Ψ_k Newsletter

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

Number 47 October 2001

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Contents

1 Editorial

Similarly to the previous newsletter, we start this newsletter with a call for scientific highlights in the section **General News**. Please do read this and try to respond positively. The section **News from the ESF Programme** contains reports on workshops, of which two include abstracts of presented papers. In this section we also have reports on recent collaborative visits. The workshop/conference announcements can be found in the **News from the RTN Network**, **News from the ESF Programme** and **General Workshop/Conference Announcements** sections. In addition, in the **News from the ESF Programme** section there is an annual report of Volker Heine, the chairman of the **ESF Programme**, on the 2001 activities of the programme. A number of position announcements can be found in the usual **General Job Announcements** section, which is followed by the **Abstracts** section with abstracts of the recently published or submitted papers. The newsletter is finished with the scientific highlight of the month by D.R.Bowler (*University College, London*), T.Miyazaki (*Tsukuba*), and M.J.Gillan (*University College, London*) on **"Linear scaling ab initio calculations: Recent Progress with the Conquest code"**. Please see the table of contents for further details.

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

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

The above contains information on the Psi-k 2001 workshops and hands-on courses. In these pages you can also find information on how to apply for funding to make collaborative visits.

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

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

	function
psik-coord@daresbury.ac.uk	**messages to the coordinators, editor & newsletter**
psik-management@daresbury.ac.uk	**messages to the NMB of all Networks**
psik-network@daresbury.ac.uk	**messages to the whole Ψ_k community**

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

2 General News

2.1 Call for Scientific Highlights for 2002

Unfortunately, our previous calls for scientific highlights for 2002 were unsuccessful, since we have had only one response from our readers. Therefore, here we repeat our appeal to all our subscribers in and outside Europe.

As you are fully aware, we publish six Psi-k newsletters a year and in each of them there is a scientific highlight. Six highlights a year may not seem that many, but it is increasingly harder to find volunteers for writing them. In addition, we find that there are only a few European groups who are willing to contribute a highlight from time to time. However, it would be beneficial to the whole community if also, until now, less visible groups would like to share the effort of producing exciting Psi-k newsletters by contributing a scientific highlight. There are many interesting things happening across the Psi-k community and it would be nice if all of it was well represented in the Psi-k newsletters.

Note that all scientific highlights published to date can, outside the newsletters, also be viewed at a dedicated web site:

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

Therefore, if you feel that you could write a scientific highlight for one of the future newsletters, please contact us on psik-coord@dl.ac.uk suggesting a topic and preferred dates. We shall get back to you with exact dates and other details as soon as possible.

3 News from the Research Training Network (RTN)

COMPUTATIONAL MAGNETOELECTRONICS

3.1 RTN Workshop/Conference Announcements

3.1.1 XRMS-2001 Workshop

International Workshop on X-ray Spectroscopies of Magnetic Solids 2001 (XRMS-2001)

Organized by:

W. Kuch, Max-Planck-Institut für Mikrostrukturphysik, Weinberg 2, D-06120 Halle, Germany
P. Strange, School of Chemistry and Physics, Keele University, Keele, Staffordshire, ST5 5BG, UK

Supported by:
Max-Planck-Institut für Mikrostrukturphysik, Halle
RTN-Network: "Computational Magnetoelectronics"

SCOPE:

The international workshop on X-ray spectroscopies of magnetic solids will bring together theoretical and experimental scientists who work in the field of X-ray spectroscopies applied to research in magnetism. The meeting provides an opportunity to discuss current advances in the field.

VENUE:

Halle, Germany, Max-Planck-Institut für Mikrostrukturphysik
(see http://www.mpi-halle.de)

DATE:

Saturday and Sunday 8 - 9th December 2001 (after the BESSY user meeting; see http://www.bessy.de/News.shtml)

SCIENTIFIC PROGRAMME:

There will be several plenary and invited talks and a poster session.

AMONG THE SPEAKERS WILL BE:

P. Carra (*ESRF*)	W. Eberhardt (*BESSY*)
H. Ebert (*München*)	J. B. Kortright (*ALS, Berkeley*)
H.-C. Mertins (*BESSY*)	H. Ohldag (*ALS, Berkeley*)
P. M. Oppeneer (*Dresden*)	M. Sacchi (*LURE*)
J. Vogel (*CNRS*)	H. Wende (*FU Berlin*)
E. Weschke (*FU Berlin*)	

REGISTRATION:

Registration fee will be 45 Euro. Please register as soon as possible via FAX or EMAIL to:

W. Kuch fax: +49 (0) 30 6392 4984
kuch@bessy.de

or

P. Strange fax: +44 (0) 1782 711093
P.Strange@phys.keele.ac.uk

If you wish to make a presentation please specify your preference:
- oral contribution (if possible)
- poster contribution

Submit the title and a half page abstract (LaTeX preferred) not later than September 30th, because a booklet of abstracts will be distributed.

FURTHER INFORMATION:

A web page will be available soon: http://www.mpi-halle.de/~xrms01

Looking forward to meet you in Halle,

Wolfgang Kuch & Paul Strange

4 News from the ESF Programme

"Electronic Structure Calculations for Elucidating the Complex Atomistic Behaviour of Solids and Surfaces"

4.1 Chairman's Annual Report for 2001

This year all the activities have been continued very actively and successfully.

The number of workshops and tutorial activities has been a record number of 17 including two still to be held before the end of the year. This includes five 'schools' and hands-on training courses and other tutorial activities.

Four workshops were held jointly with CECAM, whose cooperation we view very positively. In fact the Chairman Volker Heine has been invited to be one of a small group of 'consultants' at CECAM to help stimulate and advise on activity at CECAM in our field.

The number of individual research and training visits to date since the last report [October 2000 to the August 2001 Psi-k Newsletters] has been 12 people from seven countries to institutes in 4 countries.

The Psi-k Newsletter has been published every two months as usual, and is now regularly over 100 pages, even over 150 pages. These include detailed proceedings of some of the workshops.

The mailing list for distributing information between issues of the Newsletter is now over 900 email addresses. An increasing number of job advertisements in our field across the world now use this medium, as do quite a few conferences.

Our community continues to take an active part in the Euresco conferences in the series "Electronic Structure of Solids and Other Systems". Although not directly the responsibility of the Psi-k Programme, there is a strong overlap in the leadership and participation, with the conferences of course also including experimentalists and a wider range of theoreticians. The conference this year "Out of the vacuum into the real world" concerned surfaces in contact with fluids, and firm proposals are in place for 2002 (Biophysics from first principles), 2003 (Ab initio many-body theory for correlated electron systems) and 2004 (Micromechanics). The range of topics and the fact that our community instigates one conference per year is a witness to the breadth and vigour of our contribution.

During the year Slovenia discontinued its membership of the Programme so that we are now 16 member countries. One of the committee members, Prof Vic Van Doren, died on 24th August 2001 after a long illness. He was always a most gentle and helpful positive person.

The mid-term review report was written last year, but the result has only become known since the last report. We were warmly commended.

The biggest concern, hanging over us like a black cloud, is the future of our community after the end of the present Programme next year. ESF will now allow us to apply for a new Programme with new science. That of course is no problem. To quote someone at a recent workshop "Here we are, discussing things which five years ago we did not even dream about." And from another group, "The calculations we are doing now simply could not have been done three years ago." The success of our people in getting research grants in their own countries shows the high quality of the work, but the facts suggest strongly that European collaboration is still a dirty word among the national research councils that constitute the ESF, and that choking off our little bit of networking money that sustains the high quality of the research would not bother them.

Volker Heine, Chairman

Cambridge 17.Sept.2001

4.2 Workshop/Conference Reports

4.2.1 Report on the Berlin Workshop

Workshop on Application of Density-Functional Theory in Condensed Matter Physics, Surface Physics, Chemistry, Engineering and Biology

(Berlin, 23 july – 1 August 2001)

This ten-day course was organised by Arno Schindlmayr, Peter Kratzer, Jörg Neugebauer and Matthias Scheffler at the Fritz-Haber-Institut der Max-Planck-Gesellschaft in Berlin. Aimed especially at young researchers and Ph.D. students in the wider field of electronic-structure calculations, the workshop programme was concerned with a detailed discussion of basic aspects of density-functional theory and its application in different contexts. *Ab initio* molecular dynamics and perturbative schemes for excited states, such as the GW approximation and time-dependent density-functional theory, were also covered. Besides the lectures, there were six hands-on sessions in which the practical use of the FHI98md computer code (a plane-wave pseudopotential implementation), the construction of pseudopotentials and the calculation of quasiparticle band structures in the GW approximation were taught.

In order to guarantee individual attention during the tutorial sessions, the number of participants had to be limited to seventy, although more than twice as many applied. We tried our best to ensure a fair selection but obviously could not do justice to all applicants. Thus here comes a big "SORRY" to those we had to reject.

Instead of our own assessment of the workshop, we include below comments from some of the participants themselves. The workshop programme, complete with abstracts and full lecture notes, is available at

http://www.fhi-berlin.mpg.de/th/Meetings/FHImd2001/

Participants' Comments

This was the fourth biennial workshop on The Application of Density Functional Theory carried out by the Fritz Haber Institute Theory Group, with previous such workshops held in 1994 (Berlin), 1996 (Berlin), and 1999 (Trieste). It was financially supported by the Fritz Haber Institute, the ESF STRUC Psi-k Program together with the Wilhelm and Else Heraeus Foundation. Fifteen lectures were given addressing fundamental theory, formulations and results together with many computational issues such as convergence, choice of pseudopotentials and exchange-correlation functionals, visualization etc. These were supported by hands-on-experience with the Fritz Haber Institute's own first-principles molecular dynamics (FHIMD) computer code through six four-hour practical computer sessions. Other activities in this workshop included a poster session with 34 contributions where the participants were given the opportunity to present their research work.

The lectures on methodology were centered on three topics: (i) Density Functional Theory (DFT), (ii) *ab initio* molecular dynamics, and (iii) quasi-particle band structure schemes. The foundations of DFT methods were laid down clearly with a discussion of various pseudopotential schemes, exchange-correlation potentials and iterative diagonalization schemes for total energy minimization. *Ab initio* molecular dynamics began with a discussion of the Car-Parrinello technique, choice of fictitious mass in CP molecular dynamics linked to macroscopic phenomena through Nose-Hoover thermostats. Inherent problems of DFT in obtaining the energy gap were explained and improvements shown through the GW approach and time-dependent DFT. Specific applications of FHIMD were given in areas such as surface reconstruction and adsorption, biological systems and device physics.

All the lectures were very well organized and presented by an extremely competent scientific team. The lecturers were mainly from the FHI Theory Group together with a few from other institutions with close affiliations to this group. Tutors, who were mainly Ph.D. or post-doctoral research associates, led the six afternoon hands-on sessions and so these provided a platform to train the budding talents at the FHI. The examples of the practical sessions were chosen carefully to emphasize the salient points of the morning lectures and in particular were designed to obtain a feel for the necessary parameters. The computer resources available for the practical sessions were adequate with two persons sharing a computer. This meant that examples could be fully explored by each pair and this contributed greatly to the success of the workshop.

The team spirit of the FHI-theory group and the leadership of Prof. Scheffler of the Theory Group should be commended. We strongly urge the European Funding Agencies to continue their support of the efforts of the FHI Theory Group in disseminating their scientific expertise through such workshops. We congratulate the organizers for a superb job and we hope that this workshop will open doors to new world wide collaborations.

Chakram S. Jayanthi
Department of Physics, University of Louisville, Kentucky, USA

Gustavo Martini Dalpian
Depto. Fisica dos Materiais e Mecanica, Instituto de Fisica, Universidade de Sao Paulo, Brazil

Andrew Smith
School of Physics and Materials Engineering, Monash University, Victoria, Australia

4.2.2 Report on CECAM/ESF STRUC-Ψ_k Workshop on Ab Initio Modelling in the Biological Sciences

Summary of Workshop

A total of 37 participants from 13 countries attended the workshop from 11 to 13 June 2001. 26 talks covered a wide range of topics from new technical developments through to potential applications described by participants from biological disciplines.

The presentations and subsequent discussions ranged over four broad areas:

Technical Developments

The workshop was opened by Mike Payne, who gave a brief overview of Density Functional Theory. He cautioned the participants that first principles methods could not simulate true biological systems. In reality, biology is 'warm and wet'. A full description would require molecular dynamics simulations over milliseconds or even seconds, several orders of magnitude longer than can be simulated using current methods. Biological systems are also immersed in water and solvation effects are important in many systems. Treatment of solvent molecule in a full solvation shell would require the treatment of tens of thousands of atoms for large molecules. Current technology cannot approach these times and sizes from first principles.

The restricted time-scale over which molecular dynamics can be performed can be partially overcome through the use of techniques which explore the potential energy surface for a reaction mechanism, for example identifying transition states and barrier heights. Several speakers described such studies, identifying transition states in systems such as ribonuclease A (Anik Peeters), Lysozyme (Marco De Vivo) and Caspase-3 (Marialore Sulpizi). Janez Mavri described a method for performing calculations where the quantum nature of the nuclei, in particular protons, are important.

One approach to overcome the difficulties posed by large system size is to treat only a relatively small fragment of the system using a full *ab initio* method. This small fragment is then embedded in a larger system which is modelled using an empirical molecular mechanics approach. These QM/MM methods allow the effects of the larger 'classical' region on the 'quantum' fragment to be included, albeit in an approximate manner. Glen Martyna described a method for treating the electrostatic interactions between the classical and quantum regions in an efficient manner, within a plane wave calculation. Many of the studies presented used such QM/MM methods, for example an investigation of copper binding to the prion protein responsible for 'mad cow' disease, described by Joost VandeVondele. QM/MM methods were the subject of the CECAM workshop immediately following this.

A fully *ab initio* approach to the study of large systems is provided by linear scaling, or O(N), DFT methods. These will permit the study of several thousand atoms from first principles. A

number of groups are currently implementing such algorithms and one approach is implemented in the Siesta code. The application of this code to the study of polarons in dry A-DNA was described by Emilio Artacho.

Calculation of Experimental Observables

One area in which *ab initio* simulations can contribute to the study of biological systems is the calculation of experimental observables. Many experiments are interpreted using empirical or semi-empirical models. An *ab initio* approach to calculating these observables would provide a concrete link between experiment and hypothetical structural or mechanistic models. Examples include resonance Raman, EXAFS and optical spectroscopy, ESR and NMR.

The potential of paramagnetic NMR for rapid protein structure determination was described by Lucia Banci. The effects of a paramagnetic metal ion on NMR parameters can be used to obtain constraints on the structure of metalloproteins, which constitute 30-40% of the total number of proteins in living organisms. Furthermore, these effects can be used to characterise the dynamics of these proteins.

A method for calculating NMR chemical shifts using a plane wave pseudopotential method was described by Chris Pickard. This approach allows chemical shifts to be calculated in systems containing hundreds of atoms. The results of calculations on porphyrin systems were presented, which showed good agreement with experiment. Furthermore, the ability to visualise the current densities in these systems allows the observed chemical shifts to be rationalised in terms of abstractions such as ring currents. At present, only diamagnetic systems may be studied with this approach, but extension of the theory to paramagnetic systems in underway.

Matteo Cecarelli discussed normal mode analysis of DFT calculations, from which vibrational frequencies can be calculated for comparison with resonance Raman spectra. He described an application of this to bacteriochlorophyll type *a*.

Current Applications

A wide range of applications of *ab initio* modelling to biological systems were discussed during the workshop. These included:

- Simulations of the cleavage of RNA, described by Frank Alber, Boero Mauro and Anik Peeters. Frank Alber and Anik Peeters presented investigations of the mechanism of ribonuclease A. These compared a number of proposed reaction intermediates and rationalised the roles of residues important to the reaction. Boero Mauro simulated the self cleavage mechanism of ribosomes (analogues of enzymes composed of RNA). All of these studies identified the importance of solvent molecules in the reaction mechanism.

- A study of the isomerisation reaction of the chromophore of rhodopsin in response to absorption of a photon, presented by Carla Molteni. This investigation necessitated the extension of conventional DFT to permit the study of the first singlet excited state. This theoretical development was described in detail by Irmgard Frank. Photoreactive pro-

teins offer potential technological applications and are an excellent example of how better understanding of some biological systems may aid exploitation in non-biological fields.

- The binding of ligands to myoglobin and haemoglobin, discussed by Carme Rovira and Damian Scherlis respectively. These hemoproteins are responsible for the transport of oxygen in organisms. Carme Rovira discussed the detailed interaction of ligands such as CO, O_2 and N_2 to the haem iron in myoglobin and employed a QM/MM approach to study the effects of the haem-protein interaction. Damian Scherlis studied the hydrogen-bonding between molecular Oxygen and key residues in the active site of human haemoglobin and that of the ascaris worm. The object of this study was to understand the origins of the enormous difference in oxygen affinity between the two proteins.

Future Applications

We were very grateful for the participation of colleagues from the biological sciences, who were able to give us their views on where *ab initio* modelling could be used most effectively to further their fields.

As described previously, Lucia Banci gave a very thorough explanation of the use of paramagnetic effects in NMR for rapid protein structure determination. She described how these experimental observations were currently used in combination with classical molecular dynamics simulations and the advantages that first principles calculation of the paramagnetic effects would bring.

Peter Eddershaw, from GlaxoSmithKline Research and Development described the challenges of optimising the characteristics of a pharmaceutical compound. Other than potency against a target for treatment of a disease, the important properties can be described under the categories absorption, distribution, metabolism and excretion (ADME). The participants heard that optimising these properties is a major challenge in attempting to improve the efficiency of the drug discovery process. So-called *in silico* approaches to predicting ADME properties are now being used, which provide a dramatic improvement in throughput over traditional *in vivo* and *in vitro* experiments. This improvement in throughput allows ADME propertied to be considered earlier in the drug discovery process, improving the likelihood of a successful drug candidate emerging. The *in silico* approaches include empirical methods, which compare uncharacterised molecules with those in a database of known properties, on the basis of chemical 'descriptors'. A complementary approach is to study the mechanisms of ADME processes using quantum mechanical simulations. A better understanding of the reaction mechanisms will enable quantitative prediction of the outcomes of these processes. It is in this area that *ab initio* methods will be of most benefit.

Ashok Venkitaraman explained the field of functional genomics, the study of the link between a gene and its function. The process by which a particular genotype results in an observed phenotype is very complicated, making the relevance of a particular gene difficult to ascertain. Many processes in cells are mediated by interactions between proteins and mutations in the respective genes, which disrupt these interactions, can lead to diseases such as cancer. Understanding these interactions at an atomistic level will provide better understanding of the causes of disease and new routes for its treatment or prevention. Currently, experimental techniques

exist for the rapid identification of the regions of proteins responsible for their interactions. Coupled with accurate simulations of the interactions, this will provide an excellent approach to linking genetic structure and function. Professor Venkitaraman concluded by emphasising the importance of determining the true biological relevance of a system before beginning a detailed and potentially expensive *ab initio* study.

Conclusion

This workshop proved to be a great success. The presentations and subsequent discussions were very stimulating and provided a good overview of this rapidly growing field.

The popularity of the workshop indicates that a larger conference on this subject would be viable. Internationally, the number of groups working in this field continues to grow.

It was suggested that future workshops could include more involvement from scientists in biological disciplines. Interest in *ab initio* simulations from this community will grow, as the utility of these methods in biological research continues to be demonstrated. A better mutual understanding between the communities will be aided by another workshop. Closer contact is necessary to ensure that the systems studied are of the highest possible biological relevance.

List of Participants

Dr Frank Alber	SISSA
Dr Emelio Artacho	Universidad Autonoma de Madrid
Professor Lucia Banci	University of Florence
Dr. Bernardo Barbiellini	Northeastern University
Dr Jacqueline Berges	Université Pierre et Marie Curie
Dr Mauro Boero	Joint Research Center for Atom Technology
Mr Arrigo Calzolari	University of Modena & Reggio Emilia
Professor Paolo Carloni	SISSA
Dr Matteo Ceccarelli	MPI für Festköperforschung
Dr MariaCarola Colombo	ETH Zurich
Dr Alessandro Curioni	IBM Research, Rueschlikon, Switzerland
Mr Marco De Vivo	University of Bologna
Dr Peter Eddershaw	GlaxoSmithKline R&D
Dr Irmgard Frank	University of Munich
Professor Marcelo Galván	Universidad Autónoma Metropolitana-Iztapalapa
Dr Chantal Houee-Levin	Université Paris-Süd
Dr Joel Ireta	Fritz-Haber Institut der Max-Planck-Gesellschaft
Dr Therese Malliavin	Institut de Biologie Physico-Chimique, Paris
Dr. Janez Mavri	National Institute of Chemistry, Slovenia
Professor Michael Klein	University of Pennsylvania
Professor Glenn Martyna	Indiana University
Dr Carla Molteni	University of Cambridge
Dr Iwona Mróz	University of Wrocław
Dr Jun Nara	National Institute for Materials Science, Japan
Dr Pablo Ordejon	Universidad Autonoma de Barcelona
Professor Mike Payne	University of Cambridge
Dr Anik Peeters	University of Antwerp
Dr Chris Pickard	University of Cambridge
Professor Ursula Röthlisberger	ETH Zurich
Dr Yuriy Prylutskyy	Kyiv National Schevchenko University
Dr Carme Rovira	Universitat de Barcelona
Mr Damian Scherlis	Universidad de Buenos Aires
Dr Matthew Segall	University of Cambridge
Marialore Sulpizi	SISSA
Dr Masaru Tateno	Institute of Advanced Industrial Science and Technology
Dr Joost VandeVondele	ETH Zurich
Professor Ashok Venkitaraman	Cambridge Institute for Medical Research

Programme

Monday 9:00

9:00–9:15 Welcome and Introduction

M.D. Segall. TCM Group, Cavendish Laboratory, Madingley Road, Cambridge, CB3 0HE, UK

9:15–9:45 Introduction to Density Functional Theory

M.C. Payne. TCM Group, Cavendish Laboratory, Madingley Road, Cambridge, CB3 0HE, UK

For many years it was assumed that quantum mechanics could quantitatively predict every phenomenon in physics, chemistry, biology, and materials science. However, the complexity of the quantum mechanical wavefunction makes a direct solution of the equations of quantum mechanics intractable for all but the smallest systems. Density functional theory is a reformulation of quantum mechanics that allows calculations to be performed for systems containing up to a thousand atoms on the largest computers presently available. In this talk I shall provide a brief introduction to density functional theory and describe the strengths and weaknesses of this methodology for studying biological systems. I shall also discuss the prospects for significant developments in the capability of density functional theory calculations in the future.

9:45–10:05 An ab-initio Density Functional Study of the BgK Toxin

F. Aparicio, J. Ireta[1], **A. Rojo, A. Cedillo and M. Galván**. Departamento de Quimica, Universidad Autónoma Metropolitana-Iztapalapa, A.P. 55-534, México, D.F. 09340, México;

L. Escobar. Departamento de Fisiologia, Facultad de Medicina, Universidad Nacional Autónoma de México.

BgK is a K+ channel-blocking toxin from the sea anemone *Bunodosoma granulifera*[1]. It is a 37-residue protein that adopts a novel fold, as determined by NMR[2]. In this work, the electronic structure of this toxin is studied using the Ab-initio Total Energy Density Functional Pseudopotential (TEDFP) Method with a plane wave basis expansion.

The charge transfer capabilities of the macromolecule are analyzed within the context of its biological activity as a K+ channel blocker. Also, some features of the charge density at interstitial regions of the marcomolecule are studied by using localized and non-localized basis sets.

[1] A. Aneiros *et al.*, Biochim. Biophys. Acta **1157**, 86–92 (1993)

[2] M. Dauplais *et al.*, J. Biol. Chem. **272**, 4302–4309 (1997)

[1] Present address, Ftitz-Haber-Institute der Max-Planck-Gesellschaft, Faradayweg 4-6, D-14195 Berlin-Dahlem, Germany

10:05–10:30 Coffee

10:530–11:00 Quantum Dynamical Simulation of the Systems of Biological Interest

Janez Mavri National Institute of Chemistry, Hajdrihova 19, 1000 Ljubljana, Slovenia

Classical molecular dynamics simulation breaks down when a proton transfer, electron transfer or a high frequency vibration take place. Currently only 12 degrees of freedom can be treated full quantum-dynamically. An overview of the methods that can mix quantum and classical degrees of freedom will be given. A density matrix evolution (DME) method (Berendsen and Mavri, J. Phys. Chem., 97, 13464, 1993) to simulate the dynamics of quantum system embedded in a classical environment will be presented. The method is applicable when the quantum-dynamical degrees of freedom can be described in a Hilbert space of limited dimensionality. Selected applications of the mixed quantum-classical simulations by the method of Density Matrix Evolution will be presented:

- quantum harmonic oscillator embedded in the noble gas environment
- cleavage of the ester bond in aqueous environment
- proton transfer in the HIV-1 proteaze apoenzyme
- simulation of the vibrational spectra of hydrogen bonded systems.

11:00–11:20 RNA enzyme: a first principles molecular dynamics study of the self-cleavage mechanism

Boero Mauro Joint Research Center for Atom Technology JRCAT-ATP, Tsukuba Central, 1-1-1 Higashi, Tsukuba-shi, Ibaraki-ken, Japan

Since the discovery in the early 1980s, catalytic RNA molecules have been at the center of great attention in molecular biology and medical science. In fact, the RNA enzymes (rybozimes) can be engineered in order to cleave other target RNA molecules. In this respect, rybozimes are very promising therapeutic agents able to inhibit gene expression and can be used in gene therapy of cancer.

The fundamental chemical reaction operated by rybozimes is the hydrolysis of the RNA phosphodiester, resulting in the cleavage of the RNA at a particular target site (transesterification). Until now however, the intimate details of the reaction mechanism governing the transesterification have not yet been studied in detail, but mainly deduced on the basis of assumptions and static calculations on simplified molecular models, which never take into account the presence of the ribose ring, the temperature effects and the infulence of the solvent in which the "laboratory" reaction occurs.

In the present study we present a Car-Parrinello dynamical investigation of the self-cleavage reaction of RNA enzymes at finite temperature. We first inspect the gas phase reaction, evidencing how the reaction pathway depends on the charge state of the system. Simulations of the

reaction of the anionic species in solution, still in progress, show thet the presence of the solvent is crucial, because the hydrogen bond network prevents the pseudorotation of the competing reaction channel and drives the reaction in the desired way.

11:20–11:40 Ab initio study of the active site of the reaction between ribonuclease A and cytidyl-3',5'-adenosine

Anik Peeters, C. Van Alsenoy Department of Chemistry, University of Antwerp (UIA), Universiteitsplein 1, B-2610 Wilrijk, Belgium

Bovine pancreatic ribonuclease (RNase A) catalyzes the cleavage of the 3',5'-pho sphodiester linkage of RNA or nucleotide esters at the P-O5' bond at the 3' end of a pyrimidine in two subsequent reactions. The first reaction is a transphosph orylation to form a 2',3'-cyclic phosphate intermediate. This cyclic nucleotide can be hydrolyzed in a second reaction to yield a terminal 3'-pyrimidine nucleot ide. Despite the large number of experimental and theoretical studies involving ribonuclease A, there is still no consensus about the proton transfer in the ini tial step of the reaction mechanism.

Therefore, the catalytic mechanism of the initial step of the cleavage of cytidy l-3',5'-adenosine (CpA), one of the more reactive substrates, by ribonuclease A was studied using ab initio calculations. The geometry of the active site has be en optimized using the Hartree-Fock method. All residues proven to be important for the reaction mechanism at the active site are represented in the model. The model includes the complete substrate, interacting water molecules and parts of eight amino acids that are involved in functional and structural interactions wi th the substrate. The starting structures for the geometry optimizations were ta ken from five different snapshots along a molecular dynamics trajectory of the c omplete system. During the optimization a limited number of constraints have bee n applied to the system to guarantee a proper fit in the rest of the ribonucleas e A enzyme after the refinement.

The geometry and intermolecular interactions of the refined conformations have b een evaluated and an interesting hydrogen bonding network has been revealed. Thi s network allows the prediction of the conformation of the active site in the in itial step of the reaction mechanism. The proton from the O2'C-H2C group is tran sferred to a phosphate oxygen through a water molecule. This proton transfer has been followed in a subsequent study of the reaction barriers.

11:40–12:00 Withdrawn

Monday 14:00

14:00–14:30 Modelling photoreactions in proteins by density functional theory

Carla Molteni. Cavendish Laboratory - Theory of Condensed Matter group, Madingley Road, Cambridge CB3 OHE UK

Photoactive proteins are an important class of biomolecules that offer potential technological applications. In the first hundreds of femtoseconds of their photocycle, the absorption of a photon

produces conformational changes that trigger a cascade of chemical reactions culminating in a specific biological signal. Given the short time of the initial photoreaction, which usually implies a double bond isomerisation, it is experimentally difficult to see how this isomerisation proceeds and how it is converted in a protein-wide structural change; therefore simulations could be extremely helpful for accurately characterizing the structural and electronic changes initially induced by light.

I will present some attempts to investigate photochemical reactions by density functional theory based methods [1]. Excited states are treated within a recently developed density functional theory scheme which allows us to perform geometry optimisation and molecular dynamics in the first excited singlet state. The effects of the protein environment can be included by combining the quantum mechanical treatment of the chromophore with the classical treatment of the environment. Results on the photoisomerisation of rhodopsin will be shown [2]. The active site of the photoactive yellow protein is also under investigation.

This work has been done in collaboration with I. Frank (Institut für Physikalische Chemie, University of Munich) and M. Parrinello (Max-Planck-Institut für Festkörperforschung, Stuttgart). An accurate modelling of the rhodopsin protein environment based on a recent x-ray structure is presently in progress (by U. Röhrig, L. Guidoni and U. Röthlisberger, ETH Zurich).

[1] C. Molteni, I. Frank and M. Parrinello, Comput. Mater. Sci. **20**, 311 (2001)

[2] C. Molteni, I. Frank and M. Parrinello, J. Am. Chem. Soc. **121**, 12177 (1999)

14:30–14:50 Ab initio study of one-electron reduction of disulfide bonds in lysozyme

Jacqueline Bergès LCT, Université Paris VI, France.

Chantal Houee-Levin LCP, Univesité Paris Sud, France

One-electron redox reactions involving sulfur residues are of relevance in many essential biological processes. The protein thiol-disulfide redox couple has a great importance for numerous biological events, such as gene expression or gene inhibition. In many circumstances, protein sulfur free radicals are created in living cells and play a crucial role in the course of the reactions leading to cellular effect. The most important radical species are thiyl and disulfide radicals.

We have studied the one-electron reduction of disulfide bonds in lysozyme by gamma and pulse radiolysis, and shown that only one out the four disulfide bridges was reactive in our system. To provide an explanation of this selectivity we used the methods of quantum chemistry. The disulfide brige and its closest neighbouring residue, Arg5, were modelled. We show that this residue does stabilize the free radical anion in a configuration very close to that of the protein. Protonation weakens the SS bond which undergoes fragmentation easily. These results are in very good agreement with experimental data.

14:50–15:10 Withdrawn

15:10–15:30 Electronic properties and conductivity of guanosine assemblies

A. Calzolari, R. Di Felice, E. Molinari INFM - Dipartimento di Fisica,Université di Modena e Reggio Emilia, via Campi 213/A, 41100 Modena, Italy

A. Garbesi CNR ISOF, Area della Ricerca, via P. Gobetti 101, 40129 Bologna, Italy

Guanosine (G) aggregates are among the simplest structures constituted of DNA base pairs that are well characterized experimentally, and were recently used in the fabrication of novel biomolecular nanodevices. Understanding their electronic and transport properties is especially interesting also in view of the role played by guanine, the base with the lowest ionization potential, in charge transport and damage in DNA. We present ab-initio (plane-wave pseudopotential DFT-GGA) calculations of the stability and the electronic structure of stacked dimmers and ribbons with different geometry. We discuss the implication of π-π stacking and band dispersion in determining Bloch-type band conductance, as well as the role of macroscopic dipoles that can build up in real nanostructures. For stacked geometries, the stability is affected by the relative charge distribution of the π orbitals in adjacent guanine molecules. π-π coupling in some stacked columns induces dispersive energy bands, while no dispersion is identified in the planar ribbons along the connection of hydrogen bonds (Fig.1). The bandstructure and the calculated conductance of dispersive configurations may justify a contribution of Bloch-type band transport to the conduction of deoxyguanosine fibers, while in B-DNA-like configurations band transport is expected to be negligible, and other mechanisms for mobility must play a role.

15:30-16:00 Coffee

16:00-16:30 Structure and dynamics of paramagnetic systems: experimental constraints and theoretical background

Lucia Banci CERM and Department of Chemistry, University of Florence, Florence, Italy

The effects produced by paramagnetic centers on NMR parameters can be exploited as source of geometrical constraints in the calculation of the structure of biological molecules in solution, based on NMR data. It is important to stress that the effects originating from an open shell paramagnetic metal ion constitute the only source of information on the location of the paramagnetic metal ion within the protein frame. In any case, their use needs extensive validation on case systems. As the share of metalloproteins on the total number of proteins involved in life processes in living organisms is large (30-40%), most of them containing a paramagnetic center, the exploitation of the paramagnetic effects in structural calculations of paramagnetic metalloproteins is quite relevant. Furthermore, the presence of paramagnetic metal ion(s) can give rise to sizable molecular self- orientation in high magnetic fields. This phenomenon can be exploited to obtain further structural information on the orientation of bond vectors with respect to the principal axes of the molecular magnetic susceptibility tensor. The various contributions to the molecular magnetic anisotropy can be separated and the calculated values compared with the experimental ones.

Finally, the picture of the internal fast motions, obtained from heteronuclear relaxation measurements, can be fruitfully compared with the results of molecular dynamics simulations in order to rationalize the role of the metal ion, its oxidation state and geometry on the dynamical properties.

Examples on the structural and dynamical characterization of proteins containing paramagnetic metal ions will be presented.

16:30–17:00 Large scale first principles calculation of NMR chemical shifts: towards biological systems

Jonathan Yates, Chris J. Pickard, Matt Segall, Mike Payne, Richard Kowenicki, Nick Bampos, Jeremy Sanders Cambridge University, Cambridge, United Kingdom

Francesco Mauri Université Paris 6, Paris, France

We have recently shown that planewaves and pseudopotentials can be used to calculate NMR chemical shifts of small molecules with an accuracy comparable to that of traditional all-electron Quantum Chemical approaches [1]. In a collaboration between theorists and experimentalists, we aim to show that this methodology is applicable to the understanding of NMR chemical shift spectra of biologically relevant molecules. As progress in this direction, we present the results of calculations and experiments on synthetic porphyrins. The calculated chemical shifts are the first that we are aware of for realistic synthetic porphyrins. The first principles calculations not only confirm the experimental assignments, but also give rise to a new understanding of the role of ring currents in porphyrins.

[1] Chris J. Pickard and Francesco Mauri. "All-electron magnetic response with pseudopotentials: NMR chemical shifts." Physical Review B, 2001 (To appear).

Tuesday 9:00

9:00–9:30 Predictive in silico ADME models in Drug Discovery

Peter Eddershaw Drug Metabolism & Pharmacokinetics, GlaxoSmithKline R&D, Ware, UK

The investigation of the absorption, metabolism, distribution and excretion (ADME) of novel drug molecules is a vital part of the drug discovery process. Successful optimisation of these factors can transform a promising biologically active molecule into a clinically and commercially viable medicine. The ability to predict ADME properties in humans has long been a desire of drug metabolism and pharmacokinetics (DMPK) scientists within drug discovery organisations. In recent years, considerable progress has been made towards this goal, stemming in the main from substantial increases in data generation and capture associated with higher throughput methods for absorption, metabolism etc. Furthermore, against a background of increased front-loading and tighter deadlines, there is a growing realisation that the empirical nature of even relatively high throughput studies (the 'make it, test it' process) ultimately limits the role of DMPK scientists. Computational approaches are truly high throughput and, since they require

only a chemical structure, allow virtual screening to be carried out. Above all, they provide greater insight into the fundamental principles governing ADME which is the key to truly rational drug discovery.

Computational approaches are now an integral part of the drug discovery process at GSK, finding application in a variety of areas including the design of new compound libraries, prioritising compounds for in vivo testing and identifying potential issues which can be targeted as part of the progression strategy. Through the use of various computational and statistical methods, we have developed an array of models that covers the key aspects of ADME relevant to lead identification and optimisation.

In addition to informatics based methods, we have need of mechanistic approaches to provide greater definition and to characterise ADME issues in more detail. For instance, the challenge of predicting interactions of drug molecules with proteins such as drug metabolising enzymes and membrane transport systems, taking account of the impact of both steric and electronic factors, needs to be addressed. In particular, the ability to predict the rates of metabolic reactions in order to assess the overall significance of a given pathway to the disposition of a molecule in humans.

9:30–9:50 A Quantum Mechanical Computational Study of the Lysozyme Reaction Mechanism

Marco De Vivo[2], **Andrea Bottoni** Department of Chemistry "G. Ciamician". – University of Bologna Via Selmi 2, I-40126 Bologna, Italy

Lysozyme is a small protein (129 amino acids) belonging to the family of the β-glycosyl hydrolases. This enzyme catalyses the cleavage of β(1-4)-glycosidic bonds between N-acetylmuramic acid (NAM) and N- acetylglucosamine (NAG) of the bacterial cell wall peptidoglycan. The active site of lysozyme lies in a cleft which can accommodate six pyranose units (...-NAM-NAG-...) usually denoted as A-B-C-D-E-F (substrate). The glycosidic hydrolysis occurs between D and E. In particular, the enzyme selectively cleaves the glycosidic bond between the C-1 atom of the NAM unit (D) and the O-4 atom of the NAG unit (E). In this way, lysozyme carries out its antibacterial action, "lysing" and consequently dissolving the bacterial walls. Although the enzymatic activity of lysozyme is well known and many information about the three-dimensional structure are available [1] (lysozyme was the first enzyme whose 3D-structure was determined by a X-Ray crystallographic study), the reaction mechanism has not been well understood yet.

In the present study we have used a quantum mechanical approach to investigate the potential energy surface (PES) associated with the two reaction mechanisms commonly reported in the literature [2-3]. The model-system used here is formed by the fourth sugar ring of the substrate and the two amino acids of the active site (Glu35 and Asp52). A simplified structure of these two amino acids has been considered to obtain a higher computational expedience. The geometry of this model active site has been obtained from the crystallographic coordinates of the enzyme-substrate complex retrieved from the Protein Data Bank. The geometry of the various critical

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points of the PES have been optimized with the gradient method at the Hartree Fock level. A heterogeneous basis-set formed by the 6-31G*, 3-21G and STO-3G basis, has been used. To mimic the effect of the protein frame (structural constraint), the most external atoms of the model active site have been kept fixed during the geometry optimization. To obtain a better estimate of the energetics of the reaction (activation energies associated with the various transition states TS and relative energies of the various intermediates) DFT/B3LYP (Density Functional Theory) and MP2 computations have been carried out on the Hartree-Fock optimized structures.

We have found that only one of the two reaction mechanisms investigated here, is possible. For this mechanism the catalytic pathway has been fully established. An important structural change of the ring of the NAM (D) residue before the cleavage of the glycosidic bond has been found. Such a modification favors the cleavage of the glycosidic bond and the subsequent departure of the dimer NAG(E)-NAM(F). An important role played by the Aps52 residue in the enzymatic reaction has been demonstrated. This type of information can be of paramount importance when designing TS analogs inhibitors.

[1] N.C.J. Strynadka and M.N.G. James ; J. Mol. Biol. **220**, 401-424 (1991)

[2] M. Karplus and C.B. Post ; J. Am. Chem. Soc. **108**, 1317-1319 (1986)

[3] Andrè White and David R Rose ; Curr. Opin. Struct. Biol. **7**, 645-651 (1997)

[4] M.J. Frish, G.W. Trucks, H.B. Schlegel, P.M.W. Gill, B.G. Johson, M.A. Robb, J.A. Pople, et al. Gaussian Inc., Pittsburgh 1995

9:50–10:20 Ab initio moelcular dynamics simulations on biological systems: HIV-1 reverse transcriptase and ribonuclease A

Frank Alber. International School for Advanced studies (SISSA), via Beirut 4 341014 Trieste, Italy

Car-Parrinello molecular dynamics simulations are used to study aspects of prote in-ligand interactions and enzymatic reaction mechanisms.

1) We have studied the binding of the natural substrate to HIV-1 reverse transcr iptase (RT). Our calculations shed light on the functional role of residues involved in the R T resistance against nucleoside-analog drugs. While the mono-protonated triphosphate experien ces large rearrangements in the active site, the unprotonated form is stable and exhibits a previously unrecognised low-barrier-hydrogen bond between Lys65 and the gamma-phosphate. Ab sence of this interaction in Lys65-¿Arg HIV-1 RT might play a prominent role in the resistanc e of this mutant for nucleoside analogs. Water molecules present in the active site, not detected in the x-ray structure, form a complex H-bond network. Among these waters, one may be crucial for substrate rec ognition as it bridges Gln151 and Arg72 with the beta-phosphate. Absence of this stabilizing interaction in Gln151-¿Met HIV-1 RT mutant may be a key factor for the known drug resistance of this mutant towards dideoxy-type drugs and AZT.

2) We have also studied the hydrolysis of cyclic phospho-diester in ribonuclease A using constrained Car-Parrinello molecular dynamics simulations. Our calculations suggest that a stable,

monoanionic, trigonal bipyramidal phosph orane intermediate (TBP) is formed. Furthermore, they help rationalize the role of the catalytically important residue Lys41 in the reaction process. The side chain of the residue i s found to rearrange significantly during the reaction, stabilizing the incipient intermedi ate in the nucleophilic water attack and assisting the dissociation of the O2‘ leaving grou p in TBP.

Reference: F. Alber, Carloni, P., Protein Sci. (2000), 9: 2535-2546.

10:10–10:30 Coffee

10:30–11:00 Mixed ab initio/empirical force-field simulations

Glenn J. Martyna Department of Chemistry, Indiana University, 800 E. Kirkwood Ave. Bloomington, IN, USA.

Mixed ab initio/empirical force-field simulation studies, calculations in which one part of the system is treated using a fully ab initio description and another part is treated using an empirical description, are becoming increasingly popular. Here, the ability of the commonly used, plane wave based, generalized gradient approximation to density functional theory is extended to model systems in which the electrons are assumed to be localized in a single small region of space, that is, itself, embedded within a large chemically inert bath. This is accomplished by introducing two length scales, so that the rapidly varying, short range, electron-electron and electron-atom interactions arising from the region where the electrons are localized can be treated using an appropriately large plane wave basis while the corresponding, slowly varying, long range interactions of the electrons with the full system or bath, can be treated using a small basis. Briefly, a novel Cardinal B-spline based formalism is employed to derive a smooth, differentiable, and rapidly convergent (with respect to the small basis) expression for the total electronic energy, which explicitlycontains the two length scales. The method allows reciprocal space based techniques designed to treat clusters, wires, surfaces and solids/liquids (open, and 1D and 2D periodic boundary conditions, respectively) to be utilized. Other plane wave based “mixed ”methods are restricted to clusters. The new methodology, which scales as Nlog N at fixed size of the chemically active region, has been implemented for parallel computing platforms and tested through applications to both model and realistic problems including an enzyme, human carbonic anhydrase II solvated in an explicit bath of water molecules.

11:00–11:20 On the possible dependence between protein structures and chiral symmetry breaking

Iwona Mróz Institute of Experimental Physics, University of Wroclaw, Plac Maxa Borna 9, 50-204 Wrocław, Poland

We analyse how chiral and charged amino acid residues influence handedness of simple polypeptides and investigate how typical three-dimensional peptide structures influence electric charges of the amino acids depending on the positions of the residues along the polypeptide chains. We show that possibilities of obtaining three-dimensional protein structures having given handed-

ness depend on both: electric charges and chirality of particular amino acids in the chain and can be systematized using the idea of "charge configuration".

For given three-dimensional peptide structures, the interdependence between electric charge and chirality of the amino acids shows significant differences: the amino acids situated at the N-termini of the peptides can fit their charge configuration to the structure of the peptide, while the amino acids at the C-termini are not able to behave in that way. Glycine, which is achiral, changes its charge configuration independently on its position along the chain.

Our results suggest that proteins synthesized starting from the N-termini might create right- and left-handed conformations using only one amino acid stereoisomer. Proteins synthesized from the C-termini should rather use L-amino acids for right-handed conformations and D-amino acids for left-handed conformations. The results also suggest why the most common left-handed C-terminal endings of natural helices are created by glycine.

11:20–11:40 The intrisic electric field and the secondary structures of proteins

J. Ireta, J. Neugebauer and M. Scheffler Fritz-Haber Institut der Max-Planck-Gesellschaft, Germany

A. Rojo and M. Galvan Universidad Autonoma Metropolitana-Iztapalapa, Mexico

It is well known that alpha-helix secondary structure of proteins is stabilized by hydrogen bonds (hb). However, the effect of the intrinsic field (ief) on the stability of the secondary structure is not well stablished. In this contribution we will present an DFT-pseudopotential study of the hb strength and the hb cooperativity in the presence and in a compensate ief environment. We will discuss about the importance of the ief for the alpha-helix stabilization.

11:40–12:00 Theoretical study of thiol radicals of biological interest as some cystein derivatives

J. Bergès, N. Varmenot. Z.Abedinzadeh LCT, Université Paris VI, France.

The monoelectronic oxidation of some biological thiols was performed using gamma and pulsed radiolysis experiments in aqueous medium, specially on S,N-diacetyl L-cystetyleinate of ethyle (SNACET) and its derivatives. These compounds were oxidized by hydroxyl radicals OH obtained from the water radiolysis. The first products detected could be adducts ROH and/or radical cations. Our purpose is to characterize by ab-initio calculations and solvent modelling the species structures and the reaction mechanisms.

Tuesday 14:00

14:00–14:30 Functional Genomics

Ashok R. Venkitaraman Department of Oncology & The Wellcome Trust Centre for Molecular Mechanisms in Disease, The Cambridge Institute for Medical Research, Wellcome Trust/MRC

Building, Hills Road, Cambridge CB2 2XY, UK.

The recent decipherment of the complete sequence of the human genome has focused attention on the need to develop new, interdisciplinary approaches to identify and manipulate the biological functions of the protein products of human genes. Here, I will discuss techniques currently being used by biologists for the functional analysis of novel proteins with reference to my own group's work on cancer biology, and attempt to define key problems to which ab initio methods might fruitfully be applied.

Tuesday 14:30–15:00 Reaction Mechanism of Caspase-3: insights from a QM/MM investigation

Marialore Sulpizi International School for Advanced studies (SISSA), via Beirut 4 341014 Trieste, Italy

No abstract submitted.

15:00–15:30 Polarons of electrostatic origin in dry A-DNA

Emilio Artacho Dept. of Earth Sciences, University of Cambridge, UK

Pablo Ordejón Inst. Ciencia de Materials, CSIC, Barcelona, Spain

Daniel Sánchez-Portal Donostia Int. Physics Center, San Sebastian, Spain

José M. Soler Depto. Física Materia Condensada, U. Autónoma, Madrid, Spain

The possibility of DNA acting as a current-conducting wire both in life-related processes and in nanodevices has attracted the attention of many research groups in different areas. In spite of the work accumulated so far the situation remains controversial with recent papers claiming not only conduction but superconduction in DNA, while others observe insulating behavior. This controversy has its roots in the complexity inherent to DNA where, in addition to the complications intrinsic to the molecule, there are environment effects of at least similar importance. It is very difficult to characterize with precision the conditions DNA is under while performing nanoprobe experiments, for instance. Knowledge on DNA's electronic structure and its variability with environment conditions is still scarce albeit extremely important for understanding electronic transport.

First-principles calculations represent a powerful complement to experiment in this and other situations. The simulations allow a perfect control and knowledge of the environment conditions. Moreover, the conditions most easily accessible to simulations are hard for experiments and vice-versa. Recent developments in linear-scaling density-functional simulations have allowed us to gain insights into the electronics, electrostatics, and their interplay in dry DNA. We started simulating the simplest conditions: dry acidic A-DNA of trivial sequence, with all guanines in one strand and all cytosines in the other, in an infinite double helix (eleven base pairs per

unit cell). The electronic structure of the system at the relaxed geometry reveals narrow bands at either side of the (wide) band gap. The distortions of the structure corresponding to soft vibrations are observed to produce changes in the energy levels close to the band gap much larger than the corresponding bandwidths. The origin of this effect is electrostatic: the base pairs have important dipole moments associated to them, and the low frequency motions in DNA involve the soft and ample swinging of the base pairs within the double helix. The electrostatic potential felt on each base pair oscillates appreciably, and so do the energies of their orbitals. This suggests the formation of a small polaron for each carrier that appears in the chain (normally a hole): The carrier is self-trapped by the decrease of its eigenenergy in the distortion induced by the carrier itself.

The possibility of having polarons in DNA was already proposed in the literature [see P. T. Henderson *et al.*, Proc. Natl. Acad. Sci **96**, 8353 (1999), and E. M. Conwell and S. V. Rakhmanova, Proc. Natl. Acad. Sci **97**, 4556 (2000)], including a mechanism for charge migration based on thermally assisted polaron hopping. Our results support this possibility. However, the electrostatic origin that we find disagrees with the previous proposals. While Henderson *et al.* speculated about different possibilities (none of them electrostatic), Conwell and Rakhmanova characterized their polarons in terms of the Su-Schrieffer-Heeger Hamiltonian, meaning that the polaron originates from the fluctuations in the electron hopping energy term between base-pair orbitals. The electrostatic nature of the distortion, however, points at the coupling between the displacements and the *on-site energy term* of the base-pair orbitals as the relevant term in the Hamiltonian describing the polarons we find. It is difficult at this stage, however, to ascertain to what extent can the environmental conditions change the picture, further research being needed in this direction.

15:30–16:00 Coffee

16:00-16:20 A quantum description of the hydrogen bond

Bernardo Barbiellini Department of Physics, Northeastern University, 111 Dana Research Centre, Boston, MA, U.S.A.

In a recent x-ray Compton scattering experiment in ice Ih [1] it was unambiguously shown that the hydrogen bond is inherently quantum in nature. As a matter of fact, standard X-ray diffraction experiments studies of the charge densities cannot give such a clear picture since the charge transfer involved in the hydrogen bond can be very small (about 1% of an electron charge). The density matrix $\rho(\mathbf{r}, \mathbf{r}')$ is a fundamental property of quantum mechanical systems because it determines the degree of locality of the bonding properties. Inelastic x-ray scattering data are particular important for determining the density matrix from the experiment. The aim of this work is to develop powerful computational methods to extract the density matrix from experiments in several compound with hydrogen bond such as ice and DNA. Because the charge transfer in the hydrogen bond the electronic structure of DNA may play an important role in the replication process. The electronic structure information can be used in models for DNA and its relationship to mutagenesis. For instance one could check if mutations will be more frequent in DNA sequences where electron delocalization occurs [2]. Finally the result of

the present investigation may be useful to challenge current conventional wisdom concerning the nature of the hydrogen bond and the adequacy of widely used model potentials and numerical simulation techniques for describing H-bonded materials.

[1] E. D. Isaacs, A. Shukla, P. M. Platzman, D. R. Hamann, B. Barbiellini and C. Tulk, Phys. Rev. Lett., 82, 600-603 (1999).

[2] C.M. Chang, A. H. Castro Neto, A. R. Bishop, cond-mat/0008166.

16:20–16:40 DFT normal mode analysis applied to small biological molecules: a practical example

Dr Matteo Ceccarelli CECAM, Ecole Normale Superieure-Lyon 46, Allee d'Italie 69364 Lyon CEDEX 07 France

DFT methods constitute a powerful tool to obtain structural and dynamical inform ation of small biological molecules (one hundred atoms). This information, when compared to available experimental data, shows a good agr eement and hence constitute a precious complement to experimental investigations. In this talk I will present in detail the results of a DFT normal mode analysis of a chlorophyll derivative, the bacteriochlorophyll of type *a*, a molecules involved in the photosynthetic process of bacteria.

DFT normal mode analysis allows us to compare calculated frequencies with the ex perimental resonance Raman (RR) spectrum and provides a unique opportunity for a precise assignement of frequencies to internal modes. Moreover, DFT data are used as reference set to parametrize classical potential force fields such as AMBER. This is a preliminary step to study these molecules embedded in a solvent or in their protein environment w ith long-time (ns) and large-size (thousand of atoms) molecular dynamics simulations. The major result of our investigation is the remarkably different behavior of a region of the spectrum compared to previous empirical and semiempi rical investigations.

16:40–17:10 Ab-Initio Simulation of Photoreactions

Irmgard Frank Department Chemie, LMU München, Butenandtstr. 5-13, Haus E, 81377 München

Photoreactions are the basis of many important processes in chemistry and biochemistry. Most photoreactions in organic molecules occur in either the S_1 or T_1 states. The T_1 state is the lowest state of triplet symmetry and T_1 photoreactions are accessible to conventional ground-state Kohn-Sham theory. This is not the case for S_1 photoreactions.

We have developed an approximate scheme that extends Kohn-Sham theory to the treatment of S_1 states [1]. The method, called restricted open-shell Kohn-Sham (ROKS) method, can be used to determine excited-state geometries and to perform efficient dynamics in excited states.

Like this the treatment of many photoreactions has become accessible, not only in the gas phase but also in condensed phase. Application to protein photoreactions is possible by a combination with classical MD in a QM/MM scheme.

[1] I. Frank, J. Hutter, D. Marx, and M. Parrinello, J. Chem. Phys., **108**, 4060 (1998).

Wednesday 9:00

9:00–9:30 Ligand binding properties of myoglobin. A QM/MM density functional study

Carme Rovira Departament de Química Física. Universitat de Barcelona Martí i Franquès 1. 08028 Barcelona, Spain

Michele Parrinello Max-Plank-Institut für Festkörperforschung, Heisenbergstrasse 1, 70569 Stuttgart, Germany.

The binding of ligands to the active center of myoglobin is a complex process determined by many structural and dynamic properties of both the active center and the surrounding protein. Many essential aspects of this function, such as the the way the protein controls the binding of ligands (O_2, CO and NO) or the origin of the distinctive ligand absorptions present in the IR spectra of carbonmonoxy myoglobin, are a topic of debate [1]. In order to understand these issues, we will analyze the properties of the myoglobin active center and its interaction with the ligands by means of first principles molecular dynamics [2]. In a second step, a combined QM/MM methodology will be used to investigate the heme-protein interaction [3].

[1] J. T. Sage, P. M. Champion. In Comprehensive Supramolecular Chemistry. (K. S. Suslick, Ed.) Vol. 5, Chap. 8, Pergamon, Oxford (1996).

[2] C. Rovira, K. Kunc, J. Hutter, P. Ballone, M. Parrinello. J. Phys. Chem A **101**, 8914 (1997); C. Rovira, M. Parrinello. Chem. Eur. J. 5, 250 (1999); C. Rovira, M. Parrinello. Biophys. J. **78**

[3] M. Eichinger, P. Tavan, J. Hutter, M. Parrinello. J. Chem. Phys. 110, 10452 (1999); C. Rovira, B. Schulze, M. Eichinger, J. D. Evanseck, M. Parrinello. Biophys. J. In press.

9:30–9:50 Role of Hydrogen Bonding in the Oxygen Affinity of Hemoglobins

Damian Scherlis Departmento de Fisicoquimica, Universidad de Buenos Aires.

Hemoglobin is well known for its ability to transport dioxygen and carbon dioxide in the vascular systems of animals. However, the mechanisms that modulate the O2 affinity constant are not completely understood. By replacing a few amino-acid residues the oxygen affinity may be increased in four orders of magnitude, though the active site of the protein remains the same. An example of such an extraordinary affinity for O2 is found in the hemoglobin of the ascaris worm. It has been proposed that the abnormal equilibrium constant observed in this hemoglobin is due to the formation of hydrogen bonds between oxygen and two amino-acids of the distal pocket. In this work we use DFT-GGA computations to estimate the interaction energies associated with H-bonding in the active site of ascaris hemoglobin, as well as in the different subunits of the human hemoglobin in the R-state. Our results show that the effects of hydrogen bonding are not directly responsible for the high O2 affinity of the ascaris hemoglobin and suggest that

the usual interpretation should be revised.

9:50–10:30 Coffee

Wednesday 10:30–11:00 CPMD/MM simulations of copper binding to the prion protein

Joost VandeVondele, Alessandro Laio, Ursula Röthlisberger Laboratory of Inorganic Chemistry, ETH Zentrum, Zurich, Switzerland

The prion protein, in an incorrectly folded form, triggers neurodegenerative diseases, such as the mad cow disease (BSE). The unaltered form, also present in humans, has an unknown biological function, but an NMR structure has been resolved. Furthermore, the evidence is growing that the prion protein might play a role in the copper metabolism, and recent EPR experiments suggest that copper binds in the ordered C-terminal domain of the protein.

The problem of locating metal ions in complex structures is a more general one, and in order to complement the experimental data with suggestions of possible bindings sites and their geometries, we performed mixed ab initio-classical simulation employing a hybrid Car-Parrinello / classical approach. Three possible binding sites will be presented, and we will discuss how further connection with experiment can be made. Additionally, we give an overview of the features of our computational approach, and in particular discuss how an MM code can be interfaced with a plane wave based DFT code at a high level of the electrostatic coupling.

11:00–11:15 Closing.

4.2.3 Report on the CECAM / Psi-K workshop on "Application of Ab-Initio Methods to Geophysical Problems"

CECAM WORKSHOP "APPLICATION OF AB-INITIO METHODS TO GEOPHYSICAL PROBLEMS"

Sponsored by CECAM and by the European Science Foundation Programme "Electronic Structure Calculations for Elucidating the Complex Atomistic Behaviour of Solids and Surfaces" (Psi-k)

Organised by **Sandro Scandolo**, SISSA, Trieste, Italy
Francois Guyot, LMCP, Université P&M Curie, Paris, France
Francesco Mauri, LMCP, Université P&M Curie, Paris, France
G. David Price, University College London, UK

The workshop took place at CECAM in Lyon (France), on July 16-20, 2001. We warmly thank Mrs. Crespeau and Prof. Mareschal for the their availability and help in organizing the event.

The workshop was attended by 27 participants (plus 4 directors), and consisted of 24 long (40') presentations and 11 short (15') talks. All participants have contributed, either with a long talk, or with a short one, or both.

The workshop developed around the following main themes: spectroscopy, high-pressure structure and elasticity, thermodynamics, dynamics, transport, defects and surfaces in minerals. We also had an overview on the emerging field of geobiology. The workshop was meant to gather geophysicists and electronic-structure scientists with the aim of reinforcing interdisciplinary exchanges and create a common language for scientific discussion and advancement. This has been succesfully achieved by scheduling sessions in such a way that theory and experiment/phenomenology could be directly confronted on a specific topic.

All sessions ended up with suggestion for new experiments and new challenges for theory/modelling, indicating an increasing interest in seeing ab-initio modelling applied to geophysical problems, but also pointing to the need that activitities of this kind be repeated in the next years, possibly extended to a broader audience.

The list of participants, the detailed program, and the abstracts, are attached below.

List of Participants

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Programme

Monday, July 16

Session "SPECTROSCOPY-1"

09:00-09:40 A. Pasquarello (IRRMA, Lausanne)
"Vibrational spectroscopy of vitreous silica:
A first-principles investigation"

09:40-10:20 P. Sainctavit (Paris VI)
"Magnetic and linear x-ray dichroism in oxydes"

10:20-10:40 Break

Session "HP-ELASTICITY-1"

10:40-11:20 R. Wentzcovitch (Univ. Minnesota)
"Thermoelasticity of Minerals from DFT"

11:20-12:00 T. Duffy (Princeton Univ.)
"Elasticity and Equations of State from Experiments"

Session "THERMODYNAMICS, DYNAMICS, TRANSPORT -1"

15:00-15:40 V. Heine (Cambridge)
"Al/Si ordering in aluminosilicates"

15:40-16:20 B. Reynard (ENS - Lyon)
"Isotope fractionation: where and how ab-initio
calculations can be useful"

16:20-16:40 Break

16:40-18:00 Discussion

Tuesday, July 17

Session "HP-STRUCTURE AND MELTING-1"

09:00-09:40 M. Gillan (UCL, London)
"Temperature and composition of the Earth's core
from ab initio thermodynamics"

09:40-10:20 S. Bernard (CEA, Paris)

"The optimal potential method: applications to Fe and Sn"

10:20-10:40 Break

Session "SPECTROSCOPY-2"

10:40-11:20 J. Badro (Paris VI)
"Electronic structure at high pressure"

11:20-12:00 I. Farnan (Cambridge)
"Structure and Dynamics of Silicates Observed by 29^Si
and 17^O NMR"

12:00-12:40 F. Mauri (Paris VI)
"Silicate structure with NMR"

Session "NEW FRONTIERS: GEOBIOLOGY"

15:00-15:40 Ph. Gillet (ENS, Lyon)
"Iterations between microorganism and mineral surfaces:
main questions"

15:40-16:00 Break

16:00-18:00 Discussion / Short talks
T. Duffy - "Raman spectroscopy of phase transitions
in sesquioxides and hydroxides"
R.J. Reeder - "XAFS results on local structural relaxation
in solid solutions"

Wednesday, July 18

Session "HP-ELASTICITY-2"

09:00-09:40 R. Cohen (Geophys. Lab. / CalTech)
"Magnetism at high pressure"

09:40-10:20 L. Stixrude (Univ. Michigan)
"Elasticity of Iron at High Pressure and Temperature and
Implications for the Earth's Inner Core"

10:20-10:40 Break

Session "IMPURITIES AND DEFECTS"

10:40-11:20 J. Brodholt (London)
"Ab Initio Calculations on Defects in Mantle Minerals"

11:20-12:00 K. Wright (Royal Inst., UK)
"Modelling hydrogen defects in forsterite using embedded cluster methods"

12:00-12:40 D. Price (UCL, London)
"Miscibility of light impurities in Fe"

AFTERNOON: SOCIAL ACTIVITY (Guided tour of the "Vieux Lyon")

Thursday, July 19

Session "SPECTROSCOPY-3"

09:00-09:40 E. Balan (Paris VI)
"Simulation of powder IR spectra in phyllosilicates"

09:40-10:20 B. Winkler (Kiel)
"Crystallography with DFT"

10:20-10:40 Break

Session "MINERAL SURFACES"

11:20-12:00 S. Parker (Bath)
"Modelling the structure and stability of mineral surfaces"

12:00-12:40 R.J. Reeder (SUNY)
"Coordination of metals at mineral surfaces determined by XAFS spectroscopy"

15:00-18:00 Discussions / Short talks / Perspectives
S. Mackwell - "Intrinsic and hydrous defects in olivine: experimental constraints"
M. Matsui - "Necessity to obtain a reliable pressure standard

standard at high pressure and temperature"
S. Merkel - "Elasticity and rheology of MgO at high pressure and temperature"
M. Cococcioni - "Structural and electronic properties of fayalite Fe2SiO4"
M. Warren - "Ab-initio simulations of metal adsorption on hydroxylated alumina surfaces"
E. Balan - "Water on zircon"
R. Cohen - "Equations of state and elasticity in minerals"

Friday, July 20

Session "THERMODYNAMICS, DYNAMICS, TRANSPORT -2"

09:00-09:40 S. Wells (Cambridge)
"Rigid unit modes-dynamical effects in minerals with neutrons"

09:40-10:20 S. Mackwell (Bayreuth)
"Diffusion and deformation in the (Mg,Fe)O"

10:20-10:40 Break

Session "HP-STRUCTURE AND MELTING -2"

10:40-11:20 M. Matsui (Kyushu U., Japan)
"MD simulation of the 410 km and 660 km seismic discontinuities"

11:20-12:00 M. Catti (Milano)
"High-pressure phase transformations by periodic LCAO techniques"

END

Abstracts of Talks

Electronic Structure at High Pressure

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Abstract
High pressure research has entered the era of high-end state of the art measurements, especially in the field of synchrotron x-ray research. Nowadays, a large number of techniques are readily available and applicable in conjunction with the most widely used high pressure apparatus, namely the diamond anvil cell.
In the past years, diffraction constituted the largest part of high-pressure synchrotron-based x-ray research, along with limited efforts in the field of x-ray absorption spectroscopy. The appearance of high-energy third generation x-ray sources (ESRF, APS, SPring-8) allowed extremely brilliant x-ray beams to be focused down to very small sizes, due to the conjunction of high flux, small source size and divergence, and high coherence. With the help of an x-ray spectrometer set up in the Rowland geometry and low-Z (x-ray transparent) gaskets, a wide variety of high-resolution spectroscopic techniques can be accessed.
We will briefly present techniques such as high resolution x-ray emission as local probe for magnetism and electronic modifications, as well as resonant x-ray scattering (x-ray Raman). Inelastic x-ray scattering with ultra-high resolution allows us to access the vibrational properties (acoustic and optical phonons) of materials. These new techniques allowed us to investigate the electronic and magnetic properties of wuestite (FeO), hematite (Fe2O3) and iron (Fe) well into the megabar pressure range. FeO is shown to become a paramagnetic compound at high pressure, and a closed-loop anti-ferromagnetic stability domain is depicted [1].
The vibrational properties (longitudinal and transverse sound wave velocities, and optical phonons in some cases) of iron (Fe) [2] and iron-bearing compounds (FeSi, FeS, FeS2, and FeO) [3-4] were measured to megabar pressures by ultra-high resolution (4 meV) inelastic x-ray scattering, along with the acoustic phonon dispersion curves. This set of data provides the first direct measurement of sound velocities of the constituents of the core in the conditions of the deep Earth, and is of utmost importance to geophysics.
The electronic properties of the charge-transfer insulator NiO [5] are dramatically modified at high pressure, as shown by resonant inelastic x-ray scattering up to 100 GPa.
Last, a part of the presentation will be dedicated to future issues in synchrotron x-ray spectroscopy. Specifically, the upgrade of existing sources as well as the upcoming machines will be briefly presented.

References:
[1] Badro et al., Phys. Rev. Lett. 83:4101 (1999)
[2] Fiquet et al., Science 291:468 (2001)
[3-4] Fiquet/Badro et al., to be published (2001)
[5] Shukla et al., in prep (2001)

Simulation of powder infra-red spectra of phyllosilicates

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Infra-red (IR) spectroscopy provides information at the molecular level on the structure and properties of minerals. The interpretation of IR spectra is generally done by assigning the observed signals to the normal vibrational modes of molecules or solids, which may be assessed with classical models and group theory. However, in most cases, assignment of bands is done using empirical rules and inter-comparison between IR spectra. Alternatively, ab initio quantum mechanical calculations allow to determine the dielectric tensor of solids as a function of the light frequency. IR-spectra may then be calculated using models taking into account for shape and size effects. To date, this approach has been mainly limited to the investigation of the vibrational properties of highly symmetric or isotropic compounds.

In the present work, we use this method to investigate the IR spectra of phyllosilicates, which often show a micrometric size (clay minerals), a low-symmetry structure, and various structural defects (e.g., impurities, stacking faults). These widespread hydrous minerals play a major role in the geochemistry of the Earth's surface.

We check the accuracy of the ab initio approach in calculating the IR spectrum of kaolinite (Al2Si2O5(OH)4), a triclinic clay-mineral. Interest of the IR spectrum of kaolinite also stems from the well-defined absorption bands of OH groups. Indeed, IR-bands of OH-groups in minerals are widely used to investigate the occurrence of structural defects, which may be related to the conditions of genesis and properties of the mineral. Thus, a theoretical understanding of the IR signal of OH groups is of fundamental interest in mineral physics. Ab initio calculations were performed by using the Density Functional Theory in the generalized gradient approximation. We described the ionic cores by norm-conserving pseudo-potentials and the wave functions were

expanded in plane-waves. A remarkable agreement was obtained between calculation and experiment, including OH bands. This provides a firm basis for the interpretation of the IR spectrum of kaolinite and, in a near future, of other phyllosilicate minerals, including disordered and defective structures.

This work was performed in collaboration with A.M. Saitta (Laboratoire de Physique des Milieux Condenses, CNRS UMR 7602, Universite' Paris 6) and F. Mauri, F. Guyot, C. Lemaire, T. Allard, G. Calas (Laboratoire de Mineralogie-Cristallographie).

Reference :
Balan, E., Saitta, A.M., Mauri, F., Calas, G. First-principles modeling of the infra-red spectrum of kaolinite. American Mineralogist, 2001, 86, (in press).

The optimal potential method: application to Fe and Sn

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(2) ETHZ, Zurich (Switzerland)
(3) SISSA, Trieste (Italy)

We have recently proposed[1] a new simulation technique, which, by combining first principles and classical molecular dynamics, allows extensive classical simulations with ab initio accuracy . The method is based on the construction, by a force-matching procedure, of a classical Hamiltonian explicitly depending on a reference thermodynamic state. In a first application, we will discuss the melting curve and the thermodynamic properties of iron at earth's core conditions. We will then present the melting curve of tin and focus on the properties of the liquid with increasing pressure.

[1] A. Laio et al, Science 287, , 1027 (2000)

High-pressure phase transformations by periodic LCAO techniques

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The issue of phase stability against applied pressure has an obvious importance for the earth sciences and for geophysics in particular. In many instances, temperature has comparatevely minor effects on phase equilibria with respect to high pressure, so that static simulations at the athermal limit can be of great value to predict the stabilty ranges of mineral phases and their structural properties. Further, the study of pressure-dependent solid state transformations is beginning to shift attention from equilibrium thermodynamics to kinetic aspects and to the underlying atomistic mechanisms. In this respect, ab initio calculations are expected to give a most appreciable contribution.
In solid-state ab initio methods, the one-electron eigenfunctions are usually expanded in sets of delocalized basis functions (plane waves, PW). Their very simple analytical form affords a number of remarkable advantages. The PW approach is usually associated with use of DFT (density-functional-theory) Hamiltonians. Another scheme is based on the use of basis functions localized at atomic nuclei (atomic orbitals, AO), with the advantage of allowing a straightforward treatment of valence and core electrons at the same level. The periodic LCAO (linear combination of atomic orbitals) scheme can be associated to both Hartree-Fock and DFT Hamiltonians. We have used this all-electron computational approach, as implemented in the computer code CRYSTAL98 [1], with DFT-B3LYP and LDA Hamiltonians. Least-enthalpy optimizations at constant pressure have been performed, with full structural relaxation within the constraint of symmetry.
As thermodynamic application, the phase equilibrium Fd-3 m-MgAl2O4 <-> Fm-3 m-MgO + R-3 c-Al2O3 <-> Cmcm-MgAl2O4 has been considered, corresponding to the high-pressure transformation of cubic spinel-type magnesium aluminate into the orthorhombic CaTi2O4-type polymorph, with the periclase+corundum assemblage as intermediate step [2]. Experimental results [3] indicate 15 GPa and over 40 GPa, respectively, for the two transition pressures. Least-enthalpy structure optimizations in the pressure range 0 to 60 GPa have allowed us to predict: (i) the full crystal structure, the pV equation of state and the compressibility of Cmcm-MgAl2O4 as a function of pressure; (ii) the phase diagram of the MgO-Al2O3-MgAl2O4 system, and the equilibrium pressures for the reactions of formation/decomposition of the Fd m and Cmcm polymorphs of MgAl2O4 from the MgO+Al2O3 assemblage. Cmcm-MgAl2O4 is predicted to form

at 39 and 57 GPa by LDA and B3LYP calculations, with K0 =248 (K'= 3.3) and 222 GPa (K' =3.8), respectively.
Concerning applications to kinetics, the important transition undergone at high pressure by many binary AB compounds (e.g., tetrahedral semiconductors), which transform from the zinc blende (B3, F-4 3m) to the rocksalt (B1, Fm-3 m) structure, has been investigated. The cases of SiC [4] and ZnS are considered, for which the transition occurs at about 100 and 13 GPa, respectively. The mechanism traditionally assumed involved an intermediate rhombohedral R3m state, with motion of one of the two sublattices along the cube diagonal. However, recent molecular dynamics simulations on silicon carbide hinted at a different transition pathway with an intermediate monoclinic structure.
The main findings for SiC are the following. (i) The new mechanism actually involves an orthorhombic, rather than monoclinic, intermediate state with Pmm2 symmetry and two SiC units per cell. Such a cell is related to the zinc blende and rocksalt cubic lattices by appropriate transformation matrices. During the transition, a rigid shift of the C vs. Si sublattice is accompanied by a change of volume and of the b/a and b/c dge ratios of the orthorhombic cell. (ii) In the kinetic study, the phase transformation was monitored at constant pressure along the z(C) reaction coordinate in the range 0.25 to 0.5, by minimizing the total enthalpy H with respect to the appropriate variables according to the mechanism considered. This procedure was carried out at several pressures. At equilibrium (p=92 GPa), the activation enthalpy of the process attains 0.75 and 2.10 eV/SiC-unit for the orthorhombic and for the rhombohedral pathways, respectively. This demonstrates unambiguously that the new mechanism, based on the intermediate Pmm2 structure, is energetically favoured with respect to the traditional one. Further, a detailed analysis of the dependence of DV, b/a and b/c on z(C) along the transformation path gave the activation volume of the process and provided insight into the bottleneck transition state. Such results are confirmed by the ZnS study.

[1] Saunders V.R. et al., CRYSTAL98: User's manual. University of Torino, Italy, and CLRC Daresbury Laboratory,UK (1999).
[2] Catti M. Phys. Chem. Minerals, in press.
[3] Funamori N. et al. J. Geophys Res. 103, 20813 (1998).
[4] Catti M. Phys. Rev. Lett., in press.

Magnetism at High Pressures

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Consideration of magnetism is crucial in many transition metal-bearing materials for understanding and predicting phase diagrams, elasticity, equations of state, and electrical and thermal conductivity. Most important is whether there are local magnetic moments on the ions, rather than the ordering of the moments, though different magnetic ordering can also significantly affect the physical properties. Two end-member models have been proposed for magnetic materials, the band model and the localized Hubbard model. It appears that conventional band theory, using the GGA, is quite accurate for Fe for the phase diagram, elasticity, and equation of state. We have used a combination of methods (tight-binding, LAPW, mixed-basis pseudopotential, and a non-collinear Stoner model) to study the properties of Fe at high pressures and temperatures. The phonon contributions were included using the particle-in-a-cell (PIC) model, which is effectively a classical anharmonic Einstein model, and is accurate at high temperatures above the Debye temperature, but below temperatures where premelting effects appear. For hcp Fe, we find a non-collinear magnetic ground state at high pressures below 60 GPa. These antiferromagnetic correlations are crucial for the equation of state and for understanding the Raman spectra. FeO and CoO are examples of Mott insulators, materials for which conventional band theory predicts metallic behavior, but in fact are insulators. This is understood to arise from local correlations not included in local density functionals like LDA and GGA. There is yet no accepted solution to this problem, and there are a number of methods that can predict the correct insulating behavior at zero pressure (e.g. Hartree-Fock, self-interaction corrections, LDA+U, and dynamical mean field theory). However, high pressure may help distinguish between these models, so it is useful to make some predictions about high-pressure behavior that can be tested experimentally. We have applied the LDA+U model to FeO and CoO as a function of U and volume V. For U=0 (that is GGA) we find first-order high-spin low-spin transitions at high pressure for an antiferromagnetic phase diagrams, elasticity, equations of state lattice with a delta V of several percent, but for rhombohedrally strained lattices the transitions are continuous. Turning on U pushes the high-spin low-spin transition to much higher pressures, and depending on U one finds a metal-insulator transition at high pressures

between high-spin, AFM states. Much improved equations of state are found with LDA+U, and the strain and its dependence on pressure in FeO are reproduced well. Experiments are required to test the accuracy of the predictions of LDA+U. Also, further work is required to understand the behavior of U with compression.

This work is in collaboration with Stephen Gramsch, Oguz Gulseren, Sonali Mukherjee, Gerd Steinle-Neumann, and Lars Stixrude, and is supported by NSF. Computing was done on the Cray SV1 at the Geophysical Laboratory supported by NSF and the Keck Foundation.

Elasticity and Equations of State from Experiments

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The thermoelastic properties of minerals play a crucial role in understanding the mineralogy, structure and dynamics of the deep interiors of the terrestrial planets. Major advances in mineral thermoelasticity have occurred recently due to the development of new techniques for accurate experimental determination of thermal equations of state in both the multi-anvil press and diamond anvil cell. Many of the most important mantle minerals have been studied to temperatures up to 1000 K or more and pressures of 30 GPa or higher. here have also been major developments in the experimental study of single-crystal elastic moduli of mantle and core materials at very high pressures. This paper will review the recent developments and highlight areas where continued work is needed. Applications to understanding the Earth's deep mantle will be emphasized.

Raman Spectroscopic Studies of Phase Transitions in Sesquioxides and Hydroxides

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There has been much theoretical interest in high-pressure phase transformations in sesquioxides (e. g., Al2O3, Fe2O3, Cr2O3) and hydroxides (e.g., Co(OH)2). Here we report on Raman spectroscopic studies of Fe2O3 and Cr2O3 to pressures above 60 GPa. For Fe2O3, all Raman-active phonons show strong nonlinear pressure-induced shifts. Using Kiefer's model, we can calculate the phonon contribution to the thermodynamic parameters of hematite and estimate a bound on the magnon contribution to the heat capacity. At 54 GPa, the Raman spectrum changes drastically and the characteristics of the high-pressure phase are shown to be inconsistent with a perovskite-type structure. In the case of Cr2O3, recent Raman studies have revealed clear evidence for a high-pressure phase transition but no structural change was found by high-resolution x-ray diffraction (Mougin et al., 2001). Here we resolve this discrepancy by showing that near 18 GPa Cr2O3 transforms to a new phase not previously predicted theoretically. The high-pressure behavior of brucite-type hydroxides has attracted much theoretical and experimental interest (e.g. Raugei et al., 1999). For Co(OH)2, there is a fundamental conflict between a spectroscopic study (Nguyen et al., 1997) which suggested this material undergoes a novel form of sublattice (H-layer) amorphization at high pressures and a neutron diffraction study (Parise et al., 1999) which found it does not. Here we use x-ray and Raman data to resolve this discrepancy. Disordering restricted to the hydrogen layer is indeed induced by application of pressure, but the transition occurs at much higher pressures than suggested by earlier spectroscopic data.

Refs:
J. Mougin et al., J. Phys. Chem. Solds, 62, 553 (2001).
S. Raugei et al., Phys. Rev. Lett., 823, 2222 (1999).
J. H. Nguyen et al., Phys. Rev. Lett., 78, 1936 (1997).
J. B. Parise et al., Phys. Rev. Lett., 83, 328 (1999).

Temperature and composition of the Earth's core from ab initio thermodynamics

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We have recently proposed methods for constraining the temperature and composition of the Earth's core using ab initio techniques to calculate free energies and chemical potentials of solid and liquid iron and its alloys with sulphur, silicon and oxygen [1,2,3]. This talk will summarise the theory that underpins these methods. In particular, we will show how the technique of thermodynamic integration allows one to calculate ab initio free energies with statistical-mechanical errors that are completely controllable and can be reduced to any desired extent. New results will be presented for the melting properties of aluminium over a wide range of pressures. We will also present our latest results for the melting properties of iron up to Earth's core pressures.

[1] D. Alfe, M. J. Gillan and G. D. Price, 'Melting curve of iron at Earth's core pressures from ab initio calculations', Nature, 401, 462 (1999).
[2] D. Alfe, M. J. Gillan and G. D. Price, 'Constraints on the composition of the Earth's core from ab initio calculations', Nature, 405, 172 (2000).
[3] D. Alfe, G. D. Price and M. J. Gillan, 'Thermodynamics of hexagonal close-packed iron under Earth's core conditions', Phys. Rev. B, in press.

Si/Al ordering in tetrahedral framework silicate minerals

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The ordering enthalpy is calculated by computer simulation and its origin identified as lying mostly in local strain. The transformation temperature is often well below what would be expected from Bragg-Williams theory, due to 'low' Al concentratrion, quasi-one-dimensional structures, and structural frustration. There are some indications of how actual Si/Al interchange can take place.

Diffusion and deformation in (Mg,Fe)O

Stephen Mackwell, Nathalie Bolfan-Casanova, Steven Jacobsen and Catherine McCammon, Bayerisches Geoinstitut, Universitat Bayreuth, D-95440 Bayreuth, Germany

(Mg,Fe)O with a composition near 20 mol.% FeO:80 mol.%MgO is arguably the most abundant oxide in Earth's interior and the second most important mineral in the lower mantle. It has the added advantage of going through no structural phase transitions between ambient pressure and conditions deep within the lower mantle. At room pressure, it is probably the most defective abundant Earth mineral, containing as much as 8 at.% vacant cation sites for compositions characteristic of the lower mantle. As defects control many processes in minerals, including diffusion, electrical conductivity, chemical reactions and high-temperature deformation, this mineral provides a unique, relevant geological material in which to study the nature of defects and their effects on chemical and physical properties. Unfortunately, this is both a boon and a bane: we can measure the defect concentrations and site occupancies directly, but the defect densities are so high even under reducing conditions at room pressure that defect clusters form at even modest iron contents of around 5 mol.% FeO. It is also noteworthy that cation defect concentrations decrease with increasing pressure, complicating extrapolation of room pressure property measurements to lower mantle conditions.

At low pressure, the defect structure of (Mg,Fe)O is dominated by ferric iron in octahedrally coordinated cation sites, vacant cation sites and ferric iron in tetrahedrally coordinated interstitial sites. For a single crystal sample we can determine total iron content from the electron microprobe, ferric/ferrous iron ratios from Moessbauer, and ferric iron occupancy of interstitial sites by refinement of the single-crystal x-ray structure. Using samples characterized in this way, we have investigated iron-magnesium interdiffusion at a range of temperatures and oxygen fugacities, and measured elastic velocities using gigahertz interferometry at room pressure, as well as high pressures. Previous studies have also studied the effects of iron content and oxygen fugacity on solid state creep. From these studies, we are able to obtain additional information about the point defect behaviour of (Mg,Fe)O.

In addition to the intrinsic defect structure, we have investigated the nature of hydrous defects in (Mg,Fe)O at pressures and temperatures appropriate to the lower mantle. The infrared signatures and

dependencies of defect concentrations on the chemical environment are consistent with interstitial protons associated with octahedrally coordinated cation vacancies. Absolute hydrogen contents are low compared to transition zone minerals, but are still higher than in silicate perovskite.

MD simulation of the 410 km and 660 km seismic discontinuities

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The seismic wave discontinuities near 410 and 660 km depths in the mantle have been attributed to the pressure-induced phase transformations from (Mg,Fe)2SiO4 olivine to (Mg,Fe)2SiO4 modified-spinel, and from (Mg,Fe)2SiO4 spinel to (Mg,Fe)SiO3 perovskite plus (Mg,Fe)O magnesiowustite, respectively. In recent publications (Matsui, 1999; Matsui et al., 2000; Matsui, 2000), we have shown that the molecular dynamics (MD) simulation with realistic potential models is very successful in reproducing accurately the observed crystal structures and elastic constants of MgO periclase (Pc), the three Mg2SiO4 polymorphs, olivine (Ol), modified-spinel (Ms) and spinel (Sp), and MgSiO3 perovskite (Pv) over wide T and P ranges, including those found in the deep Earth. Here we apply MD simulation to predict the density and sound velocity jumps between Mg2SiO4 Ol and Ms, and between Mg2SiO4 Sp and MgSiO3 Pv plus MgO Pc at the high-T and high-P conditions corresponding to the 410 and 660 km discontinuities, respectively. We then compare these simulated density and sound velocity jumps with representative seismological models reported for the 410 and 660 km discontinuities, to study the mineral composition for the mantle, and to assess the seismological models.

SHORT TALK: "Necessity to obtain a reliable pressure calibration standard at high temperature and high pressure"

The equation of state (EOS) of Au, proposed by Anderson et al. (1989), has recently been widely used to estimate pressure at high temperatures (e.g. Mao et al. 1991; Fei et al. 1992; Meng et al. 1994; Funamiri et al. 1996; Irifune et al. 1998). However, it should be noted that Anderson et al. derived the EOS of Au based on the measured elastic and thermodynamic properties of Au at temperatures less than 550 K, where

the contribution from the thermal energy due to excited conduction electrons is expected to be very small. Thus their EOS of Au underestimates the pressure especially at high temperatures where the electronic thermal pressure becomes significant. Indeed $B!$ (Brecent in situ X-ray measurements (Irifune et al., 1998) of the postspinel phase boundary in Mg2SiO4, based on the Au pressure scale, suggest that the boundary is about 2 GPa lower than the pressure at the 660 seismicdiscontinuity. First-principle band structure calculations for Au are strongly recommended to estimate precisely the electronic thermal pressure in Au at high temperature. Alternatively, crosschecks of the Au EOS at high temperatures, by comparing the Au EOS with accurate EOS's obtained for non-metals such as MgO(Matsui et al., 2000), are urgent.

Structural determinations from first principles analysis of experimental NMR spectra.

Francesco Mauri
Laboratoire de Mineralogie-Cristallographie, CNRS UMR 7590, Universite' Paris 6 et 7, IPGP, Case 115, 4 Place Jussieu, 75252 Paris Cedex 05

We developed a theory for the ab initio calculation of the all-electron magnetic response in molecules and solids, with pseudopotentials and density functional theory [C. J. Pickard, F. Mauri, Phys. Rev. B 63, 245101 (2001)].
With respect to previous all-electron approaches, we can treat extended systems; moreover, the efficiency of the plane-wave pseudopotential scheme allows us to deal with systems of hundreds of atoms (including heavy elements) with a very manageable computational cost. Thanks to the accuracy of the theoretical predictions, it is possible to extract, from the experimental NMR spectra of complex solids, their microscopic structure. I will illustrate our approach with applications to the determination of the Si-O-Si bond angle distribution in amorphous silica [F. Mauri, A. Pasquarello,B. G. Pfrommer, Y.-G. Yoon, S. G. Louie, Phys. Rev. B 62, R4786 (2000)], and to the determination of the structure of icosahedral boron carbide [F. Mauri, N. Vast, C. J. Pickard, Phys. Rev. Lett, to be published (2001)].

Atomistic Simulation of Mineral Surfaces and their interaction with water

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Atomistic simulation techniques represent a powerful complementary tool for studying mineral surfaces. The aim of this presentation is to describe the recent progress in modelling the structure of oxide and mineral surfaces and in particular to review our attempts at studying the interaction of water with mineral surfaces. The approach has been to use a combination of energy minimisation and molecular dynamics techniques to model mineral surfaces at the atomic level. We find that on oxide mineral surfaces water usually adsorbs dissociatively and thus a nominally stoichiometric oxide will often exhibit hydroxide-like surfaces which is clearly significant if we wish to consider the surface stability and reactivity of minerals. A further consequence of the large adsorption energies is that the relative stability of the surfaces is modified which effects their growth and morphology. In contrast to the oxide minerals we find that calcite water adsorbs associatively. Despite this, water can have a profound effect on the surface properties. This becomes particularly evident when we consider the growth and dissolution of calcite surfaces. For example, when calcite is grown in the presence of magnesium ions we predict that if water is absent then magnesium will thermodynamically prefer to dissolve into the bulk of the resulting crystal. However, when water is present it will bind preferentially to magnesium causing the magnesium to reside at the mineral surface - inhibiting further growth. This effect may also help to suggest why difficulties are often encountered when attempting to grow dolomite in laboratory or marine conditions.

Vibrational spectroscopy of vitreous silica: A first-principles investigation

Alfredo Pasquarello
IRRMA, EPFL, CH-1015 Lausanne, Switzerland.

The vibrational properties of vitreous silica are investigated through their spectroscopic response in inelastic neutron scattering [1], infrared absorption [2], and Raman scattering experiments [3]. We use a model structure consisting of a disordered network of cornersharing tetrahedra, which we obtained by a first-principles molecular dynamics

quench from the melt [4]. Calculated and measured effective neutron densities of states are found to compare well [1]. In particular, this comparison allows us to clarify the origin of the high-frequency doublet. Applying the recent quantum polarization theory, we calculate dynamical charge tensors and obtain an infrared spectrum in good agreement with experiment [2]. In order to reproduce the distribution of experimental intensities throughout the spectrum, it is critical to include nonspherical contributions to the oxygen charge tensors. Finally, using the calculated eigenmodes, we conclusively assign the two unusually sharp lines appearing in the Raman spectrum to breathing oxygen motions in small rings embedded in the structure [3]. Using a bond polarizability model with parameters derived from first-principles calculations on crystalline SiO$_2$ polymorphs [5], we then provide an estimate for the concentration of such rings [6].

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[5] P. Umari, A. Pasquarello, and A. Dal Corso, Phys. Rev. B 63, 094305 (2001).
[6] P. Umari and A. Pasquarello, to be published.

The ab initio simulation of light impurities in Fe under the conditions of the Earth's Core

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We will show how ab initio techniques based on density functional theory can be used to calculate the chemical potentials of the leading candidate impurity elements (S, O and Si) in the Earth's solid inner core and liquid outer core. The condition that these chemical potentials

be equal in the solid and liquid phases provides values for the ratios of the impurity mole fractions in the inner and outer core. By combining the estimated ratios with ab initio values for the impurity molar volumes in the two phases, and demanding that the resulting inner- and outer-core densities agree with seismic values, we obtain estimates for the concentrations of S, O and Si in the core. The results show that O partitions much more strongly than S and Si from solid to liquid, and indicate that the presence of O in the core is essential to account for seismic measurements. We note the implication of this finding for our understanding of the Earth's magnetic field.

Coordination of Metals at Mineral Surfaces Determined by XAFS Spectroscopy

Richard J. Reeder (State University of New York at Stony Brook)

The detailed coordination of metals at the mineral-water interface is one of the major controls on incorporation during mineral growth. Because calcite is readily grown in laboratory conditions, its study offers clues to the mechanisms operating at mineral surfaces. Metal impurity incorporation at the (10-14) growth surface of calcite is known to be strongly influenced by the availability and spatial distribution of structurally distinct surface sites. Reduced symmetry and constrained orientations of monolayer growth steps result in nonequivalent vicinal faces composing polygonized growth spirals over a wide range of growth conditions. Several studies have documented consistent trends of differential incorporation of both cation and anion impurities between nonequivalent vicinals, with subsequent formation of compositionally distinct vicinal subsectors. Explanations for the step-selective incorporation have focused on differences in the geometry among different kink sites. However, several exceptions to step-selective incorporation patterns on calcite (10-14) have been noted, including Zn2+, Cu2+, and several tetrahedral metal-oxyanions. X-ray absorption fine-structure spectroscopy (XAFS) allows characterization of the local coordination of metal species sorbed at the mineral-water interface and provides new insight to its role in impurity incorporation. Zn K-edge XAFS spectra collected on moist Zn-sorbed calcite pastes reveal that Zn2+ forms a tetrahedral surface complex. This contrasts with results for Zn2+ incorporated into the calcite structure, where XAFS has shown octahedral coordination, characteristic of the host Ca, but with significant relaxation. Similarly prepared Cu K-edge XAFS spectra reveal that Cu2+ sorbs at the

surface as an axially distorted octahedral complex, consistent with a Jahn-Teller distortion. Cu2+ coprecipitated into calcite also shows a Jahn-Teller distorted octahedral coordination, but with a different degree of elongation. Other divalent transition metals having sizes similar to Zn2+ and Cu2+ (e.g., Co2+) are expected to sorb as regular octahedral complexes, and readily substitute in the octahedral site of calcite. The geometrically distinct Zn2+ and Cu2+ surface sorption complexes may explain their anomalous incorporation behavior at calcite (10-14) surfaces.

These findings indicate that coordination geometry of surface complexes must also be considered, along with surface site geometry, as factors controlling metal incorporation at mineral-water interfaces.

Isotope fractionation: where and how ab-initio calculations can be useful

B. Reynard
ENS - Lyon (France)

In Earth sciences, stable isotope fractionation of ligth elements (O, B, C, N, ...) is used to track and quantify interactions between solids and fluids or gases in terms of intensive (T, pH, ...) or extensive (e. g. fluid/rock ratios) parameters. In practice, it is mostly solids that are analysed simply because they can be preserved through time and amenable to chemical analysis. It is then necessary to know the fractionation constants between a rock or its constitutive minerals to reconstruct the fluid chemistry for various purposes ranging from understanding the circulation of deep and hot fluids in rocks and their control on seawater chemistry over geological times (1-1000 Ma) to environmental characteristics such as past seawater temperatures, composition (pH, ice volume) and CO2 concentrations of the atmosphere. If many of these aspects have been adressed within the past 50 years through experimental measurements or vibrational modelling of equilibrium constants at high temperatures where equilibrium prevails, we reach now a point where applications to low temperature systems with or without biological intercations are of increasing importance for environmental issues. These require the understanding of subbtle mechanisms such as interactions at the mineral surfaces, and accurate prediction of low temperature fractionation which are not easy to study experimentally. Ab initio calculations may help in solving this problem by providing accurate description of the interaction potentials of exchanging species in various structural environments (bulk crystal, surface, aqueous solutions, ...). Various examples are shown and potential applications

of ab initio calculations discussed.

Elasticity of iron at high pressure and temperature - Implications for the Earth's inner core

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The discovery of seismic anisotropy and possible super-rotation of the Earth's solid inner core has initi-ated considerable work on the physical state and dy-namics of this innermost portion of our planet. A de-tailed knowledge of structure and elasticity of its main constituent, iron, at appropriate pressure and tempera-ture conditions is crucial for our understanding of the processes leading to inner core anisotropy. Here we report results on the structure and elasticity of hexago-nal close packed (hcp) iron at high pressure and tem-perature from first principles calculations and their im-plications for inner core elasticity. We combined den-sity functional theory in the generalized gradient approximation with the particle-in-a-cell model, which was used to compute the vibrational contribution to the Helmholtz free energy. We find that the axial ratio c/a of hcp iron increases substantially with increasing temperature, reaching a value of close to 1.7 at a tem-perature of 5700 K, where aggregate bulk and shear moduli match those of the inner core. As a conse-quence of increasing c/a the single crystal longitudinal anisotropy at high temperature has the opposite sense from that at low temperature. By combining our results with a simple model of polycrystalline texture in the inner core in which basal planes are partially aligned with the rotation axis, we can account for seismologi-cal observations of inner core anisotropy.

Rigid Unit Mode analysis of framework structures.

Stephen Wells

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A rigid-unit mode, or RUM, is a vibrational mode which can propagate through a framework mineral structure with no distortion of the

tetrahedra, which rotate and translate as rigid units. Recently we have been using the mathematical techniques of geometric (Clifford) algebra to identify such modes as both static and dynamic distortions. Given a set of atomic positions before and after some atomic movement, we can identify contributions to the movement from RUM, bond-stretching and bond-bending motions. We have combined this approach with Mott-Littleton calculations, so as to study the propagation of strain as a structure accomodates a defect, and also with Reverse Monte Carlo techniques using models built from total neutron scattering data. This allows us to quantify the RUM contribution to phase transitions and dynamic disorder in materials such as cristobalite, quartz and zeolites.

Investigation of pressure-induced structural and electronic changes in inorganic crystals by density functional theory

B. Winkler, V. Milman
Institut f. Geowissenschaften, Uni Kiel (D)

Density functional theory-based calculations are currently the most commonly used tool to model pressure-induced changes of crystals and their properties. In this contribution, we will first discuss the reliability with which elastic properties of crystals and pressure-induced structural changes can be modelled and predicted. Quantum mechanical calculations also allow to investigate pressure-induced changes to the electronic structure. These can be analysed as changes in bond populations, and thereby offer insight into the driving force of pressure-induced phase transitions. This is especially interesting for iso-symmetric structural phase transitions, where small changes in coordination-polyhedra give rise to first-order transitions. Furthermore, changes in hydrogen bridges and the possibility of pressure-induced hydrogen bonding or pressure-induced charge-disordering can reliably be investigated. Finally, we will present a new method to systematically generate trial structures to investigate possible high pressure polymorphs. In summary, parameter-free modelling successfully complements experimental approaches and often opens the only route to determining the origin of pressure-induced structural or electronic changes.

Report on a Collaborative Visit of B. Arnaud, University of Rennes (France) to P. Bloechl, University of Clausthal (Germany)

I visited Prof. Peter Bloechl at the Clausthal University of Technology from the 9 to the 19 July, 2001 to work on the improvement of the recently implemented GW-PAW approximation[1,2].

We discussed how to make GW calculations much faster and how to get a code with a better scalability in order to treat larger systems. To achieve such a goal we explored two major issues:

1 Instead of using a direct scheme to evaluate the dielectric matrices which are necessary to build the screened interaction W, we used a scheme based on the Green's function approach [3,4] which is better adapted to the PAW formalism and which avoids the time consuming sums over conduction bands. The implementation of this scheme is not yet finished but is expected to improve the scability of GW calculations.

2 We implemented a scheme[5] which consists in forming an optimal basis set for electron states everywhere in the Brillouin zone by considering the Bloch functions at a few points in the zone. This approach was motivated by the fact that the evaluation of the self-energy in the GW approximation is rather time consuming since the computation of electron states at thousands of crystal momenta is required. Our preliminary calculations showed that this scheme is well adapted to reduce the computationnal cost of GW calculations.

Based on these methodological improvements, we hope to be able to investigate the quasiparticle and optical properties of complex systems such as molecular systems which are currently studied in Rennes.

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[3] S. Baroni, P. Giannozzi and A. Testa, PRL 58, 1861, (1987).

[4] H. Ness and A.J. Fisher, PRB 56, 12469 (1997).

[5] E. Shirley, PRB 54, 16464 (1996).

Brice Arnaud

Report on a Collaborative Visit of L. Sandratskii (Technische Universität Darmstadt) to Uppsala

Visit from August 6 to 28, 2001

I visited Olle Eriksson, Lars Nordström and Lars Bergqvist at the Uppsala University. The main topic of our discussions were magnetic excitations and thermodynamics in MeFe2 systems (Me=Y,Ce,U). These systems possess a number of interesting properties: (i) although both sublattices are magnetic the spin wave exitations are observed only on the Fe sublattice, (ii) in $CeFe_2$ both ferromagnetic and antiferromagnetic fluctuations coexist, (iii) there is very strong variation of the spin stiffness in the series. In UFe_2 the value of the stiffness exceeds the corresponding value in bcc-Fe. Further experiments are currently performed. We plan to combine the caculation of the spin-wave energies and interatomic exchange parameters with the Monte-Carlo simulation.

I gave a seminar on the non-collinear magnetism in U compounds.

Other topics of possible future collaboration have been discussed.

Leonid Sandratskii

4.4 ESF Workshop/Conference Announcements

4.4.1 Workshop on Oxide-Metal Interfaces

Final Announcement

Workshop on Oxide-Metal Interfaces, Lyon 4-6 October

Sponsored by CECAM and ESF-STRUC Programme

We draw your attention to the webpages relating to this PSIK/CECAM workshop which are linked from our home page below and from http://www.cecam.fr. The system is that all participants should make their own accommodation and travel arrangements, making use of the information on the web. There will be a limited number of bursaries to assist young researchers from the PSIK network, and substantial financial support for invited speakers. The total number of participants will be limited to about 40, but there is still space and anyone wishing to attend should get in touch with Professor Mike Finnis or his coorganiser Dr Christian Elsaesser.

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4.4.2 Hands-on CASTEP Code Workshop

Second announcement and call for registrations

"The Nuts and Bolts of First-Principles Simulation"
A one-week hands-on workshop in the theory and practice of CASTEP calculations run by those who wrote the code
6th-13th December 2001 at Durham University, UK

Organisers

Philip Lindan (Kent)
Stewart Clark (Durham)
Walter Temmerman (Daresbury)

Supporters

ESF-STRUC Psi-k Programme
The CASTEP Developers' Group
Accelrys Inc.

Overview

This course is aimed at anyone who wants to learn how first-principles simulation works and how to apply it. It is especially suitable for those embarking on a Ph.D with a substantial first-principles element. In the workshop you will use a completely new F90 version of CASTEP written to a radical modular design. For academics, the workshop package includes a copy of the academic code for you to take away and use in your own research.

Further information, including a timetable of lectures and workshops, is located at http://cmt.dur.ac.uk/sjc/caste

Registration: general points

Registration is by web-page only. The URL is `http://www.dur.ac.uk/~dph0sjc/castep_form.html`

Participation is limited to 100 delegates, the large majority of which will be young researchers. We expect the meeting to be heavily over subscribed, and therefore we will have to give preference to early registrations. Note that the allocation of bursaries is subject to further restrictions (see below).

It is not possible (or appropriate!) to register for part of the conference.

Bursaries

Thanks to generous support from the ESF through the Psi-k network we shall be able to offer many fully-subsidised places for young researchers. These bursaries will cover the conference fee and accommodation. They will be allocated according to ESF and Psi-k guidlines: the main restrictions are that recipients should be aged 35 or less, and be working in psi-k groups or groups within countries that participate in the ESF programme.

We cannot provide support for travel expenses.

Fee-paying delegates

Some places will be avalable for fee-paying delegates at the following rates:

Conference fee only: 54 pounds sterling

Accommodation

Delegates staying at the University will be housed in rooms in Grey college. Further details can be found at: http://www.dur.ac.uk/GreyCollege/

Both standard and en-suite accommodation is available to fee-paying delegates, and the costs are: Standard: 120 pounds sterling En-suite: 190 pounds sterling

Those receiving a bursary will stay in standard rooms.

Meals

Breakfast will be provided for those delegates staying at the University. All other meals must be paid for separately. It will be possible to buy lunch and/or dinner in one of Durham's colleges. Delegates wishing to take this option must book their meals at the time of registration.

The total cost, for 7 lunches and 6 dinners, is 120 pounds sterling.

Social programme

We plan to organise a conference trip and a dinner on a rather informal basis. We will advise delegates of the details of these nearer to the date of the conference.

CASTEP code

All academic delegates will be able to take away a copy of the latest version of CASTEP. For licensing reasons this will be in binary form, with executables for all major platforms. Access to the source code may be possible through collaborative arrangements with one of the CASTEP development group, or for UK-based academics, through the UKCP consortium.

5 General Workshop/Conference Announcements

5.1 Workshop in Santa Barbara

"Realistic Theories of Correlated Materials"

Institute for Theoretical Physics at the University of California, Santa Barbara

July 29, 2002 - December 20, 2002

Organized by O. Andersen, A. Georges, G. Kotliar, and A. Lichtenstein

We are happy to announce that the workshop entitled: "Realistic Theories of Correlated Materials", was approved and will take place at the Institute for Theoretical Physics at the University of California, Santa Barbara from July 29 2002 to December 20 2002, organized by O. Andersen, A. Georges, G. Kotliar and A. Lichtenstein.

The applications can be found at the URL http://www.itp.ucsb.edu/activities/future/

This ITP program will focus on quantitative methods for the treatment of electronic correlations in solids, and emphasize applications to materials of current experimental interest such as rare earth and actinides, heavy fermions, transition metal compounds and quasi one- and two-dimensional organics.

It is motivated by recent advances in the treatment of correlation effects such as dynamical mean field theory and its extensions, numerical renormalization group approaches, and their integration into electronic structure calculations. The program will stimulate discussions among experts in many body theory, experts in electronic structure calculations and experimentalists working on strongly correlated materials.

The program will balance two important components: the development of new theoretical methods, and the applications of these methods to experimentally relevant systems, in order to gain a new physical understanding of complex materials.

The participation of key researchers in the area of strongly correlated electron systems and electronic structure calculations is crucial for the success of the workshop, and we would like to invite you to participate in this workshop for an extended period of time. If you can, please fill out the application form at the URL above. Some travel and local expenses as well as office space will be provided for long term participants according to availability and ITP policies.

Notice that only the ITP director can issue official invitations, so it is essential that you submit an application soon. The ITP allows short term stays for experimentalist.

Suggestions for the workshop are welcome, please email them to kotliar@physics.rutgers.edu We look forward to seeing you in Santa Barbara in the fall of 2002.

5.2 2002 APS Special Focus Topic

2002 March Meeting of the American Physical Society

"Progress in Heterogeneous Catalysis, Fuel Cells, and Chemical Sensors"

This announcement is to bring to your attention a Special Focus Topic entitled "Progress in Heterogeneous Catalysis, Fuel Cells, and Chemical Sensors", to be held at the 2002 March Meeting of the American Physical Society. The deadline for abstract submission is Dec. 7, 2001. For information on submitting abstracts, please follow instructions on the APS website, http://www.aps.org/meet/MAR02/abs.html
The sorting number for this focus topic is 11.9.7. Please note that while contributors are welcome to send a duplicate copy of their abstract to the organizers, it is important to make sure that the original is sent to the APS, on time, ensuring that the abstract conforms to all APS regulations.

Call for papers: "Progress in Heterogeneous Catalysis, Fuel Cells, and Chemical Sensors" (11.9.7 FIAP/DCP)

While the areas of catalyst, fuel cell (both PEM and SOFC), and gas sensor development are perhaps not normally grouped together, they actually have several key issues in common. All three areas rely on complex catalytic reactions on one or two separate electrodes, atomic and molecular transport on surfaces and in the bulk, and are all faced with issues of thermal and chemical stability under harsh oxidizing/reducing environments and large temperature variations. This focus session will provide an overview of the current state of the art in these fields, and a forum for comparisons of different approaches to common problem formulations. Experimental and theoretical papers are solicited on a wide variety of phenomena, including (but not limited to) the following areas:

Structural (e.g. microstructure, mechanical properties, durability)

Chemical (e.g. surface chemistry, micro- and macrokinetics, triple-point boundaries)

Transport (e.g. bulk and surface diffusion, ionic transport, dopant interactions)

Electronic (e.g. band-gap engineering, optical properties, nanostructures)

Methodology (e.g. combinatorics, computation, nanotechnology)

Authors are encouraged to stress the relevance of their work to technological and industrial problems. Materials of interest include metals, semiconductors, and ceramics, either in bulk or at surfaces or interfaces. Contributions based on all experimental, theoretical, and computational methodologies are welcome.

Organizers

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6 General Job Announcements

Research Associate Position in Ab Initio Quantum Simulations

Theoretical Chemistry, Ruhr-Universitaet Bochum

Applications are invited for a postdoctoral research associate position (German nomenclature: promovierter wiss. Mitarbeiter, BAT IIa) including full social benefits. The appointment will be for two years in the first instance, however the position is available for a total of five years - independent of external funding. Starting date will be October 2001 or as soon as possible thereafter.

Applicants are expected to hold a doctorate in physics or a related discipline. In addition to excellent programming and computational skills the ideal candidate would have significant experience in one or several of the following fields: path integral simulations, quantum dynamics, density functional calculations, Car–Parrinello *ab initio* molecular dynamics. He or she would be involved in a number of diverse and challenging research projects including both method development and large-scale applications. The broad interests of the group are covered in the review
`http://www.fz-juelich.de/nic-series/Volume1/marx.pdf`
and additional information can be obtained from the webpage
`http://www.theochem.ruhr-uni-bochum.de`.

Candidates should send a detailed resume including an outline of their research interests and the names and email addresses of academic referees to

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

The University particularly welcomes applications from women.

Postdoctoral Position in Computational Electronic Structure Theory

Rutgers University

A post-doc opening is expected to become available in the group of Prof. David Vanderbilt at Rutgers University. The preferred starting date would be in the November 2001 to January 2002 time frame. The primary focus of the work will be on methods developments related to (i) the physics of insulators in finite electric fields, and (ii) the study of dielectric loss phenomena in oxides via density-functional perturbation theory. Familiarity with ab-initio density-functional methods is essential.

Candidates should send a CV, together with names and contact information for 2-3 references, to dhv@physics.rutgers.edu as soon as possible. Consideration of candidates will begin immediately and continue until the position is filled.

Prof. David Vanderbilt
Rutgers University
PO Box 849
Piscataway, NJ 08855-0849, USA

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Email: dhv@physics.rutgers.edu
`http://www.physics.rutgers.edu/~dhv`

Postdoctoral Research Position

National Renewable Energy Laboratory

Golden, Colorado

We invite applications for a very challenging post-doctoral position in computational chemical physics. Our newly started project involves protein systems, semiconductor quantum dots, and carbon nanotubes. The ideal candidate would have a background in the chemistry and physics of all these systems. However, we encourage ambitious young candidates with a background in any one of them to apply. The work will involve exploring new exciting ideas in the multi-discipline area based on electronic structure calculations. Molecular dynamics (both first principles and classical) may also be involved. Ability in code development is highly desired, especially after the first fiscal year. Stipend will be approximately 40K per calendar year. Candidate should send curriculum vitae, list of publications (including preprints of unpublished papers, if possible) and list of three references to

Dr. Shengbai Zhang or Dr. Barton Smith
National Renewable Energy Laboratory
1617 Cole Blvd.
Golden, CO 80401, USA

NREL is an equal opportunity/affirmative action employer. Clarifications or further details can be obtained via e-mail to szhang@nrel.gov

Postdoctoral in Computational Physics - Electronic Structure
North Carolina State University, Raleigh, USA

Qualified and motivated candidates are invited to apply for the Postdoctoral Research Associate positions in the group of Prof. Lubos Mitas at the North Carolina State University. The candidate's PhD should be in physics or quantum chemistry. Some programming, computational and electronic structure methods experience is expected. The positions will be for one year initially and are renewable up to three years based upon mutual agreement and availability of funds. The beginning is anticipated in fall or early winter of 2001, at the latest.

The group is involved in many-body computational methods for quantum systems and computational materials research. Publications from our recent projects in electronic and atomic structures of nanoclusters, molecules and solids can be found at

http://altair.physics.ncsu.edu/

Successful candidates will be involved in the development of advanced methods such as quantum Monte Carlo and their applications to forefront research problems in electronic structure including

i) nanocrystals and nanoclusters,
ii) molecular and biomolecular systems,
iii) solid state systems including ferroelectrics, magnetic systems and semiconductors.

Please send the application with Curriculum Vitae, copies two recent papers, maximum one page of research interests/plans, and contact information (address, phone and email) of three references to:

Prof. Lubos Mitas
Dept. of Physics, Cox Hall 410-D
North Carolina State University
127 Stinson Rd.
Raleigh, NC 27695-8202, USA
or lmitas@unity.ncsu.edu

More information can be found at

http://altair.physics.ncsu.edu/

Tenure Track Position

Ohio University, Athens, USA

We will have a tenure track position open starting next Fall in condensed matter theory and are now soliciting applications. Please bring this to the attention of suitable candidates. Thank you for your help in this.

David A. Drabold, Professor of Physics
Dept. of Physics and Astronomy, Ohio University
Athens, OH 45701
drabold@ohio.edu
740-593 -1715 (phone) -0433 (fax)
`http://www.phy.ohiou.edu/~drabold`

Product Manager, Quantum Physics

San Diego, CA. or Cambridge, UK

JOB CODE: PMQM

The above position is currently advertised on the Accelrys website (http://www.accelrys.com/hr/jobs.php). Position is available immediately.

As a member of the product marketing/field science organization, the Product Manager develops beneficial internal/external relationships that assist in achieving market segment revenue goals, and facilitate market research, product planning, and product strategy execution of the organization. Working closely with the product development organization, this individual will develop a plan to consolidate and transition our quantum physics tools into a modern platform. S/he will also develop a new product pipeline and maintain a profitable product line with healthy growth potential. S/he keeps abreast of new/changing technologies, tools, and web site information. This individual will also continue to maintain scientific leadership in the field, by performing research and validation studies. S/he will be an active member of the scientific field and will actively be involved with various scientific societies, presenting scientific papers in conferences, and publishing in peer-reviewed scientific journals.

EDUCATION, SKILLS AND KNOWLEDGE REQUIRED

Ph.D. in Physics or in related discipline is required, with demonstrated expertise in solid-state quantum physics and simulations area. General software/computer proficiency required including Internet technologies. Must have good written and presentation skills. Has a working understanding of the relevant scientific concepts. Able to work independently and creatively; troubleshooter and problem-solver. Business/marketing orientation is also highly desirable.

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POST-DOC and PhD POSITIONS IN SOLID STATE THEORY

Department Chemie/Physikalische Chemie

Ludwig Maximilians Universit"at M"unchen, Germany

There are several vacant positions in our group working on spectroscopic properties of magnetic solids and surfaces. Emphasis of the planned project will be on layered systems that are of interest in the field of Magneto-Electronics.

The positions are available right now and within the next few months, respectively. The salary depends on age and family status and will be around 1700 and 850 Euro for a Post-Doc or a Ph.D. student, respectively.

Applications should be sent with a curriculum vitae, list of publications and letter(s) of reccomendation to

Prof. Hubert Ebert
Department Chemie/Physikalische Chemie
Ludwig Maximilians Universit"at M"unchen
Butenandtstrasse 5-13
D-81377 M"unchen GERMANY

Fax : 0049-89-21807584
e-mail : hubert.ebert@cup.uni-muenchen.de
WWW : http://olymp.phys.chemie.uni-muenchen.de/ak/ebert

Postgraduate Studentship

NMRC, Cork, Ireland

NMRC Ireland is a specialised research centre with an agenda ranging from optoelectronics and nanotechnology to microelectronics and ICT/Life Sciences http://www.nmrc.ie Applications are invited for a postgraduate studentship at NMRC investigating chemical vapour deposition of oxides on silicon using a range of state-of-the-art modelling strategies - in particular, quantum chemical/first principles calculations. This is part of an EU-funded project to simulate the structure, properties and deposition of high k dielectrics for gate oxides in the next generation of transistors. Collaboration with partners from industry and academia around Europe is a vital part of the project.

NMRC is located in the vibrant city of Cork, near the stunning landscapes of Ireland's southern coast. Postgraduate students at NMRC receive an annual stipend of IEP12000 (EUR 15237) and register at University College Cork for M.Sc. or Ph.D.

http://www.ucc.ie

The studentship is available from October 2001. Candidates of any nationality with a strong primary degree in chemistry, physics, computational or materials science or a related discipline are welcomed. An interest in such areas as electronic structure theory, computational modelling or thin-film deposition is advantageous.

For further information please contact Dr Simon Elliott:

mail to: Simon.Elliott@nmrc.ie
Tel: +353-21-490 4246
NMRC, Lee Maltings, Prospect Row, Cork, Ireland.

Ph. D Graduate Positions

International Graduate School *Advanced Materials* University of Osnabrück, Germany

The international graduate school Advanced Materials at the University of Osnabrück situated in the historical city of Osnabrück launches a new PhD program Synthesis and Characterisation of Surfaces and Interfaces assembled from Clusters and Molecules financed by the Federal State of Niedersachsen. Starting January 2002, 10 doctoral fellowships (total grant Euro 1120.- per month plus social benefits) are available for three years. Among the projects there are two in the area of first-principles electronic structure theory.

1) Magnetic Clusters on Antiferromagnets

   Contact: Prof. S. Blügel, s.bluegel@fz-juelich.de
   further information: http://www.fz-juelich.de/iff/personen/S.Bluegel
   or http://www.flapw.de

2) Self-assembling of small metal clusters on ferroelectric surfaces

   Contact: Dr. R. Eglitis, roberts.eglitis@uos.de,
   or Prof. G. Borstel gunnar.borstel@uos.de

Applicants should hold a diploma or master degree in chemistry, physics or material science or a comparable degree. Particularly invited are applicants interested in computational physics, interested in developing new methods and techniques and candidates interested in multi-disciplinary research.

The University endeavors to employ a higher portion of female academic staff. Female candidates are therefore encouraged to apply and will be chosen if suitably qualified. Physically handicapped applicants will take precedence if equally qualified.

Interested persons are invited to send their applications indicating the project of interest and containing the customary documents until October 30, 2001 to the coordinator of the PhD program: Dr. J. Schnack, Fachbereich Physik, Universität Osnabrück, D-49069 Osnabrück,Email: jschnack@uos.de.

A list of all projects and for detailed information see http://www.physik. uni-osnabrueck.de/pp/.

7 Abstracts

Structural, electronic, and magnetic properties of a Mn monolayer on W(110)

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D-20355 Hamburg, Germany
X. Nie, G. Bihlmayer,
[b] *Institut für Festkörperforschung, Forschungszentrum Jülich,*
D-52425 Jülich, Germany
S. Blügel
Fachbereich Physik, Universität Osnabrück, D-49069 Osnabrück, Germany

Abstract

In this paper we establish a monolayer Mn on W(110) as a model system for two-dimensional itinerant antiferromagnetism. Combining scanning tunneling microscopy (STM), low-energy electron-diffraction (LEED), and *ab initio* calculations performed with the full-potential linearized augmented plane wave (FLAPW) method we have studied the structural, electronic, and magnetic properties of a Mn monolayer on W(110). Our experimental results indicate that in spite of the huge tensile strain Mn grows pseudomorphically on W(110) up to a thickness of three monolayers. Intermixing between the Mn overlayer and the W substrate can be excluded. Using this structural data as a starting point for the *ab initio* calculations of one monolayer Mn on W(110) we conclude that: (i) Mn is magnetic and exhibits a large magnetic moment of 3.32 μ_B, (ii) the magnetic moments are arranged in a c(2 $\times$ 2)-antiferromagnetic order, (iii) the easy axis of the magnetization is in-plane and points along the [1$\bar{1}$0] direction, i.e. the direction along the long side of the (110) surface unit cell with a magnetocrystalline anisotropy energy of 1.3–1.5 meV , and (iv) the Mn-W interlayer distance is 2.14 Å. The calculated electronic structure of a Mn monolayer on W(110) is compared with experimental scanning tunneling spectroscopy (STS) results. Several aspects are in nice agreement, but one cannot unambiguously deduce the magnetic structure from such a comparison. The proposed two-dimensional antiferromagnetic ground state of a Mn monolayer on W(110) is directly verified by the use of SP-STM in the constant-current mode, and the in-plane easy magnetization axis could be confirmed using tips with different magnetization directions. We compare the measurements with theoretically determined SP-STM images calculated combining the Tersoff-Hamann model extended to SP-STM with the *ab initio* calculation resulting in a good agreement.

(Submitted to Phys. Rev. B)

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FLEUR: a parallelized electronic structure code for surfaces and bulk

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Abstract

We report on the development of a parallelized *ab initio* electronic structure code, FLEUR, suitable for large scale applications on massively parallel computer systems as well as smaller applications on workstation clusters. Our program is a realization of the full-potential linearized augmented planewave (FLAPW) method. We give an account of the optimization of the code for the investigation of low-dimensional systems. It was parallelized on the **k**-point as well as on the eigenvector level with the message passing interface.

(Submitted to Comp. Phys. Comm.)
G.Bihlmayer@fz-juelich.de

Fully relativistic calculation of magnetic properties of Fe, Co and Ni adclusters on Ag(100)

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[2] *Department of Theoretical Physics, Budapest University of Technology and Economics, Budafoki út 8, H-1521, Budapest, Hungary*

Abstract

We present *first principles* calculations of the magnetic moments and magnetic anisotropy energies of small Fe, Co and Ni clusters on top of a Ag(100) surface as well as the exchange-coupling energy between two single adatoms of Fe or Co on Ag(100). The calculations are performed fully relativistically using the embedding technique within the Korringa–Kohn–Rostoker method. The magnetic anisotropy and the exchange–coupling energies are calculated by means of the force theorem. In the case of adatoms and dimers of iron and cobalt we obtain enhanced spin moments and, especially, unusually large orbital moments, while for nickel our calculations predict a complete absence of magnetism. For larger clusters, the magnitudes of the local moments of the atoms in the center of the cluster are very close to those calculated for the corresponding monolayers. Similar to the orbital moments, the contributions of the individual atoms to the magnetic anisotropy energy strongly depend on the position, hence, on the local environment of a particular atom within a given cluster. We find strong ferromagnetic coupling between two neighboring Fe or Co atoms and a rapid, oscillatory decay of the exchange-coupling energy with increasing distance between these two adatoms.

(Submitted to PRB, 31 Aug 2001)
Postscript preprints available from Bence Lazarovits: `bl@cms.tuwien.ac.at`

This paper includes acknowledgement to the RTN on "Computational Magnetoelectronics" (Contract No. RTN1-1999-00145).

Proton Migration and Defect Interactions in the CaZrO3 Orthorhombic Perovskite: A Quantum Mechanical Study

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Abstract

Quantum mechanical techniques based on density functional theory (DFT) have been used to investigate the mechanism and energetics of proton transport in the perovskite-structured $CaZrO_3$. The calculations demonstrate that the observed orthorhombic crystal structure (comprised of tilting $[ZrO_6]$ octahedra) is reproduced accurately. QM molecular dynamics simulations confirm that the diffusion mechanism involves proton transfer from one oxygen ion to the next (Grotthuss-type mechanism), and also indicate the importance of the vibrational dynamics of the oxygen sublattice. For each hopping event the oxygen-oxygen distance contracts to about 2.4-2.5 A so as to assist proton transfer. By exploring the energy profiles for proton transfer, a very low energy barrier is found for the O(1)-O(1) inter-octahedra path. However, long-range proton conduction may involve O(1)-O(2) proton transfer as the rate-limiting step with a calculated energy barrier of 0.74 eV. Binding energies for hydroxyl-dopant pairs involving Ga^{3+}, Sc^{3+} and In^{3+} dopant ions are predicted to be favourable, and are compatible with observed proton "trapping" energies from previous mSR and QENS experiments.

(Chem. Mater. **13**, 2049 (2001))
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Magnetism of Co clusters embedded in Cu(001) surfaces: an *ab initio* study

A. B. Klautau and S. Frota-Pessôa
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Abstract

We report calculations of electronic structure and magnetic properties of Co clusters (up to 50 atoms) embedded in Cu(001) surfaces, performed using the first-principles linear muffin tin orbital (LMTO-ASA) method, implemented directly in real space (RS). Co agglomerates of different sizes and shapes are considered in order to investigate the influence of the local environment around the Co sites to the magnetism in this class of systems. We find that the magnitude of the Co moments is mainly governed by two factors: the position of the site relative to the Cu(001) surface layer and the number of Cu neighbors. The results show moment enhancement for sites located above the surface and/or placed substitutionally in the surface layer, due to their reduced coordination numbers. For sites with the same coordination number, the moment tends to decrease as the number of Cu neighbors increases. As a consequence, in Co agglomerates, the magnetic moment decreases considerably as one goes from more central sites to those close to the grain boundary at the Co-Cu interface.

(Submitted to Surface Science)
Contact person: Angela B. Klautau (aklautau@usp.br)

First-principles electronic structure of rare-earth arsenides

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Abstract

The electronic properties of rare-earth arsenides have been calculated from first principles. In the calculations we have treated the rare-earth f electrons both as core-like and as valence-like electrons. We consider the changes in the energy bands and in the density of states near the Fermi level which are found to be relevant, except for the case of LuAs, and discuss this in relation with the role played from the rare-earth $5d$ derived states. Moreover we show that the rare-earth $5d$ related bands are particularly sensitive to the variation of the lattice constant; change in the lattice constant of less than 1 % leads to a different behaviour with respect to the crossing of the rare-earth $5d$ derived bands and the As $4p$ derived bands along the Δ direction. This point is discussed in connection with the possibility of having a semimetal-semiconductor transition in the rare-earth arsenides.

(The European Physical Journal B, in press)
Contact person: S. Ossicini (ossicini.stefano@unimo.it)

Probing interface electronic structure with overlayer quantum-well resonances: Al/Si(111)

L. Aballe, C. Rogero, P. Kratzer, S. Gokhale, and K. Horn
Fritz-Haber-Institut der Max-Planck-Gesellschaft, Faradayweg 4–6, 14195 Berlin-Dahlem, Germany

Abstract

Angle-resolved photoemission investigations of the dispersion of quantum-well resonances in ultrathin epitaxial, two-dimensional Al(111) films grown on Si(111) 7×7 reveal energy- and wavevector-dependent reflection properties at the Al/Si interface. The substrate electronic structure is found to strongly influence the phase shift of the electron waves upon reflection at the interface. This observation demonstrates that the details of the substrate electronic structure need to be taken into account for a complete analysis of the dispersion of metallic quantum-well resonances. Furthermore, the assumption of loss of parallel wavevector information upon reflection or transmission through a lattice-mismatched interface is challenged. This effect offers a way of probing the ground-state substrate band edges through the changes induced in the electronic structure of the metallic overlayer.

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

Identification of surface anion antisite defects in (110) surfaces of III-V semiconductors

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Fritz-Haber-Institut der Max-Planck-Gesellschaft, Faradayweg 4–6, 14195 Berlin-Dahlem, Germany

Abstract

We identify surface anion antisite defects in (110) surfaces of GaAs, GaP, and InP using scanning tunneling microscopy combined with density-functional theory calculations. In contrast to subsurface arsenic antisite defects, surface antisite defects are electrically inactive and have a very localized defect state which gives rise to a distinct feature in scanning tunneling microscopy images.

Appl. Phys. Lett. **17**, 88 (2001)
Contact person: Günther Schwarz (schwarz@fhi-berlin.mpg.de)

Molecular modeling of surfaces from first principles

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Abstract

Surfaces are the cutting edge of materials science. This statements conveys that a surface is the place where molecules from the gas phase or a liquid come in contact with a material and where chemical bonds of these approaching molecules are cut and new bonds formed. To understand how materials function, how they can be produced or improved, we have to understand surfaces. This paper describes some advances in this field, in particular the development of methodologies that *combine density-functional theory with elasticity theory, thermodynamics, or statistical mechanics*. The resulting approaches are computationally elaborate, but they enable us to treat thousands of atoms, to follow their wandering and interplay over timescales from the pico-second up to the seconds regime, and most importantly the methods enable us to analyze the results such that we achieve *insight and understanding*. The examples discussed in this paper relate to the fields of semiconductor growth and nano-technology. However, the applicability of the described methodology is much wider, and analogous studies are being performed for modeling the growth of thin magnetic metal films, catalysis, and corrosion.

Computing in Science & Engineering (in print)
Contact person: Peter Kratzer (kratzer@fhi-berlin.mpg.de)

Density-functional theory study of the cooperativity of hydrogen-bonds in an infinite alpha-helix

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Arturo Rojo and Marcelo Galván
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Abstract

We studied the energetics of finite and infinite polyalanine chains in the α-helical and extended structure employing density-functional theory. Based on these results we extracted the energy of hydrogen bonds (hb's) and their interactions taking the full peptide-peptide connectivity (back bone) of proteins into account. We focused on two limiting cases: an isolated hb and one within an infinite α-helical chain. For the isolated hb we found the bond energy to be 3.5 kcal/mol. In the infinite chain this value is 8.6 kcal/mol, i.e. the cooperativity within an infinite network of hb's strengthens each individual bond by more than a factor of two. This effect has important consequences for the stability of α-helices.

(submitted to: Phys. Rev. Lett.)
Contact person: Joel Ireta (ireta@fhi-berlin.mpg.de)

Oxygen adsorption on Ag(111): A density functional theory investigation

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[2] *Department of Physics and Astronomy, Northwestern University, Evanston, IL 60208-3112, USA*

Abstract

The oxygen/silver system exhibits unique catalytic behavior for several large-scale oxidation (and partial oxidation) industrial processes. In spite of its importance, very little is known on the microscopic level concerning the atomic geometry and chemical nature of the various O species that form. Using density-functional theory within the generalized gradient approximation, the interaction between atomic oxygen and the Ag(111) surface is investigated. We consider, for a wide range of coverages, on-surface adsorption as well as surface-substitutional adsorption. The on-surface fcc-hollow site is energetically preferred for the whole coverage range considered. A significant repulsive interaction between adatoms is identified, and on-surface adsorption becomes energetically unstable for coverages greater than about 0.5 ML with respect to gas phase O_2. The notable repulsion even at these lower coverages causes O to adsorb in subsurface sites for coverages greater than about 0.25 ML. The O-Ag interaction results in the formation of bonding and anti-bonding states between Ag-4*d* and O-2*p* orbitals where, the antibonding states are largely *occupied*, explaining the found relatively weak adsorption energy. Surface-substitutional adsorption initially exhibits a repulsive interaction between O atoms, but for higher coverages switches to *attractive*, towards a $(\sqrt{3}\times\sqrt{3})R30^\circ$ structure. Scanning tunneling microscopy simulations for this latter structure show good agreement with those obtained from experiment after high temperature and high O_2 gas pressure treatments. We also discuss the effect of strain and the found marked dependence of the adsorption energy on it, which is different for different kinds of sites.

(submitted to: Phys. Rev. B)
Contact person: Wei-Xue Li (wxli@fhi-berlin.mpg.de)

Ab initio analysis of surface structure and adatom kinetics of Group-III Nitrides

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14195 Berlin-Dahlem, Germany

Abstract

Recent results based on density-functional theory calculations concerning the structure and stability of III-nitrides surfaces are discussed. An analysis of the thermodynamically stable surface structures for this materials system reveals that the driving mechanisms behind surface reconstructions are fundamentally different to those in "traditional" (i.e. arsenic or phosphorus based) III-V semiconductors. Specifically, surfaces are always metal-rich and nitrogen atoms on and in the surface layer are thermodynamically unstable. This feature will be shown to have important consequences on surface morphology, adatom kinetics, growth, reactivity, and alloy formation.

phys. stat. sol. (b) (in print)
Contact person: Jörg Neugebauer (neugebauer@fhi-berlin.mpg.de)

Ab initio thermodynamics and statistical mechanics of diffusion, growth, and self-assembly of quantum dots

M. Scheffler and P. Kratzer
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Abstract

Recent developments in methodology enable us to extend the density-functional theory approach, that primarily focuses on the self-consistent electronic structure, to poly-atomic complexes with 10,000 and more atoms, atomic motion over time scales of seconds, and involved statistics. In this contribution we will sketch recent density-functional theory-based hybrid methods, which bridge the length and time scales from those of electron orbitals to meso- and macroscopic proportions, and present some results for crystal growth and the self-assembly of nano-scale structures.

(submitted to: Proc. NATO ARW on Atomistic Aspects of Epitaxial Growth (Corfu, Greece). Kluwer Academic Publ., Dordrecht)
Contact person: Peter Kratzer (kratzer@fhi-berlin.mpg.de)

Diagrammatic self-energy approximations and the total particle number

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[2] *Departamento de Física Fundamental, Universidad Nacional de Educación a Distancia, Apartado 60141, 28080 Madrid, Spain*
[3] *Department of Physics, University of York, Heslington, York YO10 5DD, United Kingdom*

Abstract

There is increasing interest in many-body perturbation theory as a practical tool for the calculation of ground-state properties. As a consequence, unambiguous sum rules such as the conservation of particle number under the influence of the Coulomb interaction have acquired an importance that did not exist for calculations of excited-state properties. In this paper we obtain a rigorous, simple relation whose fulfilment guarantees particle-number conservation in a given diagrammatic self-energy approximation. Hedin's G_0W_0 approximation does not satisfy this relation and hence violates the particle-number sum rule. Very precise calculations for the homogeneous electron gas and a model inhomogeneous electron system allow the extent of the non-conservation to be estimated.

Phys. Rev. B (in print)
Contact person: Arno Schindlmayr (schindlmayr@fhi-berlin.mpg.de)

8 SCIENTIFIC HIGHLIGHT OF THE MONTH

Linear scaling *ab initio* calculations: Recent Progress with the Conquest code

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Abstract

We describe recent progress in the practical implementation of linear scaling, *ab initio* calculations, referring in particular to our highly parallel code CONQUEST. After reviewing the state of the field, we present the basic ideas underlying almost all linear scaling methods, and discuss specific practical details of the implementation. We also note the connection between linear scaling methods and embedding techniques.

1. Introduction

The last ten years have seen an upsurge of interest in $\mathcal{O}(N)$ electronic-structure methods[1] for treating condensed matter both within tight-binding theory and within density functional theory [2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 13, 14, 15, 16, 17, 18, 19, 20, 21, 22, 23, 24, 25]. In these methods, the number of computer operations needed to determine the electronic ground state is proportional to the number of atoms N in the system, instead of showing the N^2 or N^3 dependence characteristic of traditional methods. $\mathcal{O}(N)$ methods are possible because electronic phase coherence is localised [14, 19, 26, 27, 28, 29]. This localisation property can be expressed by saying that the density matrix between two points, $\rho(\mathbf{r}, \mathbf{r}')$, decays to zero with increasing distance between points $\mathbf{r}$ and $\mathbf{r}'$.

Locality is the unifying theme between almost all $\mathcal{O}(N)$ methods, and it requires a local formulation of quantum mechanics (or, at least, electronic structure theory). The density matrix $\rho(\mathbf{r}, \mathbf{r}')$ mentioned above is a key quantity in this local formulation, and in terms of the Kohn-Sham orbitals, can be written as:

$$\rho(\mathbf{r}, \mathbf{r}') = \sum_i f_i \psi_i^*(\mathbf{r}) \psi_i(\mathbf{r}'), \tag{1}$$

where f_i are the occupation numbers. The Kohn-Sham energy can be easily rewritten in terms of the density matrix: the Hartree and exchange-correlation energies, which are written in terms of the charge density ($n(\mathbf{r}) = \rho(\mathbf{r}, \mathbf{r})$) do not change; the kinetic and pseudopotential energies become:

$$E_{\mathrm{KE}} = -\frac{\hbar^2}{2m} \int \mathrm{d}\mathbf{r} (\nabla_r^2 \rho(\mathbf{r}, \mathbf{r}'))_{\mathbf{r}=\mathbf{r}'} \tag{2}$$

$$E_{\mathrm{ps}} = 2 \int \mathrm{d}\mathbf{r}\ \mathrm{d}\mathbf{r}' V_{\mathrm{ps}}(\mathbf{r}, \mathbf{r}') \rho(\mathbf{r}, \mathbf{r}') \tag{3}$$

It can be shown that $\rho(\mathbf{r}, \mathbf{r}')$ decreases as the separation between $\mathbf{r}$ and $\mathbf{r}'$ increase (either exponentially, for insulators, or algebraically, for metals[27, 28, 29, 30, 31]): $\rho(\mathbf{r}, \mathbf{r}') \to 0$ as $\mid \mathbf{r} - \mathbf{r}' \mid \to \infty$. This locality implies that the amount of information scales linearly with the size of the system; an $\mathcal{O}(N)$ method can be created by making an approximation, and *enforcing* locality: $\rho(\mathbf{r}, \mathbf{r}') = 0, \mid \mathbf{r} - \mathbf{r}' \mid > R_c$. While the scaling of both memory and computational effort will allow large systems to be simulated on a workstation, for very large systems containing thousands or tens of thousands of atoms, the codes need to run efficiently on parallel computers; this aspect is discussed later in the article.

However, the six-dimensional quantity $\rho(\mathbf{r}, \mathbf{r}')$ is not the ideal variable to work with, so the assumption is made (with only the restriction that the original quantity had a finite number of non-zero eigenvalues) that it can be written in *separable* form:

$$\rho(\mathbf{r}, \mathbf{r}') = \sum_{i\alpha, j\beta} \phi_{i\alpha}(\mathbf{r}) K_{i\alpha j\beta} \phi_{j\beta}(\mathbf{r}'), \tag{4}$$

where $\phi_{i\alpha}(\mathbf{r})$ is a *support function* (or a *localised orbital*) centred on atom i, and $K_{i\alpha j\beta}$ is the density matrix in the basis of the support functions. Then locality can be enforced by applying separate cutoffs to both $K_{i\alpha j\beta}$ and the set of *support functions* $\{\phi_{i\alpha}(\mathbf{r})\}$. The minimisation of the energy with respect to each of these quantities then drives the system towards the ground state.

The support functions are *non-orthogonal*, and forced to be confined within a *localisation region*, of radius R_c. They are themselves represented in terms of other basis functions (which will be described in detail in Section 3), and it is important that they be freely varied in the search for the electronic ground state. By increasing the cutoffs and improving the completeness of the basis set representing the support functions, an $\mathcal{O}(N)$ method can be made to reproduce traditional methods with plane wave accuracy.

The minimisation itself involves three different variables: the elements of the density matrix, K; the support functions, $\phi_{i\alpha}$; and the charge density, $n(\mathbf{r})$, which must be consistent with the potential $V(\mathbf{r})$. We have chosen to decouple these variables, fixing first the support functions and the charge density, and minimising with respect to the density matrix, then achieving self-consistency (while minimising with respect to the density matrix every time that the potential changes) and finally varying the support functions. This scheme has various advantages: first, it decouples the degrees of freedom associated with the support functions and the density matrix; second, it allows us to treat regions of the system with fixed support functions (in an *ab initio* tight binding manner) while freely varying others; third, on a practical level, it allows us to optimise the procedures for the different minimisations independently.

The rest of the article is arranged as follows: in the next section, we describe minimisation of the energy with respect to the density matrix, K; then we consider possible basis sets for the support functions, and describe our choice; we then describe some practical details relating to the implementation of our scheme and conclude the article.

2. Finding the density matrix

Within the atom-centred basis of support functions, the density matrix $K_{i\alpha j\beta}$ (also called the *kernel*) is clearly equivalent to the density matrix in a non-orthogonal tight binding formulation. There has been a great deal of work investigating effective $\mathcal{O}(N)$ methods for finding the density matrix in tight binding[2, 4, 5, 6, 7, 8, 9, 10, 17, 18, 21, 22, 24, 1] which gives us a strong position to start from. However, there is an important issue, which will be addressed fully below: in the formulation described up to this point, the basis in which the density matrix, $K_{i\alpha j\beta}$, is written is *non-orthogonal*, while most tight binding methods have been primarily formulated with an orthogonal basis set. We shall first describe the methods, and then address this important question of non-orthogonality.

Tight binding techniques which have been extended to *ab initio* techniques fall broadly into four categories: recursion[10]; density matrix minimisation[5, 6, 12, 24]; orbital minimisation[7, 9]; and penalty functions[23]. These have been described in some detail by Goedecker[1], so we shall only outline the methods.

The Fermi Operator Expansion technique[10, 32, 33, 34] is a conceptually and computationally simple way of obtaining the density matrix, at the expense of introducing a finite electronic temperature and losing a variational principle. The Fermi matrix (a finite temperature density matrix) can be defined as:

$$\mathbf{F}_{\mu,\mathrm{T}} = f\left(\frac{\mathbf{H}-\mu}{\mathrm{kT}}\right), \tag{5}$$

where $f(x) = 1/(1 + exp(x))$, the Fermi function.

Now, the Fermi function only has to cover a finite width, that is the width of the density of states for the system in question (or the difference between the minimum and maximum eigenvalues of the Hamiltonian). Within this range, it can be represented by a polynomial in the energy,

$$f(x) = \sum_{p=0}^{n_{pl}} C_p E^p, \tag{6}$$

which means that the Fermi matrix $F_{\mu,T}$ can be represented as a polynomial in the Hamiltonian,

$$\mathbf{F}_{\mu,T} = \sum_{p=0}^{n_{pl}} C_p \hat{H}^p. \tag{7}$$

This then gives the expression for one element of the Fermi matrix as:

$$\langle i\alpha \mid F_{\mu,T} \mid j\beta \rangle = \sum_{p=0}^{p=n_{pl}} C_p \langle i\alpha \mid \hat{H}^p \mid j\beta \rangle, \tag{8}$$

Conceptually, then, the method works by fitting a polynomial to the Fermi function over the range of the eigenvalues. Then, using the coefficients of this polynomial and moments of the Hamiltonian, elements of the finite temperature density matrix, or the Fermi matrix, are constructed. To make the method $\mathcal{O}(N)$, the Fermi matrix can be truncated beyond a certain cutoff radius. In practice, for stability, a Chebyshev polynomial is used[32], which leads to a recursion relation for the coefficients:

$$p_{\mu,T}(H) = \frac{c_0}{2} + \sum_{j=1}^{n_{pl}} c_j T_j(H), \text{and} \tag{9}$$

$$\begin{aligned} T_0(H) &= I \\ T_1(H) &= H \\ T_{j+1} &= 2HT_j(H) - T_{j-1}(H) \end{aligned} \tag{10}$$

Once the Fermi matrix has been truncated, the forces are not exactly equal to the derivative of energy; there is, however, a formalism which gives a force which is the exact derivative of the energy[33]. In some cases the error in energy due to the high electronic temperature may be significant; a scheme is available[35] for extrapolating the T=0 energy from a high temperature which can correct this.

Density matrix minimisation (DMM)[5, 12, 37, 36, 24] seeks to find the density matrix by minimising the energy with respect to the density matrix elements (since $E_{\text{band}} = 2\text{Tr}[\rho H]$). However, two constraints must be applied to the minimisation: (i) either constant electron number or constant fermi energy; (ii) idempotency of ρ. The first is relatively easy to address; maintaining constant fermi energy is as simple as minimising $2\text{Tr}[(\rho - \mu I)H]$, with μ the fermi energy, while various schemes exist for maintaining electron number constant[38, 39].

Idempotency of ρ (which is equivalent to requiring that the eigenvalues of ρ all be either zero or one, or that $\rho^2 = \rho$) is a much harder constraint to impose during a variational minimisation, and instead use is made of McWeeny's purification transformation[40]:

$$\rho = 3\tilde{\rho}^2 - 2\tilde{\rho}^3. \tag{11}$$

Provided that the eigenvalues of $\tilde{\rho}$ lie between -$\frac{1}{2}$ and $\frac{3}{2}$, the eigenvalues of ρ will lie between zero and one. McWeeny first proposed this as an iterative procedure (so that if $\rho_n = \tilde{\rho}$ then $\rho_{n+1} = \rho$), but another technique[5] is to minimise $E_{\rm band} = 2Tr[\rho H]$ with respect to the elements of $\tilde{\rho}$. If this approach is taken, then we must assume that $\tilde{\rho}$ is also separable (as ρ is in eq. 4): $\tilde{\rho} = \sum_{i\alpha j\beta} \phi_{i\alpha}(\mathbf{r}) L_{i\alpha j\beta} \phi_{j\beta}$; then we can write $K = 3L^2 - 2L^3$. Approaches to DMM are varied: pure McWeeny iteration can be used[41] (also with a modified cubic form which preserves electron number); pure minimisation can be used[5, 6, 38]; minimisation followed by[36] or interspersed with[37] McWeeny purification is also pursued; finally, McWeeny purification (which is not variational) followed by minimisation (which is variational)[24]. It can be shown[24] that the McWeeny purification approaches a manifold of idempotent density matrices perpendicularly in its final stages, while the minimisation yields a gradient tangential to this surface (and preserves idempotency to first order).

Another method for finding the ground state density matrix is orbital minimisation, which was proposed from two different routes, leading to essentially the same formalism[9, 7]. Consider a system of N electrons, described by $N/2$ non-interacting states $\{\mid \psi_i\rangle\}$. In order to avoid an *explicit* orthonormalisation step (which scales with N^2 in a localised basis set and N^3 in a plane wave basis), the following functional is defined:

$$E = 2\mathrm{Tr}[QH] - \eta\left[2\mathrm{Tr}[QS] - N\right] \tag{12}$$

$$Q = \sum_{n=0}^{\mathcal{N}} (I - S)^n, \tag{13}$$

where $S_{ij} = \langle \psi_i \mid \psi_j \rangle$ is the overlap matrix. The orbitals $\{\mid \psi_i\rangle\}$ are represented by a basis $\{\mid \phi_\mu\rangle\}$, so that:

$$\mid \psi_i\rangle = \sum_\mu C_{i\mu} \mid \phi_\mu\rangle. \tag{14}$$

Then as the energy is minimised with respect to the coefficients $C_{i\mu}$, the overlap matrix will tend to the identity. The method can be made $\mathcal{O}(N)$ by localising the orbitals ψ_i, and only allowing contributions from ϕ_μ within a specified volume.

The drawback with the method is that it is subject to many local minima if the minimal set of orbitals ($N/2$) is used; it has been extended to more orbitals, which to some extent corrects this problem[42].

Penalty functionals apply a similar idea, but instead seek to penalise the deviation away from idempotency[19]. The original technique defined the following functional:

$$Q[\rho;\mu,\alpha] = E_{NI}[\rho] - \mu N[\rho] + \alpha P[\rho] \tag{15}$$

$$P[\rho] = \left\{\rho^2(1-\rho^2)\right\}^{\frac{1}{2}}, \tag{16}$$

where E_{NI} is the non-interacting energy. However, it was found[43] that the branch point introduced by the square root prevented minimisation using techniques such as conjugate gradients. Instead, a general functional was introduced[23]:

$$Q[\rho] = E[\rho] + \alpha P^2[\rho], \tag{17}$$

which allows use of minimisation techniques.

All of the above methods have been described using orthogonal bases, but the formalism above relies on non-orthogonal bases. Each of the methods can be reformulated in a non-orthogonal basis, but this raises various issues:

1. Matrix expressions become more complex (e.g. we now have $K = 3LSL - 2LSLSL$, where S is the overlap matrix)
2. Compound matrices (such as LSL) are longer ranged
3. When using variational methods, the inverse of the overlap, S^{-1}, is required to correct the gradients[44]

Some choose to work within the non-orthogonal basis, and derive an approximate S^{-1}[34, 25], while others convert to an orthogonal basis, using a variety of methods (incomplete inverse Cholesky factorisation[36], Cholesky decomposition[45]). All of these approaches require an approximation (either in the S^{-1} or in the Cholesky factorisation), with the former having the advantage that no basis set changes are being used, and the latter that the formalism is much simpler and shorter ranged.

We finish by noting that the localisation inherent in $\mathcal{O}(N)$ schemes makes them ideal for use in embedding[46]. By this, we mean embedding of one system within another (e.g. a point defect into perfect bulk), not embedding of one technique within another. If the system is divided into region I (the region of interest – e.g. the point defect and its surroundings) and region II (the embedding matrix – e.g. the perfect bulk) then the amount of region II required is equivalent to the range of the density matrix, and we expect the energy convergence with size of region I to scale just as the energy convergence scales with density matrix range. This is illustrated in Figure 1, which shows the convergence of the energy for a Ge substitutional defect in diamond Si with radius of region I.

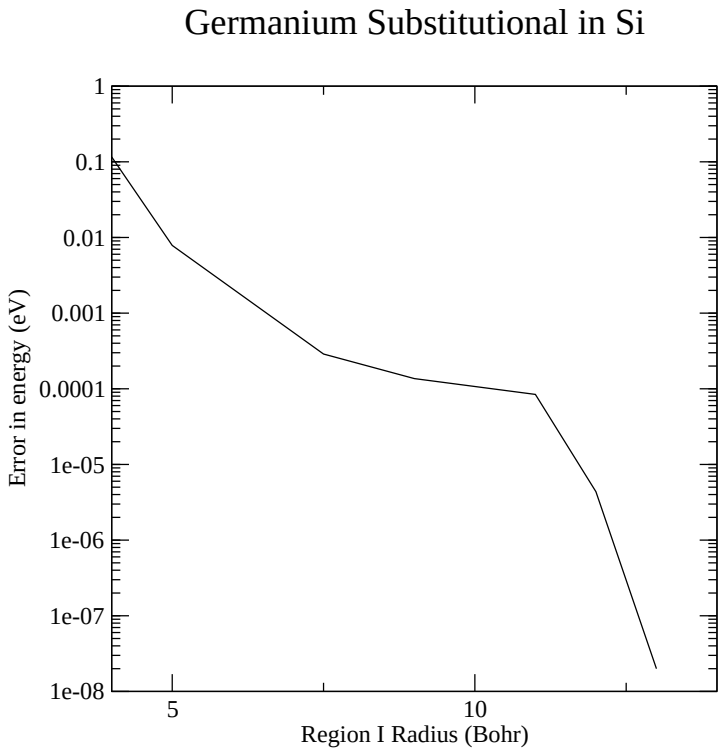

Figure 1. Convergence of energy with region I radius for a Ge substitutional impurity in Si expressed relative to result for infinite region I radius.

3. Support Functions

3.1 Representing Support Functions

As emphasised in Sec. 1, the localised orbitals $\phi_{i\alpha}(\mathbf{r})$ have to be freely varied in the search for the DFT ground state. This raises the technical problem common to all quantum calculations – the representation of the orbitals, i.e. basis sets. A peculiar feature of the basis sets needed in the scheme we have outlined is that the orbitals to be represented vanish outside the localisation region, and the basis functions clearly need to have the same property. Before discussing the approaches that have been taken to this, it is useful to consider briefly the conflicting requirements that basis functions have to satisfy.

First, they should ideally be well adapted to the function to be represented, which means that only a *few* basis functions should be needed to represent the orbitals. Second, the representation should be systematically improvable; this means not just that the basis set must be complete, but that the convergence should be rapid as the size of the basis set is increased. As a rider to this, the computational effort should not increase too fast as one increases the number of basis functions, and ideally no faster than linearly. Third, the operations to be done with the basis functions should be mathematically simple, so that the number of computer operations is small. Fourth, since some parts of a total-enegy calculation have to be done on spatial grid, which generally causes problems like breaking of translational symmetry, the basis must be designed so that as little as possible has to be done on the grid.

Several types of basis sets have been used or proposed for linear-scaling DFT calculations. When CONQUEST was first written, the support functions were represented as numerical values on a grid. A grid basis set gives a natural way of representing orbitals that vanish outside specified regions. Nevertheless, it is the ultimate in maladaption, and needs fine grids and large amounts of memory in order to achieve good precision. The kinetic energy is particularly troublesome. In more conventional DFT/pseudopotential schemes based on grid basis sets, high-order finite-difference methods are used to give an accurate representation of the Laplacian operator. Because of this, grid basis sets were replaced in CONQUEST by a scheme akin to finite elements.

This finite-element scheme represents the $\phi_{i\alpha}(\mathbf{r})$ in terms of piecewise continuous polynomials, using a technique sometimes referred to as B-splines. Full details of the scheme, with demonstrations of its effectiveness, are presented in a published report[47], so here we give only a brief summary. In one dimension, the B-spline basis consists of localised functions $\theta_s(x)$, centred on the points of a grid, s, with spacing a. The basis functions are all images of each other, displaced by an integer number of grid spacings, so that $\theta_s(x) = \theta_0(x - X_s)$. The basis function $\theta_0(x)$ vanishes identically outside the range $-2a < x < 2a$. Inside this range, it is put together out of

cubic polynomials:

$$\theta_0(x) = \begin{cases} 1 - \frac{3}{2}x^2 + \frac{3}{4}|x|^3 & \text{if} \quad 0 < |x| < a \\ \frac{1}{4}(2 - |x|)^3 & \text{if} \quad a < |x| < 2a \\ 0 & \text{if} \quad 2a < |x| \end{cases} \tag{18}$$

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

$$f(x) \simeq \sum_s b_s \theta_s(x) \tag{19}$$

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

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

$$\Theta(\mathbf{r} - \mathbf{R}_s) = \theta(x - X_s)\theta(y - Y_s)\theta(z - Z_s) \ , \tag{20}$$

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

$$\phi_{i\alpha} = \sum_s b_{i\alpha s} \Theta_s(\mathbf{r}) \ . \tag{21}$$

In the current scheme, the blip-grid on which the $\Theta_s(\mathbf{r})$ are sited is defined separately for each atom, and moves with that atom. To enforce the vanishing of $\phi_{i\alpha}(\mathbf{r})$ outside the support region, we include in eqn (21) only those $\Theta_s(\mathbf{r})$ that are non-zero only for points within the region. The reason for making the blip-grid move with the atom is that this ensures that each $\phi_{i\alpha}(\mathbf{r})$ is represented always in terms of the same set of basis functions.

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

But this is certainly not the only spatially localised basis set that is closely related to plane waves. An alternative is the spherical-wave basis proposed by Haynes and Payne[48]. Spherical waves are the energy eigenfunctions of a particle confined to a spherical box, where the radius of the box is the support region radius R_{reg}. The properties of this basis set have been explored in detail in Ref. [48, 49], where tests on molecules (H_2, HCl, Cl_2, SiH_4) and bulk silicon show reasonable convergence properties relative to plane wave results.

This scheme has the nice feature that a total-energy calculation can be converged in exactly the same way as a plane-wave calculation, by systematically increasing the plane-wave cut-off wavevector $G_{\max}$. However, it has serious objection, which may make it difficult to use in practical calculations. This is that as the size of the basis set is increased, the computational effort grows as the square of the number of basis functions. This is because the number of basis functions that are non-zero at any point in space is proportional to the total number of basis

functions, so that matrix elements $\langle\phi_{i\alpha}|O|\phi_{j\beta}\rangle$ of any operator O for any two atoms i and j grows very rapidly. Since we know in advance that at least 100 spherical waves will be needed per atom, the number of operations needed to calculate each such matrix element is likely to be at least 10^4, and this may make the calculations too slow.

Finally, we mention the pseudo-atomic basis sets used in SIESTA[50]. The basic philosophy is similar to that originally developed by Sankey and Niklewski [51]. The basis functions are the atomic orbitals obtained from a self-consistent DFT calculation on the free atom, except that, in order to ensure that the funcitons vanish identically outside the region radius, the free-atom calculation is done in the presence of a confining potential. In the original Sankey-Niklewski scheme, the confining potential is simply an infinite potential beyond the radius $R_{\rm reg}$. This makes the localised orbitals go to zero linearly as $r \to R_{\rm reg}$, so that there is a discontinuity in the first derivative, which may well exacerbate the breaking of translational symmetry in the parts of the calculation done on a spatial grid. This gives a motivation for making the confining potential go to infinity more continuously as $r \to R_{\rm reg}$, and this freedom is being exploited in the latest SIESTA basis sets[52]. In addition, in order to obtain satisfactory precision, it is essential to go beyond minimal basis sets, and to include at least two basis functions for each angular momentum (so-called 'double-zeta' basis sets), and to include also polarisation functions.

The different approaches to the problem of basis sets taken with linear-scaling DFT schemes thus reflect the tension between the four criteria outlined at the start of this Section, and particularly the tension between good adaptation of the basis set to the form of the orbitals, and resulting economy in memory use, on the one hand, and systematic improvability onthe other hand. As in more conventional DFT methods, there cannot be a 'best' approach to basis sets, since the physical problem being addressed and the resources available will place different weights on the criteria. Our view is therefore that there is great merit in a flexible approach, in which different types of basis set are employed for different problems, or at different stages of a given problem. We also believe it may be possible to combine different schemes, for example pseudo-atomic orbitals and B-splines, in the same way as mixed basis sets have long been used in conventional DFT/pseudopotential calculations.

3.2 Blip Operations

As described above, the support functions are represented in a basis of blip functions (or B-splines), defined on a grid that moves with each atom. We need to to perform integrals involving the support functions to generate matrix elements (such as $S_{i\alpha j\beta} = \int {\rm d}\mathbf{r}\phi_{i\alpha}(\mathbf{r})\phi_{j\beta}(\mathbf{r})$). For the overlap matrix and the kinetic energy part of the Hamiltonian, the integration can be performed analytically in terms of the $b_{i\alpha s}$ coefficients. For example, $S_{i\alpha,j\beta}$ can be expressed as:

$$S_{i\alpha,j\beta} = \sum_{m,n} b_{i\alpha m} b_{j\beta n} s_{im,jn} \ , \tag{22}$$

where:

$$s_{im,jn} = \int d\mathbf{r}\, \Theta_{im}\Theta_{jn} \ , \tag{23}$$

However, some parts of the Hamiltonian matrix cannot be calculated analytically, and integration must be approximated by summation on a grid. This 'integration grid' is completely distinct from the blip grid, and is a single fixed grid covering the whole simulation cell. For a

uniform cubic grid of spacing $h_{\rm int}$, a matrix element such $S_{i\alpha,j\beta}$ would be approximated as:

$$S_{i\alpha,j\beta} \simeq \delta\omega_{\rm int} \sum_{\ell} \phi_{i\alpha}(\mathbf{r}_\ell)\phi_{j\beta}(\mathbf{r}_\ell) \ , \tag{24}$$

where $\delta\omega_{\rm int} = h_{\rm int}^3$ is the volume per grid point, and $\mathbf{r}_\ell$ is the position of the ℓth grid point. As shown elsewhere [20], $h_{\rm int}$ should generally be about half of $h_{\rm blip}$.

Analytic evaluation, if possible, is preferable, but the double summation required (see eq. 22) brings a computational cost. Our strategy is to evaluate analytically the on-site ($i = j$) matrix elements of overlap and kinetic energy, and to use grid summation for all others. The thinking here is that the on-site terms are large, so that accuracy is important; but there are few of them, so that the cost of analytic evaluation is small.

The transformation from the coefficients $b_{i\alpha s}$ to the values of $\phi_{i\alpha}(\mathbf{r}_l)$, where $\mathbf{r}_l$ is a grid point, is called a blip-to-grid transform[47, 21] – using the separable form of blips shown above in eq. 20, this is extremely similar in concept to an FFT, and can be evaluated extremely efficiently. The integration can be performed efficiently by creating small blocks of integration grid points, and making partial contributions to matrix elements between all atoms touching the block with a single BLAS call, as discussed below.

4. Practical Details

In this section, we address the practical implementation of CONQUEST on massively parallel machines, as well as some of the practical problems which we have encountered in the course of writing CONQUEST, related both to efficiency on parallel computers and to robustness[21, 25, 53].

4.1 Implementation

The division of workload between processors is an important part of all parallel codes – indeed, load balancing is a large subject in its own right. Nominally, the computational effort and storage requirements of CONQUEST are divided up as follows:

1. Every processor has responsibility for a group of atoms (storing the blip coefficients for each atom and transforming their values onto the integration grid) – the primary set.
2. Every processor has responsibility for rows of matrices of these atoms (storing values and performing multiplications for these rows).
3. Every processor has responsibility for an area of the integration grid (storing data on this area and performing integrations) – the domain.

Practically, the assignment of groups of atoms and areas of the integration grid will have a large effect on the efficiency of the code – typically, we want the groups of atoms and grid points to be compact and local and we want the two groups to overlap as much as possible (to restrict communication). Below, we describe a key technique in achieving flexibility in load balancing as well as efficiency in computation – small groups.

4.2 The Use of Small Groups

In CONQUEST, there are two key areas of effort: matrix multiplication, and grid operations (integration, blip-to-grid transforms etc). In both of these areas, there are two natural levels of organisation: individual (e.g. grid point or matrix element); and global (all atoms or grid points). We have found that it is vital for efficiency to create an intermediate level of organisation – small groups of the entities (we call a small group of atoms a *partition* and a small group of integration grid points a *block*).

To understand the use of small groups, let us take an example of matrix multiplication, where we perform:

$$C_{ij} = \sum_k A_{ik} B_{kj}. \tag{25}$$

Here, each processor is responsible for calculating all elements C_{ij} for atoms i for which it is responsible – its primary set. It already has the values A_{ik} stored locally, but will have to fetch the values B_{kj} for the atoms k outside its primary set. Following the two natural levels mentioned above, there are two extremes we can consider for fetching the elements B_{kj} (and hence interleaving communication and calculation): individually (fetch a single element, compute the partial contribution to C_{ij}, repeat – fine interleaving); and globally (fetch all elements B_{kj} which will be required, then do all computations – coarse interleaving). The first of these will be overly expensive in communications (all communication involves a latency or start-up cost, so that a significant gain is made by transferring long messages) while the second will potentially be expensive in memory. Somewhere between these two extremes there will be a good balance between memory required on-processor, and the latency of short communications.

Partitions of atoms (and hence matrix elements) are extremely useful as they simplify the task of finding the compromise between the two extremes given above. For example, if a processor is responsible for several partitions, then transferring the B_{kj} according to the partitions will split up the calculation in a natural way; this will be explored more in the next section, and has been extensively discussed in a recent paper[53]. Another area where these groups are helpful is in integration: we use the highly optimised BLAS routines on all integration grid points in a block to yield extremely efficient integration routines; this is touched on later.

4.3 Matrix Multiplication

Recently, we have studied the efficiency of sparse matrix multiplication on highly parallel machines[53]. Each processor takes responsibility for several partitions of atoms, formed into its primary set. For a given matrix multiplication, we form a *halo* consisting of all atoms (or partitions) within range of *any* primary set atom, and loop over these atoms during the multiplication. It is also helpful to form a *covering set*: a super set of different matrix haloes. This simplifies searches and indexing for various different matrix multiplications. We have also identified a multiplication *kernel*: a piece of code that is repeatedly called, and which can be optimised on different machines. We have achieved 10% of peak speed on a Cray T3E, which is respectable given the pattern of matrices.

We illustrate the practical performance of the CONQUEST code in Figure 2. Here we show the time taken for various aspects of the calculation for increasing system sizes on a Cray T3E-

1200. As the technique is variational, the time to self-consistency will improve after the slow, initial search. We see that for fixed number of atoms per processor, the time taken is almost constant, showing that the matrix multiplication (which forms the bulk of the workload for these calculations) scales extremely well in parallel.

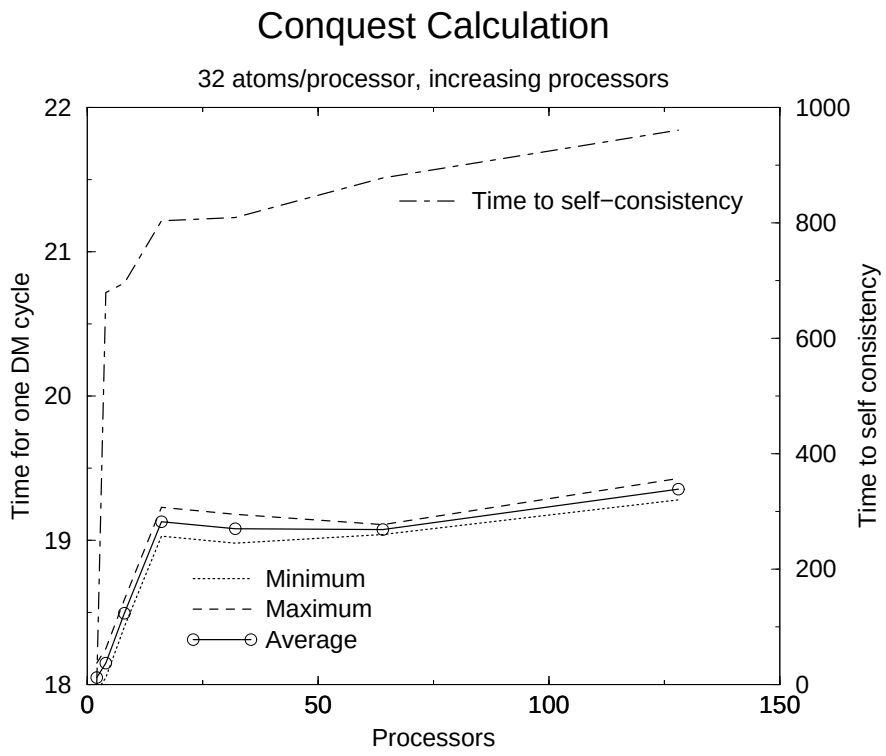

Figure 2. Time taken for CONQUEST calculations for a single density matrix minimisation (left axis, bottom three lines) and for a complete search for self-consistency, starting from scratch, fixed support functions.

4.4 Integration and Grid Operations

In the light of the recent developments with matrix multiplication, we have been considering the efficiency of blip-to-grid transforms and the indexing associated with this and with integration. Let us first consider what kind of operations this requires. The matrix elements made from support functions, projector functions, or their derivatives such as $S_{i\alpha,j\beta} = \langle \phi_{i\alpha} | \phi_{j\beta} \rangle$, $P_{i\alpha,j\beta} = \langle \phi_{i\alpha} | \chi_{j\beta} \rangle$, and $\langle \nabla \phi_{i\alpha} | \nabla \phi_{j\beta} \rangle$, are calculated by a summation over integration grid points. For example, $S_{i\alpha,j\beta}$ is calculated by

$$S_{i\alpha,j\beta} = \omega_{\rm int} \sum_{\boldsymbol{r}_l} \phi_{i\alpha}(\boldsymbol{r}_l) \phi_{j\beta}(\boldsymbol{r}_l) \tag{26}$$

Here, $\omega_{\rm int}$ is the volume per grid point and $\boldsymbol{r}_l$ is integration grid which is common to the support region of i and that of j. The above summation for a given set of indices (i,α) and (j,β) can be regarded as a matrix multiplication, where $\boldsymbol{r}_l$ serves as the column index of the left matrix and as the row index of the right matrix. As explained in Ref. [21], we use a BLAS-3 routine `dgemm` to do these matrix multiplications and we have introduced the term 'blocks' for the effective use of this routine. A block is an assembly of integration grid points and the above summation is

divided into the summation of partial contributions from all blocks and the calculation of the partial contribution by `dgemm` for each block. As we will see later again, we refer to an atom whose support region contains at least one integration grid point in a block b as a neighbour atom of a block b for support functions. For these calculations, we must have the list of the pairs of atoms (i,j) for each block b, both of which are neighbour atoms of the block. In practice, a block is a cuboid[3] containing $n_x \times n_y \times n_z$ points and its size should be determined by comparing the gain in the speed of `dgemm` by increasing the size of matrices and the loss by unnecessary operations from zero values in $\phi_{i\alpha}(\boldsymbol{r}_l)$.

To perform the integration, we also must know the values of support or projector functions on integration grid. For support functions, we have to calculate the values from a set of coefficients $\{b_{i\alpha s}\}$, where s is the index of blip grid.

$$\phi_{i\alpha}(\boldsymbol{r}_l) = \sum_s b_{i\alpha s}\Theta(\boldsymbol{r}_l - \boldsymbol{R}_{is}). \tag{27}$$

Here, $\boldsymbol{R}_{is}$ is the position of blip grid and we call this type of operations blip-grid transforms. Blip-grid transforms are performed only for $\boldsymbol{r}_l$ in the blocks which include one or more integration grid points in the support region the atom i. We refer to these blocks as neighbour blocks of the atom i.

In short, we need to consider the optimal way of performing the following tasks:

1. Making lists and tables to perform blip-grid transforms and the calculation of matrix elements: making lists of neighbour atoms of blocks; making lists of neighbour blocks of atoms; and so on.
2. Blip-grid transform
3. Calculation of matrix elements

It should be noted that the matrices calculated in this way are used to calculate other matrices, LSL, $LSLSL$, $SLSLH$ and so on.

In the new method, we use the same data structure shown in the previous sections. In the method for performing matrix multiplications, each node has a set of small groups called partitions, and each partition has its members, i.e. atoms. Obviously, we can regard a block as a small group of integration grid points. Each processor is responsible for a set of blocks which we call domain.

Table 1. How small groups are made up for different members.

members	small groups	primary sets
atoms	partitions	bundles
integration grid points	blocks	domains

Each processor has one domain and one bundle. Hereafter, we refer to a node which performs operations with respect to atoms as a bundle-responsible node, and the node doing operations

[3]This is not necessary in principle, and non-orthorhombic cells and hence blocks will be addressed in the future

regarding integration grid as a domain-responsible node. In performing the above three tasks, we have a lot of communications between bundle-responsible nodes and domain-responsible nodes. In blip-grid transforms, for example, bundle-responsible nodes first calculate $\phi_{i\alpha}(\boldsymbol{r}_l)$ for integration grid points $\boldsymbol{r}_l$ in the support region of the atoms i, because bundle-responsible nodes have a set of blip coefficients $\{b_{ian}\}$. Then, they must send these values to domain-responsible nodes which have integration grid $\boldsymbol{r}_l$. In the calculation of matrix elements, each domain-responsible node accumulates the partial contributions to matrix elements from all blocks in the domain, and these contributions are sent to bundle-responsible nodes, which accumulate the contributions sent from their halo nodes to make their matrix elements. How to organise these communications is the key point for performing the operations in this section, efficiently.

In searching neighbour atoms of blocks or neighbour blocks of atoms, and in the way of labelling, we can completely follow the scheme used in matrix multiplications. For each block b in the primary set, there are atoms i in the system whose distance from b is less than the cutoff radius of support functions or projector functions. We refer to these atoms as neighbour atoms of b. The atoms i which are neighbours of at least one block in a domain form a set which we call halo atoms of the domain. The set of partitions containing at least one halo atoms are refered to as halo partitions, and the set of nodes having at least one halo partitions as halo nodes. Further, we can define a covering set made of partitions as the one which includes all neighbour atoms of one or more blocks in a domain. We call this a domain covering set (DCS) of partitions. Following this way of naming, a grand covering set used in matrix multiplications can be refered to as a bundle covering set (BCS) of partitions. Similary, as we need a list of neighbour blocks of atoms in a primary set, we define the terms, such as neighbour blocks of the atom i, halo blocks of a bundle, and a BCS of blocks. Even in increasing the size of a simulation cell, if we increase the number of processors and keep the form of each domain, the number of members in covering sets is obviously constant. Thus, with the covering sets, the cost of searching neighbour atoms or blocks is proportional to N, not to N^2. This advantage of the new code is important for the calculations on very large systems.

5. Future Prospects

In many ways, linear-scaling DFT is now established as a viable technique. Within the CONQUEST project, we have shown how practical linear-scaling performance can be achieved on systems of many thousands of atoms. Most of the practical problems presented by the search for the self-consistent ground state for such large systems are now solved, or are close to being solved. The practical challenges of implementing the algorithms on large parallel computers, including PC clusters, have also been addressed in detail. However, one issue that is not yet solved to our satisfaction is that of the basis sets for representing support functions, and this is the main reason why CONQUEST has not yet been applied to major scientific problems.

But the ideas embodied in CONQUEST can be seen as part of a larger current of thought that is being followed by many condensed-matter groups - a move away from extended orbitals

and extended basis sets and towards a formulation in terms of localized orbitals and localized basis sets. The key issue of how to make effective localized basis sets, which is so crucial to CONQUEST, was explored in depth in the very recent CECAM workshop on 'Localized orbitals and linear-scaling calculations', which was part-funded by Psi-k. A clear message from this workshop was that the new atomic-like basis functions being developed by several groups can often compete very effectively with plane waves, while demanding far less memory and often far fewer cpu cycles. By contrast, CONQUEST is currently based on finite-element methods that are deliberately related to the plane-wave approach. The exciting recent progress with atomic-like basis sets is already making an important impact in the SIESTA[52] and PLATO[54] codes and in other codes, and will undoubtedly be important for the future of CONQUEST and for linear-scaling DFT in general. We have high hopes that the SIESTA-CONQUEST collaboration, now in its early stages, will accelerate progress in this area.

Finally, we want to emphasize the very broad importance of linear-scaling ideas. One reason for this importance is the close relation between linear scaling and the 'embedding' problem, i.e. the problem of performing quantum calculations on a limited region which is 'embedded' in a much larger surrounding region. Since embedding also demands a localized formulation of quantum mechanics, and can be seen as the problem of embedding the density matrix in one region into that of a surrounding region, it is pretty well guaranteed that progress in linear scaling can be exploited for the embedding problem. Another completely different reason for the broad importance of linear scaling is its implications for quantum Monte Carlo. It is already clear that many of the current linear-scaling ideas can be directly transferred to improve the system-size scaling of QMC. By the same token, we expect that the long-standing problem of QMC embedding will also be helped forward by some of the new ideas. The future looks exciting!

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