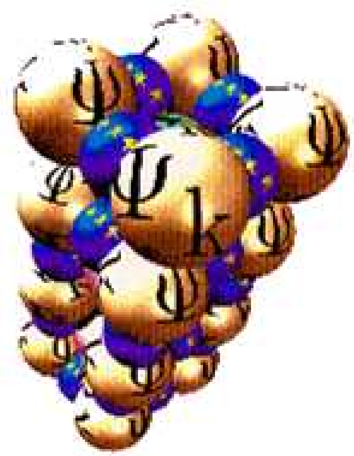
Ψ_k Newsletter

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

Number 73 February 2006



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

Contents

1 Editorial

We start this newsletter with an announcement of a workshop by the RTN on "f-electrons" to take place in April at Canterbury, UK. Further workshop/meeting announcements can be found in the section of the ESF Psi-k Programme and also in the section dedicated to workshops/conferences organized without Psi-k, RTN "f-electron" or CCP9-UK sponsorship. In this newsletter we also have five reports on recent or even quite distant workshops. Position announcements and abstracts of newly submited or recent papers are in their usual sections. This time we also advertise journals or their special issues. The newsletter is finished with the scientific highlight of the month on "Octopus: a tool for the application of time-dependent density functional theory" by Alberto Castro (Berlin and ETSF), Miguel A. L. Marques (Coimbra and ETSF), Heiko Appel (Berlin and ETSF), Micael Oliveira (Coimbra and ETSF), Carlo A. Rozzi (Modena and ETSF), Xavier Andrade (Paris, San Sebastian and ETSF), Florian Lorenzen (Berlin), E. K. U. Gross (Berlin and ETSF), and Angel Rubio (San Sebastian, Berlin and ETSF). Further details can be found in the table of contents.

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

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

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

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

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

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

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2 News from the RTN on "f-electrons"

"Ab-initio Computation of Electronic Properties of f-electron Materials"

2.1 RTN Workshop Announcements

2.1.1 Workshop in Canterbury, UK

The Physics of f-electron Solids

3rd annual workshop of RTN2

April 1-2, 2006, Canterbury, UK

Sponsors: RTN2, CCP9 and University of Kent
The Workshop's web site: **http:/www.kent.ac.uk/physical-sciences/f-electrons**

The workshop will focus on new developments in experiments and theory of f-electron solids. The workshop is organized in the frame of the RTN2 network 'Psi-k: f-electrons' but will be open for anyone interested. Financial support is available for network participants. Registration: by email to P. Strange, see below.

Invited Speakers:

S. Lebegue, Nancy, France.
I. Hughes,* Warwick, UK.
D. Rowlands,* Bristol, UK.
P. Oppeneer,* Uppsala, Sweden.
R. Windiks,* Materials Design s.a.r.l.
O. Eriksson,* Uppsala, Sweden.
M. Katsnelson, Nijmegen, Holland: *Correlation effects in actinide compounds*
W. Temmerman, Daresbury, UK: *Pr tetravalency in PBCO*
G. van der Laan, Daresbury, UK:
Probing the population of the spin-orbit split levels in the actinide 5f states
S. Brown,* ESRF, France
G. Kotliar,* Rutgers, USA
F. Wastin,* Karlsruhe, Germany
H. Eschrig,* Dresden, Germany
P. Strange, Kent, UK: *MXRS for Rare Earths*

* unconfirmed.

The workshop is still open for contributions: send your suggestions to the organisers.

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  `svane@phys.au.dk`

3 News from the ESF Programme

"Towards Atomistic Materials Design"

3.1 Reports on ESF Workshops/Conferences

3.1.1 Report on Workshop *State-of-the-art, developments and perspectives of real-space electronic structure methods in condensed matter and molecular physics*

Lyon

20th to 24th June 2005

Sponsored by CECAM and Psi-K

Eduardo Hernández (ICMAB-CSIC)

Thomas L. Beck (University of Cincinnati)

Emilio Artacho (University of Cambridge)

www.cecam.fr

The original idea of proposing this workshop to CECAM and Psi-K came after considering that CECAM had hosted previous workshops on linear scaling methods and other developments in electronic structure methodology in the past, and time was ripe for for reviewing more recent developments, not only in the field of linear scaling methods, but anything connected to the efficient implementation of electronic structure methodologies, including novel methods of representing electronic states and densities, calculation of transport, efficient schemes for combining molecular dynamics and electronic structure calculations, etc. It is nice to see that several of the participants of this workshop have now stepped forward and decided to organize new workshops on issues that were touched upon during our gathering, such as the PAW method, and electronic transport techniques.

It should also be mentioned that the journal *Physica Status Solidi* has decided to devote a special issue containing articles submitted by participants of the workshop, a sign of the interest that the workshop received. The editing of this special issue is well advanced, and we hope to see it published in the near future.

The workshop was held at the CECAM premises in Lyon, from 20^{th} to 24^{th} June 2005. There were altogether 40 registered participants from 15 countries, and, as was intended, the workshop provided a lively forum for the discussion of recent developments in electronic structure calculations. Aside from the standard format of lectures followed by discussion, we had a discussion session on the last day, chaired by Prof. Mark Tuckerman, in which all attendants were encouraged to participate. Some issues that arose during the discussion session the following issues were addressed:

- It has been recognised since the early nineties that electronic structure calculations can be formulated in different ways, and that these different ways are not necessarily of equal efficiency. Thus there has been an on-going search by the scientific community aimed at finding novel electronic structure methods of optimal efficiency. The focus of this workshop was to bring together scientists from different communities (physics, chemistry, applied mathematics) but with the common denominator of having an interest in such novel methods and techniques for electronic structure calculations. The workshop served the role of a forum for discussing recent developments in the field, and was attended by some 40 participants. Talks at the workshop covered such issues as novel types of basis sets for representing electronic states, including finite elements, Lagrange meshes and discrete variable representations, the use of wavelets in connection with electronic structure calculations, real-space implementations, large-scale methods, embedding techniques, electronic transport, etc.
- One of the observations made during the discussion that took place in the workshop was that there are a multitude of different methods being proposed as alternatives to the standard plane-wave based methodology of condensed matter physics, and it was not yet clear which method(s) would ultimately prevail. While it was argued that such a multiplicity of methods makes progress and method optimisation slow, it was also recognised that this multiplicity of alternative methods is a telling sign of the richness of ideas and activity in the field, and is a strength rather than a weakness. Ultimately, natural selection will play its role in determining which method or methods become standard techniques.
- A number of desirable features that any novel methodology should have were identified. Among these, were: i) ease of implementation, which is strongly linked with efficiency and adaptability for parallel computation; ii) it should have systematic convergence; iii) it should allow for spatial adaptivity; iv) it should have O(N) capabilities, and v) it should be easy to combine with molecular dynamics techniques.
- Other points of discussion that were raised during the workshop were the problems of accessing longer time scales than can be reached with conventional molecular dynamics, and finding ways to achieve more efficient sampling methods in dynamical or Monte Carlo simulations.
- Several talks were given on electronic transport. The real-space or localized basis approach is central to the Green's function method for transport. This work is in a preliminary stage and involves the development of efficient numerical methods, novel theoretical approaches, and careful testing vs. experiment. Real-space methods will continue to figure prominently in these computations.
- A central paradigm of density functional theory is that the ground state properties of an electronic system can be expressed in terms of the electron density alone. But the Kohn-Sham method introduces orbitals in order to obtain more accurate kinetic energies (than

say the Thomas-Fermi and related methods). There has been some research in the last ten years on orbital-free methods, but development of these approaches warrants further investigation. The theory circumvents the need for orthogonalization or related orbital-based operations and involves only one constraint on the total electron number. New difficulties arise due to oscillatory integrands in the kinetic energy expression, however. Real-space methods are well suited for further numerical work in this area.

- One recommendation was formulated during the workshop. It was thought desirable to create a list of benchmarks and test cases that any new method proposed in the literature should be able to address, so that their capabilities in terms of efficiency and accuracy could be gauged. It was suggested that such a list of benchmarks could reside in a dedicated web site, which could also serve as a base for discussion groups and probably also as a software repository. It was also suggested that sites such as that of the FSATOM project or the CSC Finnish IT centre for science could host such a database of benchmarks.
- Another recommendation made during the workshop urged developers to try to write modular codes that can easily be adapted or combined with facilities written by others, in order to facilitate code exchange and thus increase the pace of developments.

Programme

Monday 20^{th} June 2005
Session 1: **Inauguration**

- 10:00 to 11:00 Welcome
- 11:00 to 11:15 Coffe Break
- 11:15 to 12:00 Pablo Ordejón, *A bit of history on previous CECAM workshops*
- 12:00 to 14:30 Lunch Break

Monday 20^{th} June 2005
Session 2: **State of the art and developments**
Chair: Pablo Ordejón

- 14:30 to 15:30 Martin P. Head-Gordon, *Fast methods for density functional theory calculations*
- 15:30 to 16:00 Coffe Break
- 16:00 to 17:00 Jerzy Bernholc, *Multigrid simulations of nanoscale materials and devices*
- 17:00 to 18:00 Mike Gillan, *The problem of achieving linear scaling quantum Monte Carlo*

Tuesday 21^{th} June 2005
Session 1: **Novel types of basis sets I**
Chair: Jerzy Bernholc

- 09:30 to 10:30 Daniel Baye, *The Lagrange-mesh method for quantum mechanical problems*
- 10:30 to 11:00 Coffe Break
- 11:00 to 12:00 Kálmán Varga, *First principles description of electronic and transport properties of nanostructures using Lagrange basis functions*
- 12:00 to 13:00 John E. Pask, *Finite-element method for large scale scale ab initio electronic structure calculations*
- 12:00 to 14:30 Lunch Break

Tuesday 21st June 2005
Session 2: **Real space implementations I**
Chair: Jean-Luc Fattebert

- 14:30 to 15:30 Kazuhiro Yabana, *Real-time, real-space implementation of the time-dependent density functional theory calculations*
- 15:30 to 16:00 Coffe Break
- 16:00 to 17:00 Eckhard Krotscheck, *A fast configuration space method for solving local Kohn-Sham equations*

Wednesday 22nd June 2005
Session 1: **Novel types of basis sets II**
Chair: Mike Gillan

- 09:00 to 10:00 Stefan Goedecker, *Wavelets: General properties and their usefulness as a basis set for electronic structure calculations*
- 10:00 to 10:30 Alexey Neelov, *An efficient numerical quadrature for the calculation of the potential energy of wavefunctions expressed in a Daubechies wavelet basis*
- 10:30 to 11:00 Coffe Break
- 11:00 to 12:00 Mark E. Tuckerman, *Exploiting localized basis sets and unitari invariance to achieve linear scaling ab initio molecular dynamics*
- 12:00 to 12:30 Mark Rayson, *Simple, localised, adaptive, orthonormal real space basis set for electronic structure calculations*
- 12:00 to 14:30 Lunch Break

Tuesday 21st June 2005
Session 2: **Real space implementations II**
Chair: Jose M. Soler

- 14:30 to 15:30 Jens Jorgen Mortensen, *A real-space grid implementation of the Projector Augmented Wave method*

- 15:30 to 14:30 Jean-Luc Fattebert, *Real-space discretization and localized orbitals: a linear scaling practical alternative to Plane-waves for large-scale first principles simulations*
- 16:30 to 17:00 Coffe Break
- 17:00 to 18:00 Rochus Schmid, *Car-Parrinello molecular dynamics using real-space wave functions*
- 18:00 to 19:00 Leeor Kronik, *The finite-difference real-space approach: recent advances and novel applications*

Thursday 23rd June 2005
Session 1: **Progress in O(N) methods**
Chair: Martin P. Head-Gordon

- 09:00 to 10:00 Gabor Csanyi, *Multiscale embedding schemes and electronic locality*
- 10:00 to 11:00 Peter Haynes, *ONETEP outlined: linear-scaling DFT with plane-wave accuracy*
- 11:00 to 11:15 Coffe Break
- 11:15 to 12:15 Chris-Kriton Skylaris, *Algorithms for linear-scaling DFT on parallel computers: the ONETEP code*
- 12:15 to 13:15 David R. Bowler, *Linear scaling DFT calculations from ab initio tight binding to plane-wave accuracy*
- 12:00 to 14:30 Lunch Break

Thursday 23rd June 2005
Session 2: **Electronic transport**
Chair: Stefan Goedecker

- 14:30 to 15:30 Thomas L. Beck, *Real-space multigrid methods for electron transport using the constrained current approach*
- 15:30 to 14:30 Pablo Ordejón, *Electronic transport in nanostructures from first principles*
- 16:30 to 17:00 Coffe Break
- 17:00 to 18:00 Jose M. Soler, *STM/STS simulations with atomic orbitals*
- 18:00 to 19:00 Nicolas Lorente, *Total-energy calculations as the basis of electronic transport calculations: the need of self-consistent electron-vibration couplings*

Friday 24th June 2005
Session 1:
Chair: Mark E. Tuckerman

- 09:00 to 10:00 Xavier Blase, *Strictly-localized basis implementation of TD-DFT and GW approaches: The FIESTA code*
- 10:00 to 11:00 Tuomas Torsti, *Real-space electronic property calculations for nanoscaled structures*
- 11:00 to 11:15 Coffe Break
- 11:15 to 11:45 Miguel Pruneda, *Electronic stopping power from real-time evolution within time-dependent density functional theory*
- 11:45 to 12:45 Discussion
- 12:45 to 13:00 Closing words.

Abstract of presented papers

Wavelets: General properties and their usefulness as a basis set for electronic structure calculations

Stefan Goedecker

An overview will be given over the properties of several wavelet families. They will be examined under the aspect of their usefulness for electronic structure calculations. The advantages and drawbacks of adaptive wavelet schemes will be discussed. Finally some recent wavelet based electronic structure codes will be presented.

A real-space grid implementation of the Projector Augmented Wave method

Jens Jorgen Mortensen

A grid-based real-space implementation of the projector augmented wave (PAW) method of P. E. Blöchl [Phys. Rev. B 50, 17953 (1994)] for density functional theory (DFT) calculations is presented. The use of uniform real-space grids for representing wave functions, densities and potentials allows for flexible boundary conditions, efficient multigrid algorithms for solving Poisson and Kohn-Sham equations, and efficient parallelization using simple real-space domain-decomposition. We use the PAW method to perform all-electron calculations in the frozen core approximation, with smooth valence wave functions that can be represented on relatively coarse grids. The accuracy of the method is demonstrated by comparing atomization energies and cohesive energies calculated for a number of systems with other all-electron methods.

An efficient numerical quadrature for the calculation of the potential energy of wavefunctions expressed in a Daubechies wavelet basis

Alexey Neelov

We propose a numerically efficient quadrature for the approximate calculation of the potential energy when the wave function is smooth and is expanded in Daubechies scaling functions (wavelets). Our quadrature can also be used for the fast calculation of the charge density from the wave function. The quadrature scheme is also applicable with adaptive spatial resolution. We present numerical results of test calculations of the ground state energy and wave function of the harmonic oscillator in one dimension with and without adaptive resolution.

Multigrid Simulations of Nanoscale Materials and Devices

Jerzy (Jerry) Bernholc

We describe the development and applications of multigrid-based methods in large-scale, massively parallel electronic structure calculations. A real-space grid is used as a basis, together with a high-order, compact Mehrstellen discretization for the differential operators. We have also reformulated this approach in terms of variationally-optimized localized orbitals, which reduce the scaling to nearly O(N). The optimized-orbital method has been combined with an efficient Green's function technique for evaluating the quantum conductance in a localized basis, leading to nearly O(N) calculations of quantum transport. Furthermore, we have implemented Berry phases, Wannier function construction and ultrasoft pseudopotentials, enabling calculations for a wide range of systems and properties. Recent applications include nanotube-cluster-based chemical sensors, non-equilibrium electron transport through molecules, computational "design" of novel ferroelectric polymers with 100% im proved properties, investigations of optical properties of surfaces (including GW corrections) and of exciton delocalization in water.

In collaboration with W. Lu, M. Buongiorno Nardelli, J.-L. Fattebert, P. Hahn, V. Meunier, S. Nakhmanson, W. G. Schmidt, and Q. Zhao.

Real-time, real-space implementation of the time-dependent density-functional theory

Kazuhiro Yabana

Time-dependent density-functional theory (TDDFT) is now widely applied to various kinds of many-electronic dynamics. The applications are classified into two categories: one is the linear response calculations which include electronic excitations and linear optical responses of molecules and solids. The other is the initial value calculations for collision phenomena induced, for example, by ions or intense laser fields. We have developed a real-space implementation of the TDDFT and have been applying the method for problems of both categories. In my presentation, I would like to present an overview of our TDDFT calculations, putting emphasis on the methodological aspects. In our real-space implementation, we employ a uniform grid representation in the three-dimensional Cartesian coordinate. A high-order finite-difference scheme is used for the Kohn-Sham Hamiltonian with norm-conserving pseudopotential. In all applications, we first need to solve the static Kohn-Sham problem. We then evolve the wave function in time according to the time-dependent Kohn-Sham equation with an external perturbing potential. For a short time evolution, we employ a Taylor expansion method. The successive applications of the short time evolution provide a stable time evolution for a certain period that is long enough to describe various electronic dynamics. The above-mentioned real-time approach solving explicitly the time evolution is the only approach for initial value problems. The real-time approach is also very useful for linear response calculations. The information on the electronic excitations are included in the time-dependent density, and one can extract physical quantities in frequency domain by a time-frequency Fourier transformation from the density. A visualization of the electron dynamics helps us getting intuitive pictures of the electronic excitations. There are, however, several equivalent implementations of the linear response calculation of the TDDFT. In fact, the TDDFT calculation is usually achieved by solving an eigenvalue equation in the standard quantum chemistry calculations. We have implemented and com-pared three different schemes with the grid representation: a modified Sternheimer method which solves a response equation for an external field with a given frequency, an eigenvalue method which provides accurate excitation energies for several low-lying excitations, and the real-time method which is useful to obtain a spectrum for a whole frequency domain at once. These three implementations provide, of course, equivalent results. The size scaling of the calculation is also the same among three methods, $O(N^2)$, where N represents the system size. One of the advantages of the real-space method compared with others is the natural and flexible imposition of the boundary condition. For electronic dynamics of finite systems, a proper imposition of the boundary condition is a crucial issue to describe response properties above the ionization threshold. I would like to present how we treat the scattering boundary condition in the grid representation. A simple and approximate way is to put an absorbing boundary potential. We demonstrate that accurate description can be feasible for the optical response in the ultraviolet region with a careful choice of the absorbing potential.

Finite-element method for large-scale ab initio electronic-structure calculations

John E. Pask

Over the course of the past two decades, density functional theory (DFT) has proven to be an accurate and reliable basis for the understanding and prediction of a wide variety of materials properties from first principles. However, the solution of the equations of DFT remains a formidable task and this has limited the range of materials problems to which it can be applied. We discuss work on a new finite-element based method for large-scale ab initio electronic-structure calculations, with the goal of extending the range of materials systems that can be investigated by such rigorous, quantum mechanical means. The finite-element method is a general approach for the solution of partial differential and integral equations. Like the traditional planewave method which uses a Fourier basis, the finite-element method is a systematically improvable, variational expansion approach. Unlike the planewave method, however, its basis functions are strictly local in real space; and it is fr om this that the flexibility and scalability of the method derives. We discuss our work on a general finite-element based electronic-structure method, allowing Bloch-periodic, Dirichlet, and Neumann boundary conditions, or any mixture thereof; arbitrary unit cells and Brillouin zone sampling; and the treatment of metallic as well as insulating systems. We present applications of the method to non-self-consistent ab initio positron distribution and lifetime calculations for systems of over 5000 atoms, as well as initial self-consistent band structure and total energy results for metallic systems. This work was performed under the auspices of the U.S. Department of Energy by University of California, Lawrence Livermore National Laboratory under Contract W-7405-Eng-48.

Strictly-localized basis implementation of TD-DFT and GW approaches: the FIESTA code

Xavier Blase

We have developed [1] an novel real-space implementation of time-dependent density functional theory within the linear response theory. The full dielectric or susceptibility matrices are expressed on a strictly localized orbitals basis. Such a localization allows an efficient calculation of all needed matrix elements. As a first application, we study the photoabsorption spectra of small metallic clusters and semiconducting molecules. Our results show that the main absorption features such as the Mie resonance of metallic clusters or the strong $pirightarrowpi^*$ absorption peaks of benzene and fullerenes converge rapidly with respect to basis size and localization. The case of $C_{48}N_{12}$ aza-fullerenes is explored as a first step towards the study of the optical properties of doped fullerenes. Progress towards the implementation of the GW approach within an imaginary-axis treatment of the correlation frequency integral will be presented.

1. X. Blase and P. Ordej?n, Phys. Rev. B 69, 085111 (2004)

Real-space multigrid methods for electron transport using the constrained current approach

Thomas L. Beck

The Green's function method is the primary theoretical approach used so far for large-scale electronic structure predictions of electron steady-state transport. Here we utilize a new perspective on electron transport developed by Kosov in which the steady-state current is imposed as a constraint, and the potential that drives that current must be computed. This leads to a modified Schrodinger equation with a nonlocal imaginary part in the potential. The formulation is analogous to the standard view of statistical mechanics where a heat bath supplies and withdraws energy to maintain a constant temperature. The system wavefunctions decay to zero away from the conducting region, so the standard nonlinear real-space multigrid methods can be employed. We have adapted our multigrid DFT solver to handle the transport problem and have tested the method on the benzene dithiol molecule sandwiched between gold electrodes, which has been studied previously with the Green's function appro ach. Once the DFT potential is obtained for the steady-state system, we solve a fixed potential eigenvalue problem to determine the Green's function and from that obtain the transmission function T(E). The Landauer formula then yields the potential which drives the current.

Total-energy calculations as the basis of electronic transport calculations: the need of self-consistent electron-vibration couplings

Nicolas Lorente

The description of electronic transport in realistic situation needs the inclusion of vibrational effects. These vibrational effects can be of uttermost importance both for the analysis of matter at the atomic level, and for the description of the operating condition of possible molecular electronic devices.

In the present talk, I would present electron-current induced dynamics in condensed matter systems in two different regimes: low-conductance and high-conductance regimes. The low-conductance regime corresponds to inelastic effects induced in tunnelling junctions. The characteristics of the tunnelling current allow for unique control capabilities. Indeed, I will make a brief summary of the achievements and understanding attained in the spectroscopic analysis of vibrations induced on adsorbates on metallic surfaces with a scanning tunnelling microscope (STM) [1]. The ability to excite specific vibrations opens up the possibility to choose atomic dynamics by pumping up energy in specific reaction coordinates. Hence the STM parameters can be chosen to excite preferentially one type of mode with energy above a given dynamical barrier. In this way, the redistribution of energy from the excited mode to the different molecular degrees of freedom permits overcoming this barrier. On th e other hand, repeated excitation of another mode can lead to overcoming a second barrier along a different reaction pathway. I will show recent experimental and theoretical data about mode selective dynamics on ammonia molecules chemisorbed on Cu(100) [2]. The high-conductance regime corresponds to the ballistic regime. In this case the electron current is not a tunnelling current, and the mean free path of electrons is much larger than the typical dimensions of the atomic objects. Recent experimental data have shown that it is possible to excite localized vibrations in monatomic gold chains in this regime [3] akin to vibrational spectroscopy in the tunnelling regime. I will show recent theoretical work [4] that reveals the modes excited by the ballistic current, as well as the difference between the heating of atomic wires and the dynamics induced on molecules by the STM.

These calculations use the ground-state electronic structure of the different condensed matter systems, together with the self-consistent electron-vibration couplings at the Kohn-Sham level. In order to take into account the non-equilibrium conditions leading to electronic currents, many-body Green functions techniques are implemented on the results of the ground-state calculation. The heuristic approach of using the Kohn-Sham electro-vibration structure in transport calculations yields unprecedented accuracy in the description and prediction of the role of vibrations during the electron flow.

1. B.C. Stipe et al., Science 280 (1998) 1732. 2. J.I. Pascual et al., Nature 423 (2003) 525. 3. N. Agraït et al., Phys. Rev. Letters 88 (2002) 216803. 4. T. Frederiksen et al., Phys. Rev. Letters 93 (2004) 256601.

The Lagrange-mesh method for quantum mechanical problems

Daniel Baye

The Lagrange-mesh method is an approximate variational calculation with the simplicity of a mesh calculation because of the use of a consistent Gauss quadrature [1-3]. No analytical evaluation of matrix elements is needed. The accuracy is not significantly reduced with respect to the corresponding variational calculation [3,4]. Lagrange functions can be based on classical or non-classical orthogonal polynomials as well as on Fourier [1,5] and sinc functions [6]. Some singularities can be handled with a regularization technique [2,4,5]. The method can be used for quantum-mechanical bound-state [1-3] and scattering [7-11] problems with local and non-local [12] interactions or with a semi-relativistic kinetic energy [13], and for solving the time-dependent Schr"odinger equation [14,15]. Its application to three-body systems for various choices of coordinates (relative [16], hyperspherical [4], perimetric [17,18]) is discussed. The helium atom [17,19,20] and hydrogen molecular io n [17,19,21] are presented as examples.

1. D. Baye and P.-H. Heenen, J. Phys. A 19 (1986) 2041

2. M. Vincke, L. Malegat and D. Baye, J. Phys. B 26 (1993) 811

3. D. Baye, M. Hesse and M. Vincke, Phys. Rev. E 65 (2002) 026701
4. P. Descouvemont, C. Daniel and D. Baye, Phys. Rev. C 67 (2003) 044309
5. D. Baye, J. Phys. B 28 (1995) 4399
6. D. Baye, in *Innovative Computational Methods in Nuclear Many-body Problems*, Proceedings of the XVII RCNP International Symposium, Osaka, Japan, 1997, edited by H. Horiuchi et al (World Scientific, Singapore, 1998), p. 179
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11. D. Baye, J. Goldbeter and J.-M. Sparenberg, Phys. Rev. A 65 (2002) 052710
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13. C. Semay, D. Baye, M. Hesse and B. Silvestre-Brac, Phys. Rev. E 64 (2001) 016703
14. D. Baye, G. Goldstein and P. Capel, Phys. Lett. A 317 (2003) 337
15. G. Goldstein and D. Baye, Phys. Rev. E 70 (2004) 056703
16. D. Baye, Nucl. Phys. A627 (1997) 305
17. M. Hesse and D. Baye, J. Phys. B 32 (1999) 5605
18. M. Hesse, Phys. Rev. E 65 (2002) 046703
19. M. Hesse and D. Baye, J. Phys. B 34 (2001) 1425
20. M. Hesse and D. Baye, J. Phys. B 37 (2004) 3937
21. M. Hesse and D. Baye, J. Phys. B 36 (2003) 139

Linear Scaling DFT Calculations from Ab Initio Tight Binding to Plane Wave Accuracy

David R. Bowler

The key idea behind linear scaling DFT is that of quantum locality[1,2]; linear scaling tight binding methods have been in widespread use for many years[3], but linear scaling DFT has only started to emerge in recent years. Conquest is a massively parallel implementation of linear scaling DFT which uses a separable form (writing $\rho(\mathbf{r},\mathbf{r}') = \sum_{i\alpha j\beta} \phi_{i\alpha}(\mathbf{r}) K_{i\alpha j\beta} \phi_{j\beta}(\mathbf{r}'))$ to impose locality on the density matrix. We will describe the ideas underlying the code, in particular emphasising how the use of support functions ($\phi_{i\alpha}(\mathbf{r})$) allows us to use different basis sets and flexibly and easily vary the accuracy of the method from empirical tight binding up to full plane wave accuracy. We will report recent results on the implementation of a new basis set, and implementation and testing of forces at all levels of accuracy[4]. We will also report preliminary results on the application of Conquest to the "hut" clusters formed in the Ge/Si(001) system. We have recently applied Conquest to systems of nearly 10,000 atoms on the Earth Simulator.

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2. W. Kohn , Phys. Rev. Lett. 76 3186 (1996)
3. Goedecker, S. Linear scaling electronic structure methods, Rev. Mod. Phys. 71 1085-1123 (1999)
4. T. Miyazaki and D. R. Bowler and R. Choudhury and M. J. Gillan , J. Chem. Phys. 121 6186 (2004)

Electronic Stopping Power from real-time evolution within Time-Dependent Density Functional Theory

Miguel Pruneda

The electronic processes that happen during the scattering of atoms and ions propagating through materials are of considerable interest in basic research and technological applications. Two limits can be distinguished for the stopping of atomic projectiles in matter. For the very low energy limit (low velocities of the particle), collisions with nuclei in the material play the essential role. The limit of high energy ions has been extensively studied since the days of N. Bohr. Less is known about the intermediate region where the ion velocities are below the Bohr velocity. An interesting problem in this field is the electronic stopping power in insulators. Using Time-Dependent Density Functional Theory we calculate the energy loss of a localized charge propagating through materials with constant velocity. The effects of size and localization of the charge, screening of the Coulomb potential, and its velocity have been explored and compared with available experimental data.

Exploiting localized basis sets and unitary invariance to achieve linear scaling in ab initio molecular dynamics

Mark E. Tuckerman

The methodology of ab initio molecular dynamics, wherein finite-temperature dynamical trajectories are generated using forces computed "on the fly" from electronic structure calculations, has benefited significantly from developments in real-space basis sets methods and orbital-localization techniques. The latter exploit the unitary invariance of the total energy to generate orbitals with maximum spatial locality. These orbitals resemble the classic textbook picture of molecular orbitals and, hence, are useful tools for analyzing electronic structure. In addition, maximally localized orbitals, expanded in localized basis sets, are a key component in linear scaling methods. In this talk, the use of discrete-variable representation (DVR) basis set methods will be described as a means of providing a simple, orthonormal real-space basis set scheme. It will be shown how the combination of such basis set methods together with an "on the fly" orbital localization approach leads to a linear-scaling ab initio molecular dynamics method. It will be shown how techniques from quantum field theory can be used to reforumulate ab initio molecular dynamics in such a way that maximally localized orbitals are generated automatically and dynamically as the calculation proceeds. Finally, we will discuss the use of Euler-exponential spline methods as a means of improving the scaling of the non-local component of atomic pseudopotentials.

Multiscale embedding schemes and electronic locality
Gabor Csanyi

In this talk, I will describe recent work on multiscale hybrid molecular dynamics schemes, particularly focusing on covalent materials systems, and on schemes that connect a black-box quantum mechanical engine to an empirical atomistic description. Emphasis will be placed on the interplay between the embedding algorithms and the nature of locality that can be observed in the quantum mechanical models that are employed.

The finite-difference real-space approach: recent advances and novel applications
Leeor Kronik

The finite-difference, real space approach to solving the Kohn-Sham equations using ab initio pseudopotentials, first introduced roughly ten years ago by Chelikowsky, Saad, and co-workers, has now evolved into a mature, versatile, and powerful software suite which we call PARSEC (pseudopotential all-purpose real space electronic-structure code). In this talk, I will overview the basic principles of the approach and describe recent methodological advances - especially the incorporation of exact exchange via an optimized effective potential approach. The strengths and merits of PARSEC will be demonstrated via recent applications to nano-materials, spintronic materials, and organic electronic materials.

ONETEP outlined: linear-scaling DFT with plane-wave accuracy
Peter Haynes

We present an outline of the ONETEP method for linear-scaling calculations within density-functional theory (DFT). In particular we focus on the optimisation of local orbitals called non-orthogonal generalised Wannier functions (NGWFs) in terms of periodic cardinal sine (PSINC) functions. The PSINC basis is orthogonal and equivalent to a plane-wave basis set, and can therefore be improved systematically via a single parameter: the energy cut-off. We compare results from ONETEP with those from the traditional plane-wave DFT code CASTEP and demonstrate excellent agreement for both isolated and periodic systems, including molecules, metal oxide clusters and crystalline semiconductors. A further advantage of the PSINC basis set is that atomic forces may be calculated using the Hellmann-Feynman theorem without the need for Pulay corrections. We demonstrate that smooth potential energy surfaces may be obtained and show the results of geometry optimisations of molecules carried out using ONETEP.

1. C.-K. Skylaris, P. D. Haynes, A. A. Mostofi and M. C. Payne Introducing ONETEP: Linear-scaling density functional simulations on parallel computers, J. Chem. Phys. 122 084119 (2005)

2. C.-K. Skylaris, A. A. Mostofi, P. D. Haynes, O. Dieguez and M. C. Payne Nonorthogonal generalized Wannier function pseudopotential plane-wave method, Phys. Rev. B 66 035119 (2002)

Algorithms for linear-scaling DFT on parallel computers - the ONETEP code

Chris-Kriton Skylaris

We present algorithms for the implementation of the ONETEP method for linear-scaling calculations within density-functional theory (DFT) on parallel computers. We show how the properties of the PSINC basis set make it ideal for imposing localisation in real space and we describe the FFT box technique which allows us to apply localisation also in momentum space. As a consequence, the computing cost of each self-consistency iteration is linear with the number of atoms. In order for the total cost to optimise the energy to be also linear, the number of self-consistency iterations must be small and independent of the number of atoms. The kinetic energy and orbital occupancy preconditioning schemes we have developed make this possible regardless of the sizes of the localisation regions of our non-orthogonal generalised Wannier functions (NGWFs). We are able to perform our calculations on an arbitrary number of processors by using different data-parallelisation strategies for atom -localised quantities such as the NGWFs and delocalised quantities such as the charge density. Data exchange between these quantities is necessary and is achieved with an efficient communication model. Tests on a variety of different materials show that the ONETEP code scales linearly with the number of atoms and with the number of processors. Comparison of ONETEP with the conventional cubic scaling plane-wave DFT code CASTEP on systems of up to a hundred atoms shows excellent agreement. We then proceed to study with ONETEP much larger systems which include segments of metallic and semiconducting carbon nanotubes and biomolecules such as the breast cancer susceptibility proteins.

1. Introducing ONETEP: Linear-scaling density functional simulations on parallel computers, C.-K. Skylaris, P. D. Haynes, A. A. Mostofi and M. C. Payne, J. Chem. Phys. 122, 084119 (2005).

2. Preconditioned iterative minimization for linear-scaling electronic structure calculations, A. A. Mostofi, P. D. Haynes, C.-K. Skylaris and M. C. Payne, J. Chem. Phys. 119, 8842 (2003).

3. Nonorthogonal generalized Wannier function pseudopotential plane-wave method, C.-K. Skylaris, A. A. Mostofi, P. D. Haynes, O. Dieguez and M. C. Payne, Phys. Rev. B 66, 035119 (2002).

Real-space discretization and localized orbitals: a linear scaling practical alternative to Plane-Waves for large-scale First-Principles simulations

Jean-Luc Fattebert

Recent progress in computer hardware are allowing quite large first-principles electronic structure calculations. In this field, the Plane-Waves (PW) approach remains the standard numerical method for highly accurate and unbiased DFT molecular dynamics with pseudopotential. Going towards larger and larger simulations is however problematic in practice because of the $O(N3)$ scaling of this approach. As an alternative we propose to use a real-space discretization — by finite differences — and a localized orbitals representation of the electronic structure. Like in the PW approach, the discretization error can be reduced systematically by decreasing the mesh spacing, while the truncation error — due to orbital localization constraints — decreases exponentially with the size of the localization regions. Forces can be computed accurately within this framework and allow energy conserving molecular dynamics simulations. Localization regions are adapted on the fly to follow the dynamics and achieve optimal accuracy. We illustrate our approach with examples of microcanonical molecular dynamics of liquid water with 512 molecules. Our implementation, using a fourth order Mehrstellen finite difference scheme, shows an excellent O(N) scaling up to this size, as well as an excellent scaling with the number of processors.

1. J.-L. Fattebert and F. Gygi, "Linear scaling first-principles molecular dynamics with controlled accuracy", Comput. Phys. Comm. 162, p.24 (2004).

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

First principles description of electronic and transport properties of nanostrucures using Lagrange basis functions

Kalman Varga

Abstract not provided.

Simple, localised, adaptive, orthonormal, real-space basis set for electronic structure calculations

Mark Rayson

Fully ab initio calculations of systems containing thousands of atoms are becoming routine. Basis sets that generate sparse Hamiltonian offer the possibility to circumvent the orthogonalisation bottleneck and increase coarse grained parallelism in conventional $O(N^3)$ algorithms as well as being an essential ingredient in linear scaling techniques. Here I present a simple, localised, adaptive, real-space basis set that generates extremely sparse Hamiltonians whilst retaining orthonormality. Also, the local potential matrix is diagonal and its evaluation is extremely rapid without the need for explicit integration.

Mosaico: A technique for linear-scaling energy optimization in semiempirical, HF, and DFT calculations

Luis Seijo

A method is presented for the energy minimization step of semiempirical and first-principles Hartree-Fock and DFT calculations on very large molecules or solids, whose computational demands grow linearly with the size of the system. A few monitoring Extended H?ckel and Siesta/DFT calculations are presented that show some potentiallities and limits of the method.

The Mosaico method is based on the on-the-fly variational calculation of the localized orbitals (LMOs) of any localization method of choice; the LMOs are represented with orbital-specific basis sets. This basic strategy makes the method useful only to systems of not a very small gap. The full set of LMOs of a large molecule is seen as an orbital mosaic where each tile or tessera is made of only a few LMOs. The tesserae are computed out of a set of embedded cluster pseudoeigenvalue coupled equations which are solved in a building-block self-consistent fashion. In each iteration, the embedded cluster or embedded tessera equations are solved independently of each other and, as a result, the method is parallel at a high level of the calculation.

In addition to full system calculations, the method enables to perform simpler, much less demanding embedded cluster calculations. In these, one profits from the transferability of the LMOs of a given localization method between similar molecules and variationally computes only a fraction of the LMOs, while the rest are taken from a similar system and frozen.

1. L. Seijo and Z. Barandiaran, J. Chem. Phys. 121, 6698 (2004).

A fast configuration space method for solving local Kohn–Sham equations

Eckhard Krotscheck

We describe algorithmic components of a program package for solving the Kohn–Sham equations in coordinate space. A number of techniques are introduced for solving different aspects of the problem: The eigenvalue problem is solved by using a fourth order factorization of the evolution operator $e^{-epsilonH}$, which is significantly more efficient than the conventional second order factorization. The algorithm can also be applied without loss of efficiency in strong, uniform magnetic fields. The wave functions are orthogonalized using a subspace–orthogonalization procedure generating a noticeably faster convergence than the conventional Gram–Schmidt orthogonalization method. The self consistency problem arising from the nonlinearity of the Kohn–Sham equations is solved with a Newton–Raphson procedure, which is shown to be equivalent to linear response theory. A collective approximation for the static density–density response function, rooted in Feynman's theory of excit ations in quantum fluids, leads to a version of the algorithm that maintains the convergence properties and only needs the computation of occupied states of the system. This approximation makes the implementation of the algorithm in three dimensions practical. Converged solutions are obtained from very rough guesses within a view iterations.

STM/STS simulations with atomic orbitals

Jose M. Soler

Although the variational formalism of Bardeen is in principle a sound, simple, and accurate approach for tunneling, the simulation of STM images and STS spectra from DFT calculations has been burdened by technical difficulties. Since the wavefunctions are very small and energetically irrelevant in the vacuum region, extremely good convergence is required in the DFT selfconsistent solution. Furthermore, typical atomic basis sets are not complete enough in that region. Finally, a separate calculation is generally required for each relative position of the tip and the sample, and for each applied voltage, what makes the simulation of full images and spectra extremely demanding. We have developed an efficient and accurate method to avoid these difficulties [Paz et al, PRL 94, 056103 (2005)]. The wave functions are calculated separatedly for the tip and the sample, and they are propagated across the vacuum gap using the vacuum Green's function. Two Bardeen-like surface integrals a re performed close to the two systems, where the calculated wave functions are large and reliable. The surface integrals are rewritten as three-dimensional integrals in a regular grid, using smoothed delta functions. This allows to express the Bardeen matrix elements in terms of convolutions, and to obtain the tunneling current for all tip positions and bias voltages in a single calculation. The efficiency of the method opens the door to real-time determination of both tip and surface composition and structure, by comparing experiments to simulated images for a variety of precomputed tips. Some applications will be described.

Real-space electronic property calculations for nanoscale structures

Tuomas Torsti

We give an introduction to the real-space, multigrid based program package MIKA (Multigrid Instead of the K-spAce) designed in particular for the electronic structure calculations of low-symmetry nanometer-scale quantum structures. We introduce the idea of multigrid acceleration techniques and present a generalization of the Rayleigh-quotient minimization multigrid method. We describe recent technical improvements of the numerical methods, and give examples of recent applications of the program package in nanoscale systems such as quantum dots and nanowires. We also show results from a related development, where all-electron density-functional calculations are performed using a well established finite-element package called ELMER.

Among the future lines of development in the MIKA-project, the highest priority in carried by the implementation of time-dependent density-functional theory (TDDFT). Two of the original developers of MIKA are now working on their post-doctoral research projects related to TDDFT outside Finland, which is expected to bring further TDDFT experiense back to the MIKA-consortium in the long run.

The MIKA project is now expanding into a national collaboration of four finnish research groups - one group of numerical methods specialists and three condensed matter theory groups. This second phase of the MIKA-project is funded in part by the finnish technology funding agency TEKES, and coordinated by CSC – Scientific Computing Ltd.

Car-Parrinello Molecular Dynamics Using Real Space Wavefunctions

Rochus Schmid

We have shown that energy conserving Car-Parrinello MD, which is known to be efficient for planewave methods, can also be performed within a real-space approach [R. Schmid, J. Comput. Chem. 2004, 25, 799-812]. We currently employ norm-conserving pseudopotentials and use a higher-order finite-difference Laplace-operator to calculate the kinetic energy. The Hartree-potential is determined at each time step by solving the Poisson equation. Newtonian dynamics equations for both electronic and ionic degrees of freedom are integrated by a Verlet propagator in combination with the SHAKE algorithm in order to maintain orthonormality. The corresponding code is fully parallelized. The combination of a high level object oriented scripting language (Python) and a compiled language (C) for the time critical part is found to be very efficient for a rapid code development. In the presentation the current status of the project will be presented. For energy conserving Car-Parrinello MD, the accurate evaluation of the Hartree potential was found to be crucial, which was initially a bottleneck of the method. By the combination of an extrapolation scheme for the Hartree potential, and a multigrid solver, the performance could substantially be improved, solving this problem.

Fast methods for density functional theory calculations

Martin P. Head-Gordon

The problem of computing density functional theory energies efficiently for large systems will be discussed. I will first summarize the status of linear scaling approaches that employ atom-centered basis functions. Such methods are useful for very large systems, but are still not yet routinely used for chemical applications. This is because they are still very expensive for systems that are 3-dimensional in character, particularly when large basis sets are desired and when high precision is required in the solution. In an effort to address this challenge, I will describe two very new developments from my group. The first uses perturbation theory to correct a self-consistent field calculation that is performed in a small basis set. The second is directed 3-d molecular clusters and liquids, and employs orbitals that are absolutely localized to a specific molecules of the cluster or liquid. This localized orbital model appears to yield high accuracy, while at the same time offer ing large speedups over conventional methods.

The problem of achieving linear scaling quantum Monte Carlo

Mike Gillan , D. Alfe

The quantum Monte Carlo (QMC) technique provides one way of overcoming the limitations of density functional theory. For some types of system, it is capable of delivering an accuracy comparable with, and perhaps better than that of high level quantum chemistry techniques, while having a far more favourable scaling with system size. It has recently been shown that some of the linear-scaling techniques developed for tight-binding and density functional versions of electronic structure theory also work within QMC [1,2,3]. In particular, we will explain how the localized-orbital methods and the real-space basis sets developed to achieve plane-wave accuracy in the linear-scaling DFT code CONQUEST [4,5,6] have been implemented within the CASINO code [10] for performing QMC. The talk will also present examples of our recent QMC work on the formation energy of point defects and surfaces in oxide materials [7,8,9].

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Electronic transport in nanostructures from first principles

Pablo Ordejon

An important factor in the development and success of silicon based microelectronics technology was the availability of reliable simulation tools to model the behavior of devices. This is clearly reflected in the fact that modeling is one of the key issues in the International Technology Roadmap Semiconductors. Going towards molecular or nanoscale electronics, the need of modeling and simulation is even greater, due to several factors. First, quantum effects determine the transport properties at this scale, and the need for simulation is therefore increased by the more complex behavior in the quantum world. Second, the structure and chemistry at the atomic level are of paramount importance in determining the properties of devices: at these sizes, the behavior of a device can change dramatically due to very small changes on its atomic structure and/or chemical bonding. Obviously, these effects can only be described properly within a method that takes explicitly into considerat ion the quantum mechanical electronic structure of the devices (including non-equilibrium effects due to the current flow), and that treat the device at the atomic level. The interplay between the two factors (current flow and atomic structure/chemistry) is also of great importance, and must be incorporatedproperly in the simulation tools.

I will describe our efforts to develop a method, TranSIESTA, that allows for first-principles quantum mechanical modeling of molecules and nanoscale systems under non-equilibrium conditions [1] . The method is based on the non-equilibrium Green's function technique, and is implemented into the SIESTA electronic structure package [2], in such a way that the density matrix of the system (and therefore the electronic structure) is calculated selfconsistently when the system is subject to an external bias. Therefore, the method incorporates the effect of the external bias (which maintains the non-equilibrium condition) on the chemistry of the device. I will also describe recent applications of the method to several problems related to transport in nanoscale systems like wires, nanotubos and molecules.

- M. Brandbyge, J. L.- Mozos, P. Ordej?n, J. Taylor and K. Stokbro, Phys. Rev. B, 65, 165401 (2002)
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- http://www.uam.es/siesta

A bit of history on previous CECAM workshops

Pablo Ordejon

This meeting on "State of the art developments and perspectives of real-space electronic structure techniques in condensed matter and molecular physics" is the third of a series of CECAM workshops devoted to methods for electronic structure calculations based on local bases, the previous two having taken place in 1998 and 2001. The first one was entitled "Local orbitals methods for large scale atomistic simulations" [1], and was organized by myself, together with Lu?s Seijo, Giulia Galli and David Pettifor. The second was on the subject of "Local orbitals and linear scaling ab-initio calculations" [2], and was organized by Peter Haynes, David Bowler and Emilio Artacho. Despite the continuity in the general subject of this series of workshops, there is a clear drift in the focus, which of course corresponds to the evolution of the field in the last ten years. In this talk, I will briefly comment on this evolution, and on the main advances that have been made in this field.

- Psi-k Newsletter 29, Oct. 1988, pp 31-86. (http://psi-k.dl.ac.uk/index.html?newsletters)
- Psi-k Newsletter 48, Dec. 2001, pp 36-66. (http://psi-k.dl.ac.uk/index.html?newsletters)

POSTERS

Efficient phase diagram determination from atomistic simulations: Si

Marcin Kaczmarski , Natalia Bedoya, Eduardo Hernandez

The ability to undertake accurate free energy calculations employing realistic models of materials is a key objective in computational materials science, and is required if we are to make reliable predictions of the thermodynamic behaviour of materials (e.g. phase digram), which are difficult to access experimentally. This, however, is a challenging objective, because the free energy depends on the entire ensemble of configurations accessible to the system under the given conditions of temperature and pressure. In recent years there has been significant progress in the development of efficient computational techniques for free energy calculations, which now makes the calculation of phase diagrams viable. In this work we have determined , from atomistic simulations, the phase diagram of silicon in a range of temperatures and pressures spanning four phases including diamond (Si I), beta-Sn (Si II), a clathrate phase (Si C) and liquid silicon (Si L). Our simulations have been p erformed with an accurate Tight Binding model which provides a qualitatively good description of silicon at all conditions considered here. We have use efficient free energy calculation techniques which, combined with a novel strategy for dynamically integrating the Clausius-Clapeyron equation and isothermal-isobaric molecular dynamics simulations, have allowed us to map out the phase boundaries between the phases encountered in this region of the phase diagram, obtaining good agreement with the available experimental data. We expect that in the near future the combination of free energy evaluation techniques employed here with accurate first-principles electronic structure methods will pave the way toward obtaining ab-initio phase diagrams of complex materials.

Conductance in gold monoatomic wires containing carbon and oxygen impurities

Sandra Garcia Gil , E. Machado, M. Bradbyge and P. Ordejon

Different procedures are followed to obtain the samples of gold monoatomic wires in which different kinds of measurements are performed. Conductance measurements (which consistently find values very close to the quantum conductance $G0 = 2e^2/h$) are done in wires obtained in mechanically controllable break junctions. In these samples, the atomic distances are not directly measured, but can be estimated using indirect approaches to be around 2.5 Angstrom, in good agreement with theoretical predictions. On the other hand, direct visualization by TEM is possible in samples obtained by electron beam drilling in thin films, where usually long distances are observed. Several explanations for these long distances have been presented to date, and some of them involve the presence of light impurities such as O or C in the gold chain.

Here were consider the issue whether the presence of these impurities affects the transport properties of the gold wires. Our results show that the conductance changes dramatically in the presence of impurities, which leads to propose that transport measurements could be a way to verify experimentally the presence of impurities in gold wires.

Electronic States of Large Scale Nanosystems: The O(N) interior Eigenvalue problem

Canning Andrew

First-principles materials science calculations typically involve a self-consistent solution of the Kohn-Sham equations. These types of methods typically scale with the cube of the system size and can only be used to study systems of up to a thousand atoms.To study larger systems we use semi-empirical potentials or approximated ab initio potentials such as those constructed using the charge patching method. Using these types of potentials does not require a selfconsistent solution of our effective single particle equations and we can solve directly for the few states of interest around the gap. This leads to a method that is effectively O(N) if we consider the number of states we require to be fixed as the system size increases. The solution of our single particle equations now becomes an interior eigenvalue problem for a few states around a given energy rather than the self-consistent solution for the lowest n states where n is the number of bands.I will compare different me thods (conjugate gradient, Jacobi-Davidson, Lanczos) for this problem with particular emphasis on solving large nanosystems on parallel computers. Work supported by the DOE under the Modeling and Simulation in Nanoscience Initiative.

Electronic transport through Fe/MgO/Fe tunnelling junctions

Ivan Rungger

Among several possible tunnelling junctions Fe(100)/MgO(100)/Fe(100) is particularly attractive because of the formation of atomically sharp interfaces, where the exact position of the atoms is known. Different studies on the linear response transport properties of this junction are available to date [1,2,3]. In this work we calculate the I-V characteristics of Fe/MgO/Fe using our newly developed code Smeagol [4]. Smeagol interfaces the non-equilibrium Green's functions (NEGF) method with density functional theory (DFT) using the numerical implementation contained in SIESTA [5]. Smeagol includes the capability to calculate selfconsistently the current for an applied bias, and it has been specifically designed for magnetic materials. First we evaluate the zero-bias transmission coefficients as a function of the in-plane k-vector for different energies T(E). Around the Fermi level the transmission coefficients for the majority electrons are found to be almost independent from the energy. In contrast those for minority electrons are very sensitive to the exact energy position. Our results are in good agreement with those in [1,2] close to the Fermi level. In order to put our calculation in prospective we have evaluated T(E) for an interface where all the MgO layers have been removed, which corresponds to bulk Fe. It can be seen that the effect of the MgO layers is mainly to reduce the value of the transmission coefficients, whereas the qualitative dependence on the in-plane k-vector is similar.

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3.1.2 Report on CECAM/Psi-k Workshop on Ab-Initio Simulation Methods Beyond Density Functional Theory

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Description

The current efficiency of highly accurate QMC methods and also path integrals MC methods is reaching such a levl that dynamical and thermodynamical calculations of real systems within correlated wave functions/density matrices are becoming feasible and scientifically very attractive. We feel that this meeting could be a very stimulating event for realizing these research opportunities and will expose the frontiers of current developments to the CECAM participants. The aim of the present workshop is to get together a relatively small number of experts (aound 20-25) from the communities which include QMC method developers, with a few experts from quantum chemistry community and possibly from GW community, who have carried out several important methodological developments in recent years. Since there is a number of fundamental scientific questions and technical challenges to address, we are convinced that the time is ripe to exchange the ideas, share the experience and stimulate further developments of this new generation methods. The key issue to be addressed can be summarized as follows:

- Efficiency of MC vs MD in the many-body framework: energy differences vs forces
- QMC/MD with noisy forces/Langevin dynamics
- Large-scale wave function optimizations, "on the fly" optimizations
- Quantum chemical methods vs QMC for cluster, nanostructures and confined systems
- New types many-body wave functions, eficient description of correlation for dynamical simulations

The main goal of the workshop will be to

- Enable exchange of ideas and developments over the last few years
- Define promising lines of research for future developments in this field
- Envision opportunities for applications of these developments to important problems in physics and chemistry

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Presentation List

Coupled Electron-Ion Monte Carlo Study of Hydrogen Fluid

Kris Delaney

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Abstract

We present details of the Coupled Electron-Ion Monte Carlo method (CEIMC) [1,2] applied to the problem of the equation of state of pure hydrogen. The aim is to develop a method that can predict state information outside the range of temperatures and pressures that are accessible with other well-established methods, such as PIMC (T⟩5000K) or ground-state quantum Monte Carlo methods (T=0K).

The CEIMC approach couples a finite-temperature Monte Carlo simulation of atomic nuclei (classical or quantum path integrals) to a zero-temperature quantum Monte Carlo simulation of the electronic subsystem. This segregation is a good approximation at low temperatures, for which thermal excitation of electrons is negligible.

The nuclear configuration space is sampled using Boltzmann statistics. Configurational energy differences are computed within the Born-Oppenheimer (BO) approximation with variational Monte Carlo or reptation quantum Monte Carlo. Both methods supply unbiased but noisy estimates of BO energy differences, requiring a modified Metropolis algorithm to sample nuclear configurations.

Using a guiding electronic wavefunction generated through a fast band-structure calculation, we study the so-called plasma phase transition, the conditions under which a fluid of pure molecular hydrogen dissociates.

References

[1] D. Ceperley, M. Dewing and C. Pierleoni, in "Bridging Time Scales: Molecular Simulations for the Next Decade", eds. P. Nielaba, M. Mareschal and G. Ciccotti, Springer-Verlag, pgs. 473-500 (2002).
[2] C. Pierleoni, D. M. Ceperley and M. Holzmann, Phys. Rev. Lett. 93, 146402 (2004)

Linear scaling electronic structure calculations and accurate statistical mechanics sampling with noisy forces

Krajewski Florian

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Abstract

Statistical sampling of the ionic Boltzman distribution can be based either on empirical force fields or on electronic structure calculations. In the latter case the use of linear scaling algorithms is imperative in order to simulate large systems. We modify a previous stochastic linearly scaling electronic structure algorithm [F. R. Krajewski and M. Parrinello, Phys. Rev. B textbf71, 233105 (2005)] in a manner that is suitable for obtaining statistical mechanics averages over ionic configurations. We show that the noise inherent in our stochastic evaluation of the interatomic forces can be corrected. We demonstrate the accuracy of our method by performing simulations based on the Langevin equation on a tight binding model for Si in the semiconducting and in the liquid metallic phase. Our approach can be adapted to other stochastic schemes for evaluating interatomic forces such as quantum Monte Carlo.

A Test of Reliability and Efficiency of Qmc Forces

Lucas Wagner
North Carolina State University, United States

Abstract

Ab initio molecular dynamics using Density Functional theory has been very successful in the past decade; however, there are still some situations where the commonly used functionals are inaccurate. Intermolecular forces and transition metal oxides, especially, are well-known examples of such inacurracies. Quantum Monte Carlo, with its many-body treatment of electron correlation, is expected to correct a major part of these deficiencies and with its scaling similar to DFT, large simulations are possible. A major stumbling block has been the calculation of forces that are both correct and efficient within QMC. Over the past years, there have been several attempts to obtain such forces, and for small(few-atom) systems, but no systematic comparison of their efficiency, accuracy, and scaling. We show data on a set of representative systems, comparing some of the proposed approaches [1-3]. All these approaches are done within reptation Monte Carlo algorithm, which allows for unbiased estimators even for systems containing transition metals.

References

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Lattice Regularized Diffusion Monte Carlo Simulations of iron dimer

Michele Casula
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Abstract

The transition metal compounds play a crucial role in various fields, ranging from biomolecular reactions to magnetic solid state properties. On the other hand, they are extremely challenging due to the strong dynamic correlation present in the unfilled d-shell, which makes the predictions of the density functional theory completely unreliable and requires the use of more accurate post-Hartree-Fock methods, limited however to small systems. The Lattice Regularized Diffusion Monte Carlo (LRDMC) method, recently introduced [M. Casula, C. Filippi, and S. Sorella, Phys. Rev. Lett. 95, 100201 (2005)], seems to be an effective alternative, since it can provide very accurate results with a favorable size scaling. One of the main advantages of this framework is the possibility to include non-local potentials in a consistent variational scheme, substantially improving both the accuracy and the computational stability upon previous non-variational diffusion Monte Carlo approaches. Here, we apply the LRDMC framework to the iron dimer. Despite its simplicity, its neutral and anionic ground states are controversial, and we try to clarify their symmetry by comparing our LRDMC results with experimental data. We use a fully optimized Jastrow geminal wave function and we carry out LRDMC simulations to study the bond length, the binding energy and the zero point motion of the lowest energy states.

The Surface Energy of the Electron Gas

Matthew Foulkes
Imperial College London, United Kingdom

Abstract

A few years ago, in a paper in Phys. Rev. B, Yan, Perdew and co-workers wrote: ”For the surface energy of jellium at alkali-metal densities, the local-density approximation (LDA) and more advanced density-functional methods disagree strongly with the wave-function-based Fermi hypernetted-chain and diffusion Monte Carlo methods.” More recently, Sottile and Ballone extrapolated the results of their DMC simulations of jellium spheres to obtain a surface energy in agreement with density-functional theory but not with earlier DMC simulations of flat surfaces. This talk describes our investigation of the causes of these disagreements and explains why QMC calculations of surface energies are so difficult. We discuss the treatment of finite-size errors; report some unexpected problems faced during the construction and optimisation of trial wavefunctions; and explain the importance of aiding error cancellation by comparing like with like. Many of these issues are generic and will be encountered more and more often as the use of QMC methods spreads. Reassuringly, if somewhat disappointingly, our final results (variational MC only so far) agree with density-functional theory and with the DMC results of Sottile and Ballone.

Kink-based path integral studies of atoms and molecules

Randall Hall
Louisiana State University, United States

Abstract

A kink-based path integral approach has been developed for use in simulating molecular systems at finite temperatures. The goal of the approach is to alleviate the infamous “sign” problem that occurs in fermionic path integral calculations as well as offering a simulation technique that can simultaneously treat electronic and geometric degrees of freedom. The method uses Gaussian basis functions and results MP2-level accuracy in initial calculations on small molecules. Developments in the method to treat relatively weak interactions such as hydrogen bonding are

the subject of current work. The method will be described and results from test calculations will be presented.

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Ab Initio Molecular Dynamics Beyond the Born-Oppenheimer Approximation

Todd Martinez
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Abstract

The ab initio multiple spawning (AIMS) method has been developed for fist principles molecular dynamics including quantum effects such as tunneling and population transfer between electronic states (breakdown of the Born-Oppenheimer approximation). We discuss recent developments and benchmarks in the multiple spawning dynamics method which underlies AIMS. We show that accurate results can be obtained in models with hundreds of dimensions, even when the underlying electronic basis is not the "natural" adiabatic representation. We provide an overview of recent applications ranging from photoinduced cis-trans isomerization to excited state intramolecular proton transfer (ESIPT) and photodynamics of DNA bases. The role of simultaneous degeneracies of three electronic states in ESIPT is discussed. Extensions of AIMS to condensed phase systems have been pursued using a combination of reparameterized multireference semiempirical (RPMRSE) methods and hybrid quantum mechanical/molecular mechanical (QM/MM) representations of potential energy surfaces. We show that the RPMRSE methods can approach the accuracy of multi-reference perturbation theories such as CASPT2 with limited reparameterization effort. Several representative examples of nonadiabatic dynamics in solution and protein environments using this "nearly" AIMS method are presented and the influence of the solvent/protein environment on excited state reactivity is assessed.

Coupled Electron-Ion Monte Carlo Simulations of Dense Hydrogen

David Ceperley
University of illinois at Urbana Champain, United States

Abstract

Quantum Monte Carlo (QMC) methods are the most accurate and general methods for computing total electronic energies, however, they have been limited to temperatures greater than

5000K, or to zero temperature. In recent years, we and others have been working on methods that utilize the Born Oppenheimer approximation to allow simulations coupling the correlated quantum systems and a system of ions. Such an algorithm could allow the sort of progress which occurred when Car and Parrinello coupled local density functional theory with molecular dynamics of ions.

Using quantum Monte Carlo, one estimates the Born-Oppenheimer energy change which is then used in a Metropolis simulation of the ionic degrees of freedom. We modify the usual Metropolis acceptance probability to eliminate the bias caused by noise in this energy difference, allowing more noisy estimates of the energy difference and reducing the sampling time of the electronic degrees of freedom. We have implemented a method for estimating the energy change with correlated sampling technique so that the variance of the difference is smaller than of each energy individually using either variational MC or reptation MC. We have performed simulations of liquid H2 and liquid metallic H down to temperatures as low as 300K. We discuss some possible advantages of the CEIMC method relative to Car-Parrinello simulations concerning how the quantum effects of the ionic degrees of freedom can be included and how the boundary conditions on the phase of the wavefunction can be integrated over.

Towards more accurate variational wavefunctions for strongly correlated systems

Sandro Sorella
SISSA, Italy

Abstract

I will briefly discuss recent progress in describing electron correlation by means of variational wave functions, that can be simulated by the statistical method-the Variational Quantum Monte Carlo- (VMC), in an affordable computational time. I will discuss recent successful applications of so called antysimmetried geminal functions (AGP), to transition metal oxides and Hydrogen under strong pressure. These applications have been made possible thanks also to a recent advance in the energy optimization techniques. that allows to deal with many variational parameters within the VMC. Within this scheme a large part of the correlation energy can be taken into account by appropriate 2-body and 3-body Jastrow factors. I will also discuss that, based on an analogy with the Hubbard model, these type of geminal wave functions should be suitable of further improvements not only by introducing triplet correlations in the geminal (by the so called Pfaffian introduced recently, K. Schmidt, L. Mitas) but especially by adding to these wave functions the so called backflaw correlations, introduced by Feynmann long time ago for the Helium.

Noncovalent interactions: diffusion Monte Carlo study of biomolecular model systems

Martin Fuchs
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Abstract

Density-functional theory (DFT) calculations are a powerful tool for studying biomolecules. Hydrogen bonding is a key aspect in such systems where, moreover, also Van der Waals dispersion forces may play an important role. For these "non-covalent" interactions the accuracy of standard functionals like generalized gradient approximations (GGA) can be rather uncertain. Benchmarking DFT is thus essential. Accurate total energies of molecules or solids can be obtained by diffusion Monte Carlo (DMC) calculations. DMC remains computationally feasible even in larger systems where conventional correlated methods like coupled cluster will become impractical. While already applied with success to chemically bonded systems, little is known about how DMC performs for non-covalent bonds.

Here we apply DMC to biomolecular model systems that showcase the performance of present-day DFT [1]: formamide-water, tautomerizing via proton transfer; formamide chains, displaying cooperative strengthening of hydrogen bonds; (methyl-) formamide dimers, where GGAs may miss dispersion interactions dependent on the hydrogen bond geometry. For all these systems our DMC hydrogen bond strengths agree well with post-Hartree-Fock data. In addition we calculate adenine-thymine, a DNA base pair where hydrogen bonding and stacking interactions compete. GGAs and hybrid functionals are adequate for the hydrogen bonded conformers, but fail to bind the stacked pair. Second order perturbation theory (MP2) markedly overestimates the stacking energy compared to coupled cluster [CCSD(T)]. Our DMC results confirm those from CCSD(T) studies [2].

Work done with Claudia Filippi (Instituut Lorentz, Univ. Leiden, The Netherlands), Joel Ireta, and Matthias Scheffler (Fritz-Haber-Institut der MPG, Berlin, Germany).

References

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Recent developments and applications of quantum Monte Carlo techniques

Dario Alfe
University College London, United Kingdom

Abstract

I will discuss some recent development of 'linear scaling' quantum Monte Carlo (QMC) techniques based on non-orthogonal localised orbitals. I will then present some recent application of QMC, with results obtained for the structural properties, Schottky formation energy, and surface energy of the (001) surface in MgO. The results are in good agreement with the available experimental data.

Structure of fermion nodes and pfaffian wavefunctions with singlet and triplet pairs

Lubos Mitas

Department of Physics, North Carolina State University, United States

Abstract

I will talk about our effort to understand nodes of fermionic wavefunctions, in particular, about the structure of nodes and number of nodal cells for ground and excited state wavefunctions. We have also explored some of the possibilities offered by the functional forms which go beyond the Slater determinants such as singlet pairing determinats and also combination of singlet and triplet pairs in the form of a pfaffian. We find improvements in the nodal structure and consistently more systematic results for the amount of recovered correlation energy in atoms and small molecules.

The Fermion Monte Carlo: a method to alleviate the Sign Problem

Roland Assaraf

CNRS, France

Abstract

We present the results of mathematical study on the Fermion Monte Carlo algorithm, a stochastic method introduced by M. H. Kalos and coworkers to handle Fermionic systems. The role of the different ingredients of the method is discussed. It is shown that the Fermion Monte Carlo algorithm alleviates the unstability of Quantum Monte Carlo simulations by performing a mapping to a problem with a reduced fermion-bose gap. However a full stability is in general not achieved. The full stability observed when a third ingredient is included [M. H. Kalos and F. Pederiva, Phys. Rev. Lett. **85** , 3547 (2000)], namely using non symmetric guiding functions, is the counterpart of a slowly converging population control error.

References

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Hartree-Fock Revisited

Bernard Bernu

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Abstract

One-body solutions are often needed as input of various sophisticated methods. Hartree-Fock framework is (supposed to be) well understood. But the solutions of Hartree-Fock equations converge with difficulty. We discuss the convergence problems of this equation and present a new scheme which allow us to find rapidly solutions at all densities for the homogeneous electron

gas in two dimensions. The method does not need any assumption about the symmetries of the ground states.

Some combinatorial ideas for path resummations, and their application to Fermion QMC

Ali Alavi
Cambridge, United Kingdom

Abstract

By re-summing the path integral formula for the partition function, we devise a method for fermion QMC based on sampling "graphs". The sign-problem for smapling graphs is greatly improved. We show how the method works for a dissociating N$_2$ molecule.

Properties of Dense Helium at Giant Planet Interiors

Burkhard Militzer
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Abstract

The properties of hydrogen-helium mixtures at high pressure are crucial to address important questions about the interior of giant planets e.g. whether Jupiter has a rocky core and whether it was formed by core accretion. Understanding dense, fluid hydrogen and helium is also of interest for the characterization of the more than 100 extrasolar giant planets that have be detected in recent years by radio velocity measurements. Using first principles simulations, we study the properties of hydrogen-helium mixtures as a function of pressure, temperature and composition[1]. In this presentation, we focus on the equation of state calculation [2,3] of pure helium and the comparison with shock wave experiments. Shock wave measurements are the only laboratory technique available today to directly probe the conditions present in the interior of giant planets. Our calculations demonstrate that the shock properties of helium differ substantially from those of hydrogen. We make suggestions for new shock experiments of helium in order to validate the hydrogen experiments and to understand processes giant planet interiors.

Our calculations will also become relevant for the interpretation of the gravitational moments that will be measured by the Jupiter orbiter mission Juno to be launched under NASA's New Frontiers program.

References

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Quantum Monte Carlo method using Gaussian basis sets

Shiwei Zhang
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Abstract

We discuss some recent developments in an auxiliary-field Monte Carlo method for quantum chemistry type of calculations, using Gaussian basis sets. The method is based on the phaseless Slater determinant random walk approach that we have been working on in the past few years. It takes the form of an ensemble of independent-particle calculations in auxiliary fields. Each random walker is an independent-particle wave function, i.e., a Slater determinant. The random walkers evolve as auxiliary fields are sampled, and a many-body wave function is obtained as a stochastic superposition of independent-particle solutions. The random walks are constrained in Slater determinant space by a phaseless approximation to deal with the phase problem. Generalizing our previous formalism with a plane-wave basis and pseudopotentials, we cast the method in an arbitrary single-particle basis. All-electron calculations are performed on small molecules, using Gaussian basis sets, to test the method and study its characteristics.

Quantum Monte-Carlo examines the accuracy of density functionals and anisotropy effects for the diamond to beta-tin transition in silicon

Richard Hennig
Ohio State University, United States

Abstract

Under pressure silicon displays a at least twelve crystallographic phases with a steady increase of coordination number and a transition from insulating to metallic. Density functional calculations support the experimental sequence, however, the transition pressures depend strongly on the specific density functional approximations. We use diffusion Monte-Carlo calculations for silicon phases to test the accuracy of current density-functional approximations based on the local density (LDA), the density gradient (PW91, PBE), and the kinetic energy density (TPSS [1]), as well as a screened hybrid functional (HSE [2]).

The accuracy of different pseudopotentials in quantum Monte-Carlo calculations is tested for the Si dimer molecule. Hartree-Fock pseudopotentials correctly predict the experimental bond length and binding energy while LDA and GGA pseudopotentials provide bond lengths 0.02 to 0.04 A too short and show errors in the binding energy of about 50 meV.

For crystalline Si in the diamond structure Diffusion Monte Carlo predicts the correct cohesive energy, lattice constant, and bulk modulus. The pressure for the transition to metallic beta-tin is larger in diffusion Monte-Carlo than in experiments. Previous diffusion Monte-Carlo calculations gave 16.5(5) GPa [3]. Our value of 14(1) GPa is closer to the experiments ranging from 10

to 13 GPa. Diffusion Monte Carlo and density functional calculations show that the diamond to beta-tin transformation is sensitive to anisotropic stresses; an anisotropy of about 1 GPa lowers the prediction to agree with experiments. Diffusion Monte Carlo for high-pressure Si phases shows that the functionals LDA, PW91, PBE, and TPSS underestimate their energies relative to the diamond ground state. The screened hybrid functional HSE improves the description of the covalent bonds in Silicon and provides energies in close agreement with diffusion Monte-Carlo.

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Trial Wavefunctions for He3

Markus Holzmann

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Abstract

Fixed node Quantum Monte Carlo calculations for liquid He3 at zero temperature provide an important benchmark for the progress of microscopic calculations for quantum liquids. Despite many years of research the calculated equation of state and the magnetic susceptibility is still in disagreement with experimental results [1]. We will present results on more complicated trial wavefunctions to improve the nodal error which help to reduce some of the discrepancies.

References

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Mol. Phys. 101, 1705 (2003).

Energy and variance optimization of many-body wave functions

Cyrus Umrigar

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Abstract

We present a simple, robust and efficient method for varying the parameters in a many-body wave function, both for continuum and lattice problems, to optimize the expectation value of the energy$ˆ 1$. The method is compared to what is currently the most popular method for optimizing many-body wave functions, namely minimization of the variance of the local energy$ˆ 2$. The variance minimization method is far more efficient than it straightforward energy minimization because for a sufficiently flexible variational wave function, it is possible to lower the energy on the finite set of Monte Carlo (MC) configurations on which the optimization is performed, while in fact raising the true expectation value of the energy. On the other hand, if the variance of the local energy is minimized, each term in the sum over MC configurations is bounded from below by zero and the problem is far less severe$ˆ 2$. Our new energy optimization method gets around this problem by adding terms to the straightforward expression for the Hessian that are zero when the integrals are performed exactly, % Hessian of the energy that have zero expectation value, but that cancel much of the statistical fluctuations for a finite Monte Carlo sample. With the additional terms, the Hessian is written as a sum of covariances resulting in much reduced fluctuations. In case the wave function parameters are linear in the exponent, part of the Hessian can be written as a tri-covariance, as also pointed out by Sorella$ˆ 3$, making it apparent that further cancellations of fluctuations occur. The optimization of Jastrow parameters converges in two Monte Carlo steps if a sufficiently large sample is used, but, it is more computationally efficient to first do 2 or 3 iterations with small samples followed by a single large-sample iteration. The estimated gain in efficiency increases with system size, ranging from 3 orders of magnitude for small molecules to 5 orders of magnitude for the larger molecules we used as test cases.

We discuss the different problems (and their solution) that affect optimization of the Jastrow parameters vs. the optimization of the determinantal parameters – for the Jastrow, the eigenvalues of the Hessian typically span 11 orders of magnitude; for the determinantal parameters, terms in the expectation values may diverge.

References

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Excited states from Many-Body Perturbation Theory: Spectra and Total Energies

Michael Rohlfing
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Abstract

We discuss many-body perturbation theory for excited electronic states (electrons, holes, and pair states) [1]. This is realized within the GW approximation for the electronic self-energy operator and the corresponding electron-hole interaction kernel. The latter is required to solve the Bethe-Salpeter equation (BSE) for electron-hole pair states. The method yields highly accurate band-structure energies, ionization energies, electron affinities, and electron-hole excitation energies, and allows to evaluate optical spectra. In addition to the spectra, the GW+BSE approach allows to investigate the total energy of excited electronic states. This enables the discussion of excited-state geometry relaxation, spectral broadening, Stokes shifts, and excited-state dynamics. As examples, results for exciton self-trapping in the polymer PPP [2] and atom expulsion from alkali halide surfaces will be discussed.

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A method for computing forces in diffusion Monte Carlo

Shiwei Zhang
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Abstract

Computation of ionic forces using quantum Monte Carlo methods has long been a challenge. We introduce a simple procedure, based on known properties of physical electronic densities, to make the variance of the Hellmann-Feynman estimator finite. We obtain very accurate geometries for the molecules H2, LiH, CH4, NH3, H2O and HF, with a Slater-Jastrow trial wave function. Harmonic frequencies for diatomics are also in good agreement with experiment. An antithetical sampling method will also be discussed for additional reduction of the variance.

Program

Day 1: Sept. 23 2005

Session : 1

09:00 to 09:45 : Presentation
Coupled Electron-Ion Monte Carlo Simulations of Dense Hydrogen
David Ceperley

09:45 to 10:30 : Presentation
A Test of Reliability and Efficiency of Qmc Forces
Lucas Wagner

10:30 to 11:00 : Coffee Break

11:00 to 11:45 : Presentation
Kink-based path integral studies of atoms and molecules
Randall Hall

11:45 to 12:30 : Presentation
Some combinatorial ideas for path resummations, and their application to Fermion QMC
Ali Alavi

Session : 2

16:30 to 17:15 : Presentation
Linear scaling electronic structure calculations and accurate statistical mechanics sampling with noisy forces
Krajewski Florian

17:15 to 17:45 : Presentation
Quantum Monte Carlo method using Gaussian basis sets
Shiwei Zhang

15:15 to 16:00 : Presentation
Properties of Dense Helium at Giant Planet Interiors
Burkhard Militzer

16:00 to 16:30 : Coffee Break

14:30 to 15:15 : Presentation
Coupled Electron-Ion Monte Carlo Study of Hydrogen Fluid
Kris Delaney

17:45 to 18:15 : Presentation
A method for computing forces in diffusion Monte Carlo
Shiwei Zhang

Day 2: Sept. 24 2005

Session : 3
09:45 to 10:30 : Presentation
Ab Initio Molecular Dynamics Beyond the Born-Oppenheimer Approximation
Todd Martinez

09:00 to 09:45 : Presentation
Lattice Regularized Diffusion Monte Carlo Simulations of iron dimer
Michele Casula

10:30 to 11:00 : Coffee Break

11:00 to 11:45 : Presentation
Towards more accurate variational wavefunctions for strongly correlated systems
Sandro Sorella

11:45 to 12:30 : Presentation
Hartree-Fock Revisited

Bernard Bernu

Session : 4
14:30 to 15:15 : Presentation
Trial Wavefunctions for He3
Markus Holzmann

15:15 to 16:00 : Presentation
Energy and variance optimization of many-body wave functions
Cyrus Umrigar

16:00 to 16:30 : Coffee Break

16:30 to 17:15 : Presentation
Structure of fermion nodes and pfaffian wavefunctions with singlet and triplet pairs
Lubos Mitas

17:15 to 18:00 : Presentation
Recent developments and applications of quantum Monte Carlo techniques
Dario Alfe

Day 3: Sept. 25 2005

Session : 5
09:00 to 09:45 : Presentation
The Fermion Monte Carlo: a method to alleviate the Sign Problem
Roland Assaraf

09:45 to 10:30 : Presentation
The Surface Energy of the Electron Gas
Matthew Foulkes

10:30 to 10:45 : Coffee Break

10:45 to 11:30 : Presentation
Noncovalent interactions: diffusion Monte Carlo study of biomolecular model systems
Martin Fuchs

11:30 to 12:15 : Presentation
Excited states from Many-Body Perturbation Theory: Spectra and Total Energies
Michael Rohlfing

12:15 to 13:00 : Presentation
Quantum Monte-Carlo examines the accuracy of density functionals and anisotropy effects for the diamond to beta-tin transition in silicon
Richard Hennig

Organizer's report

Conclusions.

The workshop has been very successful and resulted in a lively exchange of ideas on new developments in correlated electrons numerical methods with the emphasis on new techniques to develop ab-initio simulation methods based on the QMC solution of the electronic problem. It had gathered together about 25 participants, mainly from the QMC community but the presence of several scientists from the Quantum Chemistry and DFT communities has been very much welcome and fruitful. In general, the presentations have been quite informal and open to discussion during and after the talks. This informal and stimulating exchange of ideas has been one of the most successful aspects of the meeting and highly appreciated by the participants.

Our main conclusion are as follows:

- A number of interesting and promising techniques to perform Ab-Initio Simulation beyond Density Functional Theory have been reported. The Monte Carlo route (CEIMC), in which only electronic energies are required from QMC, is the most developed so far. The method and some results have been presented in two separate talks during the workshop. Interesting progresses and benchmarks on force methods within QMC has been reported for both light and heavy elements. This study has shown that QMC forces for light elements can be computed at a level of accuracy sufficient to be used in a Molecular Dynamics simulation of the nuclei. On the contrary significant challenges are still present for heavier elements such as transition metals. The most recent results suggest that the research is going in the right direction especially using more advanced methods such as Reptation Monte Carlo.

- PIMC methods are also powerful techniques for finite temperature systems. An interesting method based on PIMC in orbitals space has shown to be capable to treat both electronic and nuclear degrees of freedom in small molecules. A related promising method in the space of determinants has been reported. In this method an analytical re summation of diagrams allow to considerably reduce the sign problem. In this respect it is very interesting to follow the future developments of the methods and its performance for large systems. Restricted PIMC for many fermions systems at temperatures above few thousand kelvin are well developed. New interesting results on high pressure helium has been reported in agreement with experimental data and in striking disagreement with ab-initio DFT predictions.

- A recently developed linear scaling method in CPMD has shown ideas on how to use noisy forces in a dynamical simulation of the nuclei. This is exactly the situation to be faced in a QMC based MD simulation. A preliminary account of a first attempt in this direction has been presented for hydrogen with very promising results.

- Another important aspect of QMC method in general is to develop new and more accurate and flexible wavefunctions. Interesting ideas on methods how to include correlations have been suggested. The functional forms which include correlations in an efficient ways such as Bardeen-Cooper-Schrieffer wavefunctions which are capable of capturing the pair correlations more consistently has been tested. Furthermore, ideas based of pfaffian wave functions has been tested out ans show promise for even higher accuracy (pfaffians are generalizations of determinants which enable to include both singlet and triplet pairing effects into a single wave function). Tests with molecular and condensed matter systems have been reported.

- A new QMC method based on lattice discretization has been proposed and tested. Its significant advantage over continuum QMC is that it enables to use the fixed node approximation for nonlocal pseudopotential while keeping the energy upper bound property. Although the current methods do handle this problem the cost is significant and the lattice reformulation enables possibly other speed-ups in efficiency.

- A number of talks on the use of QMC for real materials has been presented. Recent successes of QMC but also its limitations for these very complex situations have been highlighted. We believe the situation is still one step away from the possibility to actually explore the nuclear motion in these cases but testing of reaction paths and isomer spaces look very promising.

Recommendations.

- the CEIMC, applied so far to hydrogen, should be developed toward the direction of studying more complex systems. Important advances would be to explore the use of pseudopotentials to allow considering heavier elements.

- the next idea which is becoming of key importance is the flexibility and efficiency of the wavefunctions for dynamical calculations, bond-breaking and description of several electronic states in parallel. This will be undoubtedly one of the most active and promising areas considering the impact and interest in presented talks in this direction. Efficiency of the wavefunctions has been always at the heart of successful electronic structure methods employed in dynamical framework and it remains such for the future as well. New mathematical developments such as pfaffians and pairing wavefunctions hold a significant promise for the future.

- the dynamical calculations with the noise have also a great promise within quantum Monte Carlo techniques. These methods have inherent stochasticity which enables to merge it with Langevin-type simulations rather naturally and hold a significant potential for the successful development in the future. New ideas to explore the discretization techniques such as lattice formulations are very interesting as well. They enable to formulate the quantum problem in the language and representations which are very close to quantum field theory and therefore open door into experience and ideas which has been developed in this area of research over the past twenty years or so.

- the quantum Monte Carlo/Molecular Dynamics (QMC/MD) is a very recent development which is in its first steps to be established as a viable simulation methods. Some of the algorithmic parts are already developed; some needs more work and development. The method holds a great promise for phenomena where the character of the processes involved simply requires proper description at the quantum level such as proton and electron transfers in biomolecules, excitations in molecular dynamics, or optical properties at finite temperatures

- some work has been presented on transport and quantum dynamics. So far this field has not been much explored by the quantum Monte Carlo methods. We believe that in future this will become much more active area for research. Basically, once the static and classical ion/QMC electrons types of calculations get more established it will be natural to extend the QMC techniques to this direction.

Each of the mentioned topics could become an exciting theme for future CECAM activities such as summer workshops or summer schools for graduate students and postdocs. We hope to propose some of these ideas for a future workshop in a two or three years timeframe. We also want to mention that these are all the *most advanced* directions where the feasibility of new algorithms is being pushed beyond ordinary limits and fundamental barriers such as exponential scaling of several quantum computational problems is being attacked. This is both very challenging and very exciting field of research which has a significant potential for breakthroughs in simulation studies of real materials. We highly recommend and hope that CECAM will keep a visible presence in this unique area of research in the future.

3.1.3 Report on the Second International Symposium on Hydrogen in Matter (ISOHIM 2005)

Ångström laboratory, Uppsala University, Uppsala, Sweden

June 13-17, 2005

Sponsors:
The Royal Swedish Academy of Sciences, ESF Programme Psi-k, The Swedish Research Council, US Department of Energy, The Swedish Energy Agency, NIST, NASA/JPL, Argonne National Laboratory, Jefferson Lab, Uppsala University, City of Uppsala, as well as industrial companies, the Reference Metals Company, Inc. and ATI Wah Chang.

Organizers:
ISOHIM BOARD MEMBERS are Jim Miller (Chair, ANL, USA), Ganapati Rao Myneni (Co-Chair, JLAB, USA), Björgvin Hjörvarsson (Co-Chair, Uppsala University, Sweden), Gunter Luepke (Secretary, College of W&M, USA), Bob Bowman (JPL, Caltech, USA), Tadeu Carneiro (Reference Metals, USA), Christian Day (FZK, Germany), Ron Graham (Wahchang, USA), Bill Lanford (UNY Albany, USA), Peter Lindblad (Uppsala University, Sweden), and Matthew McCluskey (WSU, USA Richard Ricker, NIST, USA).
The LOCAL ORGANIZING COMMITTEE included:

I. Abrikosov, Y. Andersson, C. Chakon, O. Eriksson, K. Flodström, B. Hjörvarsson, E. B. Karlsson, P. Lindblad, and L. Westerberg

http://www-conference.slu.se/ISOHIM/index.htm

The Second International Symposium on Hydrogen in Matter was held June 13-17, 2005 at the ngstrm laboratory, Uppsala University, in Uppsala, Sweden.The mission of ISOHIM 2005 was to advance the basic understanding of hydrogen-matter interactions. ISOHIM operates on an international level, promoting worldwide information exchange and collaboration. The interdisciplinary nature of the conference is easily recognized. It ranges from hydrogen induced embrittlement in construction materials to quantum correlations in biological systems. It is therefore of uttermost importance to link the experimental and the theoretical efforts to obtain better understanding within the field of hydrogen in matter.

Surfaces, interfaces as well as defects play a major role for chemical affinity and fugacity as seen e.g. by the catalytic activity and selective reaction paths of designed surfaces and interfaces. The composition, structure and extension are all important, nevertheless finite size effects are only rarely discussed in this context. The quantum nature of the electronic building blocks is the fundamental entity, which can never be ignored. This is one of the main missions of the conference. As an example the photobiological activity of surfaces was mentioned. Finite size effects are apparently important for the reactivity, as well as the geometrical factors of the surfaces. This was treated in a session were we linked together specialist from different disciplines, with the aim of enlightening the field by cross disciplinary discussions.

Meeting Programme was directed to the following 6 main topics:

Fundamentals: Dynamics and thermodynamics of H in metals, semiconductors and oxides. Quantum effects. Hydrogen surface and interface interactions, Defects & doping

Hydrogen induced modifications of materials: Optical and electric properties of materials, Magnetic properties of materials, Mechanical properties of materials

Biological aspects: Hydrogen production using biological processes, Artificial photosynthesis, Other aspects

Technological aspects: Ultra pure materials, UHV applications, Alloy production, Powder production, Nuclear reactors

Energy related aspects: Hydrogen storage and purification, Energy conversion Fusion technology

New aspects

The conference attracted 95 participants from 18 countries. There were 19 plenary/invited and 33 contributed talks presented, as well as 28 poster presentations. On Friday, June 17, a Panel Discussion was organized, and most important directions of hydrogen related research in the future were discussed. The Psi-k community was well represented, e.g. we have organized a session at the conference with Invited Talk given by G. Brocks (Computational Materials Science, MESA+ Research Institute, University of Twente, 7500 AE Enschede, The Netherlands) "Excitations in metal hydrides from first principles ". But in addition, there were many other talks devoted to theoretical studies of hydrogen-related phenomena by means of first-principles methods of the electronic structure theory.

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Programme

Monday, June 13

17.00 - 21.00 Registration and welcome party

Tuesday, June 14

9.15-9.30 Welcome

Session Chairman B. Hjörvarsson

9.30 - 10.15 **C. Van de Walle (plenary)**, Universal alignment of hydrogen levels in semiconductors, insulators, and solutions.
10.15 - 10.45 Break
10.45 - 11.30 **B. Beck Nielssen (plenary)**, Hydrogen in group-IV semiconductors and its interaction with defects.
11.30 - 11.50 G. Lüpke, Vibrational lifetime of hydrogen bending mode in silicon.
11.50 - 12.10 Y. Oya, Hydrogen isotope behavior in helium ion pre-irradiated SiC.
12.10 - 12.30 M. I. J. Probert, Ab Initio Path Integral MD Simulation of Hydrogen in Silicon
12.30 - 14.00 Lunch

Session Chairman R. Kirchheim

14.00 - 14.30 **E. Babaev (invited)**, A superconductor to superfluid phase transition in the projected liquid metallic state of hydrogen.
14.30 - 14.50 G. Cao, H induced modifications of optical and electronic properties of Mg films
14.50 - 15.10 R.A.H. Niessen, Electrochemical hydrogen storage characteristics of thin film MgX (X = Sc, Ti, V, Cr) compounds
15.10 - 15.30 N. Patel, Thermal stability of hydrogenated Mg/Al this films

15.30 - 15.50 D. Milcius, The role of grain boundaries in the mechanism of plasma immersion hydrognation of nanocrystalline MgAl films
15.50 - 16.15 Break

Session Chairman E. B. Karlsson

16.15 - 16.45 **C. Rolfs (invited)**, Electronic screening in deuterated metals.
16.45 - 17.05 L. Havela, Magnetic properties of hydrides of uranium ternary intermetallics
17.05 - 17.25 P. V. Sushko, Optical absorption and electrical conductivity of H-doped 12CaO X 7Al2O3

17.25 - 17.45 Rick L. Paul, Measurement of Hydrogen in Advanced Materials by Cold Neutron Prompt Gamma-ray Activation Analysis

Tuesday, June 14

Session Chairman P. Lindblad

8.45 - 9.30 **L. Hammarström (plenary)** Hydrogen from sun and water: Biomimetic approaches to artificial photosynthesis.
9.30 - 10.15 **W. Lubitz (plenary)**, The Enzyme Hydrogenase Structure and Function as Studied by Spectroscopic and Theoretical Methods.
10.15 - 10.45 Break

Session Chairman R. L. Paul

10.45 - 11.20 **S. Seetharaman (invited)**, Hydrogen in steel making.
11.20 - 11.50 D. Fruchart, Hydrogen used s a tool to probe magnetic materials: from soft and amorphous to hard and crystallised magnetic systems
11.50 - 12.10 C. Zlotea, MgH_2 whiskers formation by hydrogen disproportionation of $Mg_{24}Y_5$.
12.10 - 12.30 R. C. Bowman, Roles of Hydrogen in Space Explorations

12.30 - 14.00 Lunch

Session Chairman W. A. Lanford

14.00 - 14.45 **P. Sofronis (plenary)**, Mechanisms and models for hydrogen embrittlement.
14.45 - 15.05 A-M. Alvarez, Hydrogen embrittlement in a metastable β-titanium alloy
15.05 - 15.25 A. V. Golubeva, Hydrogen retention in plasma-sprayed tungsten and tungsten-rhenium alloys
15.25 - 15.45 I. P. Chernov, Excitation of hydrogen subsystem in solid by external influence
15.45 - 16.05 B. Zajec, Hydrogen permeation through a metal membrane in the recombination limited regime

16.05 - 16.30 Break

Session Chairman Y. Andersson

16.30 - 16.45 J. S. Brown, Superconducting protons in metals
16.45 - 17.00 H. Londer, New high capacity Getter for vacuum insulated mobile LH2 storage tank systems

17.00 - 19.00 **P. Poster Session**

Thursday, June 16

Session Chairman S. Seetharaman

8.45 - 9.30 **K. Abiko (plenary)**, Metallurgy to discover amazing metals - ultra-purification to develop ductile metals.
9.30 - 10.15 **W. Singer (plenary)**, High-purity niobium for superconducting radio frequency resonators.

10.15 - 10.45 Break

Session Chairman D. Fruchart

10.45 - 11.30 **R. Kirchheim (plenary)**, Interaction of hydrogen with defects and their stabilization.
11.30 - 11.50 K. Sakaki, The relation between vacancy formation and phase transformation in Pd_xAg_{1-x}-H system
11.50 - 12.10 A. Talyzin, Fragmentation of C_{60} by strong hydrogenation: a route to synthesis of new materials.
12.10 - 12.30 K.O. Kvashnina, X-ray absorption and emission study of $C_{59}H_x$ and $C_{58}H_x$ fullerenes

12.30 - 14.00 Lunch

Session Chairman R. C. Bowman

14.00 - 14.30 **L. Hallstadius (invited)**, Hydrogen pickup in zirconium alloys - a nuclear fuel industry perspective.
14.30 - 14.50 J. F. Miller, Lightweight materials for hydrogen storage.
14.50 - 15.10 M.H. Sørby, Characterization of mixed alanates and the role of Ti doping.
15.10 - 15.30 O. M. Løvvik, First principles study of earth alkaline alanates.
15.30 - 15.50 C. Moysés Araújo, Vacancy mediated hydrogen de-sorption in crystalline sodium alanate

15.50 - 16.30 Break

Session Chairman I. Abrikosov

16.30 - 17.00 **G. Brocks (invited)**, Excitations in metal hydrides from first principles.
17.00 - 17.20 M.G. Shelyapina, First-principles investigation of the stability of the Ti-V-Cr ternary alloys and their related hydrides.
17.20 - 17.40 M.J. van Setten, Optical properties of hydrogen storage materials: a first principles approach.
17.40 - 18.00 H. Jonsson, Binding and diffusion of hydrogen in magnesium alloys.

Friday, June 17

Session Chairman L. Westerberg

8.45 - 9.30 **R. J. Reid (plenary)**, Why worry about outgassing?
9.30 - 10.15 **P. Chiggiato (plenary)**, Methods for reduction of hydrogen outgassing.

10.15 - 10.45 Break

Session Chairman H. S. Hseuh

10.45 - 11.30 **R. C. Bowman (plenary)**, Hydrogen outgassing behavior in the gas gap heat switches of the Planck sorption cooler.
11.30 - 11.50 S. Anakhov, Gas Distribution in High Purity Niobium EB Welded in UH Vacuum
11.50 - 12.30 **V. Nemanic (invited)**, Hydrogen outgassing from stainless steel - new experimental data

12.30 - 14.00 Lunch

Session Chairman R. J. Reid

14.00 - 14.30 **H. C. Hseuh (invited)**, Beam induced pressure rise in high intensity hadron machines.
14.30 - 15.00 **E. Mahner (invited)**, A review of heavy-ion induced molecular desorption studies for practical accelerators.
15.00 - 15.20 J. Wolf, Outgassing measurements with a prototype for a large XHV spectrometer.
15.20 - 15.40 J. Setina, Hydrogen outgassing of stainless steel vacuum chamber.
15.40 - 16.00 E. Hedlund, A comparison of published data on hydrogen outgassing from stainless steel

15.50 - 16.30 Break

16.30 - 17.00 **Panel discussion**: Status and where do we go next.
17.00 - 17.30 Summary, closing remarks, and rewards

Abstracts of presented papers can be requested from conference organizers.

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3.1.4 Report on the First Joint MolSimu-Psi-k "Quantum Simulation of Liquids and Solids" within the CECAM MC Tutorial Series

CECAM, Lyon

November 07 2005 to Nov. 18 2005

Sponsored by Marie Curie Action "MolSimu"

Organizers:
Evert Jan Meijer (University of Amsterdam, Netherlands), Igor Abrikosov (Linköping University, Sweden), and Rodolphe Vuilleumier (Universit Pierre et Marie Curie, France)

`http://www.cecam.fr/index.php?content=activities/pastTutorials&action=details&wid=23`

This course aimed at giving an introduction in the simulation of electronic structure in condensed phase materials, solids and liquids. A first series of lectures was devoted to the basics of Density Functional Theory and to the solution of the electronic structure problem in solids using plane wave basis sets and Green's function technique. This part of the tutorial was based on the book by R. M. Martin "Electronic Structure. Basic Theory and Practical Methods" (Cambridge University Press, Cambridge, 2004). A second series of lectures was focused on the simulation of liquid systems using ab initio Molecular Dynamics. These also include an introduction to advanced techniques 1) to simulate reactive processes in liquids 2) to couple quantum simulations to classical molecular dynamics (so-called QM/MM).

The tutorial was organized by Evert Jan Meijer (University of Amsterdam, Netherlands), Igor Abrikosov (Linköping University, Sweden), and Rodolphe Vuilleumier (Universit Pierre et Marie Curie, France). The invited lecturers include Sergei Simak, Sam Shallcross (Linköping University, Sweden), and Elske Leenders (University of Amsterdam, Netherlands). The morning sessions were lectures introducing the methods and in the afternoons there were computer exercises in which these methods were applied. During these practical classes the students run a few simulations using existing packages, like CPMD, KKR-ASA and VASP, to apply the techniques discussed in the morning lectures and be acquainted with these packages. In addition, a miniworkshop was organized, where 5 participants presented results of their research. Unfortunately, because of the unrests in Lyon, some evening classes and week-end sessions had to be shortened or even canceled. The course did not assume any previous knowledge in molecular simulations. However, elementary knowledge in quantum physics was assumed. Support for participation (travel and lodging) was available via the Marie Curie Action "MolSimu". The tutorial was heavily overbooked, by factor of two. In the end, 37 participants (42 including conference organizers and invited lectures) were selected, representing 12 European countries.

The need for such type of tutorials is due to the fact that a distribution of computer codes for the electronic structure calculations goes much faster than the transfer of the corresponding knowledge for the underlying theory. Unfortunately, though the codes have become really user friendly, the theory on its own has not. Therefore using the codes is not fool proof. In particular, errors produced by non-experienced users, as well as their unmotivated high expectations, may accumulate, and create overall negative impression for the possibilities of the electronic structure theory. The organizers see a real and clear necessity to **educate qualified experts in the field**. Important here is that the educational activities should be directed to qualified teaching of the underlying theory rater than (exclusively) to instructions for the use of particular codes (click this button, enter this parameter). As tutorial organizers, we were very pleased that most of participants shared this view point, showed real interest in both, lectures and computer classes, asked relevant questions, and followed the subject. Moreover, participants who had experience with the codes in question, acted very efficiently as instructors to their fellow students with less experience in the electronic structure calculations. In particular, help from Tobias Marten, Christian Gransson, Arkady Mikhaylushkin, and David Andersson is greatly appreciated by the tutorial organizers. In summary, as teachers, we were very pleased with audience responses. A student questionnaire carried out upon the completion of the tutorial also showed that the absolute majority of the participants gave positive evaluation to the tutorial. We note, that this is a remarkable result, as participants represented in approximately equal amounts two different communities, the solid state band theory (Psi-k) and molecular simulations (CECAM). Obviously, the experience gained in this first joint tutorial opens a new way for collaborations and contacts between these two communities.

Finally, we would like to acknowledge help from CECAM in organizing the tutorial, Berend Smit (CECAM Director), Emilie Bernard and Caroline Werlingshoff (administrative assistants), and Fred Barmes (computer administration). The BGFM code used for the present tutorial that implements the KKR-ASA method was developed by I. A. Abrikosov, A. V. Ruban, and H. Skriver. We are grateful to Prof. J. Hafner for the permission to using Vienna Ab initio Simulation Package (VASP) for our computer classes.

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Programme

Session 1, Igor A. Abrikosov (IAA), Sergei I. Simak (SIS), and Sam Shallcross (SSh).

Monday, November 7
9.00 - 9.45 General information and introduction into the tasks of the tutorial (IAA)
10.00-10.45 Basics of the electronic structure theory (IAA)
10.45 - 11.15 Coffee

11.15-12.45 Periodic solids and electronic bands (SIS)

12.45 - 14.00 Lunch
14.00-14.45 Introduction into computational tasks (SSh and IAA)
15.00-18.00 Computer classes: calculations of lattice parameters, compressibilities, and structural energy differences across transition metal series using KKR-ASA method.

Tuesday, November 8
9.00 - 10.45 Many-body problem and density functional theory (IAA)
10.45 - 11.15 Coffee
11.15-12.45 Self-consistent band structure calculations for periodic solids (SIS)
12.45 - 14.00 Lunch
14.00-18.00 Computer classes: Calculations of mixing and ordering energies in alloys, changes of the electronic structure upon order-disorder transition, magnetic moments in alloys, band gaps in semiconductors, simple estimates of Curie temperature of bcc Fe, etc. using KKR-ASA method.

Wednesday, November 9
9.00 - 10.45 Introduction into the multiple-scattering theory (IAA)
10.45 - 11.15 Coffee
11.15-12.45 Introduction into the pseudopotential and PAW technique, part 1 (SIS)
12.45 - 14.00 Lunch
14.00-18.00 Computer classes: optimization of c/a ratio in hcp transition metals and calculations of total energy along the Bain path using VASP.

Thursday, November 10
9.00 - 10.45 Green's function technique and the coherent potential approximation (IAA)
10.45 - 11.15 Coffee
11.15-12.00 Introduction into the pseudopotential and PAW technique, part 2 (SIS)
12.00-12.45 Miniworkshop: presentations by participants
12.45 - 14.00 Lunch
14.00-14.30 Miniworkshop presentations by participants
14.30-18.00 Computer classes: determination of interatomic interactions in random alloys using KKR-ASA-CPA method and estimation of the contribution due to local lattice relaxations to the alloy total energy using special quasirandom structure method and VASP.

Friday, November 11
9.00 - 10.45 Linear scaling methods within the Green's function approach (IAA)
10.45 - 11.15 Coffee
11.15-12.45 Alloy phase stabilities from Monte-Carlo simulations (SSh)
12.45 - 14.00 Lunch
14.00-18.00 Computer classes: calculation of order-disorder transition temperature by means of

Monte-Carlo simulations

Session 2, Evert Jan Meijer (EJM), Rodolphe Vuilleumier (RV) and Elske Leenders (EL).

Monday, November 14
09.00-10.45 Recapitulation on DFT, Plane Waves, Pseudo-Potentials... simple CPMD examples - Part 1 - 2 (EJM)
10.45-11.15 Coffee
11.15-13.00 Optimization - Part 1 - 2 (RV)
13.00-14.00 Lunch
14.00-15.00 Introduction practicals: input, output, analysis tools vmd, cube-files (EL)
15.00-18.00 Computer Classes

Tuesday, November 15
09.00-10.45 ab initio Molecular Dynamics - Part 1 - 2 (EJM)
10.45-11.15 Coffee
11.15-13.00 Atoms and Molecules - Part 1 - 2 (RV)
13.00-14.00 Lunch
14.00-18.00 Computer Classes: Generating PPs & Atoms & Molecules: optimization (EL)

Wednesday, November 16
09.00-09.45 Properties calculation(RV)
10.00-10.45 Linear Response (RV)
10.45-11.15 Coffee
11.15-12.00 Infrared and Raman Spectroscopy (RV)
12.15-13.00 Time-dependent density functional theory (RV)
13.00-14.00 Lunch
14.00-18.00 Computer Classes: Liquid Simulation: proper md, wannier centers, liquid structure, reactivity (EL)

Thursday, November 17
09.00-10.45 QM/MM techniques - Part 1 - 2 (Ivano Tavernelli)
10.45-11.15 Coffee
11.15-13.00 Reactivity - Part 1 - 2 (EJM)
13.00-14.00 Lunch
14.00-18.00 Computer Classes: Analysis electronic structure (EL)

Friday, November 18
09.00-10.45 Quickstep - Part 1 - 2 (Matthias Krack) 10.45-11.15 Coffee 11.15-13.00 Advanced topics - Part 1 - 2 (RV) 13.00-14.00 Lunch 14.00-18.00 Computer Classes: Introduction to CP2K

(EL+MK)

Miniworkshop: presentations from participants

POSSIBLE TRANSFORMATION PATHS CONNECTING THE $C11_b$, $C40$ AND $C54$ STRUCTURES IN $MoSi_2$

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We suggest three transformation paths between the ideal $C11_b$, $C40$ and $C54$ structures of transition-metal disilicides. These three structures can be regarded as different stackings of identical planes of atoms. Each suggested transformation path consists in shifting these atomic planes in three directions. The shift of planes is described by one parameter p, p lies in the interval ¡0;1¿. Along each path, we calculate the total energy of MoSi2 as a function of p. Our results confirm the structural order $C11_b$-$C40$-$C54$ in $MoSi_2$. The $C11_b$-$C54$ path exhibits the largest energy barrier, 2.5 eV/f.u (f.u. means the formula unit). The energy barrier of the $C11_b$-$C40$ path is lower, 1.7 eV/f.u. and finally the energy barrier of the $C40$-$C54$ path is the lowest one, 1.4 eV/f.u.

Magnetism of AlPdMn quasicrystal from first principles

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Electron and magnetic properties of 1/1 approximant of quasicrystalline AlPdMn are studied by means of density functional theory and all-electron PAW potentials. Magnetic moments of Mn atoms are analyzed in dependence on Mn concentration and its chemical environment. We have found that large local magnetic moment of Mn atoms is appeared at 8 at.

Ab initio studies of Mn-impurity in wurtzite-type GaN

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Investigation of electron and magnetic properties of transition metal impurities in semiconductors is of great interest due to ferromagnetic ordering of these impurities with the Curie temperature around 110K and even higher. In this work the electron structure and magnetic properties of Mn impurities in wurtzite-type GaN are studied by means of density functional theory and first principles pseudopotentiales and in dependence on concentration and chemical environment of Mn atom. We have shown that magnetic moment of Mn atom in the GaN strongly depends on whether the impurity atom is substitutional or interstitial. The magnetic moment of Mn atom on the Ga-site of GaN is $4\mu_B$. Analysis of partial density of states (DOS) has shown that there is 100% spin polarization of carriers in (Ga, Mn)N and the main contribution to the DOS at the Fermi level originates from Mn impurity.

Discontinuously Reinforced Aluminum Made by Novel Ion Exchange Process

Filippo Zuliani[1], Orteo Sbaizero[1], Alessandro De Vita[1,2]
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Scientists around the world have already assigned an important role to Nanotechnology and Materials recognising them as the driving forces for the future of the world economy. This results from the simple premise that using building blocks with dimensions in nanosize makes it possible to design and create new materials with unprecedented flexibility and improvements in their physical properties. We focused on the special case of Discontinuously Reinforced Aluminium (DRA) metal matrix made by a novel solid state exchange process of magnesium ions in magnesium aluminate spinel with aluminium. This process leads to DRA composites consisting of a nanosized, highly stable and nearly insoluble aluminium oxide phase into an aluminium matrix, with greatly enhanced elastic stiffness, yield strength, ductility and resistance to high temperature deformations. Surface to volume ratio of the spinel particles strongly influences reaction kinetics in the initial composite. Reaction rate appears to increase remarkably when the particle size is decreased. To achieve better properties, a good interface between the two phases of the composite is of paramount importance. Unfortunately, nowadays the nature of the interactions involved in metal-ceramics adhesion is still far from being understood in detail. While the cohesion of metals originates from the delocalization of electrons, oxides predominantly exhibit localized ionic bonding. An interface between a metal and an oxide, therefore, requires some sort of transition between these fundamentally different type of interatomic interaction. We investigated the hypothesis that the reinforcement efficiency is very high due to chemical processes taking place at the coherent matrix/reinforcement interface. Our aim is to reveal, from a theoretical point of view, whether and how the ion exchange process can yield enhanced interface adhesion and therefore represent a viable strengthening and toughening mechanism.

Molecular Dynamics with Quantum Transitions Using Time-Dependent DFT

Enrico Tapavicza, Ivano Tavernelli, Ursula Rothlisberger

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Many chemical reactions of organic molecules occur in electronically excited states and can only be described taking into account non-adiabatic effects. Time-dependent (TD) DFT [1] allows to calculate electronic spectra and nuclear forces for electronically excited molecules. There have been several approaches to include non-adiabatic effects in ab initio molecular dynamics codes based on surface hopping [2] or Ehrenfest dynamics [3].

Recently we presented a SH mechanism for TDDFT, based on Landau-Zener theory [4], where the probability of switching excited state is computed from the nuclear forces at the avoided crossing between two electronic states [5].

Here we present a more general TDDFT based method, using the *fewest switch* approach of Tully [6]. The non-adiabatic coupling is computed using an approximation for the excited state wavefunction.

The method has been implemented in the plane wave code CPMD [7] and applied to photoinduced cis-trans isomerizations and intramolecular electron transfer in organic model compounds.

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3.1.5 Report on a Mini-workshop on FLAPW development

Forschungszentrum Jülich, Germany

10–11 Dec. 2004

Sponsors:
European Science Foundation
Forschungszentrum Jülich, Germany

Organizers:
Stefan Blügel (s.bluegel@fz-juelich.de)
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The European FLAPW (full-potential augmented plane wave) community met at the Forschungszentrum Jülich. In the light of the rich and interesting spectrum of applications such as non-linear optics, linear response for phonons and magnons, non-collinear magnetism, and problems of strongly correlated electron systems which are currently under study by the FLAPW method and looming ahead of us, and considering the broad arsenal of approaches, techniques and concepts (GW approximation, SIC, exact exchange or LDA+U functionals, DMFT) required to address these problems, it is important to discsuss the development of the FLAPW method in an european context. The goal of the two-day workshop was to bring together the European developers of the method in order to discuss and summarize current highlights, developments and the current state of the art of each group, to exchange recent advances made and discuss the different software developments of the different groups.

The program shows contributions from most of the europeen groups actively developing FLAPW based codes including: Berlin, Jülich, Prague, Uppsala and Vienna. Approaches beyond the usual local density approximation were presented by various contributions and included the development of FLAPW based GW-codes (Berlin, Jülich) as well as efforts focused on exact exchange and LDA+U (Prague).

Program

Friday, 10. Dec. 2004

Morning session:

10:00	10:15	**Opening**	S. Blügel
10:15	11:15	*FLAPW Method for 1D systems*	Y. Mokrousov
11:15	11:30	**coffee break**	
11:30	12:00	*Distorted augmented plane waves*	Fredrik Bultmark
12:00	12:30	*Phonons and Phasetransition*	P. Blaha
12:30	14:00	**Lunch**	
14:00	14:30	**Administrational business: travel expenses etc.**	

Afternoon session:

14:30	15:30	*GF-Calculations with FLEUR*	D. Wortmann J. Enkovaara
15:30	16:30	*The GW Approximation for the Electronic Self-Energy*	A. Schindlmayr
		Implementation of the GW Approximation within the FLAPW Method	Ch. Friedrich
		Ab initio Calculation of Spin-Wave Spectra	M. Niesert
16.30	16:45	**coffee break**	
16:45	17:15	*All electron GW on LAPW: Under Construction*	R. Gomez-Abal
17:15	17:45	*Positron annihilation and interferometric EELS within WIEN2k*	J. Rusz
17:45	18:30	*Discussion*	
19:00		**Dinner**	

Saturday, December 11th, 2004

Morning session:

9:00	10:00	*LDA+U : Implementation and Applications*	A. Shick
10:00	10:30	*Exact Exchange - implementation in WIEN2k program*	P. Novak
10:30	10:50	*Comparison of LDA+U and DMFT for VO$_2$*	G. Bihlmayer
10:50	11:15	**coffee break**	
11:15	11:45	*Nonlinear bulk- and surface (magneto-)optics in FLAPW with Wien97 and Wien2k*	B. Olejnik
11:45	12:15	*Calculation of Heisenberg Exchange parameters*	M. Lezaic
12:15	12:45	*Magnetism of rare-earth multilayers*	Björn Skubic
12.45	13:30	*New challenges and new developments*	S. Blügel
13:30	15.00	**Lunch**	
15:00		**End**	

Abstracts

FLAPW Method for 1D systems

Yuriy Mokrousov
Institut für Festkörperforschung, Forschungszentrum Jülich

We present an extension of the full-potential linearized augmented plane-wave (FLAPW) method to truly one-dimensional systems. The space is partitioned into three regions, the muffin-tin sphere around the atom, a vacuum region surrounding a cylinder and the interstitial region between the atoms and the vacuum region. In each region optimal basis functions for the wave-functions, charge density and potential are used. Despite the plane-wave representation in the interstitial region we were able to include a wide class of chiral symmetries, characteristic for one-dimensional systems. The one-dimensional FLAPW method was implemented as extension of the FLAPW code `FLEUR` and parallelized for supercomputing applications. Due to the efficiently adjusted basis functions and partitioning of space, 1D code allows to achieve a significant speed-up, for instance, approximately by a factor of 150 for monowires, as compared to the super-cell approach in the bulk code.

Distorted augmented plane waves

Fredrik Bultmark
Department of Physics, Uppsala University

In order to speed up the diagonalisation of the Hamiltonian matrix, the number of basis functions has to be reduced. We have tried to implement a way of reducing the number of wave functions without reducing the resolution of the basis set by applying a unitary transformation to the Hamiltonian matrix. The transform changes the basis from a large number N plane waves to a smaller number n linear combinations of N plane waves. The new basis functions are plane waves in a curved space created by letting the atoms distort space like stars distort space-time in general relativity theory.

Phonons and Phasetransitions

P.Blaha
Inst.f.MaterialsChemistry, TU Vienna, Austria

I will review methods to calculate phonons from first principles and focus in particular on the direct method. In connection with K.Parlinskis PHONON [1] program and the FP-APW+lo code WIEN2k [2] we have calculated phonons and resulting thermodynamic properties for several compounds. Ill demonstrate that soft (unstable) modes and their corresponding displacements can be used as guideline for a search of the ground-state structure or to study phase transitions. This will be demonstrated on two fairly complicated examples, namely a detailed analysis of the Ferroelectric phase transition in Aurivillius compounds [3] and the search for Geometric frustration and electronic instabilities in Pyrochlore $Y_2Nb_2O_7$ [4].

[1] K.Parlinski, Software PHONON. [2] http://www.wien2k.at [3] J. M. Perez-Mato, P. Blaha, K. Parlinski, K. Schwarz, M. Aroyo, L. Elcoro, and Z. Izaola, Int.Ferroelectrics 62, 183 (2004); and PRB (in print) [4] P.Blaha, D.Singh, K.Schwarz, Phys.Rev.Lett. 93, 216403 (2004)

GF-Calculations with FLEUR

Jussi Enkovaara and Daniel Wortmann
Institut für Festkörperforschung, Forschungszentrum Jülich

In order to extend the FLAPW method to systems with a broken translational symmetry and to treat open systems we implemented a Green function (GF) based embedding scheme into our FLAPW program. Our approach allows to treat open systems in which semi-infinite half-spaces are attached to a central volume of interest. We discuss how to include the effects of the leads, how to calculate complex bandstructures within our method and how to apply the scheme for the calculation of ballistic transport using the Landauer equation.

The GW Approximation for the Electronic Self-Energy

Arno Schindlmayr
Institut für Festkörperforschung, Forschungszentrum Jülich

Many-body perturbation theory provides an explicit framework to calculate, in principle, the exact excitation spectrum of solids. Over the last 20 years, plane-wave pseudopotential implementations of the GW approximation for the electronic self-energy have consistently obtained quasiparticle band structures in excellent agreement with experiments for a large number of semiconducting and metallic materials. The first all-electron implementations, which were only reported very recently, appear to show systematic deviations, however. After a physical interpretation of the GW approximation, I will analyse the different contributions to the self-energy and discuss the possible sources for the discrepancy between pseudopotential and all-electron results.

Implementation of the GW Approximation within the FLAPW Method

Christoph Friedrich
Institut für Festkörperforschung, Forschungszentrum Jülich

While most GW implementations are based on pseudopotentials, the explicit inclusion of core electrons within an all-electron approach has become feasible only in recent years. The FLAPW method is considered to be one of the most accurate ways to describe the electronic structure of a solid in an all-electron DFT approach. In this talk I will present the main features of our GW implementation used as a correction on the DFT results. In particular, the mixed product basis will be explained that is used to represent the polarization and dielectric function as well as the bare and screened interaction. Furthermore, it will be shown how the frequency integration needed in the construction of the self energy is carried out by way of contour integrals.

Ab-Initio Theory of Spin-Wave Excitations

Manfred Niesert
Institut für Festkörperforschung, Forschungszentrum Jülich

Spin-waves, the elementary magnetic excitations of a spin-polarized system, are of collective nature. While the initial idea of spin waves originates in the model of localized spins described by a Heisenberg Hamiltonian, the solution of a general system involves the spin-response function and its spectral representation. This response lies beyond the scope of static density-functional theory, and must therefore be obtained by advanced methods like many-body perturbation theory. A diagrammatic approach based on the GW approximation for the self-energy yields a series of ladder diagrams for the susceptibility. This talk presents the above mentioned theory and sketches an implementation based on a proposition of Aryasetiawan and Karlsson (Phys.Rev. B 60, 7419 (1999)).

Positron annihilation studies of f-electron systems

J. Rusz
Department of electronic structures, Faculty of Mathematics and Physics, Charles University, Prague
Institute of Physics, Academy of Sciences of the Czech Republic, Prague and M. Biasini
ENEA, Via don Fiamelli, Bologna, Italy

We present our results of two-dimensional angular correlation of annihilation radiation. The measurements were analysed within the density functional theory including positron wavefunction and electron-positron correlation effects. Our calculations are based on the full-potential liearized augmented waves method and do not contain any shape approximations of potential or density at any stage. Our results support the picture of localized 5f-electrons in USb and itinerant 5f-electrons in UGa3.

Magnetic moment collapse in δ-Pu.

A. B. Shick, V. Drchal and L. Havela
Institute of Physics, Academy of Sciences of the Czech Republic, Prague

The "around-mean-field" version of the LSDA+U method is applied to investigate the electron correlation effects in δ-Pu. We found a non-magnetic ground state with zero spin and orbital magnetic moments. The equlibrium lattice constant and bulk modulus are calculated in good agreement with the experiment. Our calculations allow to explain some of the important features of the experimental photoemission spectra of δ-Pu and its thin films.

Exact Exchange - implementation in the WIEN2k program

Pavel Novak
Institute of Physics ASCR, Prague, Czech Republic

Starting from the LDA+U method we propose a hybrid between the Hartree-Fock and the Density Functional methods. Compared to LDA+U the unscreened Hartree-Fock interaction between strongly correlated electrons is inserted and complete LSDA interaction subtracted. The method is parameter free and tests on several compounds showed that the results lie between the LDA+U and the Hartree-Fock calculations.

Comparison of LDA+U and DMFT for VO_2

Gustav Bihlmayer[1] Ansgar Liebsch[1] and Hiroshi Ishida[2]
[1] Institut für Festkörperforschung, Forschungszentrum Jülich
[2] Collage of Humanities and Sciences, Nihon University, Tokyo, Japan

The rutile (R) and monoclinic (M1) phase of VO_2 have been investigated with density functional theory in the local density approximation (LDA), the LDA+U framework and the dynamical mean-field theory (DMFT). In comparison with recent photoemission studies it turns out that only DMFT correctly describes the valence-band spectrum of the R phase, but fails (in a site-diagonal form) to predict the insulating nature of the M1 phase. Only very elaborate cluster-DMFT calculations improve this result. But the insulating nature of this phase is described by the LDA+U method, also in various approximations. We conclude that the k-dependency of only the static part of the self-energy is responsible for the insulating nature of the M1 phase, while strong dynamic correlations modify the spectrum of the rutile phase.

Calculation of Heisenberg Exchange parameters

Marjana M. Ležaić
Institut für Festkörperforschung, Forschungszentrum Jülich

We will give a description of a method for calculating the Heisenberg exchange interaction parameters from the first-principles. Performing total energy calculations of spin-spirals with a particular q-vector using the force theorem for spirals of small cone-angle we are able the calculate the Heisenberg exchange parameter $J(\mathbf{q})$, and by Fourier transformation one obtains J_{ij}, which are then used to calculate the Curie temperature T_c.

Magnetism of rare-earth multilayers

Björn Skubic, Lars Nordström
Department of Physics, Uppsala University

Rare-earth elements exhibit a rich variety of non-collinear magnetic structures. Because of structural similarities, these elements are ideal for growing high-quality multilayer structures. Previous experimental studies were made, aimed at understanding the coupling of the magnetism between the layers of such systems. There is a lack of theoretical band structure calculations treating these systems. Here we present the first preliminary results of band structure calculations on Er/Lu multilayers.

List of participants

- G. Bihlmayer, Jülich (g.Bihlmayer@fz-juelich.de)
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- S. Blügel, Jülich (s.bluegel@fz-juelich.de)

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- D. Wortmann, Jülich (d.wortmann@fz-juelich.de)

3.2 ESF Workshop/Conference Announcements

3.2.1 SECOND: Psi-k/NANOQUANTA SCHOOL + WORKSHOP

Time-Dependent Density-Functional Theory: Prospects and Applications

August 27th to September 11th, 2006

Benasque Center for Physics, Spain

http://benasque.ecm.ub.es/2006tddft/2006tddft.htm

Organizers:

E. K. U. Gross
Institut fuer Theoretische Physik,
Freie Universitaet Berlin
Arnimallee 14, D-14195 Berlin, Germany

Miguel A. L. Marques and Fernando Nogueira
Dep. de Fsísica, Faculdade de Ciências e Tecnologia,
Universidade de Coimbra and Centro de Física Computacional
Rua Larga, 3004-516 Coimbra, Portugal

Angel Rubio
Dpto. Fisica de Materiales, Facultad de Quimicas U. Pais Vasco,
20018 San Sebastian/Donostia, Spain

History and Scientific motivation:

The first School and workshop was hosted by the Benasque Center for Science, Spain from August 28th to September 12th, 2004. 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.

The use of TDDFT is increasing, and it is fast becoming one of the tools of choice to get accurate and reliable predictions for excited-state properties in solid state physics, chemistry and biophysics, both in the linear and non-linear regimes. This interest has been motivated by the recent developments of TDDFT (and time-dependent current functional theory) and include the description of photo-absorption cross section of molecules and nanostructures, electron-ion dynamics in the excited state triggered by either a small or high intense laser fields, van der Waals interactions, development of new functionals coping with memory and non-locality effects, applications to biological systems (chromophores), transport phenomena, optical spectra of solids and low-dimensional structures (as nanotubes, polymers, surfaces, ...).

Following our previous experience, the most efficient scheme for training of young researchers in these techniques is to have a school where the basic theory is taught followed by a workshop that introduces them to the forefront research in the field. The school should have an equal share of theoretical and practical classes. This would ease the learning of the techniques and would provide the students with the practical knowledge of the numerical aspects and difficulties, while also introducing them to well-established open source numerical codes. At the end of the school, students should have sufficient working knowledge to pursue their projects at their home institution.

The school will be followed by an international workshop, where the new developments of TDDFT and Many-Body Techniques for the calculation of excitations will be discussed. Students attending the school will be encouraged to attend the workshop, so they can get in contact with state of the art research in the field. The purpose of the workshop is to bring together leading experts in all these fields with different backgrounds, like density functional, many-body, nuclear physics and quantum chemists. This will allow the exchange of ideas between the different fields and the creation of links between the traditionally separated communities. We believe that the intense and informal discussion which is possible in this kind of workshops can contribute to the formation of a strong community in the field of TDDFT.

Location/Timing

We plan to organize this event at the "Benasque Center for Science", Benasque, Spain, from August 27, 2006 to September 10, 2006. Benasque is a beautiful town in the heart of the Pyrenees. The school will take place from August 27 (Day 0 - arrival of students for the school) to September 6, and the workshop will start September 6 (arrival of participants to the workshop) and finish on September 11 (departure of all participants).

See http://benasque.ecm.ub.es/.

Participants

The call for participation will be mainly directed to students and scientists specialized on computational physics, quantum chemistry and biophysics. We will limit the number of students to the school to 35 and participants to the workshop to less than 100, in order to ensure a maximum interaction between all the scientists participating. Attendance of graduate students and postdocs will be strongly encouraged through the inclusion of short contributed talks and a poster session. Furthermore, we will award to PhD students who present an outstanding poster short oral presentations.

Applications/Support:

School/Workshop:

All persons who wish to participate should fill out the application form at http://benasque.ecm.ub.es/2006tddft/2006tddft.htm

In the comments section, please indicate if you wish to participate in the Summer Summer School or in the Workshop (or in both).

School only:

As we have a very limited number of places for the school (35), students will be selected from among an open pool of applicants who have demonstrated a strong interest in computational sciences, applied to chemistry, physics, materials science and biology. Therefore, in order that we can make a reasonable selection, we ask that *all* candidates include in the comments section the following information:

1) Date of birth
2) Sex
3) Motivation/Why they want to come (just a couple of lines is enough)
4) What is their current and previous positions (if PhD or Post- doc state your supervisor).

We will not accept applications that do not include this information. Furthermore, we will give priority to students willing to participate in both the Summer School and the Workshop.

We also have a certain number of grants available that cover traveling and part of the stay in Benasque. If you want to apply for a grant, please indicate explicitly that you wish to be supported in the comments section, and explain why (just a couple of lines is enough).

For participants coming from the USA, please check the following address for support:

http://www.mcc.uiuc.edu/travel/

3.2.2 Summer School on Electronic Structure Calculations and Correlated Materials

Les Houches, France

August 27th to September 8th 2006

Sponsored by: Ecole Predoctorale des Houches, Psik Network

Organized by: Silke Biermann, CPHT, Ecole Polytechnique, France

www.cpht.polytechnique.fr/LesHouches.html

In recent years, electronic structure calculations for materials with strong electronic Coulomb correlations have developed into a new research field at the border between band structure theory and quantum many-body problems. The summer school will give an introduction to different aspects of the field ranging from density functional theory and dynamical mean field concepts to the physics of the Mott transition.

For details please refer to

www.cpht.polytechnique.fr/LesHouches.html

4 General Workshop/Conference Announcements

4.1 Workshop on ”First-principles approaches to optical and photoelectron spectra”

9-12 March 2006 at the University of Munich

Organized by:

Claudia Ambrosch-Draxl (University Graz)
Hubert Ebert (Ludwig-Maximilian University Munich)
Eberhard K.U. Gross (Free University Berlin)
Elisa Molinari (University of Modena and Reggio Emilia)

The workshop aims to bring together theoreticians developing and using first-principles approaches to calculate optical and photoelectron spectra. Emphasis will be on new developments concerning the treatment of correlation effects when dealing with the underlying electronic structure as OPM, TLDA, GW, LDA+U or LDA+DMFT. Although the workshop is focused on theory, there will be several invited talks by experimentalists giving a review on new developments in the field. Further experimental contributions are welcome.

The workshop is financed by the Deutsche Forschungsgemeinschaft within the Priority Programme ”Modern and universal first-principles methods for many-electron systems in chemistry and physics”

(http://www.uni-koeln.de/spp1145/)

and by the Network ”Exciting” of the European Union

(http://www.exciting.physics.at/)

For further information see:

http://olymp.cup.uni-muenchen.de/ak/ebert/FOPS06/

Preliminary List of Invited Speakers:

M. Aeschlimann (Kaiserslautern, Germany)
S. Blügel* (Jülich, Germany)
N. Brookes* (ESRF, France)
N. E. Christensen* (Aarhus, Denmark)
E. Chulkov (San Sebastian, Spain)
R. Di Felice* (Modena, Italy)
A. Ernst* (Halle, Germany)
X. Gonze/R. Shaltaf (Louvain la Neuve, Belgium)
O. Gunnarson* (Stuttgart, Germany)

J. Henk (Halle, Germany)
U. Hohenester (Graz, Austria)
W. Hübner/Y. Pavlyukh (Kaiserslautern, Germany)
J. Inglesfield (Cardiff, England)
W. Ku (Brookhaven National Laboratory, USA)
A. Lichtenstein* (Hamburg, Germany)
M. Lindroos (Tampere, Finnland)
J. Osterwalder/M. Hensberger (Zürich, Schwitzerland)
G. Panaccione* (Trieste, Italy)
M. Potthoff (Würzburg, Germany)
P. Puschnig (Montanuniversität Leoben, Austria)
L. Reining* (Paris, France)
W. Schattke* (Kiel, Germany)
S. Sharma (FU Berlin, Germany and KFU Graz, Austria)

* to be confirmed

4.2 Science Summer Institute at LLNL

COMPUTATIONAL CHEMISTRY AND MATERIAL SCIENCE SUMMER INSTITUTE

LAWRENCE LIVERMORE NATIONAL LABORATORY

We are pleased to announce the sixth year of the Computational Chemistry and Material Science (CCMS) Summer Institute at the Lawrence Livermore National Laboratory (LLNL).

The goal of the Summer Institute is to provide an opportunity for graduate students to explore and learn some of the cutting-edge methods in computational materials sciences, computational chemistry, and other related areas of computational science during their first few years of graduate study. Each student will spend ten weeks at LLNL as the guest of an LLNL host scientist working on a computational project in the host's area of expertise. In addition, computational science leaders from universities and laboratories around the country will present a series of mini-courses for the students. These courses will cover state-of-the-art and emerging computational methods in materials science and chemistry, such as computational nanoscience, computational chemistry, computational simulation of materials based on coarse graining and multi-scale modeling, to name a few.

Students will be selected from among an open pool of applicants who have demonstrated a strong interest in computational sciences, especially materials science and chemistry. The Institute will run from June 7 to August 18, 2006. Travel funds and a salary in the range of 3500−4000 per month will be provided to the participants.

Please bring this announcement to the attention of graduate students that you feel would benefit from the experience of hands-on research in computational chemistry and materials science, working with leading researchers at a national laboratory.

To apply for the CCMS summer institute, please fill out the application form for job posting number 004965 at the LLNL jobs website, jobs.llnl.gov or click on the link below

`http://jobs.llnl.gov/psc/jobs/EMPLOYEE/HRMS/s/WEBLIB_LL.VIEW_JOBS_LL.FieldFormula.IScript_`

The application deadline is February 1, 2006.

More details about the institute can be found on the institute website

`http://www-cms.llnl.gov/ccms_summer_inst/index.html`

Please direct any inquiries to Nancy Hutcheon, the administrator for the summer institute at

hutcheon3@llnl.gov

Andrew Williamson

Academic Director, CCMS Summer Institute
williamson10@llnl.gov

Mike McElfresh
Director, CCMS Summer Institute
mcelfresh1@llnl.gov

4.3 42nd Symposium on Theoretical Chemistry

”Quantum Chemistry: Methods and Applications”

September 3 - 6, 2006

Erkner (near Berlin), Germany

The Symposium will consist of 12 invited lectures, 22 contributed lectures (20 min) selected from submissions and posters.

You are cordially invited to register and submit abstracts for posters /short (contributed) lectures.

Details can be found on the Internet:

`http://www.chemie.hu-berlin.de/ag_sauer/stc2006/index.html`

Looking forward to your application,

Joachim Sauer
(Chairman)

5 General Job Announcements

Post-doc Opening on Electronic Transport in Nanostructures

A post-doc position available in the group associated to Theory and Modeling of the FAME European Network of Excellence (www.famenoe.org) in order to work jointly with P. Ordejon (CSIC-Barcelona, Spain), R. D. Levine (HUJI, Israel), J.-C. Charlier (UCL, Belgium) and F. Remacle and Ph. Ghosez (ULg, Belgium)

- Research project

The research project concerns the quantum modeling of electronic transport properties in nanostructures. The objectives are to set up a unified software for the first-principles modeling of transport properties based on an open-version of tranSIESTA, and to apply it for the study of the electronic transport in organic molecules, carbon nanotubes and ferroelectric tunnel junctions.

- Practical aspects

The initial contract will be for one year, with possible renewal for one more year, and could start as early as January 2006. The position will be formally attached to the University of Liege (Belgium) but the candidate will share his/her time between the different partners. After an initial period at the CSIC-Barcelona (P. Ordejon), the candidate will plan scientific stays at HUJI (R. D. Levine), UCL (J.-C. Charlier) and ULg (F. Remacle & Ph. Ghosez) in order collaborate with these teams in the use of tranSIESTA for computations on the specific systems mentioned above and to implement within tranSIESTA additional theoretical approaches as developed locally.

- Candidate

The candidate should have a PhD in Physics, Applied Physics or Theoretical Chemistry, a background in the first-principles modeling of transport properties, and a good experience in coding. Knowledge of tranSIESTA is not mandatory but would be appreciated.

- Application

Candidates can send

(i) a letter of motivation,
(ii) a CV and
(iii) two recommendation letters

to Prof. Philippe GHOSEZ (Philippe.Ghosez@ulg.ac.be).

Postdoctoral Position

Chemical Engineering Department at the Pennsylvania State University

A postdoctoral position at the interface between Computational Materials Physics and Computational Fluid Dynamics is available in the Chemical Engineering Department at the Pennsylvania State University. The project has a specific focus on multi-scale modeling of catalysis at solid surfaces. It involves coupling continuum fluid-phase simulations with ab initio kinetic Monte Carlo simulations of catalysis at surfaces to understand the coupling between continuum and molecular phenomena across disparate length and time scales. Candidates should have experience with continuum simulation of fluid flow, heat, and mass transport, knowledge of chemical kinetics, and, preferably, experience with molecular-level simulations, such as kinetic Monte Carlo. They should also have a keen interest in multi-scale modeling and interacting with experimentalists. The postdoc will work jointly with Prof. Kristen Fichthorn and Prof. Antonios Armaou at Penn State, as well as with Prof. Matthias Scheffler at the Fritz-Haber-Institut der Max-Planck-Gesellschaft in Berlin, Germany. Information about these research groups can be found at:

Fichthorn: http://fenske.che.psu.edu/Faculty/Fichthorn/index.html
Armaou: http://fenske.che.psu.edu/Faculty/Armaou/index.html
Scheffler: http://www.fhi-berlin.mpg.de/th/th.html

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

For more information or to apply, please contact Prof. Kristen Fichthorn:

Prof. Kristen A. Fichthorn
Dept. of Chemical Engineering
Penn State University
University Park, PA 16802

Phone: 814 863 4807
E-mail: fichthorn@psu.edu

POST-DOC OPENING IN THEORETICAL/COMPUTATIONAL PHYSICS

IEMN, Lille, France

Starting in 2006

A post-doc position is available in the theoretical physics group at the IEMN (institute for electronics, microelectronics and nanotechnology). The work will be in collaboration with Silvana Botti (LSI, Ecole Polytechnique, Paris;

`http://theory.lsi.polytechnique.fr/`)

and with Ludger Wirtz (IEMN - Dept. ISEN, Lille;

`http://www.isen.fr/~delerue/nanocristaux.html`).

RESEARCH PROJECT: The research project concerns the calculation of electronic excitations in nanotubes and nanowires. Both ab-initio techniques and semi-empirical techniques will be used. One important aspect will be the implementation of the techniques of many-body perturbation theory (GW-method and Bethe-Salpeter equation) in the framework of a tight-binding approximation. Once the methodology is developed, it will be applied to study the optical absorption and luminescence spectra of different nanotubes (C, BN, and MoS2) and of different nanowires (e.g., Si, Ge, GaAs, GaN). The project is embedded in the NANOQUANTA European network of excellence

(http://www.cmt.york.ac.uk/nanoquanta/)

and its initiative to build a European Theoretical Spectroscopy Facility (ETSF),

http://theory.polytechnique.fr/etsf/.

PRACTICAL ASPECTS:

The position is funded by the French National Research Agency (ANR). The initial contract will be for one year with possible renewal for 1 more year. It could start as early as January 2006. The position will be formally attached to the IEMN (Villeneuve d'Ascq) but the candidate will share his/her time between the IEMN and the Ecole Polytechnique. Short visits to other nodes of the NANOQUANTA network are encouraged to develop the project.

CANDIDATE:

The candidate should have a PhD in Physics, Theoretical Chemistry, or Material Science. He/she should have a background in solid-state physics and in numerical calculation/coding.

APPLICATION:

Please send (i) a letter of motivation, (ii) a CV, and (iii) the coordinates of one or two persons willing to write a letter of recommendation to Ludger.Wirtz@isen.fr or Silvana.Botti@polytechnique.fr.

Do not hesitate to contact us for further questions.

Two postdoc positions
Donostia International Physics Center (DIPC), Spain

Two postdoc positions have been opened at the Donostia International Physics Center (DIPC). The topics of research are:

"Theory and simulation of the conduction through nanostructures", contact person Dr. D. Sanchez-Portal, sqbsapod@sc.ehu.es

"Nanophotonics and opto-electronic properties of nanostructures", contact person Dr. J. Aizpurua, aizpurua@sc.ehu.es

Opening of a postdoc position in Condensed Matter Physics at the Donostia International Physics Center, San Sebastián, Spain:

"Theory and simulation of the conduction through nanostructures"

This postdoc position is part of a long-term program to investigate theoretically several aspects of the physics of complex nanostructures. The focus will be on the description of the conduction properties through molecular bridges, nanowires and other nanostructures. The purpose of this project is twofold: on the one hand, collaborations with several experimental groups will be established (these groups are involved in the project NANOTRON, funded by the Basque Government and the Diputación de Guipúzcoa); on the other hand, a deeper understanding of the physics involved in these processes will be also pursued. To learn more about the most recent work of the group visit http://dipc.ehu.es. The candidates should have a strong background in computation and Solid State Physics.

Interested candidates should contact with Dr. Daniel Sánchez-Portal, sqbsapod@sc.ehu.es

Opening of a postdoc position in Condensed Matter Physics at the Donostia International Physics Center, San Sebastián, Spain:

"Nanophotonics and opto-electronic properties of nanostructures"

This postdoc position is part of a long-term program to investigate theoretically several aspects of the physics of complex nanostructures. The purpose of the present project is to develop and apply tools to simulate nanoscale optical microscopy and spectroscopy. This is challenging due to the need to describe light fields from the near-field to the far-field, to determine the influence of the probe, and to identify any contribution of the local environment. Metal nanostructures will be studied to develop uses in key applications such as field-enhanced spectroscopies, near-field scanning optical microscopy (NSOM), or single molecule spectroscopy. To learn more about the most recent work of the group visit http://dipc.ehu.es. The candidates should have a strong background in computation and Solid State Physics. This research is part of the NANOTRON project, funded by the Basque Government and the Diputación de Guipúzcoa.

Interested candidates should contact with Dr. Javier Aizpurua, aizpurua@sc.ehu.es

Ph. D. and Postdoctoral Openings in Condensed Matter Theory

Institute for Theoretical Physics
University of Regensburg, Germany

There are several PhD and postdoc positions available in the University of Regensburg (contact angela.reisser@physik.uni-r.de for details). In my group there are PhD and postoc positions open, one delaing with GaMnAs (ab initio band structure, in collaboration with Claudia Ambrosch-Draxl, now in Leoben), the other dealing with spin transport theory in spintronic classical and quantum device structures and spin injection. For these two positions you can contact me directly.

Prof. Dr. Jaroslav Fabian
Institute for Theoretical Physics
University Regensburg
93040 Regensburg, Germany

Tel: (49-941) 943 2028 Fax: (49-941) 943 4382 E-mail: jaroslav.fabian@physik.uni-regensburg.de
http://www.physik.uni-regensburg.de/forschung/fabian

Two Ph. D. Positions

Chair of Atomistic Modelling and Design of Materials
University of Leoben, Austria

Two PhD positions (for 3 years) are available at the recently established Chair of Atomistic Modelling and Design of Materials of the University Leoben, Austria. The main goal of the work is a first-principles study on the conformation and orientation of molecules in organic thin films. Thereby the surface terminations will be investigated as well as the interfaces with different substrates. These studies aim towards the understanding of the structural properties and growth conditions of organic thin films. Besides, the corresponding physical properties will be calculated for such structures. The methods to be applied are based on density functional theory (DFT), and include manybody perturbation theory for the description of excited state properties.

The project is part of a National Research Network of the Austrian Science Fund (FWF) including 10 research groups. Hence there will be strong interaction with experimentalists and joint workshops.

The candidates should have deep knowledge in ab-initio calculations based on DFT, a strong background in theoretical solid state physics, and preferably experience in code development. Students who enjoy working in a team, collaborate with experimentalists, and contribute to the friendly atmosphere of the group are highly welcome!

Applications should be sent via email to Claudia Ambrosch-Draxl (cad@mu-leoben.at).

Claudia Ambrosch-Draxl
Chair of Atomistic Modelling and Design of Materials
Department Material Physics, University Leoben
Erzherzog Johann - Straße 3, A-8700 Leoben
Tel. +43 3842 402 4400
Fax +43 3842 402 4402

Postdoctoral Position in Condensed Matter Physics

Multiscale Simulations of Plasticity in Glasses

Université Claude Bernard Lyon 1, Lyon, France

We would like to announce the opening of a post-doc position for one year, extendable to a second year at the ”Laboratoire de Physique de la Matière Condensée et Nanostructures”, Université Lyon 1 (France). The preferred starting date would be between Septembre 2006 and January 2007. The succesfull applicant will work in the modelisation group on the simulation and understanding of the elementary processes of glass plasticity.

The modelling techniques will include atomic scale QM/MM simulations based on the LOTF scheme as well as molecular dynamics and analytic approaches. Some development on the QM/MM code will be needed to adapt the technique to the simulations of glassy systems.

The applicants should demonstrate a solid background in condensed matter physics, mechanics and statistical physics, a good experience in ab-initio and/or molecular dynamics techniques and will preferably have some experience in scientific code development in F90 or C programming languages. Moreover, a good knowledge of random processes and diffusion equations will be greatly appreciated.

This project is founded by the french governement through the ANR framework PlastiGlass and involves close collaborations with others theoretical and experimental groups in Lyon, Montpellier and Paris (France). These collaborations as well as possible interactions with groups developping the LOTF method in foreign countries should provide an exciting and challenging working environment for young scientist.

Applicants should send to the contact below (see adress below) a detailed CV, one or two representative publications and a cover letter in which they will precise their research interests, the date of their availability and the address of at least two academic references that can be contacted confidentially.

Contacts:
Anne Tanguy et Tristan Albaret,
Laboratoire de Physique de la Matière Condensée et Nanostructures, UMR5586 Université Lyon 1 / CNRS
emails : anne.tanguy@lpmcn.univ-lyon1.fr, tristan.albaret@lpmcn.univ-lyon1.fr
tel : +33(0)4 72 43 15 71 / +33(0)4 72 43 15 65
Fax : +33(0)4 72 43 26 48

Postdoctoral Fellowship
in Condensed-Matter Atomistic Modeling
Commissariat à l'Energie Atomique, Bruyères-le-Châtel, France

Applications are invited for a post-doctoral position based in Bruyères-le-Châtel (35 km from Paris), within the atomistic simulation group of the Electronic and Optoelectronic Hardening Laboratory of Commissariat à l'Energie Atomique (CEA). Our lab consists of 10 researchers with national and international collaborations and conducts applied research in the fields of microelectronic and optoelectronic hardening.

This position is for a one-year term, extendable by one year and will start from February 2006.

The research will focus on growth of HfO_2 on silicon surface; electronic structure calculations using ab initio methods will be used to investigate the reaction of molecules containing Hf on the silicon surface. Collaborations with national and international experimental labs will allow getting an experimental validation of calculations. A Ph. D. in quantum chemistry or in condensed matter simulation and experience of ab initio (DFT) calculations are essential.

Informal enquiries about the post and how to apply can be made to Dr N Richard by e-mail (nicolas.richard@cea.fr). They should include a full CV and a list of publications.

Nicolas Richard
CEA-Bruyères-le-Châtel

Postdoctoral Position

Max-Plank-Institute for Polymer Research, Mainz, Germany

A postdoctoral position in computational materials science is available at the Max-Plank-Institute for Polymer Research, Mainz, Germany (http://www.mpip-mainz.mpg.de).

The research project concerns combining the atomistic simulations with quantum modeling of electronic transport properties. The calculations will be applied to study the electronic transport in self-assembling organic systems and conjugated polymers.

The initial contract will be for one year, with possible renewal, and could start as early as January 2006. The candidate should have a Ph.D. in Physics, Applied Physics or Theoretical Chemistry, a background in the first-principles modeling of transport properties, and a good experience in coding.

Interested scientists should send an application, a CV, and two recommendation letters to Prof. Kurt Kremer (kremer@mpip-mainz.mpg.de).

Post-Doctoral Positions

COMPUTATIONAL MATERIALS SCIENCE CENTER NATIONAL INSTITUTE FOR MATERIALS SCIENCE, TSUKUBA, JAPAN

Applications are invited for one or two post-doctoral positions at the Computational Materials Science Center, National Institute for Materials Science (CMSC-NIMS) in Tsukuba, Japan. The initial appointment will be for one year, but can be renewed every year for up to three years.

NIMS is one of the world's largest materials research centers, and CMSC is a major grouping of researchers within the Institute, having a strong focus on materials modeling using first-principles methods. The successful candidate(s) will work in the FPS1 group (First-Principles Simulation Group 1) within CMSC-NIMS, together with Dr. T. Miyazaki as well as the group leader, Dr. T. Ohno. The FPS1 group currently has five permanent members of staff and seven post-docs. For further details of the group, see http://www.nims.go.jp/cmsc/.

The aim of the research project supporting the post-doctoral positions is to apply large-scale first-principles simulations to investigate the structure and physical properties of nano-structured materials and bio-materials. The work of the post-doc(s) will include the development and application of the linear-scaling first-principles code CONQUEST for the study of such materials. CMSC has access to exceptional computational resources, and the successful candidate(s) will use supercomputers such as the Hitachi SR11K at NIMS and the Earth Simulator in Yokohama for large-scale simulations. The project will be performed in close collaboration with Prof. M. J. Gillan and Dr. D. R. Bowler at the London Centre for Nanotechnology, a joint research centre hosted by UCL and Imperial College.

Applicants must have, or expect to obtain before the start of the work, a Ph.D. in a relevant discipline. A strong background in theoretical condensed matter science and experience with electronic structure methods are essential, and a knowledge of bio-materials or biophysics is desirable.

The appointment will initially be for one year, but the available funding provides for renewal of the appointment every year for up to three years. The salary will depend on age and experience, but will not be less than 5.2 million yen per year. The initial deadline for applications is February 28, 2006, but the search for candidates will continue until the positions are filled.

Candidates should send the following by e-mail in Word, pdf or html format:

1. CV
2. List of publications
3. Reprints of three selected papers
4. Summary of past accomplishments
5. Names and e-mail addresses of two referees.

Contact Information:

Dr. Takahisa Ohno,
Computational Materials Science Center,
National Institute for Materials Science (NIMS),
1-2-1 Sengen, Tsukuba, Ibaraki 305-0047, JAPAN
e-mail: OHNO.Takahisa@nims.go.jp
e-mail: MIYAZAKI.Tsuyoshi@nims.go.jp
phone: +81-29-859-2622
fax : +81-29-859-2601

For candidates in Europe, informal enquiries to Prof. Mike Gillan (m.gillan@ucl.ac.uk) or Dr. David Bowler (david.bowler@ucl.ac.uk) are strongly encouraged.

PhD Studentship in Theoretical Chemistry

Department of Chemistry, University of Cambridge, UK

COMPUTER SIMULATION OF AQUEOUS RADICAL OXYGEN SPECIES

An EPSRC PhD studentship is available from October 2006 to work on a project in the research group led by Professor Michiel Sprik. The project involves a computational study of reactive oxygen species (hydroxyl, peroxyl and superoxide radicals) and their reactions with organic molecules in solution using density functional based ab initio molecular dynamics simulation (”Car-Parrinello”). The project is part of a wider research programme for the development of computational methods for first principle simulation of redox reactions

Candidates should have, or be about to receive, an honours degree (at least II.1 or equivalent) in chemistry, physics or a related discipline. Experience with computer simulations is helpful, but not required. The studentship offers full costs (fees plus stipend) for 42 months for UK and EU citizens, who satisfy the eligibility criteria of the UK Research Councils. The studentship is not available to citizens of non-EU countries.

Applications should include a CV and the names of two referees, and should be sent to: Professor Michiel Sprik, Department of Chemistry, Lensfield Rd, Cambridge CB2 1EW, UK. Informal enquiries may also be made to Professor Sprik (tel: +44 (0)1223 336314; email:ms284@cam.ac.uk).

Information is also available at

http://www-theor.ch.cam.ac.uk/people/sprikgroup/

Closing date for applications is February 28th, 2006.

Post-Doctoral Position
Institute of Nuclear Physics of Orsay, France

A post-doctoral position in computational materials science for one year (extendable to a second year) is available at the Institute of Nuclear Physics of Orsay (FRANCE, nearby Paris). The starting date is between September and October 2006.

The candidates should have deep knowledge in ab initio calculations based on DFT, as well as a good experience with modelling codes as Gaussian03 and/or VASP. Accomplished research work in the field of the adsorbate-surface interactions with cluster and/or periodic approaches is highly desirable.

This project is funded by the French National Research Agency (ANR). The candidate will join the theoretical team of the Nuclear Physics Institute of Orsay and will also have to collaborate with our theoretical French partner groups.

The successful candidate will have to deal with the theoretical part of a general environmental study

of the migration of toxic elements in the geosphere (radiotoxic elements are of primary importance in the field of a deep geological storage of nuclear wastes).

In this study, the considered surfaces are the titanium oxide (TiO2, rutile) and the aluminium hydroxide (Al(OH)3, gibbsite). The adsorbates under interest are water molecules, an oxocation (UO22+) and two oxoanions (SeO32- and SeO42-).

The main goals of the theoretical part are:

1) The modelling of the most stable faces of the TiO2 and Al(OH)3 surfaces with cluster as well as periodic approaches.

2) The study of the water interaction with these surfaces.

3) The investigation of the UO22+, SeO32- and SeO42 adsorptions.

Theoretical results will be correlated with experimental data obtained by our partner teams (spectroscopic techniques: XPS, DRIFT, SHG, Raman, TRLFS, and XAS).

Interested candidates are invited to send:

(1) a full CV,
(2) a list of publications,
(3) two recommendation letters

to Jerome Roques (roques@ipno.in2p3.fr)

Two Ph. D. Positions
at the Fritz Haber Institute, Berlin, Germany

The Theory Department of the Fritz Haber Institute of the Max-Planck-Society invites applications for two Ph.D. studentships funded through the newly established Marie Curie early stage training network, MONET: Molecular Networks at Phase Boundaries.

Research in our department is aimed at understanding important phenomena in surface-, materials-, and nano-science. With about 50 scientists from many countries the Theory Department provides a lively and stimulating international atmosphere for students in one of Europe's most vibrant capital cities. For more information of the Theory department see:

http://www.fhi-berlin.mpg.de/th/th.html

We are looking for highly qualified students from physics, chemistry, and materials science that hold a Masters Degree (or equivalent) and fulfill the requirements of nationality and residence as outlined on the MONET website:

http://www.sljus.lu.se/monet/index.html

Further details of the proposed PhD projects can also be found at the MONET site.

We will consider applications until the positions are filled.

Please send your application by email or regular mail to

Dr Angelos Michaelides
Fritz-Haber-Instituts der MPG
Faradayweg 4 - 6
D-14195 Berlin, Germany

E-mail: michaeli@fhi-berlin.mpg.de
WWW: http://www.fhi-berlin.mpg.de/th/th.html

TWO POSTDOCTORAL POSITIONS IN THE FIELD OF FIRST-PRINCIPLES ELECTRONIC STRUCTURE CALCULATIONS OF NANO-MATERIALS

NATIONAL INSTITUTE OF MATERIALS SCIENCE, TSUKUBA, JAPAN

We would like to encourage young motivated individuals, who have strong interest in first-principle electronic structure calculations for large systems and/or the physics of complex oxide materials to apply for two postdoctoral research positions, which will be available in the First-Principles Simulation Group II at the National Institute for Materials Science in Tsukuba, Japan.

The First-Principles Simulation Group II currently includes five permanent members: T. Sasaki, K. Kobayashi, M. Arai, R. Maezono, and I.V. Solovyev. The current topics of research interests include:

(1) THEORETICAL MATERIAL SCIENCE OF STRONGLY-CORRELATED SYSTEMS: namely, the application of the existing methods of first-principles electronic structure calculations for the analysis and design of properties of strongly-correlated materials.
(2) MODELLING OF STRONGLY-CORRELATED SYSTEMS: construction of the effective model Hamiltonians using results of first-principles electronic structure calculations, and the analysis of electronic and magnetic properties of strongly-correlated systems on the basis of the obtained models.
(3) DEVELOPMENT OF NEW METHODS OF ELECTRONIC STRUCTURE CALCULATIONS FOR STRONGLY-CORRELATED SYSTEMS: mainly the work on the development and applications of ab-initio Quantum Monte-Carlo methods.

Some details can be obtained from

http://www.nims.go.jp/cmsc/fps2/index.html.

The positions will be available for one year with the possibility of renewal up to three years.

The deadline for applications is 31 May 2006.
The expected job starting date is 1 July 2006.

Although it is relatively flexible, the successful candidate will be involved in one of the following projects:

(1) molecular magnets and magnetism of nano-materials;
(2) study of electron correlation in oxide materials using ab-initio Quantum Monte-Carlo methods;
(3) analysis of the lattice distortion and the electron-lattice interaction in transition-metal oxides and related compounds.

Tsukuba is the newly developed scientific city located in 60 km north to Tokyo (and now connected with Tokyo by fast express train).

The interested candidate should submit the curriculum vitae, list of publications, a brief description of research experience and interests, and arrange two recommendation letters addressed to

Dr. Taizo Sasaki,
Computational Materials Science Center,
National Institute for Materials Science,
1-2-1 Sengen, Tsukuba,
Ibaraki 305-0047, Japan

Further details can be obtained via e-mal to SASAKI.Taizo@nims.go.jp

Postdoctoral/Ph. D Position

Physics Department, King's College London, London, United Kingdom

Research Fellowship in Physics
Atomistic simulations of large organic molecules on crystal surfaces
using hybrid methods

Applications are invited for a post-doctoral appointment related to ab initio and semiclassical modelling of large organic molecules on crystal surfaces. This work will require development of necessary ab initio and semiempirical hybrid electronic structure methods which can be used to do realistic static and dynamic simulations of large organic molecules on metal, semiconducting and insulating crystal surfaces. The project is a part of the much bigger PICO-inside project, funded by the EU within the FP6 initiative, whose goal is to understand if it is possible to construct a computational devise out of a single, most likely large, molecule anchored to a surface. Our partners include a number of well-known theoretical and experimental groups in the UK and in Europe. Therefore, the work on the project will be done in a close collaboration with other groups within the consortium.

Applicants should have a PhD in solid state physics or chemistry and possess strong computational skills, including Unix/Linux and Fortran (77 or 90). Experience in semiclassical atomistic simulations, ab initio electronic structure methods, including the methods based on the Density Functional Theory, as well as code development skills are essential. Applicants who have experience in atomistic simulations related to surface physics/chemistry, nanotechnology, AFM and/or STM are at an advantage. The Solid State group at KCL has an attractive working environment in the centre of London and excellent computational facilities that will be supplemented by additional computational resources associated with the project.

The position is available from the 1st March 2006, initially for 18 months (with the possibility of extending it for up to 34 months). The salary is offered on the RAII from 24,352 to 36,959 plus 2,323 pa London Allowance.

Further particulars are available by contacting the Personnel Office, King's College London, Strand, London WC2R 2LS, strand- recruitment@kcl.ac.uk, fax 020 7848 1352. Please quote reference W2/CCP/XXX/05 on all correspondence.

Informal inquiries are welcomed and should be directed to
Dr. Lev Kantorovich (email: lev.kantorovitch@kcl.ac.uk,
tel: (+44) (0)20- 78482160, fax: (+44) (0)20-8482420).

The closing date for applications is 1st February 2006, but may be extended if necessary.

Equality of opportunity is College policy

Postdoctoral Research Associate

Computational Modelling of Polymer Optoelectronic Devices
Department of Physics and Astronomy, University of Sheffield, Sheffield, United Kingdom

This is a theoretical/computational project focussed on understanding the role of polymer structures on three important and related electronic processes that determine the performance and efficiency of polymer optoelectronic devices. The ultimate aim is to devise strategies to enhance the perfomance of these devices. Applicants should have a strong background in theoretical and computational condensed matter physics or chemistry.

This EPSRC funded posted is available for three years from May 2006 (or as soon as possible thereafter). Salary £23,457 - £30,607 per annum.

Closing date 3rd March, 2006.

For full details and information pack visit www.sheffield.ac.uk/jobs or e.mail jobs@sheffield.ac.uk (quoting ref. R3832).

For informal enquiries contact Dr. W. Barford (W.Barford@sheffield.ac.uk)

POSTDOCTORAL POSITION IN COMPUTATIONAL NANOSCIENCE

JYVÄSKYLÄ, FINLAND

Post-doctoral research position with the focus area of ”Electronic structure and conductance properties of molecule-metal junctions” is available immediately in the Computational Nanoscience group (nano.jyu.fi/groups/compns) in the Nanoscience Center (NSC) of the University of Jyvaskylä. Successful candidate has a background of materials physics or solid state theory, is familiar with computational aspects of modern electronic structure theory and has good programming skills (C/Fortran). Preference is given to candidates who have experience in development and/or implementation of methods suitable for calculations of conductivity through nanostructures. The position is available immediately with a mutually agreed starting date. The initial appointment is for one year with a provision of extension up to three years on a yearly basis. The starting salary will be in the range of 30000 to 36000 EUR/year (taxable) depending on the qualifications and seniority. The salary level will be evaluated on a yearly basis according to the new salary system implemented by Finnish Universities.

The applicant should send a CV, list of publications and two letters of recommendation as PDF documents to Docent Hannu Häkkinen, (hannu.hakkinen@phys.jyu.fi).

Evaluation of applications begins March 1, 2006.

For more information on the research at NSC, see nano.jyu.fi.

Hannu Häkkinen
NSC and Department of Physics
FI-40014 University of Jyväskylä, Finland
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hannu.hakkinen@phys.jyu.fi
nano.jyu.fi/groups/compns

6 Abstracts

Managing the supercell approximation for charged defects in semiconductors: finite size scaling, charge correction factors, the bandgap problem and the ab initio dielectric constant.

C.W.M. Castleton[1,2,†], A. Höglund[3] and S. Mirbt[3]
1 Materials and Semiconductor Physics Lab, IMIT, KTH, Sweden.
2 Dept of Physical Electronics/Photonics, Mid Sweden University, Sundsvall, Sweden.
3 Dept of Physics, Uppsala University, Sweden.

Abstract

The errors arising in *ab initio* density functional theory studies of semiconductor point defects using the supercell approximation are analyzed. It is demonstrated that a) the leading finite size errors are inverse linear and inverse cubic in the supercell size, and b) finite size scaling over a series of supercells gives reliable isolated charged defect formation energies to around ±0.05 eV. The scaled results are used to test three correction methods. The Makov-Payne method is insufficient, but combined with the scaling parameters yields an *ab initio* dielectric constant of 11.6±4.1 for InP. Γ point corrections for defect level dispersion are completely incorrect, even for shallow levels, but re-aligning the total potential in real-space between defect and bulk cells actually corrects the electrostatic defect-defect interaction errors as well. Isolated defect energies to ±0.1 eV are then obtained using a 64 atom supercell, though this does not improve for larger cells. Finally, finite size scaling of known dopant levels shows how to treat the band gap problem: in ≤200 atom supercells with no corrections, continuing to consider levels into the theoretical conduction band (extended gap) comes closest to experiment. However, for larger cells or when supercell approximation errors are removed, a scissors scheme stretching the theoretical band gap onto the experimental one is in fact correct.

(Accepted to appear in Phys Rev B)
Preprint available from http://teoroo.mkem.uu.se/cwmc/

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Femtosecond Dynamics in Ferromagnetic Metals Investigated with Soft X-Ray Resonant Emission

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N. B. Brookes
ESRF, B.P. 220, F-38043 Grenoble Cedex, France

Abstract

We present measurements of the magnetic circular dichroism in x-ray resonant emission in the perpendicular geometry (circularly polarized x-rays at normal incidence to the magnetization) for the $L_{2,3}$ absorption region in Fe, Co and Ni metal. The results show that spin-dependent screening of the core-hole takes place within the scattering time scale, which is supported by the absence of the effect in ionic systems. This allows an assessment of the time scale for the screening process (up to a few femtoseconds). The process is almost complete within the scattering time for Fe and Co, but this is not the case for the narrow band metal Ni which shows a much slower dynamics.

Accepted for publication in Physical Review Letters **95**, 267402 (2005).
Manuscript available from g.vanderlaan@dl.ac.uk

Oxygen adsorption and stability of surface oxides on Cu(111): A first-principles investigation

A. Soon, M. Todorova and C. Stampfl
School of Physics, The University of Sydney, Australia
B. Delley
Paul-Scherrer-Institut (PSI), Villigen, Switzerland

Abstract

As a first step towards gaining microscopic understanding of copper-based catalysts, e.g. for the low-temperature water-gas shift reaction and methanol oxidation reactions, we present density-functional theory calculations investigating the chemisorption of oxygen, and the stability of surface oxides on Cu(111). We report atomic geometries, binding energies, and electronic properties for a wide range of oxygen coverages, in addition to the properties of bulk copper oxide. Through calculation of the Gibbs free energy, taking into account the temperature and pressure via the oxygen chemical potential, we obtain the (p, T) phase-diagram of O/Cu(111). Our results show that for the conditions typical of technical catalysis the bulk oxide is thermodynamically most stable. If, however, formation of this fully oxidized surface is prevented due to a kinetic hindering, a thin surface-oxide structure is found to be energetically preferred compared to chemisorbed oxygen on the surface, even at very low coverage. Similarly to the late $4d$ transition metals (Ru, Rh, Pd, Ag), sub-surface oxygen is found to be energetically unfavourable.

(Submitted to Phys. Rev. B)

Contact person: aloysius@physics.usyd.edu.au

Anisotropy of Earth's D" layer and stacking faults in $MgSiO_3$ post-perovskite

Artem R. Oganov, Roman Martonak, Alessandro Laio, Paolo Raiteri, Michele Parrinello
Laboratory of Crystallography, Department of Materials, ETH Zürich, Switzerland

Abstract

The post-perovskite phase of $(Mg,Fe)SiO_3$ (PPv) is believed to be the main mineral phase of the Earth's D" layer (2700-2890 km depths). Its properties explain numerous geophysical anomalies associated with this layer: e.g., the D" discontinuity, its topography and seismic anisotropy. Here, using a novel simulation technique, first-principles metadynamics, we identify a family of low-energy polytypic stacking-fault structures intermediate between perovskite (Pv) and PPv. Metadynamics trajectories identify plane sliding involving the formation of stacking faults as the most favourable pathway for the Pv-PPv phase transition, and as a likely mechanism for plastic deformation of Pv and PPv. In particular, the predicted slip planes are 010 for Pv (consistent with experiment) and 110 for PPv (in contrast to the previously expected 010 slip planes). Dominant slip planes define the lattice preferred orientation and elastic anisotropy of the texture. With 110 slip planes in PPv, we obtain a new interpretation of the shear-wave anisotropy in the D" layer, requiring a much smaller degree of lattice preferred orientation and more consistent with geophysical observations.

(Nature 438, 1142-1144 (2005))
Contact person: Dr. Artem R. Oganov (a.oganov@mat.ethz.ch)

High-pressure phases of $CaCO_3$: crystal structure prediction and experiment

Artem R. Oganov, Colin W. Glass, Shigeaki Ono
Laboratory of Crystallography, Department of Materials, ETH Zürich, Switzerland

Abstract

Recently, we have developed a new simulation methodology for crystal structure prediction. This method is based on an evolutionary algorithm and uses ab initio free energy as cost funstion. Among the most important ingredients of our approach are local optimisation, representation of structures by real numbers (rather than bit-strings), and special techniques for driving the evolutionary search and for enhancing convergence to the global minimum. Importantly, the only required input is the chemical composition and the desired pressure-temperature conditions. Numerous tests have demonstrated the speed and reliability of this approach. This paper presents one of the first applications of this methodology to solving hitherto unknown crystal structures.

Experimental studies demonstrated that at pressures above 40 GPa, $CaCO_3$ adopts a new form called post-aragonite. Crystal structure of this mineral phase could not be solved using experimental data and remained a controversial issue. With our new simulation methodology, we have been able to determine the crystal structure of $CaCO_3$ post-aragonite, which explains all experimental observations and becomes more stable than aragonite above 42 GPa. This structure belongs to a new structure type, which is also adopted by the high-pressure post-aragonite phases of $SrCO_3$ and $BaCO_3$. It has 2 formula units in the orthorhombic unit cell (space group Pmmn) and contains triangular carbonate-ions and Ca2+ ions in the twelvefold coordination. Additionally, a number of energetically competitive metastable structures have been identified. Above 137 GPa, a pyroxene-like structure with chains of carbonate tetrahedra becomes more stable than post-aragonite. For $MgCO_3$ this structure becomes more stable than magnesite above 106 GPa and is a good candidate structure for $MgCO_3$ post-magnesite.

(Earth and Planetary Science Letters 241, 95-103 (2006))
Contact person: Dr. Artem R. Oganov (a.oganov@mat.ethz.ch)

Theoretical study of CO adsorption on gold/alumina substrates.

Eva M. Fernández and L. C. Balbás
Depto. Física Teórica, Atómica y Nuclear. Universidad de Valladolid. Spain

Abstract

Aiming to understand the role of the substrate in the adsorption of carbon monoxide on gold clusters supported on metal-oxides, we have started a study on two different alumina substrates: an amorphous-like $(Al_2O_3)_{20}$ clusters, and the Al terminated (0001) surface of α-Al_2O_3 crystal. In this paper we present first principles calculations for adsorption of a gold atom on both alumina substrates, and the adsorption of cluster Au_8 on $(Al_2O_3)_{20}$. Then, we study the CO adsorption on the minimum energy structure of these three different gold/alumina systems. A single Au adsorbs preferably on top of Al atom with low coordination, being the binding energy higher in the case of $Au/(Al_2O_3)_{20}$. CO adsorbs preferably on top of the Au adatom, but, in the case of $Au/(Al_2O_3)_{20}$, Au forms a bridge with Al and O substrate atoms after adsorption. We find other equilibrium sites for CO adsorption on the cluster but not on the surface. This result suggests that the Au activity towards CO may be larger for the amorphous cluster than for the crystal surface substrate. For the most stable $Au_8/(Al_2O_3)_{20}$ configuration, two Au atoms bind to Al and O atoms, respectively, and CO adsorbs on top of the Au which binds the Al atom. We find other CO adsorption sites on supported Au_8 which are not stable for the case of free Au_8 cluster.

(Submitted to Journal of Physical Chemistry B)
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Magnetism and thermodynamics of defect-free FeCr alloys

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Abstract

Density Functional Theory calculations have been used to study the mixing behaviour of FeCr alloys. The heats of formation (HOF) of 65 FeCr structures in their magnetic ground states have been determined. A positive HOF is found over most of the concentration range. From 0 12The interesting magnetic situation that arises when ferromagnetic and anti-ferromagnetic metals are mixed in different ratios is discussed, with emphasis on the magnetic frustration between nearestneighbour Cr atoms. Results of an attempt to distinguish between the normal chemical mixing energy and the influence of magnetism by comparing magnetic and non-magnetic calculations for similar systems are reported.

(Submitted to Phys. Rev. B)
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Structure, stability and electronic properties of i-AlPdMn quasicrystalline surface

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Abstract

The structure, stability and electronic properties of a five-fold surface of an icosahedral (i) Al-Pd-Mn alloy have been investigated using ab-initio density-functional methods. Structural models for a series of rational approximants to the quasicrystalline structure of bulk i-AlPdMn have been constructed using the cut-and-projection technique with triacontahedral acceptance domains in the six-dimensional hyperspace according to the Katz-Gratias-Boudard model. This leads to a real-space structure describable in terms of interpenetrating Mackay and Bergman clusters. A five-fold surface has been prepared by cleaving the bulk structure along a plane perpendicular to a five-fold axis. The position of the cleavage plane has been chosen such as to produce a surface layer with a high atomic density. The atomic structure of these surface can be described by a P1 tiling by pentagons, thin rhombi, pentagonal stars and a "boat"- in terms of a cut-and-projection model, the decagonal acceptance domain of the P1 tiling corresponds to the maximal cross-section of the triacontahedra defining the three-dimensional quasicrystal. The vertices of the P1 tiling are occupied by Pd atoms surrounded by pentagonal motifs of Al atoms. For the ab-initio calculations we have prepared slab-models of the surface based on the 3/2 and 2/1 approximants and containing up to 357 atoms in the computational cell. The analysis of the surface charge-density shows flat minima at the vertices of the P1 tiling and strong charge-depletion in some of the pentagonal tiles ("surface vacancies"). Both observations are in agreement with scanning tunneling microscopy studies of these surfaces. Structural relaxations have been performed only for the 2/1 models with up to 205 atoms/cell. The calculations demonstrate that the skeleton of the P1 tiling fixed by the transition-metal atoms represents a stable surface-termination, but considerable rearrangement of the Al-atoms and large relaxations of the interlayer distances. The analysis of the surface electronic structure shows that the deep structure-induced pseudogap just above the Fermi level is filled up at the surface as a consequence of the structural disorder in the arrangement of the Al-atoms at the surface and of a shift of both the Pd and Mn d-band to lower binding energy. The d-band shift at the surface is in good agreement with observations based on photoelectron and Auger spectroscpies.

(Submitted to Phys. Rev. B **71** 054202 (2005))

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Ab-inito study of quasiperiodic monolayers on a fivefold i-AlPdMn surface

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Abstract

We present a structural model for quasiperiodic monolayers formed on the fivefold surface of an icosahedral AlPdMn quasicrystal, based on ab-inito density functional calculations. As a starting point we have investigated the relative stability of unsupported triangular, square, and quasiperiodic monolayers. The unsupported quasiperiodic monolayers are shown to be unstable upon relaxation by interatomic forces. This result indicates the important role of the adsorbate/substrate interaction for the stabilization of a quasiperiodic layer. The structural model of a monolayer adsorbed on the fivefold surface has been constructed on the basis of a mapping of the potential-energy landscape of an isolated adatom on the i-AlPdMn substrate. The structure of a clean fivefold i-AlPdMn surface is well described by a P1 tiling, with the vertices of the tiling located in the centers of B (Bergman) clusters and occupied by Pd atoms. The potential-energy mapping emphasizes the important role of the P1 skeleton for the stabilization of a quasiperiodic adlayer: adsorption at the vertices of the P1 tiling leads to high binding energies of $\simeq 4$ eV/atom. The mid-edge positions of the P1-tiling and Mn atoms exposed at the surface are identified as further favorable adsorption sites. Altogether this leads to a structural model of the quasiperiodic adlayer with atoms at the vertices and mid-edge positions of the P1-tiling, centered pentagonal motifs decorating the pentagonal tiles, and one additional atom in the center of the pentagonal star and of the boat tile. For this structure we calculate a surface coverage of $\simeq 0.09$ atoms/Å^2 in perfect agreement with experiment. The diffraction pattern of the adlayer exhibits (pseudo)decagonal symmetry. The structural stability of a 2/1 approximant to this model has been tested for Sn, Bi, and Sb monolayers via relaxation by the Hellmann-Feynman forces from ab-initio DFT calculations. The skeleton of adsorbed monolayers based on the P1 tiling was found to be stable, although the atomic decoration inside the tiles is partially distorted, albeit without violating the overall symmetry.

(Submitted to Phys. Rev. B **71** 184207 (2005))
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Surface vacancies at the fivefold icosahedral Al-Pd-Mn quasicrystal surface: A comparison of *ab-initio* calculated and experimental STM images

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Abstract

Scanning tunneling microscopy images (STM) of the five-fold surface of the icosahedral (i) Al-Pd-Mn quasicrystal have been calculated using ab initio density functional methods. The STM signal is formed predominantly by the Al atoms in the surface plane. The Pd atoms are seen in the STM image as dark spots. The reason of their small contribution to the STM current is a small local density of states around the Fermi level and the localized d-character of the Pd states. On the other hand the local paramagnetic density of states on Mn atoms is much higher than that on Pd atoms and therefore Mn atoms are seen in the STM images as bright spots. A direct comparison of the experimental images obtained from the STM with the ab-initio calculated STM images reveals that the characteristic features of the images – the dark pentagonal holes can also be created by surface vacancies and not only by truncated Bergman clusters as it has been supposed up to now.

(Submitted to Phys. Rev. B **73** 024202 (2006))
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Ab-inito study of a quasiperiodic Bi monolayer on a fivefold i-AlPdMn surface

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Abstract

The structure and stability of a quasiperiodic Bi monolayer formed on a five-fold surface of an icosahedral AlPdMn quasicrystal have been investigated using ab-initio density-functional methods. The structural model of the adsorbed monolayer has been constructed on the basis of a mapping of the potential-energy landscape of an isolated adatom on the fivefold surface of i-AlPdMn. This leads to a structural model of the quasiperiodic adlayer with atoms at the vertices and mid-edge positions of the P1-tiling. The internal decoration of the tiles is enforced by the decoration of the circumference of the tiles.

(Submitted to Phil. Mag **86** 825 (2006))
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Ab-initio study of the surface of a decagonal AlCoNi quasicrystal

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Abstract

The structure, stability and electronic properties of the tenfold-fold surface of the decagonal AlCoNi quasicrystal have been investigated using ab-initio density-functional methods. The structural model of the surface has been derived from the recently resolved structure of the W-(AlCoNi) approximant phase. The bulk quasicrystal can be cleaved at the flat A plane or at the puckered B plane. We investigate the stability and the electronic properties of the surface for both possible terminations. The simulated STM images of the A and B surfaces show that despite their significantly different atomic structure and chemical composition of both surfaces exhibit quite similar STM images. The electronic structure of the approximant phase is characterized by a pseudogap at the Fermi level. The pseudogap at the surface is partially covered and the positions of d-bands of both transition metals undergo a substantial shift towards lower binding energies.

(Submitted to Phys. Rev. B)

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Ab-initio study of quasiperiodic Bi monolayers on a tenfold d-Al-Co-Ni surface

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Abstract

We present an ab-initio study of the formation of quasiperiodic Bi monolayers on the tenfold surface of a decagonal Al-Co-Ni quasicrystal. The structural model of the surface has been derived from the recently resolved structure of the W-(AlCoNi) approximant phase. As the bulk W-phase can be cleaved at the flat A plane or the puckered B plane we investigate the formation and stability of the monolayers on both surfaces. The structural model of a Bi monolayer adsorbed on the tenfold surface has been constructed on the basis of a mapping of the potential-energy landscape of an isolated Bi adatom on the substrate. We found stable quasiperiodic monolayers on both surfaces. The structure of the monolayer on the B-surface is less dense and more regular than that on the A surface. The surface coverages are within the experimentally determined range $\simeq 0.08 \pm 0.02$ atoms/Å^2.

(Submitted to Phys. Rev. B)

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Exchange interactions, spin waves, and transition temperatures in itinerant magnets

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Abstract

The contribution reviews an *ab initio* two-step procedure to determine exchange interactions, spin-wave spectra, and thermodynamic properties of itinerant magnets. In the first step, the selfconsistent electronic structure of a system is calculated for a collinear spin structure at zero temperature. In the second step, parameters of an effective classical Heisenberg Hamiltonian are determined using the magnetic force theorem and the one-electron Green functions. The Heisenberg Hamiltonian and methods of statistical physics are employed in subsequent evaluation of magnon dispersion laws, spin-wave stiffness constants, and Curie/Néel temperatures. Applicability of the developed scheme is illustrated by selected properties of various systems such as transition and rare-earth metals, disordered alloys including diluted magnetic semiconductors, ultrathin films, and surfaces. A comparison to other *ab initio* approaches is presented as well.

To be published in Philosophical Magazine
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Insight Into a Pressure and Materials Gap: CO Oxidation at “Ruthenium” Catalysts

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Abstract

Recent experimental and theoretical work on the CO oxidation reaction at “ruthenium” catalysts provides intriguing insight into the microscopic origins behind the frequently discussed pressure and materials gap between studies performed in ultra-high vacuum (UHV) and under realistic pressure conditions. Focusing on the Ru(0001) model catalyst, the considered system has in fact two important components to this issue. At first, an oxygen-rich environment changes the material from Ru to RuO_2. Thus, earlier ambient pressure studies on “ruthenium” catalysts were actually looking at an oxide film formed at the surface. Second, even after RuO_2 has been formed the surface composition varies strongly with pressure: Also on the formed $RuO_2(110)$ there is a low-pressure surface phase that is routinely studied in UHV, but has little in common with the catalytically active situation.

(Submitted to: Oil & Gas Science and Technology)
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Revisiting the structure of the *p*(4x4) surface oxide on Ag(111)

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Abstract

Scanning tunneling microscopy (STM) and density-functional theory are used to reexamine the structure of the renowned p(4x4)-O/Ag(111) surface oxide. The accepted structural model [Carlisle *et al.*, Phys. Rev. Lett. **84**, 3899 (2000)] is incompatible with the enhanced resolution of the current STM measurements. An 'Ag$_6$ model' is proposed that is more stable than its predecessor and accounts for the coexistence of the p(4x4) and a novel $c(3\text{x}5\sqrt{3})$rect phase. This coexistence is an indication of the dynamic complexity of the system that till now has not been appreciated.

(Submitted to: Phys. Rev. Lett.)

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Density functional theory in surface science and heterogeneous catalysis

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Abstract

Solid surfaces are used extensively as catalysts throughout chemical industry, in the energy sector, and in environmental protection. Most recently density functional theory (DFT) has started providing unprecedented insight into the atomic-scale mechanisms, helping the interpretation of the large amount of experimental data gathered over the last decades. It will be shown how DFT can be used to predict the state of the surface during reaction and the rate of catalytic reactions. It will also be shown how we are beginning to have an understanding in the variation in catalytic activity from one transition metal to the next. The prospects of using calculations to guide the development of new catalysts in industry will be discussed.

(Submitted to: MRS Bulletin)
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Ab initio approach to the ballistic transport through single atoms

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Abstract

We present a systematic study of the ballistic electron conductance through *sp* and 3*d* transition metal atoms attached to copper and palladium crystalline electrodes. We employ the *ab initio* screened Korringa-Kohn-Rostoker Green's function method to calculate the electronic structure of nanocontacts while the ballistic transmission and conductance eigenchannels were obtained by means of the Kubo approach as formulated by Baranger and Stone. We demonstrate that the conductance of the systems is mainly determined by the electronic properties of the atom bridging the macroscopic leads. We classify the conducting eigenchannels according to the atomic orbitals of the contact atom and the irreducible representations of the symmetry point group of the system that leads to the microscopic understanding of the conductance. We show that if impurity resonances in the density of states of the contact atom appear at the Fermi energy, additional channels of appropriate symmetry could open. On the other hand the transmission of the existing channels could be blocked by impurity scattering.

(Physical Review B **73**, 045428 (2006))
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Magnetic Moment Softening and Domain Wall Resistance in Ni Nanowires

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Abstract

Magnetic moments in atomic scale domain walls formed in nanoconstrictions and nanowires are softened which affects dramatically the domain wall resistance. We perform ab initio calculations of the electronic structure and conductance of atomic-size Ni nanowires with domain walls only a few atomic lattice constants wide. We show that the hybridization between noncollinear spin states leads to a reduction of the magnetic moments in the domain wall. This magnetic moment softening strongly enhances the domain wall resistance due to scattering produced by the local perturbation of the electronic potential.

This work is supported by Segate Research, NSF-MRSEC and the Nebraska Research Initiative.

(Submitted to: Physical Review Letters)

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CO adsorption on the Cu(111) surface: a density functional study

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Abstract

The adsorption of CO on the Cu(111) surface has been studied with *ab initio* density functional theory. The adsorbate-metal system was analyzed with the local density approximation, the gradient corrected functional of Perdew and Wang and the B3LYP hybrid functional, for comparison. A slab model was used for the $(\sqrt{3} \times \sqrt{3}) - R30^\circ$ pattern at a coverage of 1/3. The local density approximation and the gradient corrected functional give the fcc site as the favorable adsorption site. In contrast, the B3LYP functional results in the preference of the top site, in agreement with the experiment. These results confirm the suggested explanation for the failure of standard functionals, based on the position of the highest occupied and lowest unoccupied molecular orbital. The results of total energy calculations are presented, together with projected densities of states and Mulliken populations. In addition, the basis set superposition error is discussed for CO/Cu(111) and for CO/Pt(111).

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Surface Science, in press

7 Advertising Journals/Special Issues

7.1 Special Issues of Zeitschrift fuer Kristallographie

Zeitschrift fuer Kristallographie is one of the oldest continuously existing scientific journals and presents results of theoretical and experimental study on crystallography.

Recent Special Topic Issues include:

- **Issue 4 (2005)**: ”Future of Structural Chemistry” by Penelope W. Codding (University of Victoria, Canada)
`http://www.extenza-eps.com/OLD/toc/zkri/220/4-2005`

- **Issue 5-6 (2005)**: ”Computational Crystallography” by Artem R. Oganov (ETH Hoenggerberg, Zurich, Switzerland)
http://www.extenza-eps.com/OLD/toc/zkri/220/5-6-2005+

- **Issue 8 (2005)**: ”Phase Transitions” by Ulrich Bismayer (University Hamburg, Germany)
`http://www.extenza-eps.com/OLD/toc/zkri/220/8-2005`

- **Issue 9-10 (2005)**: ”Phononic Crystals - Sonic Band-Gap Materials” by Ioannis E. Psarobas (University of Athens, Greece)
`http://www.extenza-eps.com/OLD/toc/zkri/220/9-10`

- **Issue 12 (2005)**: ”Diffuse Scattering” by T. Richard Welberry (The Australian National University, Australia)
`http://www.extenza-eps.com/OLD/toc/zkri/220/12_2005`

For more information on Zeitschrift fuer Kristallographie, please visit our website:

`http://www.zkristallogr.de`

or contact us directly: vertrieb-zs@oldenbourg.de.

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7.2 New Journal on "Fluid Dynamics & Materials Processing"

It is my pleasure to introduce you to the upcoming new journal **"Fluid Dynamics & Materials Processing"**. being published by the Tech Science Press.

Please feel free to distribute it to those who might be interested. I hope that you find this new journal and useful to your research.

Further information is on the website:

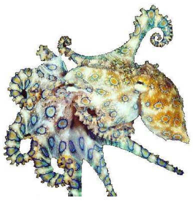
http://www.techscience.com/fdmp

Thank you for your attention.

Kind regards,

Hiroshi Mizuseki
Materials Design by Computer Simulation
Institute for Materials Research, Tohoku University
`http://www-lab.imr.edu/~mizuseki/marangoni.html`

8 SCIENTIFIC HIGHLIGHT OF THE MONTH: "Octopus: a tool for the application of time-dependent density functional theory"



`octopus`: a tool for the application of time-dependent density functional theory

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Abstract

We report on the background, current status, and current lines of development of the `octopus` project. This program materializes the main equations of density-functional theory in the ground state, and of time-dependent density-functional theory for dynamical effects. The focus is nowadays placed on the optical (i.e. electronic) linear response properties of nanostructures and biomolecules, and on the non-linear response to high-intensity fields of finite systems, with particular attention to the coupled ionic-electronic motion (i.e. photo-chemical processes). In addition, we are currently extending the code to the treatment of periodic systems (both to one-dimensional chains, two-dimensional slabs, or fully periodic solids), magnetic properties (ground state properties and excitations), and to the field of quantum-mechanical transport or "molecular electronics." In this communication, we concentrate on the development of the methodology: we review the essential numerical schemes used in the code, and report on the most recent implementations, with special attention to the introduction of adaptive coordinates, to the extension of our real-space technique to tackle periodic systems, and on large-scale parallelization. More information on the code, as well as the code itself, can be found at `http://www.tddft.org/programs/octopus/`.

1 Introduction

Both density-functional theory (DFT) [1,2], and time-dependent density-functional theory (TDDFT) [3, 4] have enjoyed a steady increase of their popularity ever since they were born, in the sixties and eighties respectively. The reason is that both theories achieve, for many problems, an unparalleled balance between accuracy and computational cost. Although the scope of applicability of traditional Quantum Chemistry techniques, or of Quantum Monte-Carlo procedures, have also increased in recent years [5,6], DFT/TDDFT is still the method of choice for large systems (e.g., molecular systems of biological interest) undergoing complex processes.

Correspondingly, numerous software packages that solve DFT/TDDFT equations are available [7]. Among them, `octopus` [8] is one with special focus on TDDFT. In the present newsletter, we describe the current status of this project, and the aims of its developing process. In brief, some of the key aspects that describe `octopus` are:

Target problems:

(i) Linear optical (i.e. electronic) response of molecules or clusters.

(ii) Non-linear response to classical high-intensity electromagnetic fields, taking into account both the ionic and electronic degrees of freedom.

(iii) Ground-state and excited state electronic properties of systems with lower dimensionality, such as quantum dots.

(iv) Photo-induced reactions of molecules (e.g., photo-dissociation, photo-isomerization, etc).

(v) In the immediate future, extension of these procedures to systems that are infinite and periodic in one or more dimensions (polymers, slabs, nanotubes, solids), and to electronic transport.

Theoretical base:

(i) The underlying theories are DFT and TDDFT. Also, the code may perform dynamics by considering the classical (i.e. point-particle) approximation for the nuclei. These dynamics may be non-adiabatic, since the system evolves following the Ehrenfest path. It is, however, a mean-field approach.

(ii) Regarding TDDFT, we have implemented two different approaches: On the one hand, the "standard" TDDFT-based linear-response theory, which provides us with excitation energies and oscillator strengths for ground-state to excited-state transitions. On the other hand, we have also implemented the explicit time-propagation of the TDDFT equations, which allows for the use of large external potentials, well beyond the range of validity of perturbation theory.

Methodology

(i) As numerical representation, we have chosen to work without a basis set, relying on numerical meshes. Nevertheless, auxiliary basis sets (plane waves, atomic orbitals) are used when necessary.

Recently, we have added the possibility of working with non-uniform grids, which adapt to the inhomogeneity of the problem, and of making use of multigrid techniques to accelerate the calculations. The adaptive coordinates implementation will be discussed in some detail in Section 4.

(ii) For most calculations, the code relies on the use of pseudopotentials [9]. We currently allow for two types: Troullier-Martins [10], and Hartwigsen-Goedecker-Hutter [11].

(iii) In addition to being able to treat systems in the standard 3 dimensions, 2D and 1D modes are also available. These are useful for studying, e.g., the two-dimensional electron gas that characterizes a wide class of quantum dots.

Technical aspects

(i) The code has been designed with emphasis on parallel scalability. In consequence, it allows for multiple task divisions. We will comment on this aspect in Section 5.

(ii) The language of most of the code is Fortran 90 (almost 50.000 lines at present). Other languages, such as C or Perl, are also used.

(iii) We have struggled to employ only standard and portable tools. The resulting code may run on virtually any Unix-like platform.

(iv) The package is licensed under the GNU General Public License (GPL). In consequence, it is available for use, inspection, and modification for anyone, at `http://www.tddft.programs/octopus/`.

Section 2 summarizes the algorithms used for ground-state calculations, while the next section handles response properties. Sections 4, 5 and 6 report some of the recent additions to the package: adaptive coordinates to numerically represent the problem, support for parallel calculations (a lot of effort is being put onto the scalability of the computations to large number of processors), and the treatment of periodic systems.

2 Ground-state DFT calculations

2.1 The Kohn-Sham equations

Kohn-Sham (KS) DFT [1, 2] provides the ground state one-particle density n_0 of a system of N electrons exposed to an external potential $v(\vec{r})$, by identifying it with the density of a non-interacting system of electrons subject to the so-called KS potential, $v_{\mathrm{KS}}(\vec{r})$. This system, being non-interacting, may be solved through a set of one-particle equations, the KS equations [1] (atomic units will be used throughout):

$$h_{\mathrm{KS}}\ \varphi_i(\vec{r}) = \varepsilon_i \varphi_i(\vec{r}) \qquad (i = 1, \ldots, N)\,, \tag{1}$$

$$n_0(\vec{r}) = \sum_{i=1}^{N} |\varphi_i(\vec{r})|^2\,. \tag{2}$$

The functions φ_i and the real numbers ε_i are the KS orbitals and KS eigenvalues, respectively. The KS state is the single Slater determinant built from those orbitals. The KS Hamiltonian is given by

$$h_{\mathrm{KS}}[n] = -\frac{1}{2}\nabla^2 + v_{\mathrm{KS}}(\vec{r})\,. \tag{3}$$

The first term, the kinetic operator, is approximated in a real-space formulation by a *finite difference* formula – details about this will be given in Section 4. The KS potential is usually separated as follows:

$$v_{\mathrm{KS}}(\vec{r}) = v(\vec{r}) + v_{\mathrm{Hartree}}[n](\vec{r}) + v_{\mathrm{xc}}[n](\vec{r})\,. \tag{4}$$

External potential. The external potential $v(\vec{r})$ is typically the sum of the Coulomb potential generated by each of the nuclei. In a pseudopotential formulation, this includes both local and non-local components. For an atom α positioned at $\vec{R}_\alpha$, the pseudopotential $\hat{v}_\alpha(\vec{R}_\alpha)$ is the sum of a local operator $v_\alpha^{\mathrm{local}}$ and a set of non-local projectors described by atom-centered functions ξ_α^κ:

$$\langle\vec{r}|\hat{v}_\alpha(\vec{R}_\alpha)|\varphi\rangle = v_\alpha^{\mathrm{local}}(\vec{r}-\vec{R}_\alpha)\varphi(\vec{r}) + \sum_\kappa \langle\xi_\alpha^\kappa(\vec{R}_\alpha)|\varphi\rangle\xi_\alpha^\kappa(\vec{r}-\vec{R}_\alpha)\,. \tag{5}$$

Note that these projectors are typically well localized in real space, so their action is computationally feasible and faster than in a plane wave formulation.

The code also allows for other "user-defined" external potentials. For example, one can attempt to model the solvent environment of a given system with the electrostatic potential generated by a set of point charges and/or dipoles (e.g. to model a chromophore in its protein environment [12]). This is the basic principle of the so-called QM/MM techniques [13]. Also, the user may define a model potential describing a two-dimensional quantum dot, and can specify it simply by writing down its mathematical function in the input file.

Hartree potential. The second term of (4), $v_{\mathrm{Hartree}}[n](\vec{r})$ is more time-consuming. There are various ways of obtaining this potential numerically, and we have investigated and implemented some of them [14]. These are explained in more detail in Section 2.2.

Exchange-correlation potential. The exchange-correlation (xc) potential, $v_{\mathrm{xc}}[n_0]$, is an unknown functional of the density, and has to be approximated. It is the first functional derivative of the exchange-correlation *energy* functional:

$$v_{\mathrm{xc}}[n](\vec{r}) = \frac{\delta E_{\mathrm{xc}}}{\delta n(\vec{r})}\,. \tag{6}$$

We have incorporated in `octopus` a wide variety of possible functionals, ranging from the standard local density approximation (LDA) [15] and generalized gradient approximations [16], to the state-of-the-art orbital-dependent functionals [17–19]. "Traditional" LDAs and GGAs are easy, since they are explicit functionals of the density and its gradient. The more recent orbital-dependent functionals, however, are explicit functionals of the KS orbitals (and so they are implicit functionals of the density *through* the orbitals) and require the use of the optimized effective potential method (OEP) [17, 18]. We have implemented these functionals in `octopus`.

Both the Krieger, Li and Iafrate (KLI) [19] approximation and the full solution of the OEP equation [20] (still in experimental phase) are available.

We are now extending the set of functionals to cope with current-density functionals [21]. At this point, we emphasize that along with the `octopus` distribution we provide a standard "exchange and correlation library," written in C. All (TD)DFT codes require an equivalent piece of software, and in our opinion, it would be mutually beneficial to share an open, reliable library. We expect that this may be a first step towards this goal.

Eigensolvers. Once we know how to construct the real-space representation of the Hamiltonian for a "trial" density n (or, in fact, for a trial set of KS orbitals φ_i from which the density is generated), we are faced with the problem of solving the Kohn-Sham equations (1) for the N lowest lying eigenpairs of this Hamiltonian operator. In real space this amounts to the solution of an eigenproblem for large sparse matrices. The literature in this field is abundant [22], and we have tried several schemes in `octopus`. The following are available in the current version of the code: conjugate-gradients based schemes [23], Lanczos-based algorithms [24] and the Jacobi-Davidson procedure [25].

Mixing. We are left with the mixing of the density, which is essential for the convergence of the self-consistent procedure. For that purpose, we employ some standard techniques. Essentially, one has to build recursively a series of densities $n^{(i)}$ that converges to the solution density n_0. Each new density is generated through a prescription of the form:

$$n^{(i+1)} = G[\tilde{n}^{(i+1)}, n^{(i)}, n^{(i-1)}, \ldots, n^{(i-s)}]\,, \tag{7}$$

where $\tilde{n}^{(i+1)}$ is the density obtained from Eq. (2) using the Kohn-Sham orbitals of step $i+1$. The simplest example of such a prescription is the so-called "linear mixing" [26], for which Eq. (7) takes the form: $n^{(i+1)} = (1-\alpha)\tilde{n}^{(i+1)} + \alpha n^{(i)}$. However, `octopus` allows for more sophisticated procedures – we refer the reader to the original references: the generalized Broyden algorithm of Johnson [27], and the "guaranteed reduction" Pulay algorithm [28].

Spin. All the previous equations were written considering no spin polarization. However, `octopus` is also able to perform calculations using spin-density functional theory, either considering complete spin alignment throughout the system or not. This latter case requires the use of the generalized local spin-density theory [29]. The wave functions are then described as two-component spinors $\Phi(\vec{r}) = (\varphi_1(\vec{r}), \varphi_2(\vec{r}))$ where the components are complex wave functions.

Finally we also mention the possibility to perform calculations including external magnetic fields. As noted above, current-density functionals are being implemented, but it is already possible to perform calculations including a static uniform magnetic field.

2.2 The Hartree potential

In 3 dimensions, the Hartree potential may be represented in two equivalent forms: as the integral:

$$v_{\rm Hartree}[n](\vec{r}) = \int\!{\rm d}^3r'\,\frac{n(\vec{r}')}{|\vec{r}-\vec{r}'|}\,, \tag{8}$$

or as the solution of Poisson's equation:

$$\nabla^2 v_{\rm Hartree}[n](\vec{r}) = -4\pi n(\vec{r})\,. \tag{9}$$

There are various ways in which these equations may be solved, and we have investigated and implemented some of them [14].

Conjugate gradients. This amounts to solving Eq. (9) via a conjugate gradients algorithm. This poses the problem of the boundary conditions for v. The standard solution is to obtain the boundary conditions by calculating the value of v at points around the simulation box by making use of a multipole expansion representation of the density n: For points outside, the potential is given by

$$\begin{aligned} v_{\rm Hartree}(\vec{r}) &= \sum_{l=0}^{\infty}\sum_{m=-l}^{l}\frac{4\pi}{2l+1}\frac{1}{r^{(l+1)}}Y_{lm}(\hat{r})Q_{lm}\,, \\ Q_{lm} &= \int\!{\rm d}^3r\, r^l Y_{lm}(\vec{r})n(\vec{r})\,, \end{aligned} \tag{10}$$

where Y_{lm} are spherical harmonics. `octopus` now offers an alternative: we subtract from n a sum of densities $Q_{lm}n_{lm}$, where Q_{lm} are the multipoles of n, and where n_{lm} are auxiliary known charge distributions whose (lm)-moment is unity, and whose other moments are zero:

$$\bar{n} = n - \sum_{l=0}^{L}\sum_{m=-l}^{l} Q_{lm}n_{lm}\,. \tag{11}$$

For a sufficiently large integer L, $\bar{n}$ has negligible boundary conditions, so that $v_{\rm Hartree}[\bar{n}]$ may be calculated with the usual Laplacian with zero boundary conditions. Since Poisson's equation is linear,

$$v_{\rm Hartree}[n] = v_{\rm Hartree}[\bar{n}] + \sum_{l=0}^{L}\sum_{m=-l}^{l} Q_{lm}v_{\rm Hartree}[n_{lm}]\,. \tag{12}$$

The functions $v_{\rm Hartree}[n_{lm}]$ can be obtained exactly (see Ref. [14] for explicit analytical expressions for n_{lm} and $v_{\rm Hartree}[n_{lm}]$).

Multigrids. Still in real-space, as a recent addition, `octopus` now also allows for the use of the multigrid method [30, 31]. Multigrid is a linear scaling iterative method to solve elliptic problems. The base of this scheme is to use a group of different grids that have less points than the original grid where the problem is discretized. In these coarser grids the corrections to the solution in the original grid are calculated using standard relaxation methods (such as Gauss-Jacobi or Gauss-Seidel). The solution process is much faster in the coarser grids, not only because of the reduced number of points, but also because relaxation operators are less local.

Currently, this technique is implemented in `octopus` only for the problem of solving Poisson's equation; our plans however are to use this technique to accelerate the convergence of our eigensolvers [32, 33].

Fourier space. `octopus` also allows to move to Fourier space and obtain the Hartree potential by making use of the well-known fact that it is simply a multiplicative function in Fourier space. This is be the best choice for fully periodic systems, since it naturally handles the periodic boundary conditions. It is a fast and efficient method thanks to the existence of the Fast Fourier Transform (FFT) algorithm.

For systems of reduced periodicity (finite systems, slabs, cylinders) plane waves can still be used efficiently to calculate the Hartree potential using the cutoff technique. The discussion of this issue is referred to Section 6.

3 Response calculations

3.1 Time-dependent DFT

TDDFT [3,4] extends the previous formulation to time-dependent phenomena; one can establish an analogous mapping between the interacting and a non-interacting system, and we obtain a set of time-dependent one-particle equations [3] (Runge-Gross equations, or time-dependent KS equations, TDKS):

$$\mathrm{i}\frac{\partial}{\partial t}\varphi_i(\vec{r},t) = h_{\mathrm{KS}}(t)\;\varphi_i(\vec{r}) \qquad (i=1,\ldots,N)\,. \tag{13}$$

$$n(\vec{r},t) = \sum_{i=1}^{N} |\varphi_i(\vec{r},t)|^2\,. \tag{14}$$

The KS Hamiltonian is similar to the static version given by Eq. (3):

$$h_{\mathrm{KS}}(t) = -\frac{1}{2}\nabla^2 + v(\vec{r},t) + v_{\mathrm{Hartree}}[n](\vec{r},t) + v_{\mathrm{xc}}[n](\vec{r},t)\,. \tag{15}$$

Note, however, that in this case we allow for an explicitly time-dependent external potential $v(\vec{r},t)$. The exchange and correlation term is now both a functional of the time-dependent density and of the initial state of the system (typically the ground state). In principle, v_{xc} should depend on the densities at all times in the past; in practice most applications of TDDFT rely on an *adiabatic* approximation:

$$v_{\mathrm{xc}}[n](\vec{r},t) = v_{\mathrm{xc}}^{\mathrm{gs}}[\rho]|_{\rho=n(\vec{r},t)}\;, \tag{16}$$

where $v_{\mathrm{xc}}^{\mathrm{gs}}$ is the ground state exchange and correlation potential functional. In this way, all the approximations implemented in the code for the ground state calculations translate immediately to the time-dependent formalism. Moreover, orbital functionals are also implemented in `octopus` for time-dependent calculations within the time-dependent KLI scheme [34].

Most applications of TDDFT are restricted to a linearized form of Eqs. (13) and (14) that assumes a small external perturbation, and attempts to obtain the first-order density-density response in frequency domain. In `octopus` we allow for both possibilities: the linear-response formalism, and the explicit integration of the TDKS equations in the time domain. The latter may not only be used to calculate linear response properties, but also permits to use high-intensity fields and to perform combined electron-ion dynamical simulations.

For the explicit integration of Eqn. (13) in real time one uses a propagation algorithm. In other words, we seek a numerical representation of the evolution operator $\hat{U}(t+\Delta t, t)$:

$$\varphi(\vec{r}, t+\Delta t) = \hat{U}(t+\Delta t, t)\varphi(\vec{r}, t)\,. \tag{17}$$

In TDDFT we are dealing with the integration of a set of coupled Schrödinger-like equations, characterized by two important facts: (i) The Hamiltonian is intrinsically time-dependent, even if there is no external potential, since the Hartree and xc parts depend on the time-dependent density; (ii) The Hamiltonian – at least a part of it – is not known *a priori*: both Hartree and xc terms depend on the solution itself.

For time-independent Hamiltonians, it is well known that the problem reduces to the calculation of the action of the exponential of the Hamiltonian on the function that describes the state. Unfortunately, since this is not the case in TDDFT, one has to approximate the full evolution operator:

$$\hat{U}(t+\Delta t, t) = \sum_{n=0}^{\infty} \frac{(-\mathrm{i})^n}{n!} \int_t^{t+\Delta t} \mathrm{d}t_1 \ldots \int_t^{t+\Delta t} \mathrm{d}t_n \mathcal{T}[\hat{h}_{\mathrm{KS}}(t_1)\ldots\hat{h}_{\mathrm{KS}}(t_n)]\,, \tag{18}$$

where $\mathcal{T}$ is the time-ordering product. We have done some research on this topic, by implementing in the `octopus` package a handful of algorithms: polynomial expansions (in the standard base or in the Chebyshev base) to approximate the exponential operator, Krylov subspace projections, the split-operator technique, higher-order split-operator-like schemes, the implicit midpoint rule, the exponential midpoint rule, and the so-called Magnus expansions.

For more details on these propagation algorithms, we refer the reader to our publication on the issue [35].

3.2 Electronic excitations by means of time-propagation

Dynamical polarizability. In `octopus` the calculation of the dynamical polarizability can be performed by propagating in real time [36]. This methodology scales well with the size of the system, and is thus our preferred scheme for large systems. Let us recall the essentials of this formulation. We will restrict hereafter to electrical (spin-independent) dipole perturbations:

$$\delta v_{\mathrm{ext},\sigma}(\vec{r}, \omega) = -x_j \kappa(\omega)\,. \tag{19}$$

This defines an electrical perturbation polarized in the direction j: $\delta\vec{E}(\omega) = \kappa(\omega)\hat{e}_j$. The response of the system dipole moment in the i direction

$$\delta\langle\hat{X}_i\rangle(\omega) = \sum_{\sigma} \int \mathrm{d}^3r\, x_i\, \delta n_\sigma(\vec{r}, \omega) \tag{20}$$

is then given by:

$$\delta\langle\hat{X}_i\rangle(\omega) = -\kappa(\omega) \sum_{\sigma\sigma'} \int \mathrm{d}^3r \int \mathrm{d}^3r'\, x_i\, \chi_{\sigma\sigma'}(\vec{r}, \vec{r}', \omega)\, x'_j\,. \tag{21}$$

We may define the dynamical dipole polarizability $\alpha_{ij}(\omega)$ as the quotient of the induced dipole moment in the direction i with the applied external electrical field in the direction j, which yields:

$$\alpha_{ij}(\omega) = -\sum_{\sigma\sigma'} \int \mathrm{d}^3 r \int \mathrm{d}^3 r' \, x_i \, \chi_{\sigma\sigma'}(\vec{r}, \vec{r}', \omega) \, x'_j \,. \tag{22}$$

The dynamical polarizability elements may then be arranged to form a second-rank symmetric tensor, $\boldsymbol{\alpha}(\omega)$. The cross-section tensor is proportional to its imaginary part:

$$\boldsymbol{\sigma}(\omega) = \frac{4\pi\omega}{c} \Im \boldsymbol{\alpha}(\omega) \,. \tag{23}$$

We consider a sudden external perturbation at $t = 0$ (delta function in time), which means $\kappa(\omega) = \kappa$, equal for all frequencies. This perturbation is applied along a given polarization direction, say $\hat{e}_j$. By propagating the time-dependent Kohn-Sham equations, we obtain $\delta\langle \hat{X}_i \rangle(\omega)$ through Eq. (20). The polarizability element $\alpha_{ij}(\omega)$ may then be calculated easily via:

$$\alpha_{ij}(\omega) = -\frac{\delta\langle \hat{X}_i \rangle(\omega)}{\kappa} = -\frac{1}{\kappa} \int \mathrm{d}^3 r \, x_i \, \delta n(\vec{r}, \omega). \tag{24}$$

Symmetry considerations. One recent addition to `octopus` [37] is the possibility of taking advantage of the possible symmetries of a given molecule when calculating its dynamical polarizability tensor, Eq. (22), through the time-propagation technique.

Let us consider three linearly-independent, but possibly not non-orthogonal, unit vectors $\{\hat{p}_1, \hat{p}_2, \hat{p}_3\}$. We define the polarizability elements $\tilde{\alpha}_{ij}(\omega)$ as:

$$\tilde{\alpha}_{ij}(\omega) = -\int \mathrm{d}^3 r \int \mathrm{d}^3 r' \, (\vec{r} \cdot \hat{p}_i) \chi(\vec{r}, \vec{r}', \omega) (\vec{r}' \cdot \hat{p}_j) \,. \tag{25}$$

This corresponds to a process in which the polarization of the perturbing field is along $\hat{p}_j$, and the dipole is measured along $\hat{p}_i$. If we know the 3x3 matrix $\tilde{\boldsymbol{\alpha}}(\omega)$, we can get the *real* tensor $\boldsymbol{\alpha}(\omega)$ by making use of the following simple relationship, which can be obtained once again from Eq. (22):

$$\tilde{\boldsymbol{\alpha}}(\omega) = \mathbf{P}^t \boldsymbol{\alpha}(\omega) \mathbf{P} \,. \tag{26}$$

$\mathbf{P}$ is the transformation matrix between the original orthonormal reference frame and $\{\hat{p}_1, \hat{p}_2, \hat{p}_3\}$. Note, that this transformation is in general not a rotation, as $\mathbf{P}$ is not unitary. Moreover, no matter how familiar it looks, Eq. (26) does not describe a change of coordinates: $\tilde{\boldsymbol{\alpha}}(\omega)$ is *not* the polarizability tensor in the new reference frame. And finally, also note that the traces of $\tilde{\boldsymbol{\alpha}}$ and $\boldsymbol{\alpha}$ do not coincide:

$$\mathrm{Tr}\left[\tilde{\boldsymbol{\alpha}}(\omega)\right] = \mathrm{Tr}\left[\mathbf{P}^t \boldsymbol{\alpha}(\omega) \mathbf{P}\right] = \mathrm{Tr}\left[\boldsymbol{\alpha}(\omega) \mathbf{P} \mathbf{P}^t\right] \,. \tag{27}$$

but $\mathbf{P}\mathbf{P}^t \neq \mathbf{1}$. Notwithstanding all this, it is the basis of our scheme, since it tells us that we may obtain the polarizability tensor by obtaining the related object $\tilde{\boldsymbol{\alpha}}(\omega)$.

Now let us assume that the molecule under study possesses some non-trivial symmetry transformations – to start with, we consider that it has two, $\mathcal{A}$ and $\mathcal{B}$. We consider an initial unit vector, $\hat{p}_1$, and define:

$$\begin{aligned} \hat{p}_2 &= \mathcal{A} \hat{p}_1 \\ \hat{p}_3 &= \mathcal{B} \hat{p}_2 \end{aligned} \tag{28}$$

We assume that this may be done in such a way that the set $\{\hat{p}_1, \hat{p}_2, \hat{p}_3\}$ is linearly independent. Next, we perform a TDDFT calculation with the perturbing field polarized in the direction $\hat{p}_1$. This permits us to obtain the row $\{\tilde{\alpha}_{11}, \tilde{\alpha}_{12}, \tilde{\alpha}_{13}\}$. Since the matrix is symmetric, we also have the column $\{\tilde{\alpha}_{11}, \tilde{\alpha}_{21}, \tilde{\alpha}_{31}\}$. The symmetry of the molecule also permits us to obtain the diagonal: $\{\tilde{\alpha}_{33} = \tilde{\alpha}_{22} = \tilde{\alpha}_{11}\}$. The only missing element is $\tilde{\alpha}_{23} = \tilde{\alpha}_{32}$, but it is easy to prove that:

$$\tilde{\alpha}_{23} = \det(\mathcal{A})\ \ \tilde{\alpha}_{1,\mathcal{A}^{-1}\hat{p}_3}\,, \tag{29}$$

which we can also obtain from our original calculation. The conclusion is that we have access to the full tensor by performing only one calculation.

Finally, we should note that these symmetry considerations may be extended to other response properties of the system, and to the calculation of the singlet and triplet excitations of paramagnetic molecules.

3.3 Electronic excitations by means of linear-response theory

We recall here the fundamental equations of the linear response formalism [38]. In the following, we work directly in the frequency domain – the variable ω denotes the frequency. A small perturbation $\delta v_\sigma(\vec{r},\omega)$ will induce a density response $\delta n_\sigma(\vec{r},\omega)$ (hereafter the Greek letters σ, τ, μ will denote spin components). They will be linearly related by the susceptibility function:

$$\delta n_\sigma(\vec{r},\omega) = \sum_{\sigma'} \int \mathrm{d}^3 r' \chi_{\sigma\sigma'}(\vec{r},\vec{r}',\omega)\delta v_{\sigma'}(\vec{r}',\omega)\,. \tag{30}$$

An analogous equation may be written for the KS system, substituting the interacting susceptibility by the KS susceptibility $\chi^{\mathrm{KS}}_{\sigma\sigma'}$ and the external perturbation δv_σ by the KS variation $\delta v_{\mathrm{KS},\sigma}$. The density response, however, is identical by virtue of the Runge-Gross theorem [3]. The KS variation is:

$$\delta v_{\mathrm{KS},\sigma}(\vec{r}) = \delta v(\vec{r}) + \int \mathrm{d}^3 r' \frac{\delta n(\vec{r}')}{|\vec{r}-\vec{r}'|} + \sum_{\sigma'} \int \mathrm{d}^3 r' f_{\mathrm{xc},\sigma\sigma'}(\vec{r},\vec{r}',\omega)\delta n_{\sigma'}(\vec{r}',\omega)\,, \tag{31}$$

where the so-called "kernel", $f_{\mathrm{xc},\sigma\sigma'}(\vec{r},\vec{r}',\omega)$, is the second functional derivative of the xc energy functional. If we now make use of the identity between densities of the real and of the KS systems, we arrive at a Dyson-like equation for the response function [39]:

$$\chi_{\sigma\sigma'}(\vec{r},\vec{r}',\omega) = \chi^{\mathrm{KS}}_{\sigma\sigma'}(\vec{r},\vec{r}',\omega) + \sum_{\tau\tau'} \int \mathrm{d}^3 r \int \mathrm{d}^3 r' \chi_{\sigma\tau}(\vec{r},\vec{x},\omega) \left[\frac{1}{|\vec{x}-\vec{x}'|} + f_{\mathrm{xc},\tau\tau'}(\vec{x},\vec{x}',\omega)\right] \chi^{\mathrm{KS}}_{\tau'\sigma'}(\vec{x}',\vec{r}',\omega)\,. \tag{32}$$

A fully self-consistent solution of this equation would provide us with the response function of the interacting system. Unfortunately, this is quite difficult numerically. Furthermore, it requires the knowledge of the non-interacting response function, $\chi^{\mathrm{KS}}_{\sigma\sigma'}$. This function is usually evaluated through an infinite summation over both occupied and unoccupied KS states. This summation may be slowly convergent. For systems with a discrete spectrum of excitations (like finite systems), it is possible to recast this equation through a series of transformations [38] into a form that is manageable and resembles the equations that are obtained in the time-dependent

Hartree-Fock and Bethe-Salpeter approaches in many-body perturbation theory [42]. We write here only the final result – which is the equation that `octopus` actually solves:

$$\mathbf{\Omega}\vec{F}_I = \Omega_I^2\vec{F}_I\,. \tag{33}$$

This is an eigenvalue equation of dimension N_{pairs}, where N_{pairs} is the number of pairs of occupied and unoccupied KS orbitals that one wishes to consider (ideally infinite). The matrix $\mathbf{\Omega}$ is defined as:

$$\Omega_{ia\sigma,jb\mu} = \delta_{ij}\delta_{ab}\delta_{\sigma\mu}(\varepsilon_{a\sigma}-\varepsilon_{i\sigma})^2 + 2\sqrt{\varepsilon_{a\sigma}-\varepsilon_{i\sigma}}K_{ia\sigma,jb\mu}\sqrt{\varepsilon_{b\sigma}-\varepsilon_{j\mu}}\,, \tag{34}$$

with the matrix elements

$$K_{ia\sigma,jb\mu} = \int\!\mathrm{d}^3r\int\!\mathrm{d}^3r'\,\varphi^*_{i\sigma}(\vec{r})\varphi_{a\sigma}(\vec{r})\left[\frac{1}{|\vec{r}-\vec{r}'|}+f_{\text{xc},\sigma\mu}(\vec{r},\vec{r}')\right]\varphi^*_{j\mu}(\vec{r})\varphi_{b\mu}(\vec{r})\,. \tag{35}$$

Here i and j run over occupied KS states, a and b over unoccupied KS states, and σ and μ are spin indexes. Upon diagonalization of this matrix, we obtain the eigenvalues Ω_I^2, which are the squares of the excitation energies of the system. The eigenvectors, in turn, contain the information that permits to obtain the transition densities and the oscillator strengths of these excitations.

We should remark, however, that Eq. (33) assumes that the $\mathbf{\Omega}$ matrix is independent of the excitation energy. This is an approximation: For exchange-correlation potentials with memory (e.g. Ref. [40]), one has to solve self-consistently a non-linear eigenvalue problem: $\mathbf{\Omega}(\Omega_I)\vec{F}_I = \Omega_I^2\vec{F}_I$, whose manifold of solutions is usually larger than the approximated one.

In order to implement the TDDFT-based linear-response equations – essentially, Eq. (33) –, one just needs to provide a means to calculate the $\mathbf{\Omega}$ matrix elements in Eq. (34). The only new difficulty is the appearance of a new ingredient, the kernel $f_{\text{xc}}(\vec{r},\vec{r}')$. Note that this is a two-point function, although it reduces to a one-point function in local approximations to the exchange and correlation energy functionals.

3.4 High-intensity fields

Now, a word about calculations in the non-linear regime (i.e. when applying large external electromagnetic fields, or when studying the scattering of a high energy projectile by a molecule). One external field is added to the "internal" KS potential; In such cases the external potential takes typically the form:

$$v(\vec{r},t) = E_0 f(t)\sin(\omega t)\hat{\mathbf{p}}\cdot\vec{r}\,. \tag{36}$$

This ansatz describes a classical laser pulse in the dipole approximation, where f is the "envelope" of the pulse and $\hat{\mathbf{p}}$ is the polarization of the light. Finally, E_0 determines the intensity of the pulse. Of course there is no problem to extend this ansatz in order to describe more general situations.

When dealing with high-intensity fields, there will be a non-negligible transition probability to unbound states. In other words, the incoming field may induce the ionization of part of the electronic cloud. The observables related to this process are the ionization probabilities, which are functionals of the time-dependent density by virtue of the Runge-Gross theorem.

Unfortunately, these functionals are unknown. There is not a fully satisfactory way to deal with this issue within a grid-based formalism, but there are some approximate methods that rely on a geometrical picture [41]: we define a bound region $\mathcal{A}$ around the system that contains the bound states, and the density that travels outside (to the rest of the space, $\mathcal{B}$) corresponds to ionized states.

In practice, there are two schemes to simulate this ionization in `octopus`. The first consists of adding an imaginary potential to the Hamiltonian, which is defined to be non-zero only in a frontier region $\mathcal{F}$ that separates $\mathcal{A}$ and $\mathcal{B}$. It varies smoothly from zero in the intersection of $\mathcal{F}$ and $\mathcal{A}$ to a maximum in the limit of the simulation region. The role of this imaginary potential is to eliminate in a smooth way the electronic density that approaches the frontier of the simulation region. The second uses a mask function to selectively remove the density close to the borders.

A classical example for the application of TDDFT within the high-intensity field regime is the calculation of the High-Harmonic Generation (HHG) spectrum of a molecule: If we shine a very intense laser field (of intensity over $10^{13}\mathrm{W/cm}^2$) on a molecule, an electron may absorb several photons, be ejected, and then return emitting one single photon. This photon has a frequency which is an integer multiple of the frequency of the external driving field. The spectrum of emitted radiation is approximately (i.e. neglecting incoherent processes) given by:

$$\sigma_{\mathrm{emission}}(\omega) = \left| \int \mathrm{d}t e^{-\mathrm{i}\omega t} \frac{\mathrm{d}^2}{\mathrm{d}t^2} \langle \hat{\vec{R}} \rangle \right|^2 . \tag{37}$$

Since the dipole $\langle \hat{\vec{R}} \rangle$ is an explicit functional of the time dependent density, the emission spectrum can then be approximated with TDDFT. A couple of examples may be found in Ref. [43].

3.5 Coupled ion-electron response

In order to study the dynamics of molecules exposed to external fields, we have implemented a mixed classical/quantum approach. The Hellman-Feynman theorem is no longer valid in this case, but we may resort to the Ehrenfest theorem; the model may be described as two coupled dynamical systems: one quantum system of non-interacting particles (the KS/TDDFT system of electrons) subject to the KS potential, and one classical system of particles describing the ions. The first system obeys Eqs. (13) and (14); the second system is described by Newton's equations:

$$m_\alpha \frac{d\vec{R}_\alpha}{dt} = \vec{P}_\alpha \, , \tag{38}$$

$$\frac{d\vec{P}_\alpha}{dt} = - \sum_j \langle \varphi_j(t) | \vec{\nabla}_{\vec{R}_\alpha} v_{\mathrm{KS}}[n] | \varphi_j(t) \rangle + \sum_{\beta \neq \alpha} \vec{F}_{\beta \to \alpha} \, . \tag{39}$$

In these equations, m_α is the mass of the nucleus tagged by α; $\vec{R}_\alpha$ and $\vec{P}_\alpha$ are their position and momentum; $\vec{F}_{\beta\to\alpha}$ is the classical electrostatic force exerted by nucleus β on nucleus α. Eq. (39) is nothing else than a reformulation of Ehrenfest's theorem.

3.6 Sternheimer's equations

One recent addition to `octopus` is the possibility of calculating response properties using density-functional perturbation theory [44–46]. Currently it is possible to calculate static polarizabilities and the first hyperpolarizabilities,

The base of this theory is that, for a given perturbative potential, we can find the first order perturbations to the wavefunctions ($\varphi_i^{(1)}$) solving the Sternheimer [47] equation

$$\left(H^{(0)} - \varepsilon^{(0)}\right) \varphi_i^{(1)} = - \left(H^{(1)} - \varepsilon^{(1)}\right) \varphi_i^{(0)} , \tag{40}$$

the $H^{(1)}$ term includes the perturbative potential and the variation of the Hamiltonian due to the variation of the density, which is

$$n^{(1)} (\vec{r}) = \sum_{i=0}^{N} \left[\varphi_i^{*(0)} (\vec{r}) \varphi_i^{(1)} (\vec{r}) + \varphi_i^{*(1)} (\vec{r}) \varphi_i^{(0)} (\vec{r})\right] . \tag{41}$$

The two equations (40) and (41) form a system that must be solved self-consistently. As the right hand side of (40) is known, this is a linear equation that can be solved by iterative methods.

Thanks to the $2n + 1$ theorem [48], using the first order perturbations of the wavefunctions, we are able to calculate properties that are second and third-order derivatives of the total energy (polarizability and the first hyperpolarizability, for instance).

This formalism is also applicable to time dependent perturbations, using TDDFT [49], where we have to solve a slightly different Sternheimer equation

$$\left(H^{(0)} - \varepsilon^{(0)} \pm \omega\right) |\varphi_i^{(1)}\rangle = -H^{(1)} |\varphi_i^{(0)}\rangle , \tag{42}$$

where ω is the frequency of the perturbative potential. We are now developing this scheme to calculate dynamical polarizabilities.

4 Adaptive coordinates

The real-space techniques for computational simulations in the condensed matter realm are usually praised for, at least, two strong advantages: On the first hand, the intrinsically local character of the "basis set" permits, in principle, large scale parallelization by dividing the space in domains. This locality is also the basis for the use of techniques aiming at the linear-scaling of the computational effort. On the second hand, the real space mesh on which the magnitudes are represented may be locally adapted to the needs of each region – one feature which is difficult to translate to the more traditional plane wave representation.

This section is centered on the second aspect: One possible route to implement curvilinear coordinates, able to adapt the local resolution to the needs of each region in space. The next section will be dedicated to the parallelization.

A real-space representation is the description of the functions involved in the calculation by the values that these functions take on a collection of points in real space (the "grid" or "mesh"). This grid can be regular – meaning that the points are equispaced between each other – or

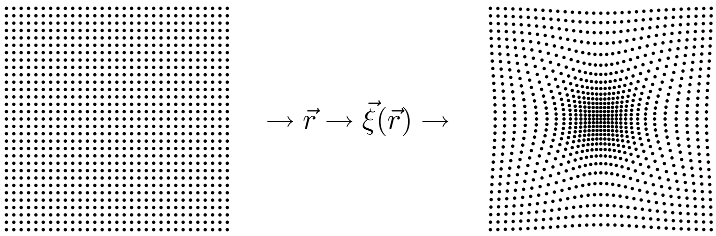

Figure 1: An adaptive-coordinates representation is constructed through the definition of a coordinate transformation function $\vec{\xi}$.

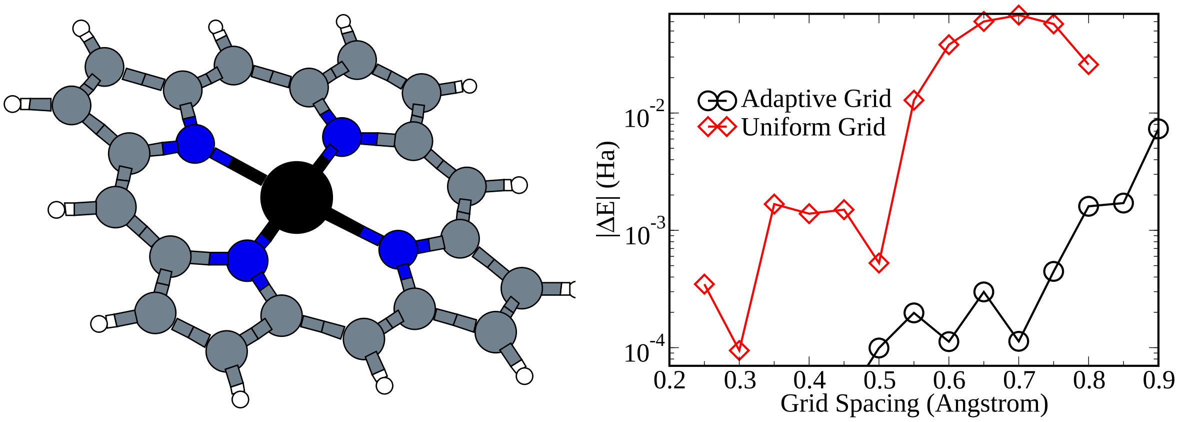

Figure 2: Left: the "basic" porphyrin molecule. Right: convergence study of the ground-state total energy of the porphyrin molecule, with and without the use of the adaptive-grid technique. In this case, we have used the transformation formula of F. Gygi [50], doubling the local cut-off near the atoms, and a 44-point stencil to represent the Laplacian operator.

curvilinear. An "adaptive" or "curvilinear" grid is the deformation of a regular grid through some transformation function (see Fig. 1), which leads to a curved distribution of points. This deformation should be intelligently done, so that the density of points increases in the regions of space where the problem requires a larger resolution.

In the last years, a number of groups have contributed to the development of these techniques in the field of electronic structure calculations. We have specially looked at the works of F. Gygi and collaborators [50], Hamann [51], Pérez-Jordá [52], Briggs and collaborators [53], E. Fattal and collaborators [54] and at the work of Waghmare and collaborators [55]. In `octopus` we have implemented one scheme based on the ideas of these works.

An example of curvilinear coordinates is based on the following transformation function, first proposed by Gygi [50]

$$\xi^i = x^i + \sum_\alpha (x^i - R^i_\alpha) f_\alpha(|\vec{x} - \vec{R}_\alpha|), \tag{43}$$

$$f_\alpha(r) = A_\alpha \frac{a_\alpha}{r} \tanh\left(\frac{r}{a_\alpha}\right) \exp\left[-\left(\frac{r}{b_\alpha}\right)^2\right], \tag{44}$$

where α runs over the atoms, and $\vec{R}_\alpha$ are the atomic positions. The parameters A_α, a_α, and b_α fine-tune the transformation – what will be the resolution enhancement, the region around each atom where the regular grid is transformed, etc.

Once that the positions of the grid points are specified, we represent each function involved in the calculation (f, g,…) by the vector formed by the values that it takes on the grid points

$(\mathbf{f}, \mathbf{g}, \ldots)$. We must then define the basic operations:

- The basic vector space operations are of course unaltered: $\alpha f + \beta g \rightarrow \alpha \mathbf{f} + \beta \mathbf{g}$.
- The integration is now a weighted sum; each grid point i has a weight ω_i, which is in fact the Jacobian of the transformations:
$$\int \mathrm{d}^3 r\, f(\vec{r}) = \sum_i \omega_i f_i \,, \tag{45}$$
$$w_i = \det \left[\frac{\partial x^i_m}{\partial r_n} \right] \,. \tag{46}$$
- The integral permits to define the dot product:
$$\langle f | g \rangle = \sum_i \omega_i f_i g_i = \mathbf{f}^\dagger \mathbf{\Omega} \mathbf{g} \,. \tag{47}$$
  We see how a metric appears naturally; it is given by the diagonal matrix $\mathbf{\Omega}$: $\Omega_{ij} = \delta_{ij}\omega_i$.
- The operators that are local in real space are trivial to represent; they are just multiplicative operators in the same way that they were for uniform grids.
- The differential operators (e.g. the kinetic operator) are the main problem. In principle, one can use the transformation laws to relate the differential operators in the new grid to the usual well-known finite-differences discretization expressions in the uniform space:
$$\nabla^2 = \sum_{ij} g^{ij} \frac{\partial}{\partial \xi^i} \frac{\partial}{\partial \xi^j} + \sum_{lik} \frac{\partial \xi^l}{\partial x^k} \frac{\partial}{\partial \xi^l} \left(\frac{\partial \xi^i}{\partial x^k} \right) \,. \tag{48}$$
  This, however, involves a lot of computations, and in general does not provide a Hermitian operator.

  Instead, we have used the following approach, valid for any grid, even unstructured ones:
    - Select a stencil: given each point in the grid, the stencil is the set of neighboring points from which we calculate the action of any differential operator $\mathcal{D}$:
$$(\mathcal{D}(f))_i = \sum_{j \in \mathrm{Stencil}(i)} C^i_j f_j \,. \tag{49}$$
    - Select a set of polynomials $\{x^\alpha y^\beta z^\delta\}$, of equal number to the points in the stencil: the coefficients C^i_j are fixed by ensuring that the action of $\mathcal{D}$ on these polynomials is *exact*.

      This amounts to solving a linear system of equations of order the size of the stencil for each point of the grid. This operation must be performed at the beginning of the calculations, or every time that the grid is redefined.
    - The Laplacian operator is Hermitian; the gradient operator is anti-Hermitian. The resulting numerical operator $\mathbf{C}$, however, is *not* (anti) Hermitian. But it can be (anti) symmetrized by transforming the matrix $\mathbf{C}$ in the following way:
$$\tilde{\mathbf{C}} = \frac{1}{2}(\mathbf{C} \pm \mathbf{W}^{-1}\mathbf{C}\mathbf{W}) \,. \tag{50}$$

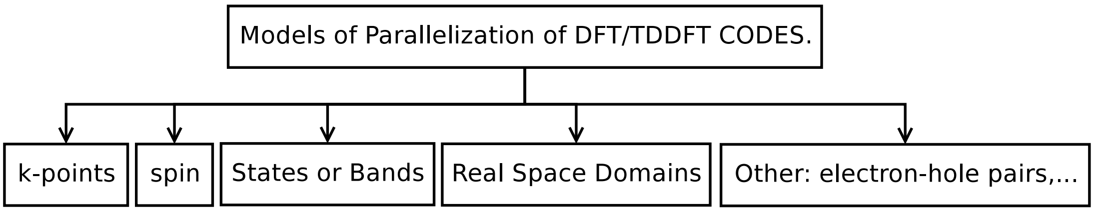

Figure 3: Parallelization modes for DFT/TDDFT codes.

More details about the selection of the stencil and of the fitting polynomials may be consulted directly in the code, and will be provided in a separate publication. Here we will finish this section by presenting an example that shows the gain that is to be expected from the use of adaptive coordinates.

For that purpose we have chosen the “base” porphyrin molecule, depicted on the left hand side of Fig. 2. We have then calculated its ground state total energy at the KS/LDA level, with varying grid spacing. We plot, on the right hand side of Fig. 2, the resulting convergence study – a plot of the error in the total energy as a function of the grid spacing.

We show two curves, one of them corresponds to the calculations with the standard uniform grid, and one of them with adaptive coordinates. The meaning of the grid spacing in the latter case is ambiguous (the spacing is no longer constant), and therefore we plot in the figure the original grid spacing, *before* the transformation is performed. In this way, at each abscissa point the number of grid points of both the uniform and the adaptive grid is the same.

In this case, we used Gygi’s transformation function, Eq. (43). The parameters are chosen in such a way that the grid resolution is doubled in the vicinity of the nuclei. The plot shows a faster convergence for the adaptive grid: The calculation can be done, with the same level of accuracy, by making use of roughly half the number of points (it is the number of points in the grid that determines the final computational cost).

5 Large-scale parallelization

The current trend in hardware technology follows a steep increase in the number of processors in each computing machine or facility, as opposed to the trend towards an increase in the clock speed or number of operations that each processing unit may perform per unit time. To use modern computing facilities efficiently, we have to ensure that our codes are able to benefit from such parallel-computing architectures.

5.1 Parallelization strategies

Recently, we have incorporated into `octopus` a multiple-way parallelization scheme that may divide the work among a given number of processors, splitting the tasks either in **k**-points, in Kohn-Sham states, in regions of real-space, or in a combination of all of them. Each single form of the contemplated parallelizations may scale by its very nature only to a certain maximum number of processors. Only combined schemes allow to overcome such limitations.

In Fig. 3 we have represented the various possible modes for which a task division within a DFT/TDDFT calculation may be obtained:

- **k**-points: In a ground-state DFT calculation each processor solves the KS equation

  $$\hat{H}^{\mathrm{KS}}_{\mathbf{k}} \, \varphi_{n\mathbf{k}}(\vec{r}) = \varepsilon_{n\mathbf{k}} \varphi_{n\mathbf{k}}(\vec{r}) \tag{51}$$

  for a given but fixed **k**-point. Communication among the nodes is only required for the calculation of the (common) density or other Brillouin-zone integrations. This is the parallelization mode that most ground-state solid-state DFT codes offer. The implementation is straightforward and scales very nicely with the number of processors. However, limitations arise for systems with very large unit cells.

- spin: The different spin subspaces may be treated by different processors. In practice this is rather similar to the **k**-point parallelization, so that both spin and **k**-points are represented as common quantum numbers and are treated on the same footing.

- Kohn-Sham states: For the ground-state a parallelization in state indices or bands is more involved than the **k**-point parallelization. Essentially, the state indices have to be divided into different state-groups. The eigenproblem is then solved for each group and a subsequent orthonormalization of the states is performed among the states of different groups. Special block-diagonalization algorithms are used for this task.

  On the other hand, in time-dependent DFT the parallelization in state indices is straightforward. Since the time-dependent Kohn-Sham equations constitute a N-fold initial value problem, each orbital/state index may be propagated on a different processor. Communication is only required for the calculation of the density and in some cases for the calculation of the current.

- real-space regions: The real-space mesh is divided into different domains, so that each processor can treat a different portion of the total mesh. This is illustrated in the left of Fig. 4, where we show a six-fold domain decomposition of a benzene molecule in the x-y plane. Apart from the distribution of the computational burden over the different nodes, this parallelization strategy also has the distinct advantage that the total memory requirement for the storage of the grid points is distributed over the nodes. Much larger systems can be treated if domain parallelization is used.

  The price one has to pay for this flexibility is the rather involved implementation which requires non-trivial communication among the nodes. On the right hand side of Fig. 4 we show the application of a finite-difference stencil of the Laplacian to a boundary point of Domain B. Due to the non-local character of the stencil this requires points of Domain A (grey shaded area) which are held in memory by a neighboring processor. These points are termed ghost points and need to be communicated among neighboring nodes every time the function values on the grid change. Low-latency high-bandwidth networks are therefore the preferred interconnects for such an implementation.

- other: electron-hole pairs, scattering states, etc: The basis set in a linear response calculation within time-dependent DFT consists of electron-hole pairs: products of occupied and

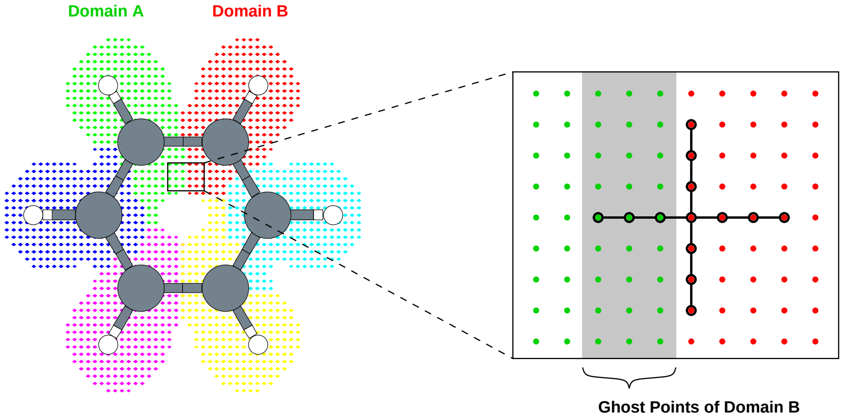

Figure 4: Ghost points in a domain parallelization.

unoccupied Kohn-Sham states. Typically a large number of matrix elements in the form of Eq. (34) is required. Since the different matrix elements are independent of each other, a parallelization may be easily obtained by simply distributing their calculation over the different nodes.

The natural description of a quantum-mechanical transport calculation is in terms of scattering states at given energies. Similar in spirit to the parallel treatment of Kohn-Sham states, the propagation of these scattering states can be distributed over different nodes.

5.2 Technical aspects

For the implementation of the multiple-way parallelization in `octopus` we have employed version 1 of the message passing standard MPI [56]. The choice was mainly motivated by the availability of this MPI variant for virtually any computer architecture, and by the fact that MPI is the de facto standard on large-scale parallel architectures. We did not make use of version 2 or newer developments in the MPI standard since these features are still not available on many platforms. Parallelization techniques like OpenMP have been ruled out from the start, since they are limited to shared memory architectures with many processors in a single machine. The current Top500 list [57] contains only a few machines of this kind.

Within `octopus` we allow for various different box shapes like spheres, cylinders or parallelepipeds in 3D, or disks and rectangles in 2D. With a recent addition to the code even arbitrary user-defined shapes can be chosen. To treat the segmentation of the real space mesh for all possible geometries and spatial dimensions on the same footing, we convert the sequence of mesh points into a structured graph. The problem of decomposing the real-space mesh into different domains is then translated into a graph-partitioning problem. Several graph algorithms are available for such tasks and we have chosen for our implementation in `octopus` a "multilevel k-way partitioning algorithm" as provided by the `METIS` library [58]. The library functions try to minimize the edge cuts while the graph partitioning is performed. Translated back to the

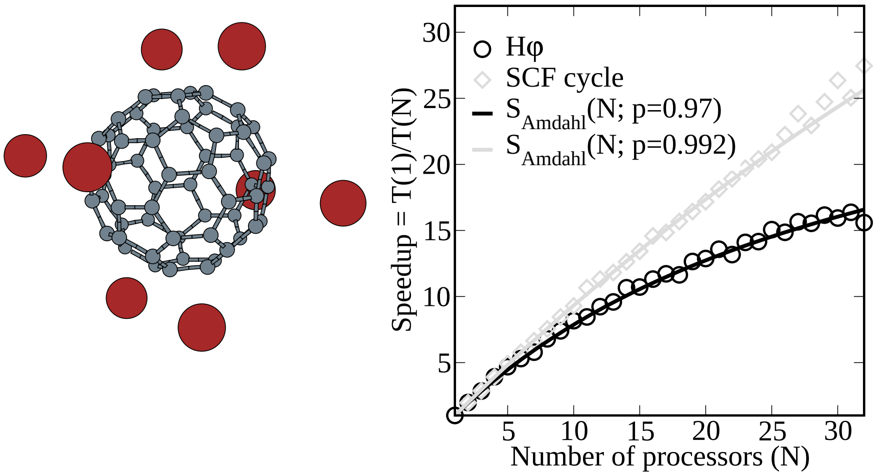

Figure 5: Measured speedups for a domain-parallel calculation of $Cs_8@C_{60}$.

real-space mesh this means that the intersection area of neighboring domains is minimized which in turn implies that fewer ghost points have to be communicated between the different nodes. This effect can be seen nicely in the example of the benzene molecule (Fig. 4) where the domain boundaries computed by `METIS` always lie between two carbon atoms, the optimal situation in this case.

5.3 Application to $Cs_8@C_{60}$

In Fig. 5 we show a sample calculation for 8 Cs atoms attached to C_{60}. Because of the size of the Cs atoms a rather large sphere with 26 Å diameter was used as enclosing computational domain. By choosing a grid spacing of Δ=0.20Å a total number of 1.177.863 grid points were contained in the calculation box.

To asses the performance of the domain parallelization we have repeated the ground-state DFT calculation of this system with a varying number of processors ranging from one to 32. On the right hand side of Fig. 5 we plot the measured speedup as function of the number of processors. The circles correspond to the timings obtained for the application of the Hamiltonian to the wavefunction and the diamonds represent the measured timings for a full SCF cycle. Both curves follow Amdahl's law [59]: Suppose that p is the fraction of a calculation that can be performed in parallel. Then $1-p$ is the percentage which is intrinsically serial. If we define the speedup $S(N,p)$ of a parallel calculation as the ratio $T(1,p)/T(N,p)$, where $T(N,p)$ is the execution time using N processors, we find

$$S(N,p) = \frac{1}{1-p+p/N}. \tag{52}$$

Note, that the speedup will always saturate to $1/(1-p)$ as function of the number of processors, if $p<1$. In Fig. 5 we have fitted our measured data to Amdahl's law (solid lines) and obtain parallel fractions $p=0.97$ for the application of $\hat{H}$ to the wavefunction and $p=0.992$ for the execution of a full SCF cycle. Both fractions indicate that a high degree of parallelization has been achieved for the domain parallelization in `octopus`. Nevertheless, since the saturation is very sensitive to the value of p there is still room for improvement in the future.

6 Periodic systems

DFT has been extensively applied to bulk systems, as much as it has been to clusters or molecules. TDDFT for solids, however, has a smaller history [42]. We intend to provide a tool for DFT and TDDFT on extended systems. In the definition of "extended systems," however, we include systems of intermediate dimensionality: systems that are periodic in one and two dimensions. These systems are still 3-dimensional (3D), but their quantum properties are those of a finite system in one or more directions, and those of a periodic system in the remaining directions.

It is possible to implement periodic boundary conditions also in real space, but we have to take special care of (i) the proper implementation of the the operators that are non-local in real space, and (ii) the correct treatment of the long-range Coulomb interaction. Regarding the first issue, we must worry about the differential operators (i.e., gradient and Laplacian), and the non-local components of the pseudopotentials. In both cases, the action of the operator on a function for a given point may need the values of the function at points that belong to a neighboring cell. The periodicity is thus enforced by identifying the "mirror" points.

Regarding the second issue – the correct treatment of the long-range Coulomb interaction – it is convenient to resort to a dual methodology, that allows to move back and forth from real to reciprocal space. In particular, the integration of Poisson's equation is more conveniently performed in Fourier space, but it is easier to impose different boundary conditions in different directions in real space.

6.1 Implementation details for bulk systems

Most of the numerical machinery described in Section 2 for finite systems can be also be used for periodic systems. In the following we will just review the main differences.

Kinetic term. For what concerns the kinetic part of the Hamiltonian, for periodic systems, we have to modify the kinetic operator used for finite systems. The feature that remains common to both cases is that, differently from what happens in plane waves codes, the kinetic energy is entirely calculated in real space. We must however remember that only the periodic part $u_{n\mathbf{k}}(\mathbf{r}+\mathbf{L}) = u_{n\mathbf{k}}(\mathbf{r})$ of the Bloch states $\psi_{n\mathbf{k}}(\mathbf{r}) = \mathrm{e}^{-i\mathbf{k}\cdot\mathbf{r}}u_{n\mathbf{k}}(\mathbf{r})$ is used as the working quantity within the cell, and, accordingly, the kinetic operator used for finite systems has to be modified in the following way:

$$\hat{T} = -\frac{1}{2}\nabla^2 \to \hat{T}_{\mathbf{k}} = -\frac{1}{2}(\nabla^2 + 2i\mathbf{k}\cdot\nabla - k^2). \tag{53}$$

External potential The total local part of the ionic potential of the infinite system is given by

$$v^{\mathrm{local}}(\vec{r}) = \sum_{\vec{n}\in P}\sum_{\alpha}^{N_a} v_{\alpha}^{\mathrm{local}}(|\vec{r} - \vec{d}_{\alpha} - \vec{L}_{\vec{n}}|)\,. \tag{54}$$

The inner sum runs over the N_a atoms of the unit cell: the index α runs over the atoms in the unit cell, and $\vec{d}_{\alpha}$ indicates the position of the α-th atom. We also use the notation $\vec{L}_{\vec{n}}$ to mean

$(n_x \vec{L}_x, n_y \vec{L}_y, n_z \vec{L}_z)$, and the outer sum is just the sum over the set $\{P\}$ of all the cells allowed by the Born-Von Kármán periodic-boundary conditions.

Evaluation of this expression either in real space or in Fourier space leads to well known convergence problems. The solution consists in splitting $v_\alpha^{\text{local}}(\vec{r})$ into a short range, and a long range part. The long range tail of each atomic potential must behave asymptotically like Z_α/r, where Z_α is the number of valence electrons for the atom α, and the long range part can be chosen in such a way that its Fourier transform is analytical, adopting a suitable representation. This representation is obviously not unique.

A convenient representation turns out to be the following:

$$v_\alpha^{\text{local}}(r) = \Delta v_\alpha(r) - Z_\alpha \frac{\text{erf}(ar)}{r}, \tag{55}$$

where a is chosen in such a way that $\Delta v_\alpha(r)$ is sufficiently localized within the cell, but is also well approximated by its Fourier series when it is truncated to N_i points per each i direction.

The Fourier transform can be performed numerically on the localized part, and analytically on the long range part

$$v_\alpha^{\text{local}}(G) = 4\pi \int_0^R \text{d}r\, r^2 \frac{\sin(Gr)}{Gr} \Delta v_\alpha(r) - 4\pi Z_\alpha \frac{\exp\left(-G^2/4a^2\right)}{G^2}. \tag{56}$$

Alternatively, the term $\Delta v_\alpha(r)$ can be directly handled in real space.

Hartree potential Let us now turn our attention to the Hartree part of the potential. The solution of Poisson's equation in real space can be achieved, for example, with a conjugated gradient minimization method (see discussion in Section 2.2), but, for infinite systems, it is more convenient to transpose the problem to Fourier space, where we can take advantage of the efficient Fast Fourier Transform, that scales like $N \log(N)$ with the number of grid points N. Applying the convolution theorem, we can write Eq. (8) in Fourier space as

$$v_{\text{Hartree}}(\vec{G}) = n(\vec{G}) w(G)\,, \tag{57}$$

where $v(G)$ is the Fourier transform of the Coulomb interaction

$$w(G) = \frac{4\pi}{G^2}\,. \tag{58}$$

The treatment of the singular point $G = 0$ is particularly simple in the case of bulk crystals, since $v(G = 0)$ corresponds to the average value of the potential, which is determined up to an arbitrary constant, and it can set to 0 by observing that the overall charge neutrality of the unit cell imposes $v(G = 0) = 0$. Note that, as the density is periodic, Eq. (57) needs to be evaluated only at the reciprocal primitive vectors $\vec{G}$. The case of systems that are periodic in less than three dimensions is considered below.

6.2 Systems with reduced periodicity: the cutoff problem

In this sub-section we call *nD-periodic* a 3D system, that can be considered infinite and periodic in n dimensions, being finite in the remaining $3 - n$ dimensions. In order to simulate this kind of systems, a commonly adopted approach is the supercell approximation. In the supercell approximation the physical system is treated as a fully 3D-periodic one, but a new unit cell (the supercell) is built in such a way that some extra empty space separates the periodic replica along the direction(s) in which the system is to be considered as finite.

This approach has several major drawbacks. For instance, it is well known that the response function of an overall neutral solid of molecules is not equal, in general, to the response of the isolated molecule, and converges very slowly to it, when the amount of vacuum in the supercell is progressively increased [42, 60]. Another problem arises when studying slabs, as a layered system (i.e., a supercell) is in fact equivalent to an effective chain of capacitors. These issues become particularly evident in the approaches that involve the calculation of non-local operators or response functions because, in these cases, two supercells may effectively interact even if their charge densities do not overlap at all. Moreover, even in those cases in which good convergence can be achieved, the supercell can be considerably larger than the system, affecting the performance, and wasting computational resources.

Some of the available methods used to avoid these problems have been mentioned in Sec. 2.2, but, with special regard to the periodic case, and considering that the Fourier space method is still the fastest available to solve the Poisson problem, some of us [61] have recently developed a new reciprocal space analytical method to cutoff the long range interactions in supercell calculations, extending previous works for finite systems [14]. This method has been implemented and tested in `octopus`.

Our goal is to transform the 3D-periodic Fourier representation of the Hartree potential

$$v_{\mathrm{Hartree}}(\vec{G}) = n(\vec{G})w(\vec{G})\,, \tag{59}$$

into the modified one

$$\tilde{v}_{\mathrm{Hartree}}(\vec{G}) = \tilde{n}(\vec{G})\tilde{w}(\vec{G})\,, \tag{60}$$

such that all the interactions among the undesired periodic replica of the system disappear. The present method is a generalization of the method proposed by Jarvis and collaborators [62] for the case of a finite system.

In order to build this representation, we want to: (i) define a screening region $\mathcal{D}$ around each charge in the system, out of which there is no Coulomb interaction; (ii) calculate the Fourier transform of the desired effective interaction $\tilde{w}(r)$, that equals the Coulomb potential in $\mathcal{D}$, and is 0 outside $\mathcal{D}$

$$\tilde{w}(r) = \begin{cases} \frac{1}{r} & \text{if } r \in \mathcal{D} \\ 0 & \text{if } r \notin \mathcal{D} \end{cases}. \tag{61}$$

Finally, we must (iii) modify the density $n(\vec{r})$ in such a way that the effective density is still 3D-periodic, so that the convolution theorem can be still applied, but densities belonging to undesired images are not close enough to interact through $\tilde{w}(r)$.

The choice of the region $\mathcal{D}$ for step (i) is suggested by symmetry considerations. It is a sphere (or radius R) for finite systems, an infinite cylinder (of radius R) for 1D-periodic systems, and an infinite slab (of thickness $2R$) for 2D-periodic systems.

Step (ii) means that we have to calculate the modified Fourier integral

$$\tilde{w}(\vec{G}) = \int \mathrm{d}^3 r\, \tilde{w}(r) e^{-\mathrm{i}\vec{G}\cdot\vec{r}} = \int_{\mathcal{D}} \mathrm{d}^3 r\; w(r) e^{-\mathrm{i}\vec{G}\cdot\vec{r}}\,. \tag{62}$$

Still, we have to avoid that two neighboring images interact by taking them far away enough from each other. The cutoff functions are analytical in Fourier space except some particular sets of points (the $G_x = 0$ plane in the 1D-periodic case, and the $G_\parallel = 0$ plane in the 2D-periodic case), for which a suitable limiting procedure has to be followed in order to get finite results (explained in Ref. [61]). The results of the integral (62) are the following

- 0D-periodic

$$\tilde{w}^{0D}(G) = \begin{cases} \frac{4\pi}{G^2}[1 - \cos(GR)] & \text{for } G \neq 0 \\ 2\pi R^2 & \text{for } G = 0 \end{cases} \tag{63}$$

- 1D-periodic ($G_\perp = \sqrt{G_y^2 + G_z^2}$)

$$\tilde{w}^{1D}(G_x, G_\perp) = \begin{cases} \frac{4\pi}{G^2}\big[1 + G_\perp R J_1(G_\perp R) K_0(|G_x|R) & \text{for } G_x \neq 0 \\ \qquad - |G_x| R J_0(G_\perp R) K_1(|G_x|R)\big] & \\ -4\pi \int_0^R \mathrm{d}r\; r J_0(G_\perp r)\log(r) & \text{for } G_x = 0 \text{ and } G_\perp > 0 \\ -\pi R^2 (2\log(R) - 1) & \text{for } G_x = 0 \text{ and } G_\perp = 0 \end{cases} \tag{64}$$

- 2D-periodic ($G_\parallel = \sqrt{G_x^2 + G_y^2}$)

$$\tilde{w}^{2D}(G_\parallel, G_z) = \begin{cases} \frac{4\pi}{G^2}\left[1 + e^{-G_\parallel R}\left(\frac{|G_z|}{G_\parallel}\sin(|G_z|R) - \cos(|G_z|R)\right)\right] & \text{for } G_\parallel \neq 0 \\ \frac{4\pi}{G_z^2}\left[1 - \cos(|G_z|R) - G_z R \sin(|G_z|R)\right] & \text{for } G_\parallel = 0 \text{ and } G_z \neq 0 \\ -2\pi R^2 & \text{for } G_\parallel = 0 \text{ and } G_z = 0 \end{cases} \tag{65}$$

A suitable supercell consists in increasing the cell in the non-periodic directions (in the 1D-periodic case the supercell size is actually $(1 + \sqrt{2})L$, and in the 0D-periodic it is $(1 + \sqrt{3})L$), and setting to zero the density in this extended area. Again, since the density naturally falls off to zero at the border of a finite system, doubling the cell size in all periodic directions is sufficient.

Figure 6 illustrates the effect of the cutoff on the potentials. The left panel shows the ionic potential, the Hartree potential, and their sum for a Si atom in a parallelepiped supercell with side lengths of 2.5, 11, and 11 a.u. respectively in the x, y and z directions. No cutoff is used here. The ionic potential is roughly behaving like $1/r$ in the area not too close to the nucleus (where the pseudopotential takes over). The total potential, on the other hand, falls off rapidly to an almost constant value at around 4 a.u. from the nuclear position, by effect of the electron screening.

In the right panel of Fig. 6 the cutoff is applied to the all the potentials consistently. The radius of the cylinder is $R = 5.5$ a.u. such that there is zero interaction among the replica of the system along the y and z axes. The ionic potential now behaves like it is expected for a potential of

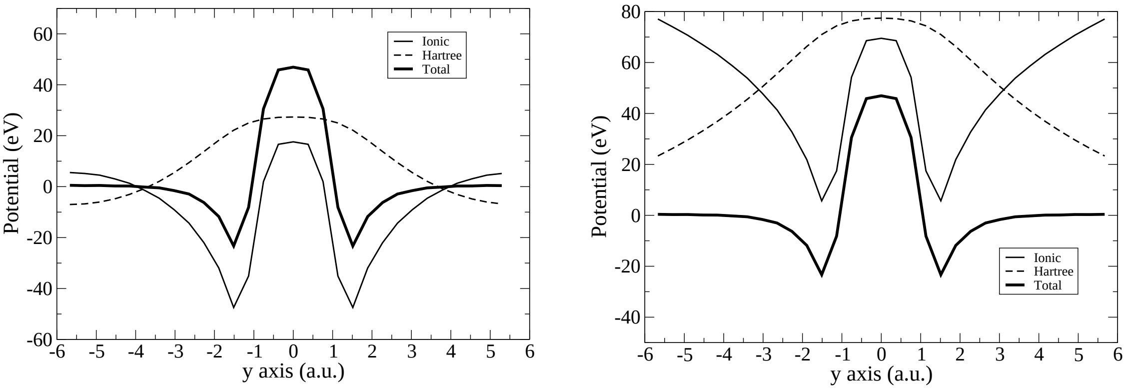

Figure 6: Calculated total and ionic and Hartree potentials for a 3D-periodic (left) and 1D-periodic (right) Si chain.

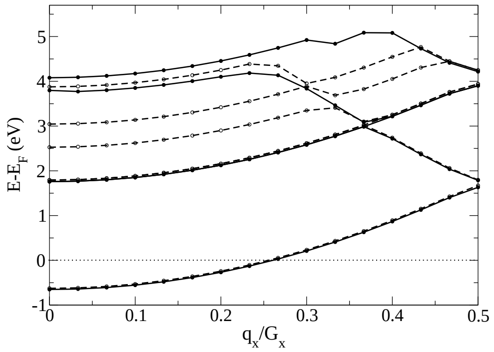

Figure 7: Effect of the cutoff in a Na linear chain in a supercell size of 7.5x19x19 a.u. The bands obtained with an ordinary supercell calculation with no cutoff (dashed line) are compared to the bands obtained applying the 1D cylindrical cutoff (solid line).

a chain, i.e. diverges logarithmically, and is clearly different from the latter case. Nevertheless, the sum of the ionic and Hartree potential is basically the same as for the 3D-periodic system. In the static case the two band structures are found to be the same, confirming that, as far as static calculations are concerned, the supercell approximation is good, provided that the supercell is large enough. In static calculations, then, the use of our cutoff only has the effect of allowing us to eventually use a smaller supercell, which provides clear computational savings. In the case of the Si-chain a full 3D calculation would need a cell size of 38 a.u. whereas the cutoff calculation would give the same result with a cell size of 19 a.u. Of course, when more delocalized states are considered, like higher energy unoccupied states, larger differences are observed with respect to the supercell calculation.

In Fig. 7 a Na chain with lattice constant 7.5 a.u. is considered in a cell of 7.5x19x19 a.u., and the effect of the cutoff on the occupied and unoccupied stated is shown. As expected, the occupied states are not affected by the use of the cutoff, since the density of the system within the cutoff radius is unchanged, and the corresponding band is the same as it is found for an ordinary 3D supercell calculation with the same cell size. However there is a clear effect on the bands corresponding to unoccupied states, and the effect is larger the higher the energy of the states. In fact, the high energy states, and the states in the continuum are more delocalized, and therefore the effect of the boundary conditions is more sensible.

In summary, the proposed cutoffs are functions in Fourier space, that are used as a multiplicative factor to screen the bare Coulomb interaction. The functions are analytic everywhere but in a sub-domain of the Fourier space that depends on the periodic dimensionality. In Ref. [61] we show that the divergences that lead to the non-analytical behavior can be exactly canceled when both the ionic and the Hartree potential are properly screened. This technique is exact, fast, and very easy to implement in already existing supercell codes.

7 Conclusions

`octopus` was officially born on the 1st of January 2002. Since then, the code has grown at a steady pace, both in the number of lines of code (that will soon reach the 50.000 lines of Fortran 90), and in the kind of problems it is able to tackle. In this article we gave a brief overview on the code, mentioning some of the algorithms used and their numerical implementation. Some of the most recent developments were discussed in more detail, namely (i) the use of curvilinear coordinates, that can improve dramatically the efficiency of the calculation; (ii) the multiple parallelization approach, that allows the code to scale in some situations to several hundred processors; and (iii) the extension of the code to periodic systems. Nevertheless, `octopus` is still, and will always be, a work in progress. In fact, our TODO list already includes, among others, (i) the extension to all-electron calculations, either using the Projector Augmented Wave technique, or by using specially crafted curvilinear transformations able to describe adequately the core wave-functions; (ii) the possibility of performing fully-relativistic (i.e., Dirac-level) calculations; (iii) the possibility of using hybrid exchange-correlation functionals; etc.

Note, however, that the code is not important *per se*, but due to the physics and chemistry we can learn from it. We believe that `octopus` has already reached a high level of maturity when it comes to the calculation of linear optical properties in nanostructures. In fact, we, and several other groups around the world, routinely use `octopus` to study the optical spectra of large nanocrystallites, bio- chromophores, and even aromatic molecules with astrophysical implications. `octopus` can also be efficiently used to study the interaction of molecules with strong lasers, to calculate (hyper)polarizabilities, etc. However, experimentalists have nowadays at their disposal numerous probes to study physical systems – infrared, visible and ultra-violet light, X-ray radiation, magnetic fields, electron beams, etc. It would be certainly helpful if a tool could describe consistently this whole plethora of spectroscopies. With `octopus` we are still far from this objective, but by adding new features and by making the code more user friendly, we expect to provide a code that is useful to a large scientific community.

Acknowledgements

We have employed the computing facilities of the Barcelona Supercomputing Center. The authors were partially supported by the EC Network of Excellence NANOQUANTA (NMP4-CT-2004-500198), by the Research and Training Network EXC!TING (HPRN-CT-2002-00317), and by the Deutsche Forschungsgemeinschaft in SFB 450. AR thanks the 2005 Bessel research award of the Humboldt Foundation.

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- ABINIT: `http://www.abinit.org/`
- ADF: `http://www.scm.com/`
- DACAPO: `http://www.camp.dtu.dk/`
- EXC!TING: `http://exciting.sourceforge.net/`
- GAMESS: `http://www.msg.ameslab.gov/GAMESS/GAMESS.html/`
- GAUSSIAN: `http://www.gaussian.com/`
- PWSCF: `http://www.pwscf.org/`
- SIESTA: `http://www.uam.es/departamentos/ciencias/fismateriac/siesta/`
- TURBOMOLE: `www.chem-bio.uni-karlsruhe.de/TheoChem/turbomole/intro.en.html/`
- VASP: `http://cms.mpi.univie.ac.at/vasp/`
- WIEN2K: `http://www.wien2k.at/`

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