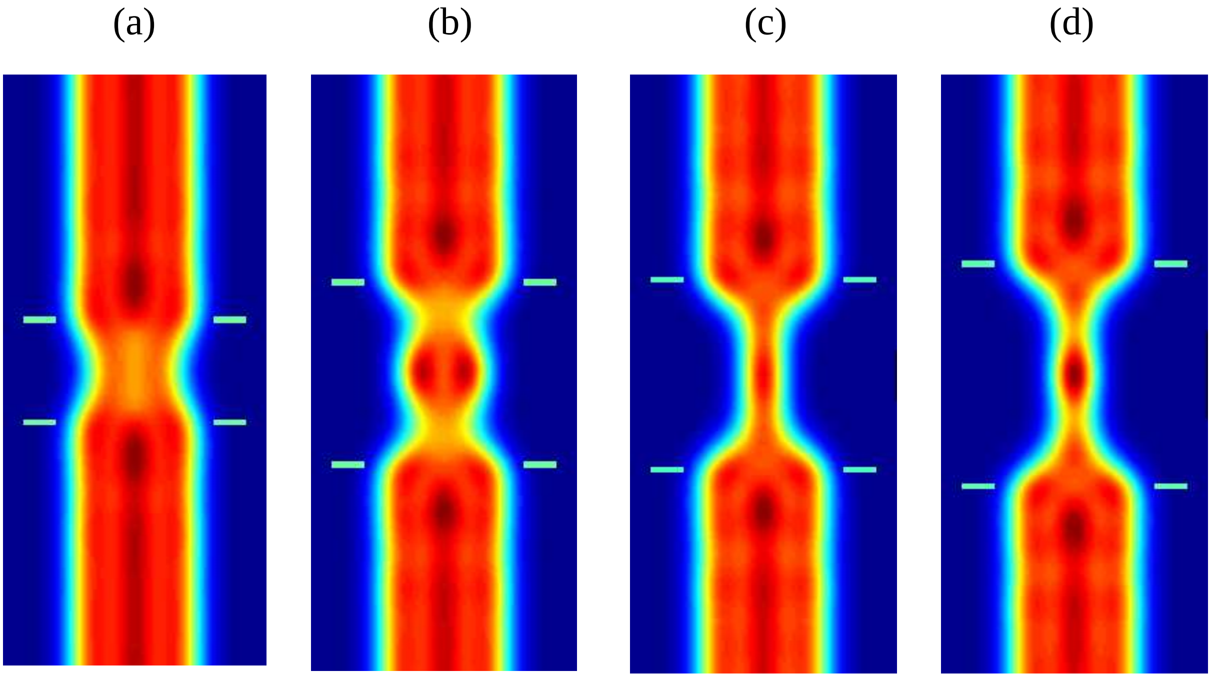

Figure 7: Snapshots from a simulation of nanowire breaking by the ultimate jellium model. A catenoid surface (a), cluster-derived structures (b) and (d), and uniform cylindrical shape (c) can be seen. Green rectangles mark the lead-constriction boundary.

quantum dots or, as in the present work, quantum wires. The model advocates the idea that the electronic structure determines via the shell structure, the geometry and ionic structure also in a partially confined system.

First, we have analyzed the stability of infinite periodic quantum wires pointing out the ability of the electronic band structure to stabilize the nanowires at magic radii, *i.e.* any small deformation of the nanowire along the z axis always increases the energy. At the unstable radii corresponding to maximum values in the energy oscillations, the wire is uniform up to a critical value of the unit cell length. The critical values found are close to $L_{\text{cell}}/R = 4.5$. Above this limit the local energy minimum disappears and a deformation of the wire lowers the total energy. This length is shorter than the classically expected 2π value, thus the wire electronic structure also has a destabilizing effect.

Then we have investigated the elongation process of finite nanowires between two leads. The elongation force, conductance and effective radius of the constriction have been calculated simultaneously. The importance of the charge relaxation in order to obtain results in agreement with experiments has been shown, *e.g.*, in the case of the elongation force. The ability of the ultimate jellium (electron density) to acquire the optimal shape allows the selection of magic radii wires that stabilize the nanocontact, as well as the formation of cluster derived structures (CDS) showing the importance of electron states in the formation of these structures. The related resonance states and their origin was also shown. We have found CDS's that can be linked with the eight- and two-electron free-standing clusters.

In summary, three different types of nanocontact stabilization mechanisms have been found

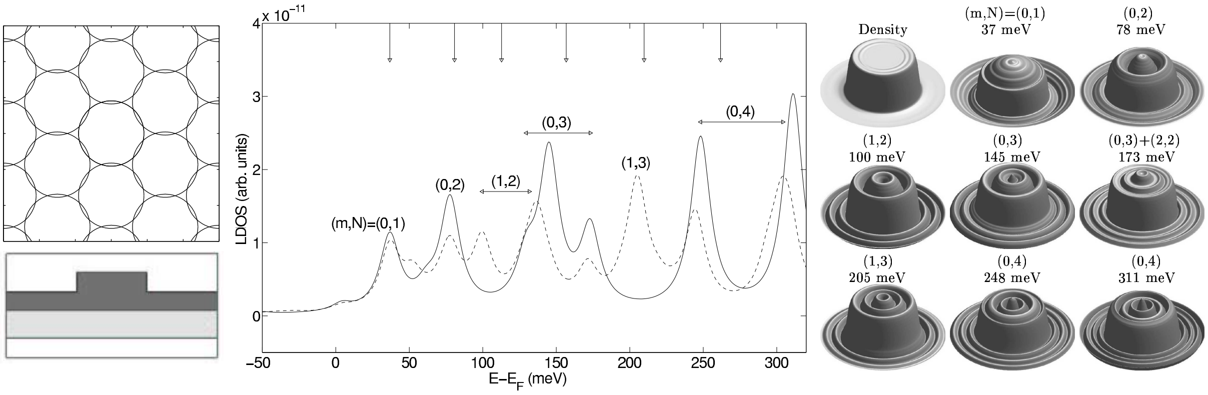

Figure 8: Top left: Hexagonal lattice of area-covering circles. Bottom left: Schematic view of the background charge density in a plane containing the z-axis in our two-density model for a quantum-dot on top of a full monolayer of Na on Cu(111) Middle: Local density of states on top of a cylindrical QD of 550 electrons on two-jellium substrate calculated at a height of 18 a_0 above the jellium edge at the axis (solid line) and at $r = 20a_0$ (dashed line). The (shifted) experimental peak positions are given by vertical arrows pointing downwards. The peaks are identified with (m, N) resonance states having two horizontal node planes in the QD. Right: Calculated isosurfaces of the electron density (upper left corner) and LDOS at the energies corresponding to the dominant peaks of the middle panel.

during the breaking process: catenoid-like shape stabilized by classical *surface tension*, straight magic wires stabilized by the *wire electronic shell structure* and CDS's stabilized by *cluster electronic shell struture.*

7.2 Adsorbed Na quantum dots on Cu(111)

In Ref. [106], we model electronic properties of the second monolayer Na adatom islands (quantum dots) on the Cu(111) surface covered homogeneously by the wetting layer of one monolayer of Na. An axially-symmetric three-dimensional jellium model, taking into account the effects due to the first Na monolayer and the Cu substrate, has been developed. The model enables the study of systems consisting of thousands of Na-atoms.

We have modeled quantum dots as small cylindrical jellium islands, and the underlying Na monolayer and Cu substrate as a two-density jellium slab. The two parameters of the model have been chosen to fit experimental spectroscopic data and calculated first-principles band structures for one and two completed monolayers of Na on the Cu(111) surface.

The calculated results are compared with experimental findings in scanning tunneling microscopy and photoemission experiments. The model gives local densities of states which are in a quantitative agreement with constant current topographs and dI/dV spectra and maps. Thereby the idea of surface states which are localized as resonances at the quantum dots is supported. The future applications of the model will include studies of the adsorption and dissociation of molecules in the vicinity of alkali metal quantum dots.

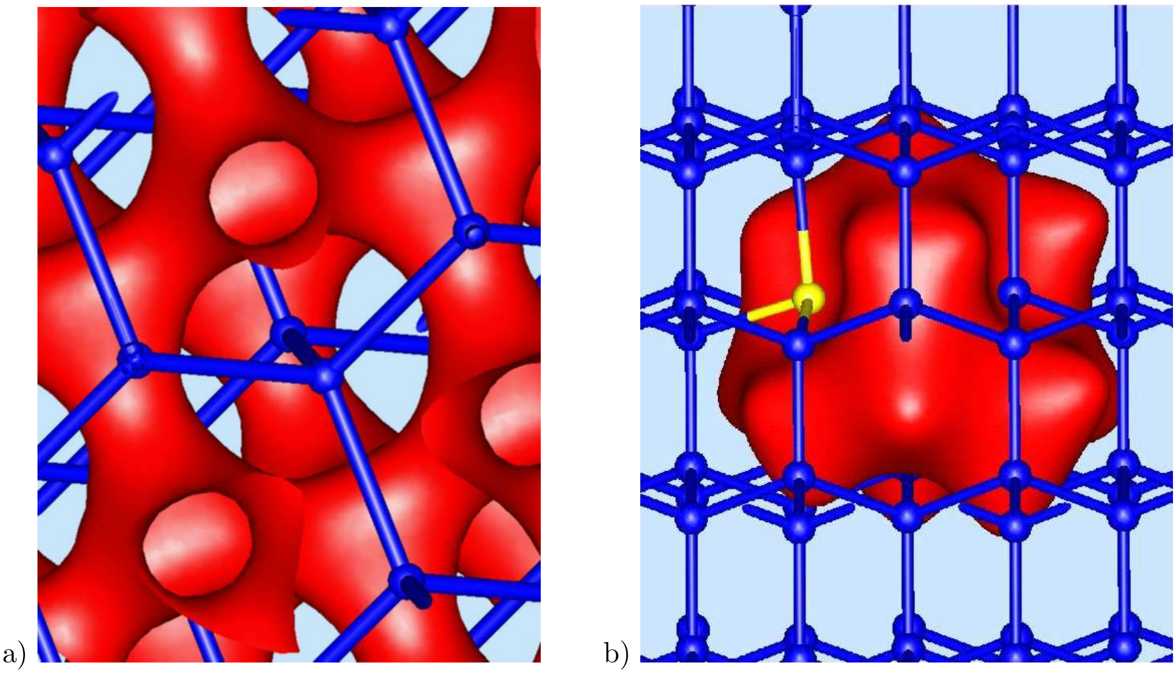

Figure 9: a) An isosurface of the positron wave function in a perfect Si lattice. The positions of the Si atoms are denoted by blue spheres, and the electronic interatomic bonds as blue sticks. The positron lifetime in this state is according to experiments and theory about 220 ps. b) An isosurface of the positron wave function at a vacancy surrounded by one Sb impurity. The Sb atom is denoted by a yellow sphere. The positron lifetime in this state is according to theory about 230 ps.

8 Positron calculations

The use of positron annihilation in defect studies is based on the trapping of positrons from a delocalized bulk state to a localized state at the defect (see Fig. 9). The trapping is due to the reduced nuclear repulsion at the open-volume defects. Because the electronic structure seen by the positron at the defect differs from that in the perfect bulk crystal the annihilation characteristics change. The positron lifetime increases because the average electron density decreases. For the same reason the momentum distribution of annihilating electron-positron pairs becomes more peaked at low momenta (see Fig. 10a). However, the positron density may sample the different atomic species of a compound material with different relative probabilities in the bulk and at a defect. The defect may be surrounded by impurity atoms. In these cases the high-momentum region of the distribution, which is mainly due to annihilations with core electrons, reflects the chemical structure of the defect (see Fig. 10b). The changes in the bond structure between the atoms neighboring the defect may also affect the low-momentum part of the distribution. In order to understand these changes and fully benefit from them in defect identification, theoretical calculations with high predictive power are indispensable.

The description of the electron-positron system can be formulated as a two-component density-functional theory [111]. In the measurements there is only one positron in the solid sample at the time. Therefore the density-functional scheme has to be properly purified from positron self-interaction effects. Comparisons with the two-component and experimental results have shown

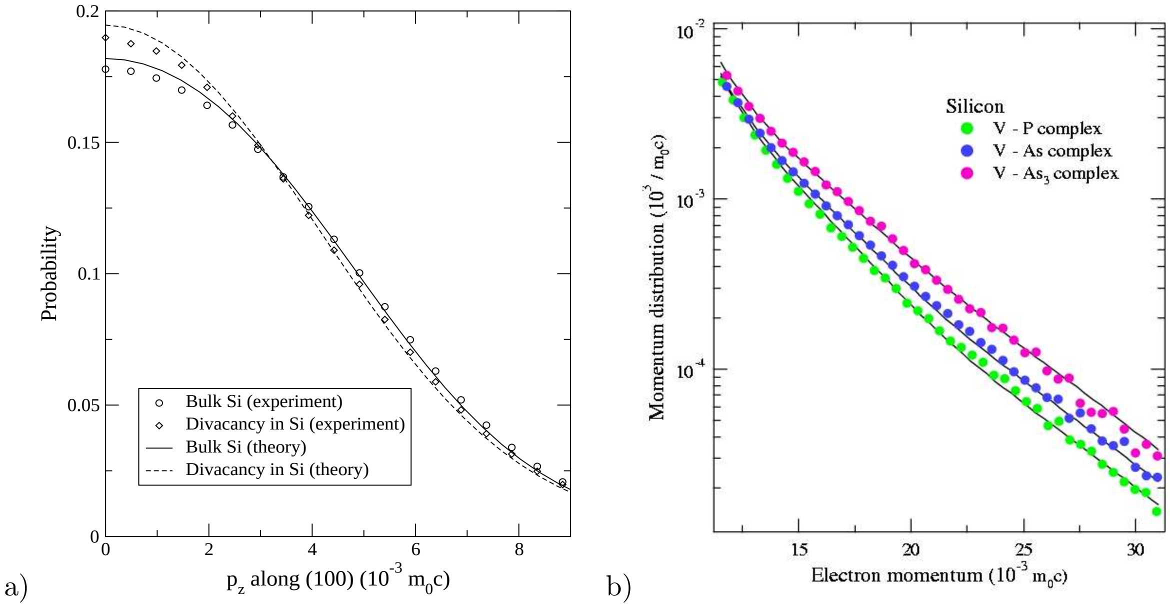

Figure 10: Momentum distributions of annihilating electron-positron pairs in Si. a) Low momentum parts. The theoretical predictions [108] (lines) are compared with the spectra measured by the Doppler broadening technique (markers) [109]. b) High-momentum parts (K. Saarinen *et al.* [110]). The theoretical predictions (solid lines) are compared with the spectra measured by the Doppler broadening techniques (markers). The comparison identifies vacancy-P complexes in electron-irradiated P-doped Si (green circles), vacancy-As complexes in electron-irradiated As-doped Si (blue circles), and vacancy-As_3 complexes in as-grown highly As-doped Si (red circles). The annihilation with As 3d electrons raises the intensity. The study concludes that the saturation of the free electron density in highly As-doped Si is mainly caused by the formation of vacancy-As_3 complexes.

that the following scheme is adequate. First the electron density $n(\mathrm{r})$ of the system is solved without the effect of the positron. This can be done using different (all-electron) electronic structure calculation methods. A surprisingly good approximation for the positron lifetime and core-electron momentum calculations is to simply superimpose free atom charges. Then the potential $V_+(\mathrm{r})$ felt by positron is constructed as a sum of the Coulomb potential $\phi(\mathrm{r})$ and the so-called correlation potential $V_{corr}(\mathrm{r})$ which is treated in a local density approximation, i.e.

$$V_+(\mathbf{r}) = \phi(\mathbf{r}) + V_{corr}(n_-(\mathbf{r})), \tag{43}$$

The ensuing single-particle Schrödinger equation can be solved using similar techniques as the electron states. For example, we use the three-dimensional real-space Schrödinger equation solver of the MIKA package.

When the electron density $n(\mathrm{r})$ and the positron density $n_+(\mathrm{r}) = |\psi^+(\mathrm{r})|^2$ are known the positron annihilation rate is calculated within the LDA as an overlap integral

$$\lambda = \pi r_0^2 c \int \mathrm{d}\mathbf{r}\, n_+(\mathbf{r}) n_-(\mathbf{r}) \gamma(n_-(\mathbf{r})), \tag{44}$$

where r_0 is the classical electron radius, c the speed of light, and γ the enhancement factor taking into account the pile-up of electron density at the positron (a correlation effect). The inverse of the annihilation rate is the positron lifetime.

The momentum distribution of the annihilating electron-positron pairs is calculated as

$$\rho(\mathbf{p}) = \pi r_0^2 c \sum_j \left| \int \mathrm{d}\mathbf{r}\, e^{-\mathrm{i}\mathbf{p}\cdot\mathbf{r}} \psi^+(\mathbf{r}) \psi_j(\mathbf{r}) \sqrt{\gamma(n_-(\mathbf{r}))} \right|^2. \tag{45}$$

Good results, especially for high-momentum part due to the core electrons, are obtained using a state-dependent constant enhancement factor by replacing $\gamma(n_-(\mathbf{r}))$ above with a constant γ_j, which is determined from the annihilation rate of the state j [112]. It is this state-dependent form, which we use in practice.

The `doppler`-program delivered within the MIKA package uses the atomic superposition method. The scheme cannot be used for the low-momentum part due to valence electrons. For that purpose self-consistent all-electron wavefunctions have to be constructed. For example, we have used the projector augmented-wave (PAW) method implemented in the plane-wave code VASP [10, 11, 113, 114].

9 Summary and outlook

We have given an overview of the real-space, multigrid-based program package called `MIKA`, and several examples of its applications in research of quantum dots, nanostructures and positron physics. We hope that the work invested in developing these codes could be useful to a wider group of researchers than our own. Therefore, following the model given e.g. by the `octopus`-project [4], and advocated by the `fsatom` -project [2], we have decided to license the code with the GNU general public license (GPL), and distribute the software on a web-page [1]. This does not mean, that we claim our codes to be easy to use or of commercial quality, neither does it include any promise of user support. On the contrary, we hope that other researchers will take parts of the code, inspect them critically, modify them for their purposes, and distribute the derived product further. Such a distributed mode of development should accelerate the development and adoption of real-space methods in our community.

10 Acknowledgements

We are grateful to J. J. Mortensen, M. Marques, A. Castro and J. Wang for useful discussions on real-space methods, to M. Aichinger and E. Krotscheck for collaboration in the implementation of the response iteration technique to the MIKA-package, and to J. J. Mortensen and M. Aichinger for sharing their manuscripts [57, 77] prior to publication. B. Hellsing and N. Zabala are acknowledged for collaboration in the research reported in Section 7. M. Hakala, A. Harju, V. Lehtola, V. Ranki, S. Riikonen, K. Ritvanen, P. Valminen and T. Hakala are acknowledged for their contibutions to the MIKA-package through individual student projects, Masters projects or other activity. S. F. McCormick, M. Lyly, J. Ruokolainen, T. Eirola, M. Huhtanen and A. Knyazev are acknowledged for discussions on numerical methods. There should be more such discussions between researchers in the (emerging) real-space electronic structure community and specialists in numerical methods. A. Harju deserves a special acknowledgement for providing us results from accurate many-particle methods and also for constructive criticism on density-functional theory in general and the MIKA-package in particular. Special thanks are due to M. Heiskanen for his original development of the multigrid subroutines. Apologies to those people, whose names should have appeared above, but have been accidentally left out.

References

[1] `http://www.csc.fi/physics/mika`.

[2] `http://fsatom.org; http://www.tddft.org/fsatom`.

[3] `http://www.abinit.org`.

[4] `http://www.tddft.org/programs/octopus`.

[5] M. Heiskanen, T. Torsti, M. Puska, and R. Nieminen, Phys. Rev. B **63**, 245106 (2001).

[6] E. Ogando, N. Zabala, E. V. Chulkov, and M. J. Puska, Phys. Rev. B **69**, 153410 (2004).

[7] E. Ogando, N. Zabala, E. V. Chulkov, and M. J. Puska, submitted to Phys. Rev. B (2004).

[8] F. Nogueira, A. Castro, and M. Marques, in *A Primer in Density Functional Theory*, edited by C. Fiolhais, F. Nogueira, and M. Marques (Heidelberg, 2003), 218–256.

[9] M. C. Payne, M. P. Teter, D. C. Allan, T. A. Arias, and J. D. Joannopoulos, Rev. Mod. Phys. **64**, 1045 (1992).

[10] G. Kresse and J. Furthmüller, Phys. Rev. B **54**, 11169 (1996).

[11] G. Kresse and J. Furthmüller, Comp. Mat. Sci. **6**, 15 (1996).

[12] R. Car and M. Parrinello, Phys. Rev. Lett. **55**, 2471 (1985).

[13] R. N. Barnett and U. Landman, Phys. Rev. B **48**, 2081 (1993).

[14] B. Delley, J. Chem. Phys. **113**, 7756 (2000).

[15] G. te Velde, F. Bickelhaupt, E. Baerends, C. F. Guerra, S. van Gisbergen, J. Snijders, and T. Ziegler, J. Comput. Chem. **22**, 931 (2001).

[16] R. Ahlrichs and M. V. Arnim, in *Methods and Techniques in Computational Chemistry: METECC-95*, edited by E. Clementi and G. Corongiu (1995).

[17] High Performance Computational Chemistry Group, NWChem, A Computational Chemistry Package for Parallel Computers, Version 4.1 (2002), Pacific Northwest National Laboratory, Richland, Washington 99352, USA.

[18] J. M. Soler, E. Artacho, J. D. Gale, A. García, J. Junquera, P. Ordejón, and D. Sánchez-Portal, J. Phys. : Condens. Matter **14**, 2745 (2002).

[19] T. L. Beck, Rev. Mod. Phys. **72**, 1041 (2000).

[20] S. R. White, J. W. Wilkins, and M. P. Teter, Phys. Rev. B **39**, 5819 (1989).

[21] J. Pask, B. Klein, C. Fong, and P. Sterne, Phys. Rev. B **135**, 1 (1999).

[22] E. Tsuchida and M. Tsukada, Phys. Rev. B **52**, 5573 (1995).

[23] E. Tsuchida and M. Tsukada, J. Phys. Soc. Jap. **67**, 3844 (1998).

[24] K. Tagami, E. Tsuchida, and M. Tsukada, Surf. Sci. **446**, L108 (2000).

[25] J. R. Chelikowsky, N. Troullier, K. Wu, and Y. Saad, Phys. Rev. B **50**, 11355 (1994).

[26] A. P. Seitsonen, M. J. Puska, and R. M. Nieminen, Phys. Rev. B **51**, 14057 (1995).

[27] E. L. Briggs, D. J. Sullivan, and J. Bernholc, Phys. Rev. B **54**, 14362 (1996).

[28] F. Ancilotto, P. Blandin, and F. Toigo, Phys. Rev. B **59**, 7868 (1999).

[29] Y.-G. Jin, J.-W. Jeong, and K. Chang, Physica B **274**, 1003 (1999).

[30] J. Wang and T. L. Beck, J. Chem. Phys. **112**, 9223 (2000).

[31] U. V. Waghmare, H. Kim, I. J. Park, N. Modine, P. Maragakis, and E. Kaxiras, Comp. Phys. Comm. **137**, 341 (2001).

[32] T. A. Arias, Rev. Mod. Phys. **71**, 267 (1999).

[33] D. Bai and A. Brandt, SIAM J. Sci. Stat. Comput. **8**, 109 (1987).

[34] E. J. Bylaska, S. R. Kohn, S. B. Baden, A. Edelman, R. Kawai, M. E. G. Ong, and J. H. Weare, in *Proceedings of the 7th SIAM Conference on Parallel Processing for Scientific Computing*, edited by D. H. Bailey *et al.* (1995), 219.

[35] J.-L. Fattebert, J. Comput. Phys. **149**, 75 (1999).

[36] F. Gygi and G. Galli, Phys. Rev. B **52**, R2229 (1995).

[37] I. Babuska and Rheinboldt, Int. J. Num. Meth. Engng. **12**, 1579 (1978).

[38] I. Babuska and B. Szabo, Int. J. Num. Meth. Engng. **18**, 323 (1982).

[39] I. Babuska and M. Suri, Comp. Meth. Appl. Mech. Engng. **80**, 5 (1990).

[40] A. Brandt, Math. Comput. **31**, 333 (1977).

[41] A. Brandt, S. F. McCormick, and J. W. Ruge, SIAM J. Sci. Comput. (USA) **4**, 244 (1983).

[42] S. Goedecker, Rev. Mod. Phys. **71**, 1085 (1999).

[43] J.-L. Fattebert and J. Bernholc, Phys. Rev. B **62**, 1713 (2000).

[44] A. D. Becke, J. Chem. Phys **76**, 6037 (1982).

[45] A. D. Becke, Phys. Rev. A **33**, 2786 (1986).

[46] L. Laaksonen, P. Pyykkö, and D. Sundholm, Comp. Phys. Rep. **4**, 313 (1986).

[47] D. Sundholm, Comp. Phys. Comm. **49**, 409 (1988).

[48] J. Kobus, L. Laaksonen, and D. Sundholm, Comp. Phys. Comm. **98**, 346 (1996).

[49] E. L. Briggs, D. J. Sullivan, and J. Bernholc, Phys. Rev. B **52**, R5471 (1995).

[50] W. Hackbush, *Multi-Grid Methods and Applications* (Springer-Verlag, Berlin, 1985).

[51] P. Wesseling, *An Introduction to Multigrid Methods* (John Wiley & Sons, Inc., New York, 1992).

[52] W. L. Briggs, V. E. Henson, and S. F. McCormick, *A Multigrid Tutorial, Second Edition* (SIAM, 2000).

[53] T. L. Beck, K. A. Iyer, and M. P. Merrick, Int. J. Quantum Chem. **61**, 341 (1997).

[54] S. Costiner and S. Ta'asan, Phys. Rev. E **51**, 3704 (1995).

[55] S. Costiner and S. Ta'asan, Phys. Rev. E **52**, 1181 (1995).

[56] J. Wang and K. Marthinsen, Unpublished (2003).

[57] J. J. Mortensen, L. B. Hansen, and K. W. Jacobsen, submitted to Phys. Rev. B (2004).

[58] J. R. Chelikowsky, N. Troullier, and Y. Saad, Phys. Rev. Lett. **72**, 1240 (1994).

[59] X. Jing, N. Troullier, D. Dean, J. R. Chelikowsky, K. Wu, and Y. Saad, Phys. Rev. B **50**, 12234 (1994).

[60] J. R. Chelikowsky, X. Jing, K. Wu, and Y. Saad, Phys. Rev. B **53**, 12071 (1996).

[61] G. H. Golub and C. F. V. Loan, *Matrix Computations* (The Johns Hopkins University Press, London, 1989), second edition.

[62] A. Stathopoulos and S. Ögüt and Y. Saad and J. Chelikowsky and H. Kim, Comput. Sci. Eng. (2000).

[63] A. Knyazev, Siam. J. Sci. Comput. **23**, 517 (2001).

[64] A. Knyazev and K. Neymeyr (2003).

[65] J. Mandel and S. McCormick, J. Comput. Phys. **80**, 442 (1989).

[66] J. L. B. Cooper, Q. Appl. Math. **6**, 179 (1948).

[67] T. Ono and K. Hirose, Phys. Rev. Lett. **82**, 5016 (1999).

[68] P. Pulay, Chem. Phys. Lett. **73**, 393 (1980).

[69] P. Pulay, J. Comp. Chem. **3**, 556 (1982).

[70] D. R. Bowler and M. J. Gillan, Chem. Phys. Lett. **325**, 473 (2000).

[71] G. P. Kerker, Phys. Rev. B **23**, 3082 (1981).

[72] M. Manninen, R. M. Nieminen, P. Hautojärvi, and J. Arponen, Phys. Rev. B **12**, 4012 (1975).

[73] J. Arponen, P. Hautojärvi, R. M. Nieminen, and E. Pajanne, J. Phys. F **3**, 2092 (1973).

[74] R. M. Nieminen, J. Phys. F **7**, 375 (1977).

[75] J. Auer and E. Krotscheck, Comp. Phys. Comm. **118**, 139 (1999).

[76] J. Auer and E. Krotscheck, Comp. Phys. Comm. **151**, 139 (2003).

[77] M. Aichinger and E. Krotscheck, submitted to Comp. Phys. Comm. (2004).

[78] H. A. van der Vorst, *Iterative Krylov Methods for large linear systems* (Cambridge University Press).

[79] T. Torsti. unpublished (1997); M. Heiskanen. unpublished (1998).

[80] J. Dongarra, in *Templates for the solution of Algrebraic Eigenvalue Problems: A Practical Guide*, edited by Z. Bai, J. Demmel, J. Dongarra, A. Ruhe, and H. van der Vorst (Philadelphia, 2000), 372.

[81] J. Auer, E. Krotscheck, and S. A. Chin, J. Chem. Phys. **115**, 6841 (2001).

[82] M. A. L. Marques, A. Castro, G. F. Bertsch, and A. Rubio, Comp. Phys. Comm. **151**, 60 (2003).

[83] J. R. Chelikowsky, L. Kronik, and I. Vasiliev, J. Phys. Cond. Matt. **15**, R1517 (2003).

[84] S. Riikonen, T. Torsti, M. J. Puska, and R. M. Nieminen, unpublished (2002).

[85] J. P. Perdew, K. Burke, and M. Ernzerhof, Phys. Rev. Lett **77**, 3865 (1996).

[86] J. A. White and D. M. Bird, Phys. Rev. B **50**, 4954 (1994).

[87] For an overview, see L. Jacak, P. Hawrylak, and A. Wójs, *Quantum dots* (Springer, Berlin, 1998).

[88] See, e.g., L. P. Kouwenhoven, D. G. Austing, and S. Tarucha, Rep. Prog. Phys. **64**, 701 (2001); S. M. Reimann and M. Manninen, Rev. Mod. Phys. **74**, 1283 (2002).

[89] H. Saarikoski, E. Räsänen, S. Siljamäki, A. Harju, M. J. Puska, and R. M. Nieminen, Phys. Rev. B **67**, 205327 (2003).

[90] C. Attaccalite, S. Moroni, P. Gori-Giorgi, and G. B. Bachelet, Phys. Rev. Lett. **88**, 256601 (2002).

[91] B. Tanatar and D. M. Ceperley, Phys. Rev. B **39**, 5005 (1089).

[92] E. Räsänen, H. Saarikoski, M. J. Puska, and R. M. Nieminen, Phys. Rev. B **67**, 035326 (2003).

[93] C. E. Creffield, W. Häusler, J. H. Jefferson, and S. Sarkar, Phys. Rev. B **59**, 10719 (1999).

[94] E. Räsänen, H. Saarikoski, V. N. Stavrou, A. Harju, M. J. Puska, and R. M. Nieminen, Phys. Rev. B **67**, 235307 (2003).

[95] D. G. Austing, S. Sasaki, S. Tarucha, S. M. Reimann, M. Koskinen, and M. Manninen, Phys. Rev. B **60**, 11514 (1999).

[96] A. Harju, E. Räsänen, H. Saarikoski, M. J. Puska, R. M. Nieminen, and K. Niemelä, Phys. Rev. B **69**, 153101 (2004).

[97] T. H. Oosterkamp, J. W. Janssen, L. P. Kouwenhoven, D. G. Austing, T. Honda, and S. Tarucha, Phys. Rev. Lett. **82**, 2931 (1999).

[98] E. Räsänen, A. Harju, M. J. Puska, and R. M. Nieminen, Phys. Rev. B **69**, 165309 (2004).

[99] S. M. Reimann, M. Koskinen, M. Manninen, and B. R. Mottelson, Phys. Rev. Lett. **83**, 3270 (1999).

[100] H. Saarikoski, A. Harju, M. J. Puska, and R. M. Nieminen, Phys. Rev. Lett. **93**, 116802 (2004).

[101] H. Saarikoski, S. M. Reimann, E. Räsänen, A. Harju, and M. J. Puska, submitted to Phys. Rev. B.

[102] H. Saarikoski, A. Harju, M. J. Puska, and R. M. Nieminen, to appear in Physica E.

[103] M. Toreblad, M. Borgh, M. Koskinen, M. Manninen, and S. M. Reimann, Phys. Rev. Lett. **93**, 090407 (2004).

[104] E. Räsänen, J. Könemann, R. J. Haug, M. J. Puska, and R. M. Nieminen, Phys. Rev. B **70**, 115308 (2004).

[105] P. Havu, T. Torsti, M. J. Puska, and R. M. Nieminen, Phys. Rev. B **66**, 075401 (2002).

[106] T. Torsti, V. Lindberg, M. J. Puska, and B. Hellsing, Phys. Rev. B **66**, 235420 (2002).

[107] E. Ogando, T. Torsti, M. J. Puska, and N. Zabala, Phys. Rev. B **67**, 075417 (2003).

[108] M. Hakala, M. J. Puska, and R. M. Nieminen, Phys. Rev. B **57**, 7621 (1998).

[109] K. Saarinen and V. Ranki, J. Phys.: Condens. Matter **15**, S2791 (2003).

[110] K. Saarinen, J. Nissilä, H. Kauppinen, M. Hakala, M. J. Puska, P. Hautojärvi, and C. Corbel, Phys. Rev. Lett. **82**, 1883 (1999).

[111] E. Boroński and R. M. Nieminen, Phys. Rev. B **34**, 3820 (1986).

[112] M. Alatalo, B. Barbiellini, M. Hakala, H. Kauppinen, T. Korhonen, M. J. Puska, K. Saarinen, P. Hautojärvi, and R. M. Nieminen, Phys. Rev. B **54**, 2397 (1996).

[113] G. Kresse and D. Joubert, Phys. Rev. B **59**, 1758 (1999).

[114] I. Makkonen, M. Hakala, and M. J. Puska, to be published.