Ψ_k Newsletter

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

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

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1 Editorial

One of the Psi-k networks, the TMR1 Network on *Interface Magnetism*, finished its activity at the end of August. A detailed final report on its fruitful five years is given in the **News from the TMR1 Network** section. The report contains also short scientific highlights. In the **News from the RTN Network** section readers will find an announcement of *'Hands-on Course: KKR Bandstructure and Spectroscopy Calculations'*. In the **News from the ESF Programme** we have four elaborate reports on some ESF supported workshops. The one on Local Orbitals contains also abstracts of presented papers, some of which include plots and spectacular figures. In the same section we advertise a number of forthcoming workshops. Note especially the announcements of the Brighton Conference Mini-Colloquia, whose deadline for abstracts submission is December 10. In the **General Workshop/Conference Announcements** section we have more announcements of the Brighton Conference Mini-Colloquia, an announcement of the *'Euro Winter School on Quantum Simulations'*, and an announcement of *'9th International Conference on Theoretical Aspects of Catalysis'*. In the **General Job Announcements** section we have a few available positions, and the **Abstracts** section contains as usual abstracts of newly submitted or recently published papers from members of the Psi-k community. The newsletter is finished with a scientific highlight by J. M. Soler (*Madrid, Spain*), E. Artacho (*Cambridge, UK*), J. D. Gale (*London, UK*), A. García (*Bilbao, Spain*), J. Junquera (*Madrid, Spain*, and *Liège, Belgium*), D. Sánchez-Portal (*Donostia, Spain*), and P. Ordejón (*Bellaterra, Spain*) on "**The SIESTA method for linear scaling ab initio simulations**". 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**
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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 News from the TMR1 Network

"Interface Magnetism"
"Ab Initio Calculations of Magnetic Properties of Surfaces, Interfaces and Multilayers"

2.1 Final Report on the Activity of the TMR1 Network

Final Report TMR Network on Interface Magnetism

The Network ran from 01-09-1996 to 31-08-2001,i.e. for a total duration of 60 months. Below is part of the report which was submitted to Brussels. The full report can be viewed on http://psi-k.dl.ac.uk/TMR1

SCIENTIFIC HIGHLIGHTS

A Highly Sensitive GMR-Device

The Giant Magnetoresistance (GMR) effect discovered by Peter Grünberg and Albert Fert in the late 80's forms the basis for sensors which in the space of 10 years have developed into a billion dollar industry. These devices typically consist of artificially grown magnetic multilayers, the main ingredient being two magnetic layers (such as Co) separated by a non-magnetic spacer layer (such as Cu), in this case a Co/Cu/Co sandwich. The GMR effect then utilizes the fact that the resistance is very different depending on whether the magnetic moments of the two magnetic layers are parallel or anti-parallel. When used as a read head in a hard disk drive, the magnetic stray field of the magnetic bits stored on the hard disk switches the magnetization direction of one of the magnetic layers in the sandwich. This change is detected by measuring the changed electrical resistance of the sandwich. These devices can be made very small using the same lithographic techniques used to make semiconductor devices smaller. It is this miniaturization which makes it possible to continue to increase the storage density of magnetic hard disks.

Although the GMR effect has been very successful, there is still an ongoing strive to optimize these magnetic multilayers, both regarding efficiency and production costs. In a recent article in Nature "Non-collinear states in magnetic sensors" (**Nature 406, 280-282, (2000)**) Adrian Taga, Lars Nordström, Peter James, Börje Johansson, and Olle Eriksson, of the Uppsala node of the Network, presented results of ab-initio calculations for an asymmetric magnetic trilayer of the type Fe/V/Co. In such an asymmetric combination the local magnetic anisotropy may favor different easy axes. In the vicinity of the non-magnetic vanadium layer the iron magnetic moment prefer a direction in the plane of the layer while the moment of the cobalt prefer a perpendicular direction, out of the plane. When these moments are combined in a trilayer they will interact, through the so-called interlayer exchange coupling, resulting in a non-collinear ordering, which depending on the vanadium thickness vary from close to collinear to almost perpendicular. These calculations suggest that by tuning the anisotropy and the interlayer exchange interaction independently, trilayers can be manufactured that are very sensitive to the stray field, which in principle may make more efficient sensor devices possible. The actual chemical composition as well as spacer layer thickness which will give the most optimized asymmetric trilayer has to be decided by future experimental studies

A Very Close Look at Magnetic Nanostructures

The invention of scanning tunneling microscopy (STM) has revolutionised our knowledge about surfaces. Suddenly being able to see the atomic structure of surfaces in all details with atomic resolution has been like making a blind man see and has lead to strong advances in fields like molecular beam epitaxy or catalysis. Yet for the magnetic structures of surfaces and ultrathin magnetic films STM has remained blind, since only the chemical structure, but not the magnetic structure, could be resolved atomistically. Thus despite many efforts, no spin-polarised STM images with atomic resolution could be obtained in the past.

In a recent article in Science "Real-space imaging of two-dimensional antiferromagnetism at the atomic scale" ((**Science 288, 1805-1808 (2000)**) an experimental group at the University of Hamburg and Blügel's group of the Jülich node of our Network have demonstrated that spin-polarised STM is possible on the atomic scale and that the resulting magnetic contrast is much larger than expected. More than 10 years ago Blügel et al. had predicted by ab-initio calculations that Mn or Cr monolayers on noble metal surfaces form ideal two-dimensional antiferromagnets. However, until now these predictions remained unconfirmed, basically because the available bulk techniques like neutron scattering cannot detect such minute amounts of magnetic materials. With a spin-polarised tip the Hamburg group was now able to confirm the magnetic superstructure for an antiferromagnetic Mn-monolayer on W(110). In advance the Jülich group had calculated the expected spin polarised STM intensity and predicted an unusually strong superstructure intensity. This was indeed observed, i.e. the magnetic contrast measured with the spin-polarised Fe-tip, produced by coating a W-tip with a thin Fe-layer, suppressed the chemical contrast obtained with a non-magnetic W-tip. Blügel et al. gave a very clear explanation of the strong magnetic contrast. The measured corrugation of the STM current is determined by the Fourier components of the smallest reciprocal lattice vectors, since these components decay most slowly into the vacuum region where the tip is located. The magnetic superstructure introduces new reciprocal lattice vectors, being smaller that the ones of the chemical structure, so than the related spin-current decays more slowly than the charge current.

The availability of the spin-polarised STM offers a bright outlook for surface magnetism. It allows the direct observation of antiferro- and ferrimagnetism on surfaces, non-collinear structures, magnetism at steps, nanostructures etc. All we could only calculate in the past, will now be accessible to the experiment. A true test for theory (and the theorists)

The INVAR Effect- after 100 years finally understood

In 1897 the Swiss physicist Charles Edouard Guillaume discovered that fcc Fe-Ni alloys with a Ni concentration around 35 atomic % exhibit anomalously low, almost zero, thermal expansion over a considerable temperature range. This effect is now known as the Invar effect. Guillaume's discovery immediately found widespread application in the construction of calibrated, high-precision mechanical instruments, such as seismographs and hair springs in watches. Today, Invar alloys are used in many temperature-sensitive devises, such as surveying tapes and shadow masks for television and computer screens. In 1920 Guillaume was awarded the Nobel Prize in Physics for the discovery of these Fe-Ni alloys.

The Invar effect has now been found in various ordered structures, random alloys or even in amorphous materials. Other physical properties of Invar systems, such as atomic volume, elastic modulus, heat capacity, magnetization, Curie (or Néel) temperature, also show anomalous behavior. It was realized early on that the explanation of the Invar effect is related to magnetism. Yet, though it has been 100 years since this effect was discovered, it was not understood. In a recent article published in Nature "Origin of the Invar effect in iron-nickel alloys (**Nature 400, 46 (1999)**), I. Abrikosov and B. Johansson from Uppsala node of the Network, in collaboration with Mark van Schilfgaarde from Sandia National Laboratories, Livermore, USA, presented results of ab initio calculations of volume dependences of magnetic and thermodynamic properties for the most typical Invar system, a random fcc Fe-Ni Invar alloy, where they allowed for noncollinear spin alignments, i.e. where the spins may be canted with respect to the average magnetization direction. They have found that the evolution of the magnetic structure already at zero temperature is characterized principally by a continuous transition from the ferromagnetic state at high volumes to a disordered noncollinear configuration at low volumes, and that there is an additional, comparable contribution to the net magnetization from the changes in the amplitudes of the local magnetic moments. The noncollinearity gave rise to an anomalous volume dependence of the binding energy curve, and this allowed Mark van Schilfgaarde, I. Abrikosov and B. Johansson to explain the well-known peculiarities of Invar systems.

PROJECT SUMMARIES

We believe that the width and quality of research in our network represents the highest international state-of-the-art. It is very well comparable, in fact superior as we believe, to any other theoretical activities in the field of magnetic multilayers and surface magnetism. Below we give a summary of the major accomplishments of our flagship projects.

Interlayer Coupling: Seeing the Fermi Surface in Real Space

The phenomen of interlayer exchange coupling of two magnetic layers by a non-magnetic metallic spacer was discovered by Gruenberg more than 10 years ago. In a now classic paper our Network member P. Bruno showed that the oscillations of the interlayer coupling in real space are attributed to stationary calipers of the spacer Fermi surface. Due to the establishment of our network a substantial increase of the theoretical activities on interlayer coupling occured to which all six network nodes contributed. A particular strong effort came from the combined Austrian, German and French teams. Among the highlights are a careful study of the alloying effects on interlayer coupling due to interdiffusion at the interface, due to alloying of the magnetic layer and of the spacer material. An off-spring was e.g. the vertex cancellation theorem, which proves that in disordered systems the coupling can be calculated by the ensemble averaged Green's function. Other highlights are the direct relation of interlayer coupling to the spin-dependent reflectivity at the interface as well as to the occurance of quantum well states in the spacer material. Excellent agreement was obtained between the calculated quantum well states of Co/Cu(001) and the experimental results of our collegues at Juelich. In detail and in parallel to experimental studies of the industrial partner Philips the oscillatory dependence of the coupling with magnetic layer thickness were studied, and in addition an oscillatory dependence with the thickness of caplayers was predicted. A recent interesting study concerns the temperature dependence of the interlayer coupling, where considerable progress in the understanding was achieved. The Swedish group made among others some important contributions to quantum well states. In addition to mediating the coupling of the magnetic layer these can lead e.g. to the on-set of magnetism in an otherwise non-magnetic layer. They also showed that quantum well states can lead to an oscillatory dependence of the magnetic anisotropy on the thickness of the magnetic caplayer. The UK node focussed on the ab-initio calculation of the asymtotic expression for the interlayer coupling, i.e of the period, amplitude and phase of the oscillation and their relation to the Fermi surface. In particular they showed, that the periods in the Fe/Cr and Fe/$\mathrm{Cr}_{1-x}\mathrm{V}_x$ system are directly related to the hole pocket at the N-point of the Brillouin zone. Moreover they point out that the oscillatory coupling is an important new technique for probing the Fermi surfaces of random alloys. In total the contributions of our Network have greatly improved the understanding of interlayer coupling. It is an exemplary case that complimentary contributions from six different nodes lead to a large synergetic effect, so that one can now say that interlayer coupling is well understood. Therefore, without exaggeration we can claim, that the most important theory contributions came from our Network. Summarizing: (i) the pioneering paper of Patrick Bruno showing the connection of the oscillation periods with the Fermi surface of the spacer, (ii) the enormous amount of calculations by the Austrian-Czech group about the effects of interdiffusion at the interface and of alloying in both the spacer and the ferromagnetic layer, (iii) the detailed studies of the Swedish, British and French groups for the understanding of the complex Fe/Cr systems, (iv) the calculations of the spin dependent reflection and transmission coefficients of the Dutch and German groups, etc. Very many of these papers have been published in Physical Review Letters and are widely recognised.

News from Perpendicular Magnetism and Magnetocrystalline Anisotropy Energy

The spin-orbit induced Magnetic Anisotropy is of vital importance for the fundamental understanding of magnetism as well as for practically all technological applications. For these reasons four Network nodes have concentrated their efforts towards an understanding of the magnetic anisotropy in layered systems. Of special interest is the Ni_n/Cu(001) system, since it is the only known system in which the orientation of the magnetisation switches with increasing thickness from in-place to perpendicular. As the Austrian team found, the secret for this peculiar behaviour turned out to be a tetragonal distortion in the Ni-film, namely a contraction of the interlayer distance as compared to the one in the Cu substrate. The Swedish team complemented these thin film results with calculations for bulk Ni, being tetragonally distorted as to resemble the geometry of epitaxial films. Both calculations basically came to the same conclusions, and the calculated anisotropy constants of the Ni film are in excellent agreements with experimental values. The Swedish team also made an extensive study of the magnetic properties (spin and orbital magnetic moments and magneto crystalline anisotropy-MAE) of $\mathrm{Fe}_n/\mathrm{V}_m$ multilayers for various values of n and m. Experimental data show that when n=2 and m=5 the MAE gives the out of plane direction as the easy axis, whereas for n=4 and m=4 the MAE gives a moment in plane. The experimental data have successfully been reproduced using a highly accurate first principles full potential electronic structure method. The microscopical reason for this spin reorientation transition has been analysed in detail, and it has been established that both structural effects (lattice distortion and lattice expansion) in combination with the Fe-V interaction (hybridization) are crucial for the MAE. In addition a novel method, based on elasticity theory, for calculating the in-plane and out-of-plane lattice constant of any multilayer has been developed and shown to agree with experiments with good accuracy.

The Austrian team also studied the reorientation transition in the alloy system $(\mathrm{Fe}_x\mathrm{Co}_{(1-x)})_n/\mathrm{Cu}(001)$, which with increasing thickness and varying composition shows a very rich reorientation phasediagram. The calculations show that the driving force for the reorientation is closely related to the occurrence of antiferromagnetic ordering between the layers which naturally depends strongly on the concentration of Fe. Thus, the theory gives an astonishingly simple explanation of the complicated thickness and composition dependence observed experimentally.

An exciting highlight concerns the manipulation of the magnetic anisotropy of Fe, Co and Ni layers by applying an electric field. Extensive calculations by the Juelich group show that it is possible to switch the magnetisation direction by applying an electric field to the layers. This might e.g. be realised by applying a voltage on an STM tip. The effect represents a completely new discovery and could be of interest for technical applications, e.g. magnetic writing with an STM tip.

Another technologically interesting system are (CoPt) layers on Pt substrates which are used in most magneto-optical devices. Here it could be shown by the Austrian team that - as compared to Co films on Pt(001) and Pt(111) - only for (CoPt) superstructures with tetragonal symmetry the magnetisation is strongly oriented perpendicular to plane, where as interdiffusion reduces this effect very strongly. Complimentary calculations were performed by the UK team for disordered CoPt bulk alloys, showing that the inclusion of short-range order of the (CoPt) superstructure type increased the anisotropy by orders of magnitude, in qualitative agreement with the film results of the Austrian team.

In summary the large number of highly interesting results on perpendicular magnetism show that our Network has internationally the leading position in this important field.

GMR: Spindependent Propagation versus Spindependent Scattering

Although the Giant MagnetoResistance (GMR) effect was discovered only ten years ago, it was developed very rapidly into a technology which is now found in all hard-disk drives, in many navigation devices which measure the earth's magnetic field and as a motion sensor in numerous automotive products. The explanation of GMR has been the subject of some controversy with early phenomenological theories concentrating on spin-dependent scattering to explain the effect. The early discussions focussed on the issue of the importance of bulk versus interface scattering; the origin of the spin-dependent scattering and the influence of the complex transition metal bandstructure were almost completely neglected. A scientific highlight of our Network is the insight gained into the origin of GMR by the Dutch and German groups. Both have demonstrated that bandstructure effects make a major contribution to GMR. Within the framework of (semiclassical) Boltzmann transport theory, the German team calculated Fermi surface velocities and wavefunctions to analyse the effect of impurity scattering at different sites in Co/Cu (001) multilayers in the current-in-plane (CIP) and the current-perpendicular-to-plane (CPP) configurations. They conclude that the CIP transport is particularly sensitive to the presence of impurities at the interface. The Dutch team demonstrated the importance of bandstructure effects by showing that a GMR effect exists even in the absence of impurities - the "ballistic" regime. To interpret transport measurements in the CPP configuration, a so-called "resistor model" formulated in terms of bulk resistivities and interface resistances is very successful. In most situations, the interface resistance dominates the GMR and it is important to understand its spin-dependence. By expressing it in terms of the transmission and reflection matrices which describe how propagating Bloch states are scattered by interfaces, as well as by impurities, and by formulating methods for calculating these matrices using a Green's function embedding method, the Dutch team could calculate values of the interface resistances and found good agreement with experiment.

The Austrian Group concentrated on evaluating the CIP resistance of disordered magnetic multilayers and spinvalves using the Kubo formula. The method uses the TB-KKR Green's function method, with the disorder being described by the CPA for layered systems, in this way allowing a realistic description of both the band propagation as well as the disorder scattering. Of specific interest was a simulation of the Motorola Spin Valve, yielding a GMR value in excellent agreement with experiment.

In the second phase of the Network, research on magnetic structures and devices continued using phenomenological approaches to study transport in the mesoscopic and nanoscopic regimes. On the one hand, the Network considered how metallic ferromagnets in contact with conductors inject a spin-polarised current into a variety of other materials such as simple normal metals, semiconductors and superconductors. On the other hand, the Network studied how transport in mesoscopic devices could be used to test basic concepts of quantum mechanics such as charge and conductance quantization. The behaviour of a collection of electron spins in small structures combines these two fields. We focused our attention on transport in hybrids of normal and ferromagnetic metals as well as ferromagnets and superconductors, our aim being to develop novel or improved theoretical methods for understanding transport and other phenomena in such systems. The main applications of this phenomenological theory were to: single-electron tunnelling in magnetic systems; ferromagnetic/superconducting devices; non-collinear diffuse transport. Simultaneously, practical schemes for calculating the scattering matrices used in the phenomenological theory were developed based on TB-LMTO and TB-KKR methods. The TB-LMTO schemes developed by the collaboration of the members of the Dutch node and the Czech scientists of the Austrian node was so efficient that disorder could be modelled using large lateral supercells. This methodology was applied to the study of the interface resistance of a variety of magnetic/non-magnetic interfaces including disorder. Within the framework of the Landauer-Büttiker formalism, the same methodology of transmission and reflection matrices has been used to study transport through magnetic domain walls; transport through interfaces between ferromagnets and superconductors; current-induced magnetization reversal (spin-mixing) and spin injection into semiconductors.

The success of our activities resulted in an RTN on Computational Magnetoelectronics which focusses even more on spin-dependent transport and will include calculations of the Tunneling Magnetoresistance (TMR). In concluding these highlights we note that in the field of spin-dependent transport members of our network belong to the international top players.

Spectroscopic Studies of Interface Magnetism:

Spectroscopies play a crucial role in studying the magnetic properties of magnetism at interfaces. The discovery of the sum rules in the dichroism spectra has lead to the 'experimental' determination of site-dependent orbital moments and magneto-crystalline anisotropy energy. One of the discovers of these sum rules, G. van der Laan of Daresbury Laboratory, is part of the Network. The Network has devoted considerable resources to this project. Two Network post-docs, the Austrian and English ones, are specifically working on this project. Moreover, the Swedish Network post-doc is a photoemission expert, the French node has re-directed its flagship project towards dichroism studies and GW calculations with the FP-LMTO and finally, a substantial German effort is centered around the work of the Muenchen group. In particular, the Muenchen group is looking at dichroism in the EXAFS regime, which allows for the study of magnetic SRO. Whilst there is an excellent through-put of new code developments of these five groups together with applications to the systems of current interest, such as the above mentioned Ni/Cu(001), it might be more exciting for this highlight to select some of the more speculative findings of the theoretical calculations. Firstly, the Austrian node has studied the possibility of using spin-resolved Auger spectroscopy as a possible tool for magnetic domain mapping. Secondly, the Swedish node found that magnetic dichroism in threshold photoemission provides a contrast mechanism for imaging of magnetic domains. Thus, photo-electron emission microscopy could become feasible with laboratory light sources, in addition to synchrotron facilities.

Quantum size effects can be studied in electronic quantum-well states which considerably affect the magneto-anisotropy of ultra-thin films and manifests in distinct effects in photoemission. For example, intensity oscillations in constant-initial-state spectroscopy allow for the identification of quantum well states and provide information on film thickness and film quality, as has been investigated for the prototypical system Cu/fcc-Co(001) by the Swedish team. Moreover this team also found in spin-polarized LEED from Co/W(110) - in both experiment and theory - intensity oscillations due to electron confinement. The UK team has completed a set of new codes to study photoemission and applied these to the study of quantum-well systems. This team made a systematic study of the quantum well states upon deposition of an increasing number of Ni layers upon a Cu substrate. Moreover, the UK and Swedish post-docs, now both at the MPI in Halle are collaborating on a study of the quantum well states of Ag on V(100) and in particular they see a cross-over of quantum well states into interface states.

Moreover, the breadth of the spectroscopies since the inception of the Network has increased. A promising new project on STM is taking place in a German/ Austrian collaboration focussing on the understanding of STS spectra and the chemical identification of surface atoms. In the UK node a project on magnetisation-induced second harmonic generation has been started.

A Series of New, Highly Accurate and Efficient KKR-Codes

The tight-binding KKR-Green's function method represents an original and unique product of our Network, which has lead to a series of new, highly accurate and efficient KKR codes which are not matched by any other program worldwide. The project was started with a joint publication of the Vienna and Juelich team, who showed that the well-known Korringa-Kohn-Rostoker (KKR) theory can be exactly transformed into a "screened" representation with structure constants decaying exponentially in space. This concept has proved to be extremely powerful for layered systems since the numerical effort scales linearly with the number of monolayers and since it allows for an exact solution of the halfspace problem. Thus, the project has lead to exciting activities in three nodes of the network. The Austrian team has performed with this method extensive fully-relativistic calculations for the magnetic anisotropy of layered systems and for the Giant Magnetoresistance which are reported elsewhere. Their scheme was recently extended to include the layer relaxations. The Juelich-Dresden teams has developed TB-codes for the slab-, halfspace- and multilayer-geometry and applied them in very accurate calculations for interlayer coupling and quantum well states. Based on the Green's functions of these reference systems codes for the calculations of impurities at surfaces and interfaces have been developed. In parallel to this a full-potential code for ideal surfaces and defects on surfaces has been constructed by the Juelich group. The Munich-Juelich teams have extended practically all existing scalar relativistic KKR programs into a fully relativistic Dirac scheme with spin polarisation. At present fully relativistic codes exist already for the bulk, for impurities in the bulk, for surfaces and for impurities on surfaces, layered systems. Finally, the Daresbury group is working on a flexible real space code using sparse matrix techniques for applications to photoemission and other spectroscopies. Moreover, the Daresbury post-docs incorporated the GW approximation into the KKR codes. All these coherent and complementary program developments open up a bright perspective for the application of the KKR-Green's function method, which is not restricted to typical ground state calculations, but just allows as well applications to problems connected to spectroscopy, transport and linear response. Most of the above activities would not have happened without the existence of this Network and in particular the Graphical User Interface (so-called GUI) constructed by the Muenchen team allows for a wide dissemination of this code and a hands-on course is already planned for early 2002.

Non-Collinear Magnetism at the Fe/Cr Interface

The Fe/Cr interface is an extremely complicated system due to amongst others topological defects caused by the steps at the interface. Not so long ago, a full conference on the Fe/Cr interface was organized in Strasbourg. Non-collinear magnetism has been largely investigated by the Strasbourg TMR node using a semi-empirical tight-binding method. It has been shown experimentally that magnetic frustrations will induce non-collinear magnetism. For instance imperfect interfaces with single steps in Fe/Cr lead to complicated topological defects with non-collinear spin arrangements. The large number of inequivalent atoms in these systems inhibits ab-initio computations and makes the empirical tight-binding approach the method of choice for the study of physical properties.The French team showed that the phenomenological variation law, proposed for the change of the total energy as a function of the misalignment of the two ferromagnetic layers coupled through a non-magnetic or antiferromagnetic spacer, can well be applied to FeCo/Mn systems and less to the Fe/Cr one within the framework of the semi-empirical method. The so called ”perpendicular” coupling, observed experimentally, has been described in details for Fe/Cr and FeCo/Mn systems. In fact, the magnetic behavior of each individual atom can be quite complex but the general trend of the spin magnetic moments near the interface is simple and is now well understood.

AWARDS:

The excellent work within our Network is also reflected in several recent awards presented to Network members:

- Prof. Gerrit van der Laan (Daresbury Laboratory) shares Europe’s Most Prestigious Physics Prize, the ”Agilent Technologies Europhysics Award for the Discovery of Magnetic X-ray Dichroism”. Paolo Carra (ESRF, Grenoble, France), Gerrit van der Laan (Daresbury Laboratory, Warrington, UK) and Gisela Schutz (Institute of Physics, Wurzburg, Germany) have won the Agilent Technologies Europhysics Award for the year 2000 for their ”Pioneering work in establishing the field of magnetic X-ray dichroism”.
- Prof. P. Weinberger (TU Vienna) received the Ernst-Mach Medal of the Czech Academy of Sciences. Moreover he was elected in 1998 as a Fellow of the American Physical Society.
- Prof. B.L. Gyorffy (University of Bristol) was awarded in 1998, together with the Oak Ridge group (USA), the Gordon Bell Award for the efficient scientific use of supercomputers. Furthermore Prof. Gyorffy received the prestiguous Hume-Rothery Award 2000 from the Metals, Minerals, and Materials Society of America.
- The Czech scientists Drs. V. Drchal, J. Kudrnovsky, I. Turek and M. Sob, which due to a joint appointment are staff members of the TU Vienna, received the 1998 Price of the Czech Academy of Sciences for Physics.
- The Swedish scientists received the following awards: Anna Delin received a price for ’Best Swedish thesis of the year’ (1998), Lars Fast received Bjurzons premium (1998), Anders Niklasson received Bjurzons premium (1999), Igor Abrikosov received Oscars price (2000),

Borje Johansson received the Celsium medal (2000), Rajeev Ahuja received Benselius price (2001), Olle Eriksson received the Wallmarkska price (2001)

- In the French node Brice Arnaud who obtained his PhD under the supervision of M. Alouani in fall 2000, has been awarded by the "Prix de these ADRERUS" which recognizes every year the five best PhD thesis in all four universities of Alsace (covering all subjects: "hard" science, social and human sciences, law, medicine...). This amount of this prize is almost 2000 Euros.

PROMOTIONS:

The excellency of our Network shows also up in the fact, that during the lifetime of the Network seven members received promotions to the position of a Full Professor or to a similar prestigious position (in the case of Patrick Bruno):

1. Patrick Bruno (French node) was appointed Director in the Max-Planck-Institut für Mikrostrukturphysik in Halle (Germany).
2. Stefan Blügel and Ingrid Mertig (German node) became Professors in the Universities of Osnabrück and Halle respectively.
3. Olle Eriksson (Swedish node) became Professor of Theoretical Magnetism at Uppsala University.
4. Paul Kelly (Dutch node) became Professor at the University of Twente.
5. Julie Staunton and Paul Strange (UK node) became Professors at the Universities of Warwick and Keele respectively.

NETWORKING

The Network organized four annual meetings. These annual meetings were extremely successful in establishing cohesion in our scientific endavours. These annual meetings were attended by all, resulting in attendance numbers of 80 and more. These were occasions were all young researchers active in our groups were given the opportunity to give talks. These annual meetings also gave the opportunity to the senior members of the Network to review progress. The last annual meeting was incorporated in the psi-k2000 conference which attracted in excess of 400 participants thus ensuring that out work reached out to the European computational electronic structure community at large. These annual meetings were augmented by 8 Network workshops, one hands-on course for experimentalists in our spectroscopy codes and one winter-school. Through the workshops we focussed on topical issues and these were also occasions experimentalists participated. A list of all meetings and workshops is added as an appendix.

The psi-k newsletter was also a very important network activity. It is published every 2 months. Here we reported on our scientific results and our workshop activities. This newsletter went out to more than 900 e-mail addresses, mostly in Europe and is also available on the web (http://psi-k.dl.ac.uk/psi-k/newsletters.html). This ensured that our activities reached out to the scientific community at large and this also ensured that young researchers were very attracted to work in our Network. Given the crucial role of the psi-k newsletter in the networking within the Network and with the scientific community outside, it is rather disappointing that the small cost item charged for this activity was not acceptable to the EU auditors.

ASSESSMENT: WORKING TOGETHER AT A COMMUNITY LEVEL

The Network was given collaborative opportunities not available from any other funding agency. In all of our flagship projects: Interlayer Exchange Coupling, Magnetocrystalline Anisotropy Energies, Giant Magnetoresistance, Spin-Polarised Spectroscopies, Tight-Binding KKR and Full Potential LMTO substantive collaborations between the nodes occurred. This is amply documented in the project summaries of Section 2. The most important aspect was the access to travel funds for regular meetings that allowed plenty of time for new collaborations to develop. Four annual meetings, 14 workshops and 5 mini-workshops took advantage of this. Important was also the funding that allowed us to send young and also senior researchers to other nodes to be trained in new techniques allowing to perform more thorough and complete studies. Visits by senior researchers allowed new projects to develop. From most of these visits significant publications resulted. Less tangible and quantifiable are the enormous benefits acquired by the Nodes in forming part of a Network with a common purpose of performing our science to the highest standards.

Whilst in general we felt positive by the opportunities offered, we would like to make a criticism against the restrictive policies concerning how the funding can be applied. We are happy to see that several of these restrictions are lifted in Framework V, notably funding for travel within the same country and employment of young researchers from Central European countries. Also allowing researchers of non-EU nationality, but who have been resident in a country for 5 years can now become eligible for young researchers-positions. But, still we believe, that also in the V Framework there are too many restrictions, which help very little, but cause problems for the Networks.

INTERACTIONS WITH INDUSTRY

Philips Research Laboratories Eindhoven (PRLE) is the only industrial participant in the Network. A PhD student K.M. Schep and a postdoc J.B.A.N van Hoof, both from the Technical University of Delft (TUD), spent most of their time at PRLE working under the supervision of P.J. Kelly and with very strong interaction with the senior experimentalists R. Coehoorn and M.A.M. Gijs. The Dutch node postdoc A. Brataas was located with Bauer in Delft and interacted mainly with P.J. Kelly (PRLE and University of Twente) and K. Xia a postdoc working on GMR in Twente.

PRLE was involved in the field of Interface Magnetism from the start. Pioneering experimental work on magnetic multilayers in the mid-eighties led to the discovery of perpendicular magnetic anisotropy in Co/Pd and Co/Pt systems. This formed the starting point for the theoretical study of magnetic anisotropy from first-principles calculations at PRLE which culminated in the theoretical prediction and experimental confirmation of perpendicular anisotropy in a novel

Co1/Ni2 multilayer. This led to the award of a patent. The experimental emphasis at Philips shifted to the study of exchange-coupling and there were a number of very fruitful collaborative publications between members of the Network and researchers from Philips, in particular Coehoorn. By the time the Network started up in September 1996, interest at Philips had moved on to the study of Giant Magnetoresistance (GMR) which now became the topic of a theoretical study by PRLE (Kelly) and TUD (G.E.W. Bauer). The subject of this theoretical collaboration was to combine phenomenological theories of transport in GMR systems with first-principles calculations of the electronic structure. Again, a fruitful collaboration between theory and experiment led to a number of patents and patent applications as well as to publications which have had an important impact in the field. All along there has been a useful interaction allowing systems with application potential to be identified for analysis with the help of first-principles calculations.

Some adjustments were called for by the acceptance by Kelly of a chair at the University of Twente (UT) in 1997 and the reorganization of the magnetism related research activities at PRLE. With PRLE moving away from magnetism related research, new partnerships were developed between members of our Network and other industrial partners. In particular, fruitful collaborations with Thomson in France and Siemens and Bosch in Germany have been established in Europe while further afield collaborations with IBM and Toshiba have also started.

ASSESSMENT: TRAINING AND MOBILITY OF YOUNG RESEARCHERS

Overall we believe that we have given our young researchers a thorough training in a new technique, namely accurate and ab initio computational calculations, for the electronic and magnetic properties of new and exciting materials which are part of a billion EURO industry of magnetoelectronics. That this training was valued can be seen by the future career of these young people: from the UK node: A. Ernst went to the MPI in Halle, M. Lueders and N. Lathiotakis became young researchers in other TMR networks in Italy and Germany respectively; from the Swedish node: J. Henk went also to the MPI in Halle and O. LeBacq started a permanent scientific career in Grenoble; from the French node: Iosif Galanakis received his PhD in June 2000 and is since Sept. 1, 2000 a post-doc in Jülich, Manuel Jigato is back in Spain where he is a teacher in a secondary school, Leon Petit became from Sept. 99 a post-doc in Aarhus, Alberto Bernardi is, after his stay in Strasbourg, post-doc in Trieste since January 1, 2001 and Peter Jensen has a temporary position as "chercheur invite" in Toulouse. After spending a number of years in Harvard, A. Brataas, the post-doc from the Dutch node, has obtained a tenured position at the University of Trondheim; from the German node: Roland Abt went back to the TU Graz and works now as a software consultant, Nikos Papanikolaou has now a position at the University of Halle, Phivos Mavropoulos came back on a post-doc position to Jülich after his military service in Greece, Timo Korhonen has a permanent position in the Technical University of Helsinki, Michel Freyss obtained a permanent research position in the CEA-Cadarache, and Ivan Cabria is now a post-doc at the George Washington University in Washington. From the Austrian node: Ute Pustagowa is looking for a position in Vienna since her family wants to stay there.

It is not only the young researchers directly employed in the Network who benefited, but also the resident young researchers benefited by participating in the Network activities. Moreover, several of these young researchers went on to positions in other European countries.

STATISTICAL SUMMARY

20 young researchers were employed for 429.5 months in total, 24 researchers went on secondement to another node of the network for one month or more, 82 joint papers were published, 14 workshops and annual meetings were held, augmented by 5 mini-workshops.

3 News from the Research Training Network (RTN)

COMPUTATIONAL MAGNETOELECTRONICS

3.1 RTN Workshop Announcements

3.1.1 Hands-on Course: KKR Bandstructure and Spectroscopy Calculations

Organised by:
Hubert Ebert (München) and Walter Temmerman (Daresbury)

Funded by:
ESF Psi-k-Programme and RTN-Network: Computational Magneto-electronics

18th - 23th February 2002

Univ. München, Inst. for Phys. Chem.

Purpose: teach theoreticians and experimentalists the use of the Munich SPR-KKR package.

Registration: FAX: +49-89-2180-7584
or email: Michal.Kosuth@cup.uni-muenchen.de

No attendance fee will be charged.

Financial support for some participants is possible.

The code will be available free of charge after signing a license agreement.

`http://olymp.phys.chemie.uni-muenchen.de/ak/ebert/kkr_course.html`

Program:

- Morning: Lectures on DFT, KKR and electron spectroscopies
- Afternoon: Calculations guided by the tutors.

	TUE	**WED**	**THU**	**FRI**	**SAT**
8^{45}	Welcome	DFT	KKR4	DFT+SPEC	access to the computer system possible – some tutors will be present
9					
9^{15}	KKR1				
9^{30}		XAS (Expt.)	XMO (Expt.)	PES (Expt.)	
9^{45}					
10					
10^{15}		COFFEE	COFFEE	COFFEE	
10^{30}					
10^{45}	COFFEE	SPEC1	SPEC2	SPEC3	
11					
11^{15}	KKR2				
11^{30}		KKR3	KKR5	KKR6	
11^{45}					
12					
12^{15}	FAQ/Exerc.	FAQ/Exerc.	FAQ/Exerc.	FAQ/Exerc.	
12^{30}	LUNCH	LUNCH	LUNCH	LUNCH	
12^{45}					
13					
13^{15}					
13^{30}					
13^{45}					
14	xband SCF	E(k) DOS	XAS EXAFS	VB-XPS CL-XPS	
14^{15}					
14^{30}					
14^{45}					
15					
15^{15}					
15^{30}					
15^{45}	COFFEE	COFFEE	COFFEE	COFFEE	
16					
16^{15}	SCF CPA	ground state properties	XMO XRS XES	MCP APS AES	
16^{30}					
16^{45}					
17					
17^{15}					
17^{30}					
17^{45}					
18				closing	

Speakers:

KKR1	W.M. Temmerman	Introduction to bandstructure calculations
KKR2	H. Ebert	The Munich KKR-package
DFT	N.N.	Density functional theory for magnetic solids
KKR3	B.L. Gyorffy *	CPA and relativistic effects
KKR4	J.B. Staunton *	Finite temperature magnetism
KKR5	L. Szunyogh	Surface magnetism
KKR6	P. H. Dederichs	Applications in magneto-electronics
SPEC1	P. Weinberger *	Single particle description of electron spectroscopies
SPEC2	P. Strange *	Calculation of electronic excitation spectra
SPEC3	G. van der Laan *	Electron spectroscopy from the atomic point of view
DFT+SPEC	N.N.	Electron spectroscopy within density functional theory
XAS (Expt.)	K. Baberschke	Magnetic dichroism in X-ray absorption
XMO (Expt.)	Ch. Mertins *	X-ray magneto-optical effects
PES (Expt.)	C. M. Schneider *	Magnetic dichroism in photoelectron spectroscopy

(*: to be confirmed)

4 News from the ESF Programme

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

4.1 Reports on ESF Workshops

4.1.1 Report on Oxide-Metal Interfaces Workshop

Oxide-Metal Interfaces – Progress and Challenges

Workshop in Lyon, 4-6 October 2001

sponsored by

The European Science Foundation with the PSIK network

and

CECAM

organized by

M. W. Finnis
Atomistic Simulation Group
School of Mathematics and Physics, Queen’s University Belfast
BT7 1NN, Northern Ireland, UK

and

C. Elsässer
Max-Planck-Institut für Metallforschung
Seestraße 92, D-70174 Stuttgart, Germany

Introduction

The following is a commentary on the scientific programme and outcomes. The programme itself, with abstracts and timetable, can be viewed from the website of CECAM, http://www.CECAM.fr, or at:
http://titus.phy.qub.ac.uk/Oxide_Metal_2001/short_prog.html
http://titus.phy.qub.ac.uk/Oxide_Metal_2001/final_prog.html

Since it is rather unusual for a CECAM workshop to include the participation of so many experimentalists, it seems worth remarking that this was generally regarded as an extremely positive aspect of the workshop. Especially in this interdisciplinary field, progress is most rapidly achieved by experimentalists and theorists working together. Several participants commented on the benefits of the workshop and we note some of these comments at the end.

Industrial Challenges

Roger French introduced the roadmap and problems of the microchip industry, and he reminded us of some breathtaking recent progress. The 2GHz Pentium 4 has a source-drain distance of just 90 nm, with 42M transistors on a CPU. The price of a 1.4 GHz Pentium 4 has tumbled from US$900 to US$200 since its introduction this year. These observations indicate both the speed of progress but also that in theory we should be able to squeeze out another order of magnitude from further reduction in physical dimensions. Important gate dielectrics are SiON (near term) and ZrO_2 or HfO_2 (long term). The problems of oxide-metal interfaces mentioned were: under what conditions do we get amorphous material deposited and when is it crystalline (kinetics and thermodynamics)? Mechanical adhesion is an issue when wafers are polished after creating layers - they should not delaminate.

From the automobile industry, Thorsten Ochs told us about how exhaust gas sensors work, based on solid state electrochemistry, for monitoring the richness of the mixture and concentrations of e.g. NO_x. The issues for us here seem to be optimizing electrode materials and studying the reaction of gases with the electrolyte (eg. ZrO_2) interface. The most complex problems presented had to do with the adhesion of oxide scales in high temperature structural materials such as FeAl and FeCrAl. Theses alloys form protective coatings of alumina. Industry requires a knowledge of the lifetime of components under normal and fault conditions in order to reduce the error bars in these numbers and thereby to extend the safe life of operation of components. It is a matter of improving the level of *confidence* in the materials. Mike Bennett and Peggy Hou presented different aspects of this problem, which is strongly related to the segregation of impurities (particularly sulphur) to boundaries and their role in decohesion. It is still not clear whether S for example segregates only to void surfaces or to all internal interfaces, since the smallest voids are below the probe size. One can see how calculations could contribute at least to this part of the problem. More experimental work on model systems such as Fe and Ni would be valuable for testing theories. Good adhesion is not always desirable in industrial processes, indeed the opposite may be required. An example (Don Siegel) is the interaction of Al with ceramics in the process of rolling, where one wants the least possible adhesion of roller to metal in order to minimize surface damage to the aluminium sheet.

Other challenges from experiment

Rainer Waser introduced aspects of dielectric behaviour which are in need of theoretical work, some certainly of the ab initio electronic structure kind. They are interested in charge storage in the cap of a dielectric with DRAM and the roadmap in mind. Much work has been done in controlling the morphology and texture of thin films of $Ba_xSr_{1-x}xTiO_3$ (BST) on metal crystal substrates. Atomically flat interfaces have been formed. Although there is an abrupt discontinuity in structure and composition from one phase to another, the interface contributes to the dielectric properties as if it were a phase of low dielectric constant, several nm thick. This phenomenon, the so-called "dead-layer effect" is also under active investigation by many experimental and theoretical groups around the world, including Finnis and coworkers, because there is still controversy about its origin, eg. whether interface phonon modes are involved or field penetration into the metal or what.

The strong current interest in these low-dimensional perovskite structures was also apparent on the posters presented by Susanne Hoffmann-Eifert, Hermann Kohlstedt, Xavier Jonquera, Christina Scheu and Thomas Classen. A new X-ray technique for determining the structure of small clusters in real time as they nucleate and grow on a substrate was presented by Gilles Renaud (Pt, Pd, Ag on MgO). This kind of data leads to questions of kinetics versus thermodynamics. To what extent are the equilibrium structures of small clusters, which, as we have seen, can be calculated in some cases based on ab initio methods, relevant to the structures formed during dynamic growth, for which other theoretical methods are needed? The 3D atom probe is also raising challenges for atomistic calculations, as discussed by David Seidman, since it is able to detect the positions and species of atoms through a sample with 60-80% atomic efficiency. Spatially resolved electron energy-loss spectroscopy in scanning tranmission electron microscopes is posing similarly ambitious challenges for electronic-structure calculations, since it relates local electronic spectra to local atomic arrangements and interatomic bonding types, as presented by Christina Scheu for Cu/Al_2O_3 contacts. The energy of adhesion has been subject to much experimental investigation.

For example in anti–solar and low emissive coatings, an intermediate layer can strengthen the bonding. An example is Ag on alumina, where the inclusion of a predeposited Ti film greatly improves the adhesion. Ab initio calculations of Elsässer and coworkers for Ag/spinel contacts have helped to clarify this kind of effect. Tony Tomsia has greatly clarified the issue of the role of the atmosphere in work of adhesion. Measurements of surface and interface energy versus oxygen partial pressure p_{O_2} have been made and reveal a strongly dependent regime as well as the "non-reactive wetting" regime (Nicholas Eustathopoulos), which is where the interfacial energy is insensitive to p_{O_2}. Calculations must clearly take p_{O_2} into account when comparing to experiment. The formation of grooves and craters when a metal island rests on an oxide substrate complicates the simple picture of a sessile droplet (Jaques Jupille). The morphology of this situation is size dependent (Suzanne Giorgio). High resolution TEM revealed for example how Au polyhedra on TiO_2 are accommodated to the substrate at least in the four closest layers. This introduces the question of kinetics again, but also the roles of edge and corner energies and elastic strains, all of which may also be of relevance to catalysis. Dominique Chatain also showed elegant results on the morphology of small clusters and cavities.

Theoretical Progress

DFT calculations using LDA or GGA were of course represented in the familiar form with periodic boundary conditions, using all-electron or pseudopotential approaches with plane-wave or/and local-orbital basis-set representations.

The complexities of free oxide surface structures with respect to their chemical stoichiometry were illustrated by cases of TiO_2 surfaces in the presentation of Philip Lindan and in the poster of Steve Elliott. The systematics of adsorption energies of metals on TiO_2 was the subject of ab iniitio calculations and simple models presented by Fabio Finocchi. Interestingly, the relaxation of the surface switched the sites of lowest Madelung energy from surface to subsurface, with an associated shift of the extra electron associated with Na adsorption. The correlation of shorter bond length with degree of covalency was made, so that the charge transfer could be simply modelled in terms of a linear combination of nearest neighbour bond lengths. This suggested a promising semi-empirical ionic model with variable charge transfer. A simple semi-empirical model was presented by Jacek Goniakowski to describe the Pd-MgO interaction, assuming a rigid oxide substrate. This enabled the energetics to be surveyed of a large range of cluster sizes and morphologies, providing a useful database for analysing and comparing with experimental data. Ab-initio calculations for noble-metal clusters on ZrO_2 were presented on the poster of Maria Alfredsson. Ivan Oleinik showed results for Co(111) on alumina(0001) which showed the metal-metal bonds in this case can give greater adhesion than metal-oxygen bonds. He also showed the only calculations at the workshop on magnetic systems, using the local spin density approximation, with which he has investigated the transfer of magnetic moments into insulating spacer materials. An unexpected feature was the change in sign with depth, at about 1nm, of the net magnetic moment. How to go beyond periodic boundary conditions parallel to interfaces was syggested by Roy Benedek. The brute force approach of larger and larger supercells gets us some way. His 497 atom calculations of a misfit dislocation at the Cu/MgO interface go in that direction, and are the largest of their kind. However, with this approach it will never be possible to treat general or irrationally incommensurate boundaries in a direct way. A possible alternative which is being explored is to use the short period ab initio calculations to provide a set of data on unstable or metastable interface structures. Real interfaces might then be built of an appropriate linear combination of such building blocks. It remains to be tested how well they prove able to deal with the regions of misfit and even inhomogeneous misfit, for example as a boundary structure changes from 'atom on atom' to 'atom on hollow' configurations. With the approaches under discussion for treating larger systems, one sometimes forgets the inherent errors in GA and LDA approaches that still leave us with considerable uncertainties in even the best calculations for periodic structures. Some of the boundary energies reported (Don Siegel) showed that LDA results can be up to about 30% higher than GGA. For calculating properties at non-zero temperature, statistical mechanical properties must be taken into account. One line of attack is to calculate vibrational frequencies and obtain quasi-harmonic free energies. Kersti Hermannson in her talk and Arnaud Marmier (in a poster) showed how this can be done for surfaces both with classical potential models and with LDA. The other statistical mechanical aspect, more difficult to treat, is configurational entropy. It manifests itself firstly in the bulk properties which are subtracted to calculate surface excess quantities, that is in the chemical potentials of the components, including the role of p_{O_2}. This aspect is actually rather straighforward to calculate in comparison to the configurational entropy of defects or local structures at the boundary itself. Monika Backhaus in her talk showed how she has estimated the contribution of the latter within a regular solution model. One needs to define a reference structure of relatively short period, on which various defects may form which constitute the actual structure. This approach is limited to defects which conserve lattice sites. One talk gave us a glimpse of the dynamics of interfaces: their formation, coalescence and reorientation, within a model which is far from atomistic. This was Craig Carter's contribution on the phase-field approach to materials modelling. The challenge to atomistic theory was actually to build a theory which links such a model to atomic scale quantities that can be calculated. Since these kinds of models of materials may be unfamiliar to electron theorists, for anyone interested the basic idea, based on Michael Finnis' notes taken during Craig Carter's talk, are summarised in an appendix to this report.

Closing Discussion

The closing discussion was lively. We structured it under two headings:

- What can the experimentalists do to guide theory, eg. by providing more results on model systems?
- How can the theorists be more realistic and useful in their choice of systems or methods of calculation?

The first topic was rather shortly dealt with, but an important point was made. Namely, that there is a convergence between what used to be called model systems (simple crystals with perfect interfaces), and systems of practical interest at the nanoscale. The second point provoked more discussion and questioning of the theorists by the experimentalists. An issue which arose again, as it did during the talks and at the posters, was how we can deal with the effect of p_{O_2}, which often seems important in practice. It raised the topic of the various statistical mechanical approaches to calculating the free energy of real interfaces. Rather large scale ab initio calculations will be necessary, but an approximate scheme based on the segregation energy of oxygen to a boundary is feasible. It requires the calculation of all the configurations and stoichiometries of the boundary which might reasonably be expected to occur, or at least a good sample of them, in the manner of some recent work by our own groups and others. Apart from this various other discussion points were revisited, so that everyone felt that they had had a chance to air their 'wish-lists'. See also the comments below.

Comments of Participants

We invited participants to contribute any constructive comments and criticisms in writing.

From Dr. Mike Bennett, a materials research consultant:

“In my field of research, the corrosion of high temperature metals/alloys, the microchemistry and microstructure of metal-oxide interfaces are crucial parameters governing alloy lifetimes in industrial service. In fact it is now clearly apparent that alloy lifetime extensions, currently required by developing technologies, can only stem from optimisation of minor alloy constituents (additives as well as impurities) and detailed understanding of their role in improved metal-oxide and oxide-oxide interface properties. The first CECAM workshop, bringing together theoreticians and experimentalists working in this area, proved most opportune in timing as far as my research interests were concerned. Further such dialogue between researchers from these disciplines should be both widened and encouraged.”

From Dr. Maria Alfredsson, a theoretician:

“The idea of bringing together experimentalists and theoreticians on the subject ’Metal-Oxide Interface’ was excellent and I believe it was very useful to listen to presentations on experimental work as well as the resulting discussions. It was also very useful to listen to other groups working with different computational techniques on the subject. I think the idea of having an ’on-going’ poster session during coffee breaks was a very good idea, which resulted in many useful discussions. However, I am disapointed that a few experimentalist left after the second day and that a few theoreticians arrived not until the second day. I also hoped that the concluding discussion would have merged the two communities closer. Now the experimentalist asked many questions to the theoreticians but not the opposite. On the other hand, this is probably not a major problem but something that was taken care of in the lively discussions during coffee breaks and dinners. In conclusion this was a very succesful workshop, bridging the two communities.”

From Dr. Roy Benedek, a theoretician:

“The objective of this workshop was to bring together experimentalists as well as theorists interested in the modeling of oxide-metal interfaces. I believe that the idea of including experimentalists in such a workshop was worthwhile for at least two reasons: (i) the field of real-interface simulation is strongly coupled to practical applications, and (ii) arguably, the value of such simulations will increasingly be judged by how well they can address the challenge of the applications. My impression is that the meeting was successful. Those doing simulation were informed about the technologically important interfaces in the fields of sensors, integrated circuit design, supported catalysts, and structural alloys, while experimentalists were informed about state of the art simulations based on MD, first-principles, and other approaches. The discussion was lively, and the experimentalists encouraged the simulators to address the full complexity of the relevant systems, including particularly the effect of oxygen partial pressure variation. As in any such workshop, there were several organizational issues that could possibly be fine-tuned, such as the optimal ratio of theoretical to experimental contributions, the juxtaposition of theoretical and experimental presentations in the program, the time allocated to general discussion, and the length of the meeting. All of these questions, as well as others, could be debated at great length, and it is not my purpose to do so here. Just a few somewhat random comments: Any detailed critique of the program would need to take into account the three participants who were forced to cancel at the last moment, because of unique external circumstances. Most of the speakers appeared to prepare presentations that ran well over the 25 minute timeslots, which cut into discussion time. It would perhaps have been better to insert some of the theory presentations after experimental talks on the same subjects. In retrospect, it appears that a slightly longer meeting would have been beneficial in order to allow discussion of future directions to be carried a little further. The hall used for the poster session had excellent lighting, but the acoustics and traffic flow were less than optimal. However one judges these points, they do not detract from the overall success of the meeting."

From Dr. Dominique Chatain, experimentalist:

"Some talks have detailed the needs and the challenges of understanding these oxide-metal interfaces. This is a very important aspect which is rarely included in such a meeting. The experimental talks were dealing with different systems: real and model ones. The real systems need experimental studies which should deal with the complexity of the studied materials. The talks about these systems showed very smart approaches. The model systems are studied from two points of view: energetic (thermo scale) and structure (TEM Scale). They are complementary and (in my opinion) have to find a way of converging: Acquisition of energetic data are needed for checking the models. Measurement of the work of adhesion requires the melting of the metal, what means high temperature and consequently, activation of diffusion (or/or reaction)processes. Because of the intrinsic impurity of the oxide (Al2O3 always contains some ppm of Si,Ca,Mg,...) we do not know about the exact chemistry which takes place at the interface (segregation of CaO or other oxide is probable) and I am not sure about the "chemical" meaning of the contact angle measured. What we know the best is about the RELATIVE effect of p_{O_2}. On the other hand the TEM people can control the chemistry by performing deposition of the metal after cleaning the oxide. They get the atomic structure but questions remain about the equilibrium of the atomic structure of interfaces.

It seems to me that these two approaches have to converge. One way is to use small particles of one phase (metal or oxide), to measure the solid wetting and to look at the structure in a TEM. The equilibrium shape of such particles can be achieved even at low temperature, keeping the interface "chemically controlled". The energetic data could come from the knowledge of the surface energy of the solid metal and the vapour phase composition (p_{O_2}, p_{H_2O}?....).

As discussed at the end of the meeting, the simulation talks pointed to several important features:

- the stoichiometry of the oxide interface (and surface) or in other words the p_{O_2}.
- the misfit and the " forced" epitaxy role of the interfacial energy
- the order, chemistry and width of the interfacial zone
- the state of the element of the system (oxygen in the oxide or in solution in the metal)
- the requirement of mixing several type of calculations
- the difficulty of having a "good" potential on both sides and a large quantity of atoms.

To conclude, I went back to Marseille with a lot of questions but with the positive feeling of convergence "entre personnes de bonne volonte"."

Appendix: Phase-field model (Level Sets)

The approach to materials modelling which Craig Carter described is phenomenological in nature. This model can be applied to simulate an entire sequence of events in an alloy, from precipitation to grain growth. It is exciting, but the challenge is to give it some quantitative basis in atomistic theory! For those unfamiliar with the approach, I summarize from my notes here, believing I have understood at least the flavour of it and with apologies for my misrepresentations and errors. The basic equation for describing the advance of a boundary is

$$\frac{\partial \phi}{\partial t} = -\frac{1}{\tau}\frac{\partial F}{\partial \phi} \tag{1}$$

where ϕ is a phase field, t is time, F is a free energy function and τ is a timescale. The free energy function takes the form

$$F = \int [f(p, T, \phi, params)]. \tag{2}$$

The phase field can be a concentration or the indicater of which phase we are in. Eg. $\phi = -1$ for precipitate, $\phi = 1$ for matrix. The $\phi = 0$ surface (the level set) defines the phase boundary. To deal with crystal grains a vector formulation is required. The simplest possible scalar model, which is very easy to program, is Landau:

$$F = \int [f(\phi)]\, dV \tag{3}$$

However, all that happens in his model is that an initially smeared out boundary becomes sharp. The second simplest model is Landau–Ginzburg

$$F = \int [f(\phi)]\, dV + g \int |\nabla \phi|^2\, dV \ . \tag{4}$$

This gives nice pictures of second phase precipitation but no anisotropic effects. To include anisotropic effects a second order–parameter is required. Say η. Now it gets tricky because the free enery must be rotationally invariant, so it is not good simply to give η the orientational symmetry of a crystal. Consider the energy of a grain boundary. η should vary smoothly from one side to the other, with a $|\nabla \eta|$ term to smooth out the transition. One might think of ϕ as a complex number in 2D, but we want to do 3D problems. Craig showed a formulation in which η does not enter the first term in Ginzburg–Landau but only the second. This enables the free energy to be rotationally invariant. The other critical thing seems to be that you need an energy which is linear in $\nabla \eta$, reminiscent of (but in no way derivable from!) the energy of a gamma surface near a cusp. In Craig's formulation there is a scalar order parameter ϕ which somehow represents the crystalline order, whose gradient tells you how close you are to a grain boundary. This factor multiplies a $|\nabla \eta|$ term, so you get a term like (as far as I remember) $g|\nabla \phi|\,|\nabla \eta|$. The fascinating question is that, although this kind of model gives strikingly realistic pictures, eg. of second phase nucleation and growth, followed by coalescence and grain growth, there is no theory which derives it by coarse graining from a more elementary theory! It is easy to see how to extend the model in a phenomenological way, with other parameters, eg to describe segregation of impurities to the boundaries. But none of the basic parameters can yet be derived from theory.

(Notes by Michael Finnis taken during Craig Carter's lecture)

List of participants

Alfredsson, Maria	mariaa@ri.ac.uk
Backhaus, Monika	monika.backhaus@glvt-cnrs.fr
Benedek, Roy	benedek@anl.gov
Bennett Mike	c/o: s.l.mcguire@cranfield.ac.uk
Carter, Craig	ccarter@pruffle.mit.edu
Chatain, Dominique	chatain@crmc2.univ-mrs.fr
Cheynet, Marie	mcheynet@ltpcm.inpg.fr
Classen, Thomas	classen@marvin.mpi-stuttgart.mpg.de
Elliott, Simon	simon.elliott@nmrc.ie
Elsässer, Christian	elsaesser@mf.mpg.de
Eustathopoulos, Nicolas	nikos@ltpcm.inpg.fr
Fabio Finocchi	finocchi@lps.u-psud.fr
Fahmi, Adil	adil.fahmi@hydro.com
Finnis, Mike	m.finnis@qub.ac.uk
French, Roger	roger.h.french@usa.dupont.com
Ghetta, Veronique	veronique.ghetta@ltpcm.inpg.fr
Giorgio, Suzanne	giorgio@crmc2.univ-mrs.fr
Goniakowski, Jacek	jacek@crmc2.univ-mrs.fr
Hermansson, Kersti	kersti@kemi.uu.se
Hoffmann-Eifert, Susanne	Su.Hoffmann@fz-juelich.de
Hou, Peggy	pyhou@lbl.gov
Junquera, Xavier	javier.junquera@uam.es
Jupille, Jaques	jupille@ext.jussieu.fr
Kohlstedt, Hermann	h.h.kohlstedt@fz-juelich.de
Kotomin, Eugene	eugene.kotomin@fkf.mpg.de
Lindan, Philip	p.lindan@ukc.ac.uk
Marmier, Arnaud	a.marmier@qub.ac.uk
Noguera, Claudine	noguera@lps.u-psud.fr
Ochs, Thorsten	thorsten.ochs@de.bosch.com
Oleinik, Ivan	ivan.oleinik@materials.ox.ac.uk
Renaud, Giles	grenaud@cea.fr
Scheu, Christina	scheu@hrem.mpi-stuttgart.mpg.de
Seidman, David	d-seidman@northwestern.edu
Siegel, Don	d-siegel@uiuc.edu
Tomsia, Tony	aptomsia@lbl.gov
Waser, Rainer	waser@we.rwth-aachen.de

4.1.2 Report on DFT Workshop in Spain

9th International Conference on the Applications of the Density Functional Theory in Chemistry and Physics

September 10-14, 2001

San Lorenzo de El Escorial, Madrid, Spain

The 9th International Conference on the Applications of the Density Functional Theory in Chemistry and Physics (DFT 2001) was held in San Lorenzo de El Escorial, a picturesque village and an important historical site near to Madrid from September 10 to 16, 2001. This is the 9th in a Series of successful Conferences, and follows recent ones that took place in Paris (1995), Wien (1997) and Roma (1999).

The Conference was sponsored by the ESF Psi-K Program, EC Cost Action D9, Universidad Autónoma de Madrid, Universidad Politécnica de Madrid, Universidad de Cantabria, Escuela Técnica Superior de Ingenieros de Telecomunicación de Madrid, European Physical Society and Ministerio de Ciencia y Tecnologia (Spain).

The Conference was devoted to a broad and balanced overview of new results, emerging trends and perspectives pertaining to the applications of Density Functional Theory to Chemistry and Physics. The main topics covered by the Conference were new and recent advances on:

-Methodological developments. New exchange-correlation and kinetic energy functionals. Excited states.

-Computational advances. New codes.

-Isolated systems: molecules, reactivity, dynamics, small clusters.

-Condensed phases: mesoscopic systems, solids, assembled materials.

-Complex molecular systems: biomolecules, molecular materials.

-Electric and magnetic properties.

The Conference was divided into 3 poster sessions and 13 oral sessions covering a number of topical areas: 3 devoted to Fundamentals Aspects of DFT, 3 to Applications to Chemistry, 3 to Applications to Physics, 3 to Applications to Complex Systems and 1 to Van der Waals Interactions. A total of five Plenary conferences (one each day), 20 Invited Talks, 13 Oral communications were developed and 207 Posters were presented. The number of participants was of 238 coming from 31 countries all over the world. A number of grants (61) covering full and/or a part of lodging and registration fees were conceded. This fact was possible by the help of the sponsors. Communication with speakers and participants was managed by e-mail and the DFT2001 web page (http://www.uam.es/dft2001), containing all the information about the Conference and abstracts of the talks.

The usefulness of the DFT2001 was highly appreciated by most participants. The symposium gave a good overview of the state of the art. It was evident that considerable progress has been made in this area in last years and that much more can be expected in the near future. As a conclusion, we believe that this Congress has been a wonderfully rich conference, where excellent talks and posters have presented. A good balance between physics and chemistry was attained in a quiet and beautiful place (Colegio Maria Cristina behind the Monastery de El Escorial) and with a fine weather.

The main problems discussed into the Conference were DFT plus kinetic Montecarlo method, methods devised to treat systems in the non-scalable regime, the time-honored standard model, applications to the determination of electronic and structural properties of molecules, development and application of order-N DFT (linear-scaling DFT), improvements on the Car-Parrinello QM/MM simulation method, orbital-free molecular dynamic method, methods devised to treat large molecules in solution, internal coordinate method, DFT-based extensions to treat 4f crystal fields levels, a time-dependent DFT method for the treatment of molecular wires, the problem of nuclear motion in DFT, concepts related to information theory, the problem of exchange, the problem of van der Waals interactions, the nature of the non-interacting kinetic energy functional.

The Organizing Committee.

Committees

SCIENTIFIC COMMITTEE:
E.J. Baerends (Amsterdam, The Netherlands)
R. Car (Princeton, USA)
P. Fantucci (Milano, Italy)
P. Geerlings (Brussels, Belgium)
E.K. Gross (Wurzburg, Germany)
N.C. Handy (Cambridge, UK)
S.G. Louie (Berkeley, USA)
B.I. Lundqvist (Goteborg, Sweden)
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LOCAL ORGANIZING COMMITTEE:
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B. Miguel (Universidad Autónoma de Madrid)
A. Zarzo (Universidad Politécnica de Madrid)

Invited speakers

E. Artacho (Cambridge, UK)
R. Baer (Jerusalem, Israel)
R. Bartlett (Florida, USA)
V. Barone (Napoli, Italy)
E.A. Carter (Los Angeles, USA)
M.E. Casida (Montreal, Canada)
M.L. Cohen (Berkeley, USA)
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R. Godby (York, UK)
A. Goerling (Munchen, Germany)
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E.K. Gross (Wurzburg, Germany)
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U. Rothlisberger (Zurich, Switzerland)
A. Rubio (San Sebastian, Spain)
A. Savin (Paris, France)
M. Scheffler (Berlin, Germany)
J. Schofield (Toronto, Canada)
M. Teter (Cornell, USA)

Proceedings

A special issue of the *International Journal of Quantum Chemistry* (Wiley) will be published with a selection of accepted papers.

Programme

MONDAY SEPTEMBER 10th

9.00 - 9.25 Opening

Morning Session I: Fundamental Aspects of DFT - I (Chairman: M. Moreno)

9.25 - 10.15 Plenary Conference 1 (Robert G. Parr, University of North Carolina): Information Theory and the definition of atoms in molecules.

10.15 - 10.55 Invited Talk 1 (E. K. U. Gross, University of. Würzburg): Density functional theory beyond the Born-Oppenheimer approximation.

10.55 - 11.20 Break

Morning Session II: Applications to Complex systems - I (Chairman: A. Bencini)

11.20 - 12.00 Invited Talk 2 (Vincenzo Barone, University of Napoles):New perspectives in the study of large systems in condensed phases by DFT methods.

12.00 - 12.40 Invited Talk 3 (Angel Rubio, University of the Bask Country): Electronic and atomic properties of nanotubes from first principles.

12.40 - 13.05 Oral Communication 1 (T. Krüger, Universitt Graz): Microstructure of local defects in amorphous Si:H. A DFT- based QM/QM study.

13.05 - 15.30 Lunch

Afternoon Session: Applications to Chemistry - I (Chairman: H. Chermette)

15.30 - 16.10 Invited Talk 4 (Rodney Bartlett, University of Florida): Ab initio DFT.

16.10 - 16.50 Invited Talk 5 (Jeremy Schofield. University of Toronto): Efficient ab- initio calculations of kinetic isotope effects in intramolecular proton transfer reactions.

16.50 - 17.15 Oral Communication 2 (David J. Tozer, University of Durham): The calculation of magnetic and electrical molecular properties from theoretical electron densities.

17.15 - 17.35 Break

17.35 - 19.15 Poster Session A

TUESDAY SEPTEMBER 11th

Morning Session I : Applications to Complex Systems - II (Chairman: N.C Handy)

9.00 - 9.50 Plenary Conference 2 (Uzi Landman, Georgia Institute of Technology): Symmetry breaking, dynamics and reactivity of Nanosystems.

9.50 - 10.30 Invited Talk 6 (Emilio Artacho, Cambridge University): Linear scaling DFT applied to dry DNA.

10.30 - 10.55 Oral Communication 3 (J. Andzelm, Molecular Simulations Inc): Efficient algorithms to study chemical processes of large systems with DFT.

10.55 - 11.20 Break

Morning Session II: Fundamental Aspects of DFT - II (Chairman: D. Salahub)

11.20 - 12.00 Invited Talk 7 (Andreas Savin, University Pierre and Marie Curie): Adiabatic connections.

12.00 - 12.40 Invited Talk 8. (O. Gritsenko, University of Amsterdam): Effect of the Pauli and Coulomb repulsion on the exchange-correlation potential:a landscape with steps, peaks, counter dissociation and counter-field ultra- nonlocal terms.

12.40 - 13.05 Oral Communication 4 (J. Ortega, Universidad Autónoma de Madrid): Exchange-

correlation energy as a function of the orbital occupancies: Implementation of first-principles Local Orbital methods.
13.05 - 15.30 Lunch
Afternoon Session: Applications to Physics - I (Chairman: V. Sidis)
15.30 - 16.10 Invited Talk 9 (Paul Madden, University of Oxford): A study of metallic phase equilibria using orbital-free Ab initio Molecular Dynamics.
16.10 - 16.50 Invited Talk 10 (Jose Luis Martins, Instituto Superior Tecnico de Lisboa):Simulation of simple liquid metals and their alloys.
16.50 - 17.15 Oral Communication 5 (Patrizia Calamicini, CINVESTAV, México): Photoelectron spectra simulation of V3 and V3O from Density Functional calculations.
17.15- 17.35 Break
17.35- 19.15 Poster Session B

WEDNESDAY SEPTEMBER 12th

Morning Session I: Van der Waals interactions (Chairman: R.G. Parr)
9.00 - 9.50 Plenary Conference 3 (Walter Kohn, University of California at Santa Barbara) : Generalized Van der Waals theory using TD-DFT.
9.50 - 10.30 Invited Talk 11 (Bengt Lundqvist, Chalmers Institute of Technology Gotteborg): Density functionals incorporating Van der Waals interactions at long range.
10.30 - 10.55 Oral Communication 6 (Pablo García-González, UNED Madrid): Study of quasi-two-dimensional electron systems and Van der Waals forces using the GW approximation.
10.45 - 11.20 Break
Morning Session II: Applications to Physics II (Chairman: E. Ludeña)
11.20 - 12.00 Invited Talk 12 (Andreas Görling, Technical University Munich): Exact exchange methods for molecules and solids.
12.00 - 12.40 Invited Talk 13 (Michael Teter, Cornell University): Advantages and disadvantages of potential based density functional.
12.40 - 13.05 Oral Communication 7 (M. Colaretti-Tosti, Uppsala University): Crystal field levels by means of density functional Theory.
13.05 -15.30 Lunch
15.30 Excursion to Segovia

THURSDAY SEPTEMBER 13th

Morning Session I: Applications to Complex systems - III (Chairman: P. Geerlings)
9.00 - 9.50 Plenary Conference 4 (M. Scheffler, Fritz-Haber Institut Berlin): The role of the environment (beyond T=0 K and P=0 Pa) on the composition of surfaces and the function of materials.
9.50 - 10.30 Invited Talk 14 (U. Rothlisberger, ETH Zurich) : QM/MM Car- Parrinello Simulations of Enzymatic Reactions in Ground and Excited States.
10.30 - 10.55 Oral Communication 8 (Lothar Fritsche, University of Clausthal): A DFT-consistent solution to the gap problem of antiferromagnetic metal oxides and parent compounds of high-Tc superconductors.

10.55 - 11.20 Break

Morning Session II: Applications to Physics - III (Chairman: L.C. Balbás)

11.20 - 12.00 Invited Talk 15 (Marvin L. Cohen, University of California at Berkeley): Recent applications of the plane wave pseudopotential method.

12.00 - 12.40 Invited talk 16 (Roi Baer, University of Jerusalem): Real time electron dynamics in molecular wires using the time dependent density functional theory.

12.40 - 13.05 Oral Communication 9 (A. Bergara, University of the Bask Country): Magnetic instability in polymeric light-alkali chains.

13.05 - 15.30 Lunch

Afternoon Session: Applications to Chemistry - II (Chairman: S. Trickey)

15.30 - 16.10 Invited Talk 17 (Emily Carter, University of California at Los Angeles): Chemical degradation and protection of metal surfaces.

16.10 - 16.50 Invited Talk 18 (R. Nalewajski, University of Krakow): The information theoretic termodynamics of molecules and their fragments.

16.50 - 17.15 Oral Communication 10 (V. Van Speybroeck, University of Gent): Ab initio static and dynamic molecular simulations on elementary radical reactions in the coke formation.

17.15 - 17.35 Break

17.30 - 19.00 Posters Session C

20.30 Congress Dinner

FRIDAY SEPTEMBER 14th

Morning Session I: Fundamental Aspects of DFT - III (Chairman: E.K. Gross)

9.00 - 9.50 Plenary Conference 5 (Rex Godby, University of York): Ab initio total energies from many-body perturbation theory.

9.50 - 10.15 Oral Communication 11 (S. Kurth, Lund University): The time- dependent Talman-Shadwick scheme applied to atoms and solids.

10.15 - 10.40 Oral Communication 12 (M. Seidl, Universitt Regensburg) : Density Functional Theory from the extreme limits of correlation.

10.40 - 11.05 Oral Communication 13 (T. S. Van Erp, Universiteit vam Amsterdam) : Ab initio molecular dynamics study of the acid- catalyzed hydration of ethylene in aqueous solution.

11.05 - 11.30 Break

Morning Session II: Applications to Chemistry - III (Chairman: J.Weber)

11.30 - 12.10 Invited Talk 19 (M. Casida, University of Montreal): Molecular applications of the optimized effective potential.

12.10 - 12.35 Invited Talk 20 (C. Daul, University of Fribourg): Photochemical and photophysical properties of coordination compounds: a DFT study.

12.35 - 13.10 Concluding Remarks (E. Ludeña, IVIC, Caracas)

13.10 Lunch

16.00 Visit to the Monastery

http://www.uam.es/dft2001

4.1.3 Report on the CECAM/ESF Local Orbitals Workshop

Report on the CECAM/ESF STRUC-Ψ_k Workshop on Local Orbitals and Linear-scaling *ab initio* Calculations

Summary of Workshop

A total of 33 participants from 8 countries attended the workshop from 3 to 7 September 2001. 22 talks covered a wide range of topics from new technical developments to applications of local orbital-based methods.

The presentations and subsequent discussions ranged over five areas:

Atomic type orbitals

The workshop began with an introductory talk given by Pablo Ordejón, reviewing some of the ideas which arose from the CECAM workshop in 1998 on “Local Orbital Methods for Large Scale Atomistic Simulations”, and the progress which has been made in the field since then. The remaining talks on the first day concerned the use of *numerical* atomic type orbitals. Gotthard Seifert and Javier Junquera discussed the use of confining potentials to suppress the long-range tails and thus obtain *local* orbitals. Steven Kenny presented a different approach based upon maximizing the overlap of the Hilbert spaces spanned by the local orbitals and the Kohn-Sham wavefunctions. Stan van Gisbergen described recent improvements in the scaling of calculations based on Slater type orbitals.

Gaussian type orbitals

The second day focussed on the use of Gaussian type orbitals. Roberto Dovesi and Gustavo Scuseria described the advantages of such basis sets for *ab initio* calculations on periodic as well as molecular systems. Jürg Hutter and Martin Head-Gordon presented linear-scaling methods for building Hamiltonian matrices, including fast multipole methods and the use of auxiliary basis sets for the electronic density. Peter Reinhardt also described how Epstein-Nesbet perturbation theory may be employed to study localization. One issue which arose in discussion was that of obtaining sparse matrices when using numerical atomic type orbitals and Gaussians. With the former, the orbitals are truncated at a particular radius so that matrix elements between non-overlapping orbitals are strictly zero and the sparsity pattern is predictable. With Gaussians however, bounds on the value of matrix elements are calculated first, and those below a certain threshold are subsequently neglected.

Systematic basis sets

The topic for the third day was the use of "systematic" basis sets. Jerzy Bernholc began by outlining the use of multigrid acceleration techniques when orbitals are represented on real-space grids, in which the most expensive steps scale linearly with system-size. Chris-Kriton Skylaris described a linear-scaling method for optimizing local orbitals based upon the use of fast Fourier transforms applied to smaller regions of space than the entire simulation cell. Philip Sterne presented the application of finite-element methods for solving the Schrödinger and Poisson equations in large-scale electronic structure calculations, and Stefan Goedecker explained the potential of wavelets as a basis set for linear-scaling calculations.

Linear-scaling methods

The fourth day was devoted to the development and application of linear-scaling methods. Mike Gillan described the relation between linear-scaling and the embedding problem, applied to point defects and surface reconstructions in silicon. Oswaldo Diéguez presented a new linear-scaling method for metals based upon using a fictitious electronic temperature to localize the density-matrix. Matt Challacombe outlined a linear-scaling algorithm for factorizing the overlap matrix which is needed for calculations based on non-orthogonal basis sets. Richard Martin presented results based upon simulations of high pressure phases of nitrogen using local orbital methods, and Weitao Yang described the divide-and-conquer linear-scaling method, as well as introducing a variational approach for obtaining non-orthogonal localized orbitals.

Linear-scaling applications and Wannier function analysis

Andrew Horsfield began the final day by presenting the results of density-functional calculations on cobalt in silicon using local orbitals. The last two talks both concerned methods for obtaining generalized Wannier functions from the results of traditional calculations. Alberto Bert described how Wannier functions can be constructed from wavefunctions expressed in terms of Gaussian type orbitals, and how they can be used to study the bonding and dielectric properties of materials. Ivo Souza presented a method for obtaining Wannier functions from entangled energy bands, and the results of applying this to silicon and copper.

Conclusions

This workshop proved to be a great success. The presentations covered the spectrum of different local orbital methods currently being used to develop linear-scaling schemes, and stimulated useful discussions, particularly between those approaching the field from the physics and chemistry communities.

The popularity of the workshop and the growing number of international groups working in this area suggest that another workshop or symposium at a larger conference should be held on this topic within the next three years.

Peter Haynes, *Cavendish Laboratory, University of Cambridge, UK*

David Bowler, *Department of Physics and Astronomy, University College, London, UK*

Emilio Artacho, *Department of Earth Sciences, University of Cambridge, UK*

List of Participants

Emilio Artacho	Universidad Autónoma de Madrid, Spain
Maxime Barrault	Ecole Nationale des Ponts et Chaussées, France
Alberto Bert	Università di Torino, Italy
Jerzy Bernholc	North Carolina State University, USA
David Bowler	University College London, UK
Eric Cances	Ecole Nationale des Ponts et Chaussées, France
Matt Challacombe	Los Alamos National Laboratory, USA
Oswaldo Diéguez	University of Cambridge, UK
Roberto Dovesi	Università di Torino, Italy
Julian Gale	Imperial College London, UK
Mike Gillan	University College London, UK
Stan van Gisbergen	Vrije Universiteit Amsterdam, The Netherlands
Stefan Goedecker	Commissariat à l'Energie Atomique, France
Peter Haynes	University of Cambridge, UK
Martin Head-Gordon	University of California at Berkeley, USA
Andrew Horsfield	Fujitsu European Centre for Information Technology, UK
Jürg Hutter	Universität Zürich, Switzerland
Javier Junquera	Universidad Autónoma de Madrid, Spain
Steven Kenny	Loughborough University, UK
Rouslan Kevorkiants	Die Mülheimer Max-Planck Institut, Germany
Richard Martin	University of Illinois at Urbana-Champaign, USA
Arash Mostofi	University of Cambridge, UK
Gana Natarajan	University of Cambridge, UK
Pablo Ordejón	Institut de Ciència de Materials de Barcelona, Spain
Chris Pickard	University of Cambridge, UK
Peter Reinhardt	Université Paris VI, France
Gustavo Scuseria	Rice University, USA
Gotthard Seifert	Universität Paderborn, Germany
Chris-Kriton Skylaris	University of Cambridge, UK
Ivo Souza	Rutgers University, USA
Philip Sterne	Lawrence Livermore National Laboratory, USA
Mike Towler	University of Cambridge, UK
Weitao Yang	Duke University, USA

Programme

Speakers gave 30 minute talks, followed by 15 minutes for questions and discussion.

Monday, 3 September		
Chair:	**Richard Martin**	**Atomic type orbitals**
9.30	David Bowler	Welcome and opening remarks
9.40	Pablo Ordejón	Introduction to Local Orbitals and Linear-scaling *ab initio* Calculations
10.15	Gotthard Seifert	Optimized Atomic Orbitals for Solid State and Molecular Density-Functional-based calculations
11.00		Coffee
11.30	Steven Kenny	Transferable Atomic Type Orbitals
12.15	Javier Junquera	Optimized Numerical Atomic Orbitals for Linear-Scaling calculations
13.00		Lunch
14.30	Stan van Gisbergen	Linear scaling and parallelization in ADF
15.15		Coffee
15.30		Discussion
16.30		Close

Tuesday, 4 September		
Chair:	**Gotthard Seifert**	**Gaussian type orbitals**
9.30	Roberto Dovesi	Periodic *ab initio* calculations with the CRYSTAL program. Recent improvements.
10.15	Jürg Hutter	Reducing Prefactors in Linear Scaling DFT Calculations
11.00		Coffee
11.30	Gustavo Scuseria	Linear Scaling Electronic Structure Methods Based on Gaussian Orbitals
12.15	Peter Reinhardt	Useful aspects of Epstein-Nesbet perturbation theory
13.00		Lunch
14.30	Martin Head-Gordon	Some Recent Developments in Linear Scaling Methods using Gaussian Orbitals
15.15		Coffee
15.30		Discussion
16.30		Close

Wednesday, 5 September		
Chair:	**Pablo Ordejón**	**Systematic basis sets**
9.30	Jerzy Bernholc	Grid-optimized localized orbitals and nearly $O(N)$ *ab initio* calculations of quantum conductance
10.15	Chris-Kriton Skylaris	Optimisation of nonorthogonal generalised Wannier functions during order-N DFT calculations with plane-waves
11.00		Coffee
11.30	Phil Sterne	A Finite-Element Approach to Large-scale Electronic Structure Calculations
12.15	Stefan Goedecker	Wavelets, a potentially interesting basis set for $O(N)$ electronic structure calculations
13.00		Lunch
14.30		Discussion
15.30		Close

Thursday, 6 September		
Chair:	**Julian Gale**	**Linear-scaling methods**
9.30	Mike Gillan	Linear-scaling and its relation with the embedding problem
10.15	Oswaldo Diéguez	$O(N)$ calculations in metals with the finite temperature method
11.00		Coffee
11.30	Matt Challacombe	On the linear scaling computation of orthogonality transformations with Gaussian-Type Atomic Orbitals
12.15	Richard Martin	Simulation of High Pressure Phases of Nitrogen using SIESTA
13.00		Lunch
14.30	Weitao Yang	Linear Scaling Approaches with the Divide-and-Conquer Method and with Localized Orbitals
15.15		Coffee
15.30		Discussion
16.30		Close

Friday, 7 September		
Chair:	**Mike Gillan**	**Linear-scaling applications and Wannier function analysis**
9.30	Andrew Horsfield	A DFT study of Co on Si(001)
10.15		Coffee
10.45	Alberto Bert	Electronic structure characterization of crystalline compounds through their localized Wannier Functions
11.30	Ivo Souza	Maximally-localized Wannier functions for entangled energy bands
12.30		Close

Abstracts

Introduction to Local Orbitals and Linear-scaling *ab initio* Calculations

Pablo Ordejón
Institut de Ciència de Materials de Barcelona – CSIC, Spain

In July 1998, we organized a CECAM workshop on *Local Orbital Methods for Large Scale Atomistic Simulations.* At that time, there was renewed interest in the methods based in localized orbitals, from empirical tight-binding (TB) to accurate *ab initio* calculations. Part of the motivation of this interest was the realization that localization concepts provide a road towards *low complexity* electronic structure algorithms (by that meaning a low scaling of the computational workload involved). The workshop was devoted to a wide range of aspects, including TB parametrizations, applications of TB formulations, approximate density-functional theory (DFT) methods, fully self-consistent DFT calculations, quantum chemistry methods, linear-scaling algorithms and non-standard localized basis sets.

However, one of the key questions that arose was the issue of the optimal basis sets for exploiting the localization properties in *ab initio* electronic structure methods. Since that date, much work has been done in different lines, and this is the subject of the present meeting.

As a matter of introduction to this workshop, I will review some of the ideas that were discussed in the previous one, and advances made in the field since then.

Optimized Atomic Orbitals for Solid State and Molecular Density-Functional-based calculations

G. Seifert[1] and H. Eschrig[2]
[1] *Universität-GH Paderborn, Paderborn, Theoretische Physik, D-33095 Paderborn, Germany*
[2] *Institute for Solid State and Materials Research Dresden, P. O. Box D-01171 Dresden, Germany*

During the past about 20 years enormous progress has been made in the development of efficient methods of computations of molecules, clusters and solids within Density-Functional Theory (DFT). There is a lot of experience of the performance of exchange-correlation energy (E_{XC}) functionals, though from a 'first principles' point of view the status is still unsatisfactory. Although only approximate model density-functionals are known, even for their application work has to be done to improve the efficiency and numerical accuracy of the solution of the Kohn-Sham (KS) equations. Nowadays, local orbital basis sets for the KS-orbitals are widely used in DFT methods. Atomic orbitals (AO's) and their modifications, though they have been used since the early days in the quantum mechanical treatment of molecules and solids, are far from obsolete in the age of high performance computing of quantum mechanical many particle systems. Their advantages are clearly their physical meaning, allowing the smallest basis sets of all basis set based methods and their general suitability and flexibility, making them easily applicable for systems containing any type of atom of the periodic table. These advantages are contrasted by the cumbersome numerical handling and by the practical problems in basis set extensions for high energy excited states. For the highest accuracy demands the AO's are represented numerically on a radial mesh [1]. Numerical handling of the AO's can be much improved by the use of linear combinations of analytical functions as Gauss type functions (GTO) or Slater type functions (STO). The advantage of the STO's is their correct asymptotic behaviour on cost of a higher computational effort for the integral calculations, compared to GTO's. But usually the basis sets of STO expansions can be considerbly smaller than GTO expansions at the same level of accuracy.

We often use STO expansions of AO's (Φ_μ) in the form [2]:

$$\Phi_\mu = \sum_m^M \sum_n^N A_{mn} r^{n-l-1} e^{-\alpha_m r} Y_L$$

Y_L are the spherical harmonics, the α_m are chosen as a geometric series with $\alpha_1 \leq 1.0$ and $\alpha_M \sim Z$ (Z – nuclear charge of the atom), $M, N \leq 5$. Such representation gives AO's with a quality comparable to numerical AO's. The integrals can be calculated to a large extend analytically – see e.g. [3]. The representation of the ψ^{KS} in molecular and solid state calculations allows small basis sets:

$$\psi^{KS} = \sum_\mu C_\mu \Phi_\mu$$

down to minimal sets, considering the valence orbitals of the corresponding atoms, but treating the atomic core states as "thawed" core states with an valence-core orthogonalization between different centers in the system. The long range part of the valence AO's or polarization functions (unoccupied valence states) can be suppressed by using an additional artificial confinement potential (V_{cf}):

$$V_{cf} = \left(\frac{r}{r_0}\right)^{n_0}.$$

In practice $n_0 = 2, 4$ are used. For close packed solids $r_0 \sim r_{WS}$ (r_{WS} – Wigner-Seitz radius) and for molecules and less dense packed solids $r_{WS} \leq r_0 \leq 2r_{cov}$ (r_{cov} – covalent radius of the atom) have been found as optimal choices. In principle r_0 can be determined by variation to minimize the final total energy.

This concept of confined AO's can be applied to 'first principles' solid state as well as molecular calculations, but also for semiempirical DF-based schemes. Order-N type realizations have been realized also, as well as relativistic or semi-relativistic formulations for heavy atoms.

1. K. Koepernik and H. Eschrig, *Phys. Rev. B* **59**, 1743 (1999).
2. H. Eschrig, *Optimized LCAO Method and the Electronic Structure of extended Systems* (Springer, Berlin, 1989).
3. H. Eschrig, *phys. stat. sol. (b)* **96**, 329 (1979).
4. G. Seifert, D. Porezag and Th. Frauenheim, *Int. J. Quant. Chem.* **58**, 185 (1996).
5. M. Elstner, D. Porezag, G. Jungnickel, J. Elsner, M. Haugk, Th. Frauenheim, S. Suhai and G. Seifert, *Phys. Rev. B* **58**, 7260 (1998).

Transferable Atomic Type Orbitals

Steven Kenny
Department of Mathematical Sciences, Loughborough University, Loughborough, Leicestershire LE11 3TU, UK

Plane wave basis sets have a number of very useful features, one of these is their transferabilty across a range of bonding enviroments and another the fact that a single parameter, the cutoff energy, determines the convergence of the basis set in a straightforward and stable fashion. One of the great challenges for localised orbital basis sets is to achieve compact transferable basis sets which can also be scaled to give greater accuracy. Ideally we would like a suite of basis sets that take us from minimal basis sets, with reasonable accuracy through to fully converged basis sets. To do this we need to find some form of "optimal" basis set for a given accuracy which gives a similar accuracy when used in a wide range of bonding enviroments. We will present work [1] on producing optimal localised atomic type basis sets using the concept of spillage [2]. We have done this for C, Si and Al, which allows us to investigate these issues for systems that range from wide band gap semiconductor through conventional semiconductor through to nearly free electron metal. To test the transferability of the orbitals we looked at both a number of different structures within these materials and also at the description of SiC using the orbitals generated for bulk Si and C. We will also discuss the implementation of these localised orbital methods for transition metal systems.

The true test of any methodology is when it is employed to perform real calculations. We will look at how well the method performs when used to for calculations on two different systems, the problems that were encountered and the implications for the orbital optimisation. The two systems that we have investigated are the bonding of C_{60} to Si (100) [3] and the adhesion of Co on Si (100) [4]. Both these systems are large enough that the advantages of the localised basis sets over the plane wave basis sets both in cpu time and memory are considerable.

1. S. D. Kenny, A. P. Horsfield and H. Fujitani, *Phys. Rev. B* **62**, 4899 (2000).
2. D. Sánchez-Portal, E. Artacho and J. M. Soler, *Solid State Commun.* **95**, 685 (1995).
3. P. D. Godwin, S. D. Kenny and R. Smith, *Surf. Sci.* (accepted for publication).
4. A. P. Horsfield, S. D. Kenny and H. Fujitani, submitted to *Phys. Rev. B.*

Optimized Numerical Atomic Orbitals for Linear-scaling Calculations

Javier Junquera[1], Eduardo Anglada[1], Óscar Paz[1], Daniel Sánchez-Portal[2], José Soler[1] and Emilio Artacho[3]
[1]*Departamento de Física de la Materia Condensada, C-III, Universidad Autónoma, 28049 Madrid, Spain*
[2]*Departamento de Física de Materiales and DIPC, Facultad de Química, UPV, Apdo. 1072, 20080 San Sebastián, Spain*
[3]*Department of Earth Sciences, University of Cambridge, Downing Street, Cambridge CB2 3EQ, UK*

A requirement for linear-scaling calculations is the use of localized basis sets. Bessel functions, Gaussians [1-3], and real space grids [4] have been proposed, as well as strictly localized numerical pseudo-atomic orbitals (NAOs) [5]. The latter are the solutions of the one-dimensional radial Kohn-Sham pseudoatomic Hamiltonian under some confining constraint that makes them zero or negligible beyond some radii. These radii control the quality and the efficiency of the calculations. It is therefore important to find the radial shapes of the orbitals that optimize both the quality and the convergence cutoff-radius. Different confinement options proposed in the literature are analyzed, including confining potentials as $\left(\frac{\mathrm{r}}{\mathrm{r_c}}\right)^{\mathrm{n}}$ $(\mathrm{n} = 2, 6, \infty)$, [5-7] or direct confinement of the atomic wavefunctions [8,9]. They are compared with a new proposal that overcomes previous drawbacks [10]. Variational optimizations have been performed for the different schemes in different systems. The results are compared with fully converged plane-wave calculations on a significant variety of systems, including covalent, ionic and metallic. Optimal double-ζ plus polarization basis sets show very good agremeent with the plane-wave structural parameters and cohesion energies. The transferability of the obtained basis sets is tested in several cases and it is found to be satisfactory. A balanced way to define globally the confinement conditions for all the orbitals in a system is also presented, based on applying a fictitious pressure on the orbitals and then minimizing the corresponding enthalpy.

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Linear scaling and parallelization in ADF

S. J. A. van Gisbergen[1], C. Fonseca Guerra[2] and E. J. Baerends[2]

[1] *Scientific Computing & Modelling NV, Theoretical Chemistry / FEW, Vrije Universiteit, De Boelelaan 1083, 1081 HV, Amsterdam, The Netherlands*
[2] *Theoretical Chemistry / FEW, Vrije Universiteit, De Boelelaan 1083, 1081 HV, Amsterdam, The Netherlands*

The Amsterdam Density Functional (ADF) program [1] is based on Slater type orbitals and uses numerical integrations throughout. This has its consequences for the used algorithms, such as a density fit for the Coulomb potential, and subsequent evaluation of the Coulomb potential in the grid.

By straightforward distribution of the grid and atom pairs over processors an efficient parallelized version of ADF became available around 1997 [2]. A later project was concerned with removing the computational bottlenecks in the most time-consuming parts of the code: the calculation of the Kohn-Sham potential in the grid, the Fock matrix build, density fits, etc. This led to a near-linear scaling implementation [3], even though bottlenecks such as matrix diagonalization are still present. The description of the used techniques and applications to DNA can be found in C. Fonseca Guerra's thesis [4].

A third step involved the combination of the near linear scaling code with the parallelization. The problem here is the disturbed load balance, due to the fact that the computational weight of a block of grid points depends on its position in the molecule. To counteract this, the points were first localized using a space-filling curve, and then statically distributed according to an estimate for their weight. Using time-dependent DFT calculations as an example, it is demonstrated that good scaling with the number of CPUs and system size is obtained both for the SCF and for property calculations [5]. The talk summarizes these previous developments.

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Periodic *ab initio* calculations with the CRYSTAL program. Recent improvements.

R. Dovesi[1], R. Orlando[2], C. Roetti[1], V. R. Saunders[3], G. Mallia[1] and B. Civalleri[1]
[1] *Dipartimento di Chimica IFM, Università di Torino, via Giuria 5, I-10125 Torino, Italy*
[2] *Dipartimento di Scienze e Tecnologie Avanzate, Università del Piemonte Orientale "Amedeo Avogadro", c.so Borsalino 54, I-15100 Alessandria, Italy*
[3] *Daresbury Laboratory (CLRC), Daresbury, Warrington WA4 4AD, UK*

CRYSTAL [1] is a periodic *ab initio* program that expands the Crystalline Orbitals (CO) in Bloch functions built from local functions ("atomic orbitals", AOs). Each AO is a contraction of Gaussian Type Functions (GTFs), which in turn are the product of a Gaussian and a real solid spherical harmonic. It can treat systems periodic in one, two and three dimensions, and solve both the Hartree-Fock (HF) and Kohn-Sham (DFT) equations. All the most popular local and non-local exchange and correlation functionals can be used in any combination; also "hybrid" schemes, such as the so called B3-LYP, which combines the Hartree-Fock exchange term with the Becke [2] and Lee-Yang-Parr [3] functionals according to the formula proposed by Becke [4], are available.

The Coulomb infinite series are always evaluated analytically, by using for the long range interactions a scheme based on multipolar expansions, spherical harmonics and Hermite polynomial recursion relations and Ewald type summations.

In the DFT calculations two options are now available for the construction of the exchange-correlation matrix elements: either direct numerical integration or the use of an auxiliary basis set of GTFs in which the exchange-correlation potential is expanded. For the numerical integration, the atomic partition method proposed by Becke [5] has been adopted, combined with Gauss-Legendre (radial) and Lebedev (angular) quadrature.

A basis set of symmetry adapted crystalline orbitals (SACO's) is used for obtaining a block-diagonal representation of the Hamiltonian matrix at each **k**-point in reciprocal space, with a consequent reduction in computational time when large unit cell and high symmetry systems are considered [6-8]. In these conditions, it is possible to numerically optimise the geometry of complex structure at a relatively low cost. Recent improvements with respect to the public version of the code [1] include the evaluation of the analytic gradients of the HF Energy with respect to the internal coordinates [9-11] and the construction of well localised Wannier functions [12].

Three different examples will be discussed during the workshop:

(1) F-centre defects in LiF, by using supercells containing 8, 16, 32, 64, 128, 256 and 512 atoms; the geometry is optimised at the HF level; the convergence of the defect properties with respect to the defect-defect distance is documented.

(2) Perfect MgO supercells containing 2-512 atoms; it is shown that all the intensive properties are stable as a function of the supercell size; the scaling properties of the code are discussed.

(3) The optimisation of the structure of various zeolites with and without adsorbates.

The following tables and figure refer to the first example, treated at the HF level with a basis set containing 5 and 13 atomic orbitals/atom for Li and F, respectively.

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S_n	Li_{100}	F_{110}	Li_{111}	ΔE	E_{form}	N_{var}	N_{cyc}
8	–	–	–	-0.00000	0.25554	0	–
16	0.024	–	–	-0.00063	0.25481	1	5
32	0.039	0.013	0.000	-0.00103	0.25386	2	5
54	0.039	0.011	-0.003	-0.00105	0.25319	6	7
64	0.043	0.015	-0.003	-0.00115	0.25265	6	12
128	0.043	0.014	-0.004	-0.00122	0.25039	12	9
216	0.045	0.011	-0.005	-0.00124	0.24739	20	22
250	0.045	0.011	-0.004	-0.00128	0.24618	24	17
256	0.045	0.016	-0.004	-0.00149	0.24575	21	15

Table 1: Effect of relaxation for an F-centre in LiF as a function of supercell size S_n. In the Li_{100}, F_{110} and Li_{111} columns, the variation of the distances of the first three neighbors from the defect is reported; a positive value indicates larger distance. ΔE and E_{form} (in hartree) are the energy gain with respect to the unrelaxed geometry and the defect formation energy. N_{var} and N_{cyc} are the number of variables to be optimised and of optimisation cycles.

S_n	INT	SCF	GRAD	N_{cyc}	TOT_{cyc}
16	52.3	81.4	295.3	5	429.0
32	113.1	110.4	515.9	5	739.4
54	229.7	224.8	876.5	7	1331.0
64	308.4	220.1	1074.1	12	1602.6
128	764.4	656.2	2095.9	9	3516.5
216	1647.8	2127.2	3980.1	22	7755.1
250	1959.3	2660.8	4648.1	17	9268.2
256	2067.4	2540.8	4758.8	15	9367.0

Table 2: CPU time required for the evaluation of the bielectronic and monoelectronic integrals (INT), for the scf cycle (SCF) and for the analytical gradient (GRAD) as a function of the supercell size S_n on a *Pentium* III 1000MHz (256 KB cache) PC. In the N_{cyc} and TOT_{cyc} columns, the number of optimisation cycles and the total time for a cycle are reported. Data refer to HF calculations.

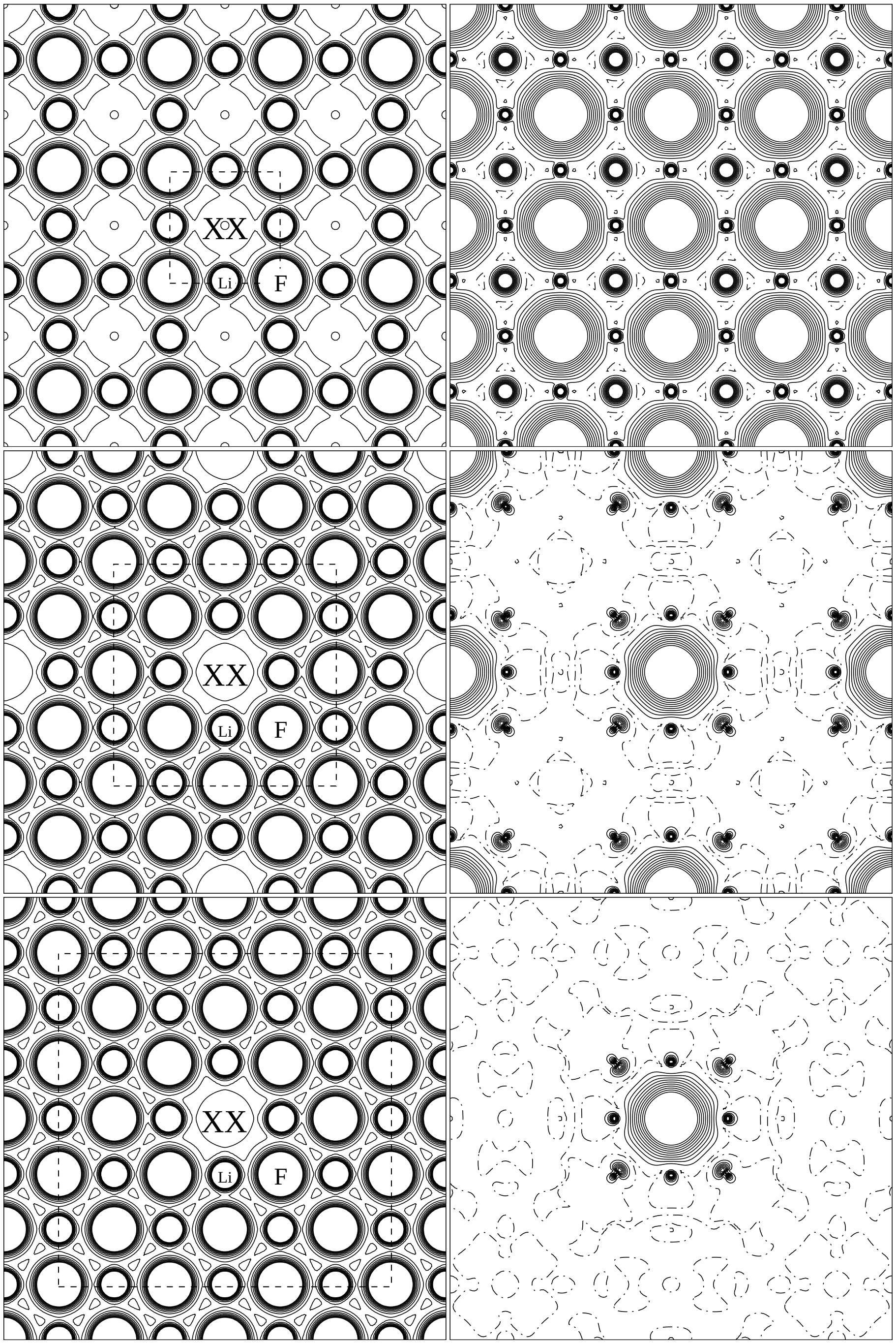

Figure 1: Electron charge (left) and spin (right) density of an F-centre in LiF, investigated at the HF level and using three different supercells: S_8 (top), S_{64} (middle) and S_{216} (bottom). The section is parallel to a (100) plane through the defect, labelled as XX. The dashed squares indicate the supercell sizes in the plane. The map side is 16.08 Ålong. The separation between contiguous isodensity curves is 0.01 and 0.001 e/bohr^3, for the electron charge and spin densities, respectively. The density range is 0.01/0.1 (left) and -0.01/0.01 (right) e/bohr^3; continuous, dashed and dot-dashed lines denote positive, negative, and zero values, respectively.

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Reducing Prefactors in Linear Scaling DFT Calculations

Jürg Hutter
Institute of Organic Chemistry, University of Zurich

In recent years progress has been made towards density functional calculations with computational costs proportional to system size [1]. The electrostatic problem is solved by fast multipole or fast Fourier/wavelet transform methods. Direct search methods for the density matrix and projection methods have replaced diagonalization of the Kohn-Sham matrix.

However, accuracy, numerical stability, and performance of these methods have to be further improved. We will discuss these items in connection with our implementation of the Gaussian and Augmented-Plane Wave (GAPW) method [2,3].

In the first part we will discuss two methods applied in the calculation of elements of the Kohn–Sham matrix. Most atomic orbital based methods use fast multipole methods [4,5] to achieve linear scaling in calculating electrostatics or make use of auxiliary basis functions to expand the electron density [6,7]. The GAPW method uses a special combination of all these methods together with techniques transfered from solid state calculations. In a first step projector techniques [8,9] are used to separate the electron density in atomic and interstitial contributions

$$n(\mathbf{r}) = \tilde{n}(\mathbf{r}) + \sum_I \left(n^I(\mathbf{r}) - \tilde{n}^I(\mathbf{r}) \right) ,$$

where n^I are densities localized on atom I. Using additional charge distributions with compensating multipole moments the electrostatic energy can be decoupled into non-interacting local terms and a single long-ranged contribution of a smooth charge distribution. The interaction energy of the core charges with the electron density and the core – core interactions are also included. This has a twofold advantage. In periodic systems two conditionally convergent sums are replaced by a single rapidly converging sum (the Ewald method) and the long-ranged part of the ionic core with the electronic density is handled together with the electron-electron interactions. Finally, the remaining long-ranged term is calculated using fast Fourier transform techniques, which can be interpreted as using an auxiliary basis of plane waves. Besides providing an overall linear scaling scheme, these methods greatly reduce the prefactor of the calculation by requiring only local nuclear attraction integrals and a much smaller plane wave cutoff. An all electron implementation was shown to be almost as efficient as pseudopotential calculations [10].

In the second part the problem of calculating the density matrix from a given Kohn-Sham matrix is discussed. Many different methods have been proposed to solve this task with linear scaling [1]. All of these methods suffer from the slow decay of off-diagonal matrix elements of the density operator. A problem greatly enhanced by ill-conditioned overlap matrices encountered in calculations with larger localized basis sets [11]. The polarized atomic orbital (PAO) method [12,13] provides a partial solution to these problems. However, the accuracy of the calculation is reduced. Test calculations and possible new fields of applications will be presented.

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Linear Scaling Electronic Structure Methods Based on Gaussian Orbitals

Gustavo E. Scuseria

Department of Chemistry, Rice University, Houston, Texas 77005-1892, USA

This presentation will address our recent efforts towards developing linear scaling electronic structure methods for the quantum mechanical modelling of large molecules and periodic systems, using Gaussian-type orbitals. In particular, we will discuss our recent advances in density functional theory methods and seconder-order perturbation theory (MP2). Time permitting, applications to fluorinated carbon nanotubes will be presented.

Useful aspects of Epstein-Nesbet perturbation theory

P. Reinhardt[1], J.-P. Malrieu[2]

[1]*Laboratoire de Chimie Théorique, Université Paris VI, 4 place Jussieu, F — 75252 Paris, France*

[2]*IRSAMC, Université Paul Sabatier, 118 route de Narbonne, F — 31062 Toulouse, France*

In Epstein-Nesbet perturbation theory several aspects of localization and delocalization can be studied. In canonical orbitals (completely delocalized) Epstein-Nesbet perturbation theory presents some defaults, which lead to the fact that nowadays the method is rarely employed. With respect to Møller-Plesset perturbation theory, Epstein-Nesbet perturbation theory needs Coulomb and Exchange integrals between hole-hole, hole-particle, and particle-particle pairs, which, when concentrated on only a few terms, lead to the inclusion of essential interactions found in CEPA-0 or MP4, but with much less effort. In canonical orbitals these integals are dispersed on many individual terms, and, compared to Møller-Plesset perturbation theory, no further correlation correction can be calculated in the limit of large systems. In order to obtain a useful method, a mixture of Møller-Plesset perturbation in canonical orbitals (or the orbital-invariant formulation) may be coupled to the additional interactions from the Epstein-Nesbet perturbation series, the latter being expressed in a localized basis.

A corresponding intermediate between Epstein-Nesbet and Møller-Plesset $\mathbf{H}_0$ is investigated, and applied to a few test cases.

Some Recent Developments in Linear Scaling Methods using Gaussian Orbitals

Martin Head-Gordon

Department of Chemistry, University of California, Berkeley; and

Chemical Sciences Division, Lawrence Berkeley National Laboratory, Berkeley CA 94720, USA

Linear scaling methods based on Gaussian orbitals vary greatly in their maturity and their extent of relevance to chemists who perform routine applications of electronic structure methods. In this talk, I shall focus first on the construction of effective Hamiltonian matrices, which is without doubt the most mature area. The status of fast Coulomb and exchange methods will be reviewed for energies and analytical gradients, and compared with grid-based quadrature for exchange-correlation contributions. In the second part of the talk, some new developments in diagonalization-free methods for updating the one-particle density matrix will be discussed. These methods are at this stage significantly less relevant to most chemical applications. Finally, if time permits, I shall discuss the use of localized orbital methods in describing highly correlated wavefunctions, and an interesting theorem about the structure of the exact wavefunction.

Grid-optimized localized orbitals and nearly *O(N) ab initio* calculations of quantum conductance

J. Bernholc[1], M. Buongiorno Nardelli[1] and J.-L. Fattebert[2]
[1] *North Carolina State University, Raleigh, NC 27695-8202, USA*
[2] *CASC, Lawrence Livermore National Laboratory, CA 94551, USA*

We have developed an *ab initio* nearly $O(N)$ method that combines an accurate optimized-orbital solution of the electronic structure problem with an efficient Green's function technique for evaluating the quantum conductance. The method has been implemented on massively parallel computers and enables studies of very large systems. This talk will describe both the methodological developments and applications to carbon nanotube-metal contacts.

The electronic structure problem is solved using a generalization of the Galli-Parrinello approach [1] to real-space grids, where powerful multigrid-based convergence acceleration techniques can be used. Briefly [2], we minimize the total energy functional

$$E[\{\phi_i\}_{i=1}^N] = 2\mathrm{Tr}(H^{(\phi)}\bar{\rho}^{(\phi)}) - \frac{1}{2}\int \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}d\mathbf{r}' - \int \mu_{xc}(\rho)\rho(\mathbf{r})d\mathbf{r} + E_{xc}[\rho]$$

for a set of nonorthogonal orbitals $\{\phi_i\}_{i=1}^N$. Here, $\bar{\rho}^{\Phi}$ is the density matrix in the basis $\{\phi\}$ and $H^{(\Phi)}$ is defined by $H_{ij}^{(\Phi)} = \langle\phi_i|H\phi_j\rangle$. The electronic density is then given by

$$\rho(\mathbf{r}) = 2\sum_{j,k=1}^{N} (\bar{\rho}^{\Phi})_{jk}\phi_j(\mathbf{r})\phi_k(\mathbf{r}).$$

The conjugate orbitals, defined by $\overline{\phi}_i = \sum_j S_{ji}^{-1}\phi_j$ where S is the overlap matrix, satisfy the relation $\langle\overline{\phi}_i|\phi_j\rangle = \delta_{ij}$. It has been shown recently [3] that orbitals generated by this procedure decay faster than either orthogonal Wannier functions or the density matrix. If the orbitals ϕ_i are constrained to be zero outside of fixed localization radii, one obtains a variational $O(N)$ expression for the total energy whose accuracy, compared to the full density-functional solution, depends on the size of the localization radii. Our orbitals are variationally optimized using multigrid preconditioning techniques until they accurately describe the ground state of the system. This procedure allows us to use a small number of orbitals per atom, much smaller than in LCAO or gaussian-based calculations, because the orbitals are optimized on the grid

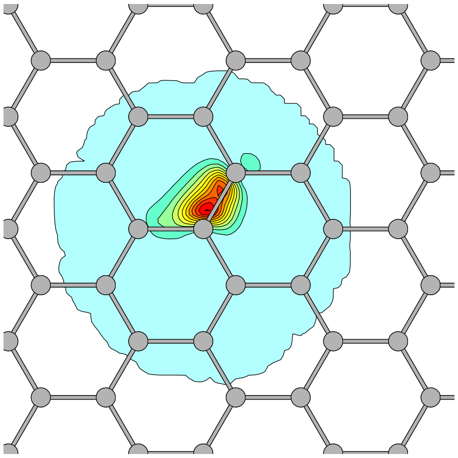

Figure 1: An optimized electron-density function for a carbon nanotube. Note that although the allowed localization region extends over 6 Å, this function is largely confined to one carbon-carbon bond. The plotting plane is along the surface of the nanotube.

according to their environment. In order to ensure fast convergence and accuracy – even for metallic systems – we use both occupied and unoccupied orbitals. The scaling of the most expensive parts of the calculations is still $O(N)$ due to localization, but there is a small $O(N^3)$ part, which is dealt with by parallelizing the necessary subspace diagonalization across many processors on a massively parallel supercomputer.

The conductance G of the full open system (infinite left lead, conductor, infinite right lead) is evaluated via the transmission function as $G = \frac{2e^2}{h}\mathcal{T} = \frac{2e^2}{h}\mathrm{Tr}(\Gamma_L G_C \Gamma_R G_C)$, where G_C is Green's function of the conductor (C) and $\Gamma_{\{L,R\}}$ are functions that describe the coupling of the conductor to the left (L) and right (R) leads. In a general non-orthogonal localized orbital scheme, the Green's function of the whole system can be explicitly written as

$$G_C = (\epsilon S_C - H_C - \Sigma_L - \Sigma_R)^{-1},$$

where Σ_L and Σ_R are the self-energy terms due to the semi-infinite leads, and H_C and S_C are the Hamiltonian and overlap matrices for the localized orbitals in the conductor. The expressions for the self-energies are derived using the formalism of principal layers in the framework of the surface Green's function matching theory. The coupling functions $\Gamma_{\{L,R\}}$ can be easily obtained once the self-energy functions are known. A full description of the method is given in Ref. 4.

The conductance calculations are carried out by expanding all quantities in the above basis of optimized, localized orbitals. It is then possible to efficiently evaluate the quantum conductance of a lead-conductor-lead system in $O(N)$ steps, by dividing the system into principal layers that interact only with their nearest neighbors. Due to the small number of orbitals, the size of the matrices that enter the quantum conductance calculation and the computational cost of the whole procedure are thus minimized, while maintaining the high accuracy of *ab initio* calculations. This allows for *ab initio* treatment of the infinite leads in full atomistic detail, and for a complete and consistent description of the coupling of the conductor to the leads.

As an important illustrative example, we have investigated carbon nanotube-metal contacts and explained the anomalously large contact resistance observed in nanotube devices as due to the spatial separation of their conductance eigenchannels. The results for various contact geometries will be briefly described, and strategies for improving device performance will also be discussed.

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Optimisation of nonorthogonal generalised Wannier functions during order-N DFT calculations with plane-waves

Chris-Kriton Skylaris, Arash A. Mostofi, Peter D. Haynes, Oswaldo Diéguez and
Mike C. Payne
Theory of Condensed Matter, Cavendish Laboratory, Madingley Road, Cambridge CB3 0HE, UK

Mixing the constituent functions of a band over **k**-points affords a set of orthonormal Wannier functions. If also a linear transformation between different bands is applied, the result is a set of Nonorthogonal Generalised Wannier functions (NGWFs). Various kinds of Wannier functions have been calculated in a post-processing context in pseudopotential plane-wave calculations [1]. The desirable property of these functions is their spatial localisation. The charge density can be written in terms of the NGWFs $\{\phi_\alpha\}$ and the density kernel $K^{\alpha\beta}$ as

$$\rho(\mathbf{r}) = \sum_{\alpha\beta} \phi_\alpha(\mathbf{r}) \mathbf{K}^{\alpha\beta} \phi_\beta(\mathbf{r}) \,.$$

The $\{\phi_\alpha\}$ are expanded in a plane-wave basis

$$\phi_\alpha(\mathbf{r}) = \frac{\mathbf{1}}{\mathbf{V}} \sum_{\mathbf{G}} \tilde{\phi}_\alpha(\mathbf{G}) \mathbf{e}^{\mathbf{iG\cdot r}} \,, \tag{1}$$

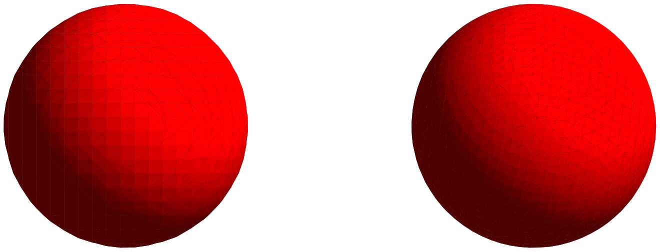
which is also equivalent to a representation in terms of bandwidth limited delta functions $D_{KLM}(\mathbf{r})$

$$\phi_\alpha(\mathbf{r}) = \sum_{\mathbf{K=0}}^{\mathbf{N_1-1}} \sum_{\mathbf{L=0}}^{\mathbf{N_2-1}} \sum_{\mathbf{M=0}}^{\mathbf{N_3-1}} \mathbf{C}_{\mathbf{KLM},\alpha} \mathbf{D}_{\mathbf{KLM}}(\mathbf{r}) \tag{2}$$

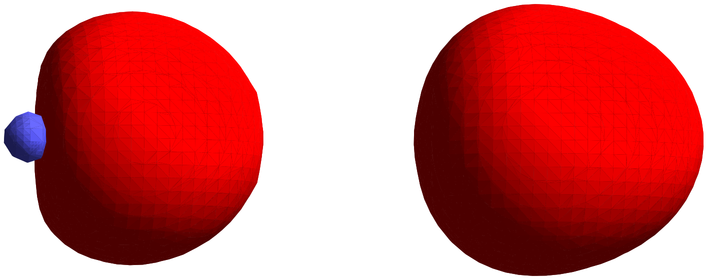
where the sum over the K, L, M indices runs over the points of a regular real space grid. $D_{KLM}(\mathbf{r})$ is centred on point $\mathbf{r_{KLM}}$ and is defined as

$$D_{KLM}(\mathbf{r}) = \frac{\mathbf{1}}{\mathbf{V}} \sum_{\mathbf{G}} \mathbf{e}^{\mathbf{iG\cdot(r-r_{KLM})}} \,.$$

When the NGWFs decay exponentialy we expect that the restriction of the sum of equation (2) only to delta functions centred within a spherical region would be a good approximation. In



H s-fireball Li s-fireball



H NGWF Li NGWF

Figure 1: Example: NGWFs of LiH. Top: Initial guesses. Bottom: After the completion of a total energy calculation with this method.

this case the number of delta functions used for each NGWF will be independent of the size of the system. The same can be achieved with the number of plane waves in (1) with our FFT box method [2].

A new code we are developing performs density functional calculations by optimising both the density kernel and the NGWFs using the above formalism. It is thus closely related to the traditional plane-wave pseudopotential approach with familiar advantages such as an orthonormal basis specified by a kinetic energy cutoff, calculation of energy terms in real or in reciprocal space and natural applicability to any lattice symmetry. The optimisation of the NGWFs is essential in order to obtain plane-wave accuracy.

Since each NGWF is expanded in an orthonormal basis set which is independent of the size of the system it should be possible to construct a linear-scaling method with variational dependence on the size of the spherical confinement regions and the sparsity of the density kernel.

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A Finite-Element Approach to Large-scale Electronic Structure Calculations

Philip A. Sterne[1], John E. Pask[2], C. Y. Fong[3] and B. M. Klein[3]
[1]*Lawrence Livermore National Laboratory, Livermore, CA 94550, USA*
[2]*Naval Research Laboratory, Washington DC 20375, USA*
[3]*University of California, Davis, CA 95616, USA*

This talk presents the application of the finite-element (FE) method to large-scale ab initio electronic-structure calculations in solids [1,2]. Conventional electronic structure calculations involve the solution of two differential equations – the Schrödinger equation and Poisson's equation. The FE method is used to solve differential equations in a vast range of engineering applications, and as a result has an extensive set of algorithms and codes for a wide range of problems. We have used a Galerkin approach, which casts the FE method into a variational form, to solve the Schrödinger equation and Poisson's equation for the Bloch-periodic boundary conditions that arise in electronic structure calculations on solids. The approach can be understood as an expansion method that uses a strictly local, piecewise-polynomial basis. Because the basis is polynomial in nature, the method is completely general and its convergence can be controlled systematically. Because the basis is strictly local, it produces sparse, structured matrices, enabling the effective use of iterative solution methods. The result is a variational real-space method that requires no Fourier transforms and is well suited for parallelization. The method thus combines the significant advantages of both basis-oriented and grid-based approaches.

We discuss the construction and properties of the required FE bases, and show how they can be used for the solution of the Schrödinger and Poisson equations in solid-state ab initio electronic structure calculations. We present results for the Schrödinger equation demonstrating the optimal and variational convergence of the method in electronic band structure calculations, and results for the Poisson equation demonstrating its optimal convergence and linear scaling with system size. We indicate the steps that are currently under way to develop a fully self-consistent program based on this approach. We conclude with recent applications of the method to large-scale ab initio positron distribution and lifetime calculations [3] for systems of over 4000 atoms.

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

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Wavelets, a potentially interesting basis set for *O(N)* electronic structure calculations

S. Goedecker
CEA Grenoble, France

Wavelets are a new and versatile basis set in electronic structure calculations. Being localized in both real and Fourier space, wavelets combine the advantages of conventional localized basis sets such as Gaussians or finite elements with the advantages of plane waves. Wavelets are therefore an ideal basis set for the localized orbitals that are the basic quantity in $O(N)$ schemes. Due to the data compression properties of wavelets localized orbitals and density matrices can be represented in a very compact way.

Linear-scaling and its relation with the embedding problem

Mike Gillan and David Bowler
Department of Physics and Astronomy, University College London, Gower Street, London WC1E 6BT, UK

A summary will be given of the current state of the CONQUEST linear-scaling code, which performs full first-principles calculations of total energy and forces, using DFT and the pseudopotential method. Examples will be given of its practical performance on systems of over 10,000 atoms. Then the close relation between the linear-scaling and embedding problems will be analysed. Practical examples will be presented, in which embedding calculations based on CONQUEST methods have been performed on a substitutional impurity and the vacancy in silicon, and the Si(001) reconstructed surface.

O(N) calculations in metals with the finite temperature method

Oswaldo Diéguez[1] and Pablo Ordejón[2]
[1] *Cavendish Laboratory, University of Cambridge, UK*
[2] *Institut de Ciència de Materials de Barcelona – CSIC, Spain*

The localization of the density matrix or the electronic wave functions is the key concept behind linear scaling algorithms. The fact that these quantities are not localized for metals at zero temperature is what hinders their application to these systems. Localization is recovered in metals at high electronic temperatures, and therefore linear scaling algorithms can be used to describe metals when T is large enough [1]. However, the temperatures required to make linear scaling calculations feasible are very high, so much that the energetics and dynamics obtained are significantly different from those at zero temperature. Horsfield and Bratkovsky [2] suggested the possibility of using the approximation due to Gillan [3] to obtain an estimate of the $T = 0$ energies and forces from the free energy at finite temperatures.

In this work, we revisit the problem, and show that the entropy term in the free energy shows localization properties that allow it to be computed in $O(N)$ operations, for large enough temperatures. We implemented these ideas in the context of the Li-Nunes-Vanderbilt functional [4], and show that the errors associated with the approximation and truncation of the entropy and the extrapolation from finite to zero temperature are small, and comparable to those of the localization approximation for insulators. This makes it possible to study metallic systems at zero temperature with linear scaling, with errors similar to those in insulating systems.

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On the linear scaling computation of orthogonality transformations with Gaussian-Type Atomic Orbitals

Matt Challacombe
Theoretical Division, Los Alamos National Laboratory, New Mexico, USA

Use of the inverse Cholesky factor $\mathrm{S}^{(-L)}$ is a promising approach to the transformation between orthogonal and non-orthogonal representations defined by the overlap matrix S of Gaussian-Type Atomic Orbital (GTAO) basis functions. However, linear scaling methods for the computation of $\mathrm{S}^{(-L)}$ have not been forthcoming.

For diagonally dominant overlap matrices that fall off from the diagonal, $\mathrm{S}^{(-L)}$ is typically much more sparse than $\mathrm{S}^{(-1)}$ and has matrix elements that fall off exponentially from the diagonal. Rate of this fall off is controlled by Cond(S).

In this talk I will introduce a sparse-blocked version of Benzi and Tuma's AINV [1] for directly computing the inverse Cholesky factor in $O(N)$, avoiding an incomplete linear solve which would otherwise be necessary. The sparse-blocked AINV employs (1) atom-blocked DGEMMs for efficiency, (2) ordering with a space filling curve to achieve diagonal dominance, and (3) *a priori* spatial thresholding (distance based truncation) to achieve an $O(N)$ complexity for well conditioned matrices.

I will show that well constructed GTAO basis sets, in which primitive exponents are related by geometric progression (i.e. even tempered [2] or well tempered [3] sequences), yield well conditioned overlap matrices and an early approach to linear scaling computation of $\mathrm{S}^{(-L)}$, while other more popular basis sets such as 6-31G have a much larger condition number and approach linear scaling slowly.

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Simulation of High Pressure Phases of Nitrogen using SIESTA

Richard M. Martin, William Mattson and Daniel Sánchez-Portal*
Department of Physics and Materials Research Laboratory, University of Illinois at Urbana-Champaign, Urbana, Illinois 61801, USA

Recently there has been renewed excitement in experimental studies [1-3] of nitrogen that have apparently found high-pressure non-molecular phases similar to those predicted long ago [4-6]. The experiments also show that there is a remarkable hysteresis that apparently was the reason the phases were not observed before in low temperature experiments [7] even though a transition was identified in high temperature shock wave experiments [8]. However, the structure of the new phase is not established experimentally. To study the metastability issues and search for possible new forms of nitrogen at high pressures, we are carrying out simulations using the SIESTA local orbital code. Results established so far are: agreement with previous LDA plane wave calculations; modifications of previous theoretical predictions due to inclusion of GGA functionals; general agreement with shock wave data and other recent high temperature simulations [9]; results for several potential molecular and non-molecular structures; quenching of a disordered non-molecular phase under conditions similar to experiments; and strong temperature dependence of the transition rates indicating the tendency for long-time-scale metastability below room temperature.

* Present address: Departamento de Física de Materiales and DIPC, Facultad de Química, UPV/EHU, Apdo. 1072, E-20080 San Sebastián, Spain.

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Linear scaling approaches with the divide-and-conquer method and with localized orbitals

Weitao Yang
Department of Chemistry, Duke University, Durham, NC 27708-0346, USA

We will present our effort in the development of linear scaling methods and their applications to biological systems. The divide-and-conquer method we developed in 1991 was the first linear scaling solution to electronic structure calculations. Its recent applications to the simulation of protein dynamics will be presented. We also will describe our variational linear scaling approach with nonothorgonal localized molecular orbitals, and its comparison with other localized orbital approaches. Our numerical calculations demonstrate the advantages of this method.

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A DFT study of Co on Si(001)

A. P. Horsfield

FECIT, Hayes Park Central, Hayes End Road, Hayes, Middlesex UB4 8FE, UK

CoSi2 is already an important material for metalization in VLSI devices. This industrial interest provides a strong incentive to understand in detail the behavior of Co during deposition and annealing. In this talk I will discuss two sets of calculations using Plato: (1) those performed to study the relative stabilities of a number of surface and subsurface sites; (2) those performed to study the diffusion of Co in Si.

Electronic structure characterization of crystalline compounds through their localized Wannier Functions

Claudio M. Zicovich-Wilson[1], Alberto Bert[2], Roberto Dovesi[2,3] and Victor R. Saunders[4]
[1] *Departamento de Física, Universidad Autónoma del Estado de Morelos, Av. Universidad 1001, Col. Chamilpa, 62210 Cuernavaca (Morelos), Mexico*
[2] *Dipartimento di Chimica IFM, Università di Torino, Via Giuria 5 I 10125 Torino, Italy*
[3] *Unità INFM di Torino, Sezione F*
[4] *CLRC Laboratory, Daresbury, Warrington, Cheshire WA4 4AD, UK*

A method for obtaining spatially localized crystalline orbitals starting from delocalized Bloch Functions has been implemented in the periodic LCAO CRYSTAL code [1]; it provides a set of well localized Wannier functions (WF) through an iterative mixed Wannier-Boys scheme [2].

The WFs of seven oxygen containing compounds with increasing degree of covalent character (MgO, MnO, ZnO, Al_2O_3, SiO_2, $AlPO_4$ and $CaSO_4$) [3] and of six semiconductors (Si, C, BP, AlP, SiC and BN) [4] are analyzed in terms of various indices (centroids positions, second order central moment tensor, its eigenvalues and principal axes, Mulliken population analysis and atomic localization indices) and through their graphical representations. Systematic trends are observed along the series.

As an example, Fig. 1 gives the *atomic delocalization index* [5] (top) defined as:

$$\lambda = \left[\sum_{A,\mathbf{g}} (q_A^{\mathbf{g}})^2 \right]^{-1}, \tag{1}$$

of the considered oxygen containing compounds; this quantity is a measure of the extent of the WF in terms of number of "contributing" atoms. Fig. 1 (down) provides additional information concerning the size of the WFs, through the index:

$$\Sigma = \frac{\sigma}{d_{OX}}, \tag{2}$$

where:

$$\sigma = \sqrt{\int d\mathbf{r} \, |\omega_s(\mathbf{r})|^2 \, (\mathbf{r} - \mathbf{o})^2}$$

is the spatial spread of the WF, d_{OX} is the bond distance, and $\mathbf{o}$ is the centroid position. Note that in SiO_2, $AlPO_4$ and $CaSO_4$ there are two types of WFs, identified as *covalent* (cv) and *lone-pair* (lp), whereas in MgO, MnO, ZnO and Al_2O_3 there is only one type, classified as *ionic* (io).

An example of graphical representation is given in Fig. 2 for the diamond valence WF; the electronic density map and profile (see the caption for more details) are reported.

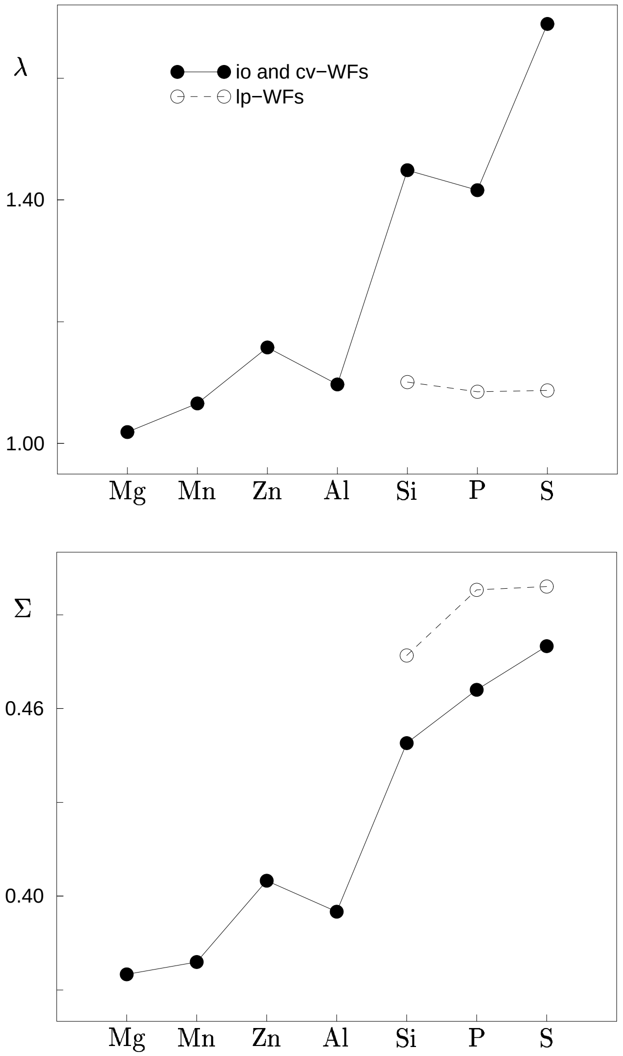

Figure 1: Atomic delocalization index λ (eq. 1; in $|e|^{-2}$) and "normalized" standard deviation Σ (eq. 2) of the considered oxygen containing compounds. Full and open circles refer to *ionic/covalent* (io, cv) and *lone pair* (lp) WFs, respectively.

The WFs have also been used for the calculation of dielectric properties of various compounds, in alternative to the Berry phase scheme based on the Bloch functions formalism [6,7]. The effective Born charges, spontaneous polarization and dielectric constants of various compounds are easily derived simply from the coordinates of the WF centroids [8,9].

Table 1 provides an example referring to $KNbO_3$; Fig. 3 shows the dependence of the centroid position of a valence and a core WFs of BeO, on the strain ε_3.

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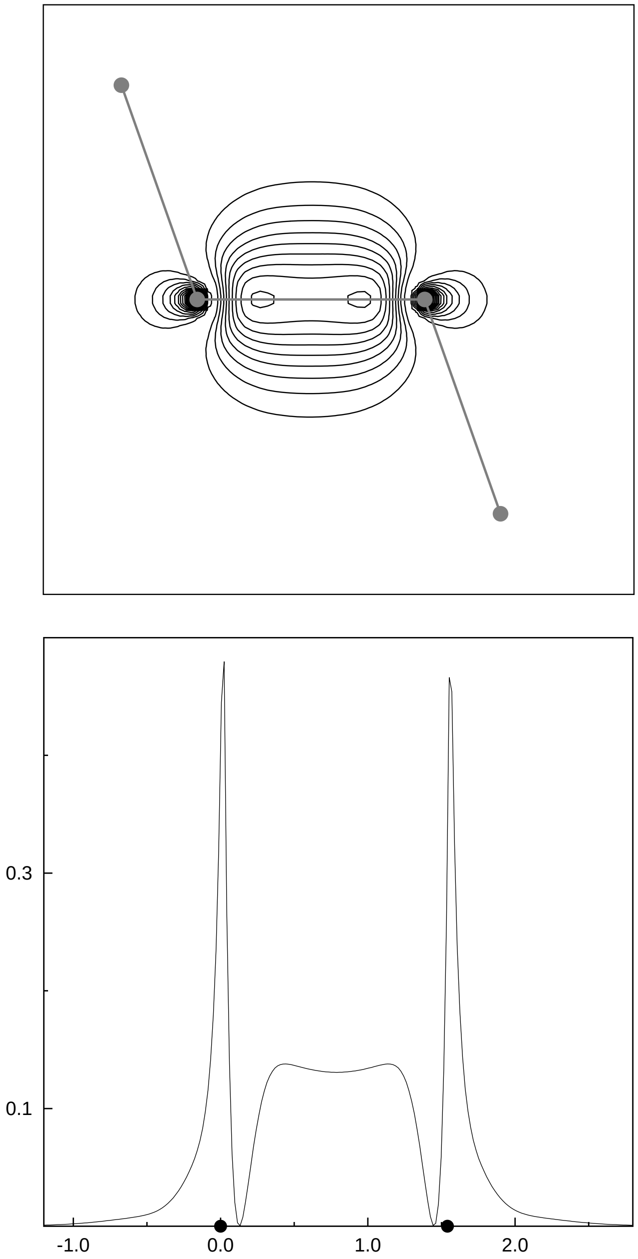

Figure 2: Electron density map in the (111) plane (top) and profile along the bond axis (down), of one of the four diamond valence WFs. In the map (4 Å wide), iso-lines differing by 0.015 $|e|/\text{bohr}^3$ in the range 0.015–0.3 $|e|/\text{bohr}^3$ are represented. Gray dots and lines indicate nuclei positions and the bond axes, respectively. Density in $|e|/\text{bohr}^3$ and distances in Å.

Method	Z^*_{Nb}	Z^*_K	$Z^*_{O_I}$	$Z^*_{O_{II}}$	S_a	ΔP_{tot}
BP	8.073	1.001	-5.964	-1.556	-0.0003	0.347
LWF	8.089	1.000	-5.985	-1.552	0.0004	0.348

Table 1: Born effective charges Z^* (in $|e|$), acoustic sum rule S_a (in $|e|$) and ΔP_{tot} (in C/m^2) obtained for KNbO_3, by using the BP and LWF schemes.

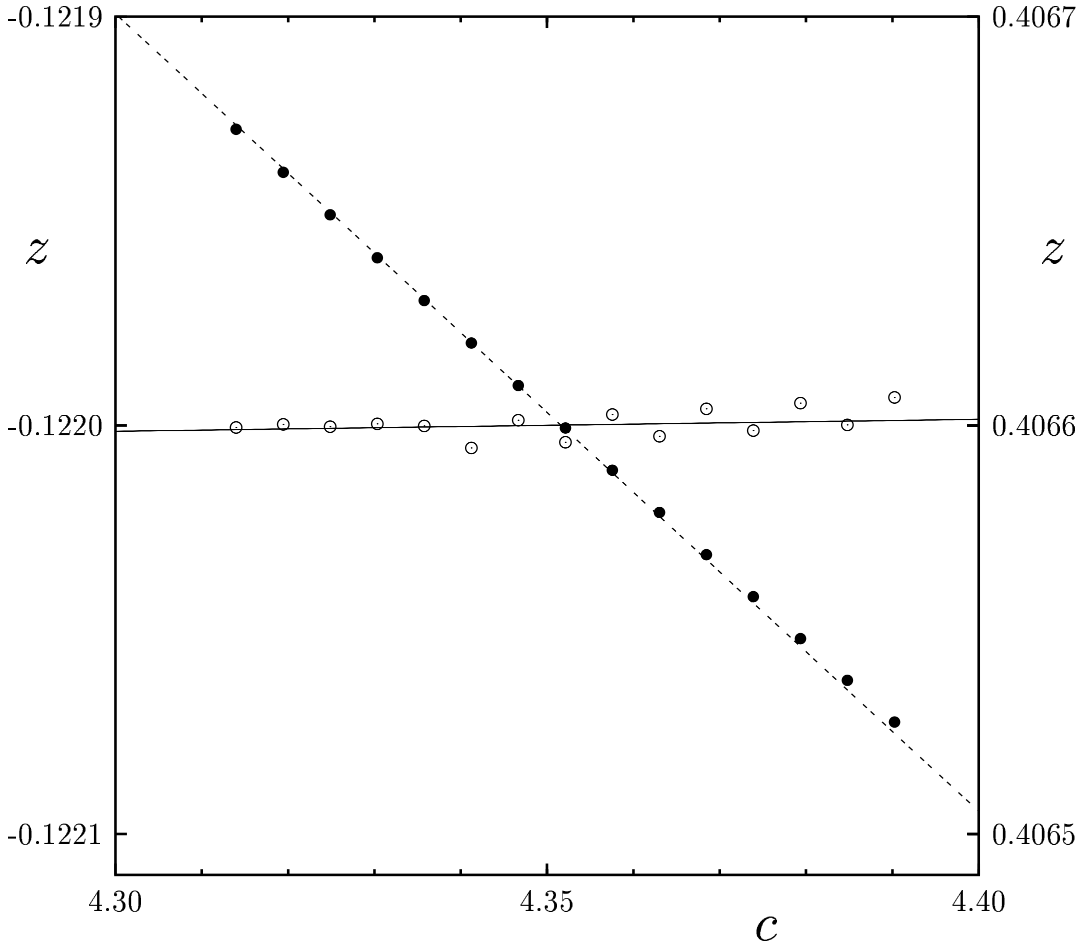

Figure 3: Dependence of the centroid z fractional coordinate for a core (left scale, continuous line and open circles) and a valence (right scale, dashed line and full circles) LWF of BeO centered on oxygen, as a function of the cell parameter c (in Å). $\partial z/\partial c = 2.0 \times 10^{-3}$ and 3.0×10^{-5} Å^{-1} for valence and core centroids, respectively.

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Maximally-localized Wannier functions for entangled energy bands

Ivo Souza[1], Nicola Marzari[2] and David Vanderbilt[1]
[1] *Department of Physics and Astronomy, Rutgers University, New Jersey, USA*
[2] *Department of Chemistry, Princeton University, Princeton, New Jersey, USA*

We present a method [1] for obtaining well-localized Wannier-like functions (WFs) for energy bands that are attached to or mixed with other bands. The present scheme removes the limitation of the usual maximally-localized WF method [2] that the bands of interest should form an isolated group, separated by gaps from higher and lower bands everywhere in the Brillouin zone. An energy window encompassing N bands of interest is specified by the user, and the algorithm then proceeds to disentangle these from the remaining bands inside the window by filtering out an optimally connected N-dimensional subspace. This is achieved by minimizing a functional that measures the subspace dispersion across the Brillouin zone. The maximally-localized WFs for the optimal subspace are then obtained via the algorithm of Marzari and Vanderbilt [1]. The method, which functions as a postprocessing step using the output of conventional electronic-structure codes, is applied to the s and d bands of copper, and to the valence and low-lying conduction bands of silicon. For the low-lying nearly-free-electron bands of copper we find WFs which are centered at the tetrahedral interstitial sites (see right panel of the figure), suggesting an alternative tight-binding parametrization.

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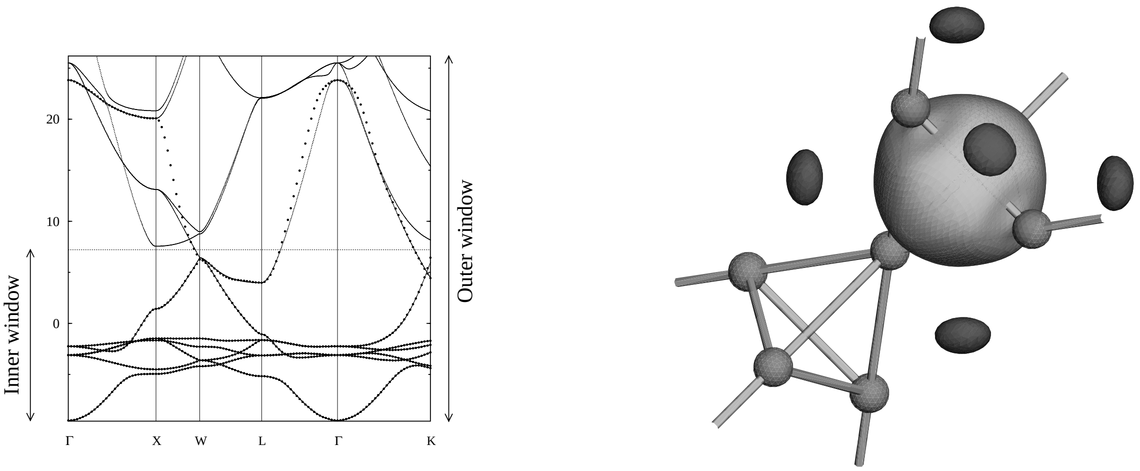

Figure 1: Left Panel: Solid lines: Calculated band structure of copper. Dotted lines: Seven Wannier-interpolated bands obtained from our procedure, by choosing an optimal seven-dimensional space from the states inside the outer energy window, while constraining the states inside the inner window to be included in that subspace. The maximally-localized WFs consist of five atom-centered d-like orbitals plus two equivalent s-like orbitals, each centered at one of the two tetrahedral interstitial sites. The contour-surface plot of one of the latter is shown in the right panel. The amplitudes are $+0.5/\sqrt{v}$ (light gray) and $-0.25/\sqrt{v}$ (dark gray), where v is the volume of the primitive cell.

4.1.4 Report on a EuroConference on Computer Simulation of Complex Interfaces

in the series
"Electronic Structure of Solids and Other Systems"

How we made it out of the vacuum into the real world

Philip Lindan
University of Kent at Canterbury, Kent CT2 7NR, UK

Background and motives

This meeting was focused on the application of first-principles computer simulation to the study of real-world surfaces and interfaces–those found outside a vacuum chamber. In this context, the current situation has three defining characteristics that reveal both the challenges that must be overcome in the next few years, and the great opportunities open to us. These characteristics are: a large armoury of maturing, complementary but largely separate methodologies; the convergence of simulation and experiment; and the desire to tackle problems that span traditional scientific disciplines. Working outside the vacuum involves a leap in complexity, non-zero and sometimes extreme temperatures and pressures and extended length and time scales, all without the sacrifice of chemical accuracy. Furthermore, in this arena simulations are particularly valuable to experiment, and may indeed provide sole or primary data. Above all, "real-world" interfaces are those found in real-world applications and problems, from electrochemistry to catalysis, tribology to corrosion.

So what were we trying to achieve? These are the aims we presented to the ESF in the conference proposal, two years ago:

- To bring together internationally-eminent and authoritative simulation practitioners, experimentalists and industrial researchers
- To give young researchers access to these experts
- To define the state of the art, identify weaknesses, opportunities, bottlenecks
- To understand scope of current methods and what developments are required
- To initiate cross-disciplinary dialogue and partnerships
- To strengthen and enrich collaborative networks, formal and informal
- To export ideas, methods and theories from science to industry

As the Chaiman I really shouldn't be the one saying this, but the meeting was exceptionally good, and the delegates met these aims with great distinction. Everyone seemed to have come prepared to take a fresh look and to challenge themselves and each other to make progress; theory and experiment really did get down to business; brilliant, innovative research was on show; dozens of ideas and plans were hammered out and new collaborations formed; young researchers were spoilt for choice of experts happy to teach and explain.

We had about 70 delegates representing 25 countries. Of these more than half were young researchers under 35 years of age, and about one third were female: these were key targets in the original proposal and we were very pleased to exceed our expectations. Another cornerstone of the meeting was the mix of theorists, experimentalists and indistrialists. I'll try here to give you a flavour of what we did.

Hghlights

Instead of highlighing individuals or particular contributions I want to single out three very strong themes that came to define our meeting:

- Challenges from experiment to theory
- Simulators tackling big problems
- A flourishing dialogue between theory and experiment

These were evident from the first talk onwards. The opening day was in itself a highlight, setting the tone for the rest of the meeting. “Real catalysis” was under scrutiny, a field where simulations are beginning to get to grips with the inherent complexities. Thus we heard about studies of subsurface processes and free-energy calculations for nanocrystals in solution to name but two. The experimentalists almost stole the show though. Perhaps it is because at last simulation can tackle real problems, but for whatever reason there was a tangible excitement about bringing simulation and experiment together. One clear message from an experimentalist was that we simulators can make a great impact in the interpretation of experiment. The day finished with a tour-de-force on microscopy of real catalysts in action. These studies have thrown up radical ideas: steps and kinks may not affect catalytic activity in a real catalyst, and quite possibly regions of oxide material may be responsible for catalytic activity in some circumstances. These suggestions may turn a few well-set ideas on their heads, and it's no surprise that they aroused intense debate.

Tackling processes with long timescales came to prominence in the context of thermodynamics. Kinetic Monte-Carlo, underpinned by first-principles calculations, is one way forward. Timescales of seconds or minutes are within its scope, though the difficulty is to capture all of the essential atomic-scale processes when setting up the model. Two impressive applications were discussed, thermal desorption and semiconductor growth. We were also reminded from classical simulations of polymers, and thermodynamic studies of extremely complicated clay materials, what challenges we face regarding lengthscales, and from first-principles calculations on solutions that sometimes a few picoseconds are enough if you are smart. Solid-liquid interfaces are ubiquitous and are the key players in a diversity of fields that includes electrochemistry, heterogeneous catalysis, gas sensing, mineral and soil science, geochemistry, corrosion, tribology and biophysics. It is fair to say that first-principles work in this area has only recently become feasible. Classical simulations can play a guiding role here, a review of many of the forementioned topics produced excellent "tension" in the debate on where first-principles practitioners are going and what they may achieve. A good way down this road lies pre-biotic chemistry and the "surface science of life". Again experiment brought us back to Earth, this time with remarkably delicate electrochemical studies. This contribution was one of several to prompt an "I can do that" response from a theorist during a break, and concrete steps were taken on the spot to arrange a collaboration.

We enjoyed several contributions on mechanical properties. An atomic-scale picture of friction, such a familiar concept, is only recently emerging. It appears that phonon processes at an interface are the key ingredients in this theory, and surely simulation can contribute ideas here: this topic was extremely challenging and though-provoking. Other areas we covered included non-contact AFM and fracture. Calculations on the intriguing phase behaviour of nanocrystals under pressure were also presented, picking up a theme opened on the first day. As one speaker put it, we enter this small world because new science emerges.

Yet more challenges were set for the theorists by comprehensive presentations on oxide surfaces and surface processes. Variable stoichiometry leads to complex, condition-dependent structures. Some recent progress has been made in simulating these structures and understanding their stability, for example as a funtion of oxygen partial pressure, but much more remains to be done. This is a prerequisite to the realistic simulation of oxide surface processes. Two very appealing studies revealed more ways of strengthening the theory-experiment link. In one, simulations of carbon nanotubes in liquids were related in detail to microscopy images, leading to better interpretation. In the other we were shown how to calculate x-ray emission spectra. Throughout the meeting a critical eye was cast on standard DFT (LDA or GGA) and whether it was accurate enough for the many purposes we are putting it to. Perhaps a glimpse of the future was given in a talk on dynamical mean-fied theory in solids, one of the most promising developments in many-body electronic structure. We even had time to hear some very practical advice on trends in supercomputing. We had two poster sessions that were a gerat showcase for new research, and as well as reflecting the subjects of the talks several other topics were presented.

By definition I cannot tell you everything that was discussed during breaks, in the afternoons and over meals. I can tell you the discussions were many, and varied, and searching, and honest: these discussions set EURESCO meetings apart, and I an certain every delegate took away new ideas from them.

Looking forward

In this series we have a special system to select the topic and organisers of a subsequent series meeting. All delegates are invited to present ideas they think are timely and which need the impetus goven by a EURESCO meeting. The ideas must push the field forward: that is the EURESCO remit.

Four suggestions were put forward on the Monday evening. The topics were: “New horizons in computational earth sciences”; “Beyond $S = 0$”; “Micromechanics”; and “Friction, contact mechanics and lubrication”. Each group presented its ideas and rationale, and each theme was debated. The discussion resulted in proposals three and four being combined into “Micromechanics and friction”, and the three were put to the vote. That the meeting had thrown up two very similar proposals was perhaps a clue to the outcome: “Micromechanics and friction” under the auspicies of Ruben Perez, Jackie Krim, Carla Molteni and Joost Frenken was chosen and they will propose the idea to the ESF for the 2004 meeting.

It takes a lot of courage to lay out an idea in this way, an idea that has been developed on the spot (with perhaps some cajoling from the organising committee). All of the ideas were highly imaginative, each had many strengths and they all staked a strong claim. We are very grateful to those who proposed them and stood up to tough questions and the merciless voting system.

Hot topics

So what were the hot topics at this meeting? By way of summary, and in no order of importance, these are some:

- The accuracy of current DFT approaches
- Finding reaction paths, simulating rare events
- The best help to experiment is interpretation
- What is the active component of a catalyst?
- Multiscale modelling
- Embedding
- Dramatic advances in microscopies, and in *in situ* experimental work
- How recruitment policy (short-term contracts) inhibits research ability
- A sudden expansion of ambition in simulation; assault on complex systems
- Theory and experiment are talking
- How do we tackle cross-disciplinary problems?

We didn’t find all the answers, but we think we have launched ourselves on the journey out of the vacuum.

Thanks

As organisers all we do is to assemble the participants and pooint then in a certain direction. It is they who made the meeting a success with top-quality contributions and discussions, so thank you all. I also thank the speakers for doing a fantastic job and for provoking so much debate and the Chairs for keeping that debate on the rails.

Running a conference with the ESF is a delight: I did all the enjoyable things, such as inviting speakers, and the ESF did all the hard work. I want to thank in particular Anne-Sophie Gablin and Caroline Grimont, who guided me and the meeting to readiness with infinite patience, and Anthea Richards, our conference secretary, who was so kind to all the participants. I also thank everyone at the ESF who worked on this meeting, there must be many I don't know. The VVF staff were excellent hosts, and even the weather behaved well. Finally, thanks to my co-organisers who have done som much behind the scenes to make the meeting a reality.

This meeting was very generously supported by the ESF, the European Commission and the Psi-k Network. This enabled an unusually large number of young researchers to attend. We are deeply grateful for this support.

We were at our meeting on the 11th of September. We had six US-based delegates, and for them the events and uncertainty were very hard. I am especially grateful to the ESF and the staff of the Centre VVF in Giens for the looking after these people in so many ways: I know they appreciate your help very much indeed. To the participants, thank you all for being so kind at this time.

Organisation

A EURESCO Conference held at Giens (near Toulon), France,
7 - 12 September 2001
Supported by the European Commission, Research DG, Human
Potential Programme, High-Level Scientific Conferences
(Contract No: HPCF-CT-2000-00231)

Chaired by: Philip J. D. Lindan
Centre for Materials Research,
University of Kent at Canterbury,
Canterbury CT2 7NR, UK

Co-chair: Anne M. Chaka
National Institute of Standards and Technology (NIST),
Gaithersburg, US

Vice-chair: Claudine Noguera
Universit Paris Sud,
Orsay, France

Steering committee: Andrew Fisher, Axel Gross,
Balazs Gyorffy, Volker Heine, Risto Nieminnen and Matthias Scheffler.

See also `www.esf.org`

Participants

Hideaki Aizawa
Elena Akhmatskaya
Tristan Albaret
Juan Amir
Tayeb Amriou
Gary Attard
Joerg Behler
Blanca Biel
Jose Manuel Blanco Ramos
Camelia Borca
Konstantine Bourchteine
Anne Chaka
Juarez Da Silva
Ulrike Diebold
Elizabeth Duplock
Feng Yuan Ping
Anna Maria Ferrari
Kristen Fichthorn
Andrew Fisher
Joost W.M. Frenken
Francesco Frigerio
Bertrand Fritz
Antoine Georges
Livia Giordano
Pascual Cesar Gonzalez
Axel Gross
Karoliina Honkala
Adam Kiejna
Marina Koudriachova
Jacqueline Krim
Walter Langel
Michele Lazzeri
Tsan-Chuen Leung
Weixue Li

Philip Lindan

Markus Lischka

Haozhe Liu

Lars Menken

Ian Alan Merrick

Carla Molteni

Christian Mosch

Christine Mottet

Marcus Mller

Claudine Noguera

Jaime Oviedo Lopez

Jeff Penfold

Ruben Perez

Lars Pettersson

Michael Philpott

Laurent Pizzagalli

Trevor Rayment

Karsten Reuter

Antha Richards

Philippe Sautet

Matthias Scheffler

Hannes Schweiger

Zeljko Sljivancanin

Daniel Spisak

Michiel Sprik

Mira Todorova

Hervé Toulhoat

Daniel Tunega

Dimitrios Vlachos

Elwira Wachowicz

Luhong Wang

Michele Warren

Mark Wilson

Changjun Zhang

Programme

Friday 7 September
Supper, Get-together-drinks

Saturday 8 September
Overview, challenges, real catalysis
Chairs: Axel Groβ, Anne Chaka

Philippe Sautet(F, CNRS, Villeurbanne, F)
Metal and oxide catalytic properties from first principles

Trevor Rayment(UK, Cambridge University, UK)
Electron Spectroscopy techniques for surface XAS studies of working catalysts operating under ambient conditions

Hervé Toulhoat(F, Institut Franais du Petrole, F)
Ab initio study of water-boehmite interfaces in the context of catalyst support manufacture

Laurent Pizzagalli (Université de Poitiers, F)
Modelling semiconductor surfaces and nanoparticles using first-principles simulation

Joost Frenken(NL, University of Leiden, NL)
A model catalyst in action

Poster session I

Sunday 9 September
Thermodynamics and liquids
Chairs: Matthias Scheffler, Philip Lindan

Michiel Sprik(NL, Cambridge University, UK)
Ab initio molecular dynamics study of redox reactions in solution

Marcus Mller(D, Institut fr Physik, Mainz, D)
Surface and interface properties of polymer solutions:
Monte Carlo simulations and self-consistent field theory

Kristen Fichthorn(US, Penn State University, US)
Molecular-dynamics simulation of nanoscopically confined fluids: from crankshafts to colloids

Matthias Scheffler(D, FHI-MPG, Berlin, D)
Get real: A perspective on the role of simulations

Poster session II

Monday 10 September

Solid-liquid interfaces

Chair: Claudine Noguera

Jeff Penfold(UK, Rutherford Appleton Lab., UK)

Surfaces, interfaces, colloids, surfactants and self assembly

Michael Philpott(US, National U. of Singapore, SG)

Theory of electrochemical interfaces

Gary Attard(UK, Cardiff University, UK)

Electrochemical characterisation of surface chirality
and structure in supported platinum nanoparticles

Excursion: boat trip to Porquerolles

Special discussion about the future of this conference series

Tuesday 11 September

Mechanics at the atomic scale

Chair: Andrew Fisher

Jacqueline Krim(US, North Carolina State U., US)

STM-QCM studies of the atomic-scale origins of friction

Ruben Perez(E, Univ. Autonoma de Madrid, E)

Two macroscopic probes for atomic bonding: noncontact
atomic force microscopy and brittle fracture

Carla Molteni(I, Cambridge University, UK)

Pressure induced structural transformations in semiconductor nanocrystals

Complex surface processes

Chair: Philip Lindan

Ulrike Diebold(A, Tulane University, US)

The interplay between bulk defect structure and surface
reactions on reducible metal oxides

Lars Pettersson(S, University of Stockholm, S)

Studying adsorption and reactions on metal-oxides
using embedded and gas phase cluster models

Conference dinner

Wednesday 12 September

General session

Antoine Georges(F, ENS Paris, F)

Dynamical mean-field theory applied to condensed matter

Mark Wilson(UK, University College London, UK)

Modelling the formation of low-dimensional crystallites in carbon nanotubes

Elena Akhmatskaya(UA, FUJITSU, UK)

Achieving high performance in computational chemistry
codes on modern computers

Bertrand Fritz(F, University of Strasbourg, F)

Thermodynamic simulations of clay materials

4.2 ESF Workshop/Conference Announcements

4.2.1 Workshop on Catalysis

We announce the 3rd workshop on

"Catalysis from first principles"

Universität Wien, February 21-23, 2002

Sponsored by

Ψ_k-ESF Network
Research Center and Science College "Computational Materials Science"
Institut für Materialphysik, Univ. Wien
Groupement de Recherche "Ab-initio MD applied to Catalysis"
(CNRS and Institut Français du Pétrole)
Center for Atomic Scale Materials Physics, DTU
Fritz-Haber-Institut der MPG

Scientific committee:

Jürgen Hafner
Jens Nørskov
Matthias Scheffler

Workshop secretariate:

Andreas Eichler, Tina Branis

Objective of the workshop

The aim of the meeting is to review the status of ab-initio total-energy calculations as a basis for the modelling and understanding of chemical reactions on solid surfaces at a microscopic level. Particular emphasis will be laid on the prospect of ab-initio simulations for finding and designing new catalysts. A further objective of the workshop will be to confront theoreticians with the challenges arising from new-experimental results and from practical applications in industry.

Participation will be by invitation only. However, at this time please feel free to suggest invited speakers and the topic of their contributions and/or participants (including yourself!) by sending an e-mail to Andreas Eichler (andreas.eichler@univie.ac.at) or Jürgen Hafner (juergen.hafner@univie.ac.at). For a preliminary list of speakers, consult the home-page of the workshop (http://cms.mpi.univie.ac.at/catconf/).

4.2.2 Workshop on Total Energy Methods in Computational Condensed Matter

"TOTAL ENERGY METHODS IN COMPUTATIONAL CONDENSED MATTER" TENERIFE 2002

Universidad de La Laguna, Tenerife (Canary Islands)
10-12 January 2002

Sponsored by

ESF-STRUC Psi-k Network
Universidad de La Laguna (ULL)
Universidad del Pais Vasco (UPV/EHU)

Scientific Committee

A. Baldereschi (EPFL, Laussanne, Switzerland)
S. Baroni (SISSA, Trieste, Italy)
M. Gillan (University College of London, London, UK)
K. Kunc (CNRS, University P. and M. Curie, Paris, France)
S. Louie (University of California - Berkeley, USA)
R. M. Martin (University of Illinois at Urbana-Champaign, USA)
M. Methfessel(Institut fur Semiconductor Physics, Frankfurt-Oder, Germany)
R. Needs(Cambridge University, Cambridge, UK)
P. Ordejon (ICMAB-CSIC, Barcelona, Spain)
M. Parrinello (Max Planck Institut fur Festkorperforchung, Stuttgart, Germany)
K. Terakura (NAIR, Tsukuba, Japan)
D. Vanderbilt (Rutgers University, New Jersey, USA)
E. Wimmer (Materials Design, Le Mans, France)

Organizing Committee

Alfonso Munoz (ULL, amunoz@ull.es)
Andres Mujica (ULL, amujica@ull.es)
Angel Rubio (UPV/EHU, arubio@sc.ehu.es)

The aim of this workshop was to bring together researchers of different backgrounds: density functional, many-body, and nuclear physics approaches in order to assess the present status of the ab-initio computation of, and to make connection with, up-to-date experimental characterization techniques. The workshop will have 20 invited talks and a poster session.

Young researchers and PhD students are encourage to participate. Make inquires for partial finantial support to: tfe2002@marengo.dfis.ull.es. Please include a small CV and a presentation from your advisor. A two days tutorial in the pseudopotential plane wave method will be organized on 14 and 15 Jaunary (depending on the number of students).

WEB PAGE: http://laguna.dfis.ull.es

List of speakers:

Carme Rovira (*Dept. Quimica Fisica, Universitat de Barcelona, Spain*), "First principles simulations of ligand binding to hemeproteins".

Risto M. Nieminen (*Helsinki University of Technology, Finland*), "Quantum dots in magnetic field - current-DFT calculations in real space".

Francesc Illas (*Universitat de Barcelona, Spain*), "Ab initio study of magnetic interactions and determination of effective hamiltonian parameters in high T_c superconductors".

Pedro Etxenike (*UPV/EHU, Spain*), "Lifetime of elecrons at surfaces".

Richard Needs (*Univ. Cambridge, U.K.*), title pending.

Luciano Colombo (*Universita degli Studi di Cagliari, Italy*), "Structural and electronic properties of a-Si/c-Si interface".

Lucia Reining (*Ecole Polytechnique, France*), title pending.

Nicola Marzari (*Department of Materials Science and Engineering (MIT), USA*), "Real-time chemical reactions via ab-initio molecular dynamics".

Nicolas Llorente (*Laboratoire Collisions, University Paul Sabatier (France)*), "Study of molecule chemisorption on noble metal surfaces".

Carla Molteni (*Cavendish Laboratory, TCM, Cambridge, U.K.*) "Nanostructures under pressure ".

Ferdi Aryasetiawan (*Research Institute for Computational Sciences Tsukuba Japan*), "Total energy method from many-body formulation".

R.Perez or J. Ortega (*UAM Madrid, Spain*), "Exchange-correlation Energy as a function of the orbital occupancies: Total Energy Calculations and Quasiparticles".

E. Chulkov (*Rusia*), "Quasiparticle dynamics at bulk and interfases".

A. Georges (*Ecole Normale, France*), "Recent advances in the dynamical mean-field theory of strongly correlated electron systems".

F. Mauri (*Paris, France*), title pending.

E. Koch (*Max Planck Sttutgart, Germany*), "Physics of the superconducting Fullerenes".

J. Gale (*Imperial College , UK*), "Towards large-scale electronic structure calculations with parallel SIESTA (or How many SIESTAs can you have at once?)".

Make inquires to:

tfe2002@marengo.dfis.ull.es
voice +34 922318275
Fax +34 922318320

4.2.3 Hands-on-FPLO Workshop

March 3-7, 2002, IFW Dresden

Supported by:	ESF-STRUC psi-k and IFW Dresden e.V.	
Purpose:	Introduction into the concept, the code, and the handling of the FPLO package	
Organizers:	Helmut Eschrig	h.eschrig@ifw-dresden.de
	Klaus Koepernik	k.koepernik@ifw-dresden.de
	Ulrike Nitzsche	u.nitzsche@ifw-dresden.de
	Manuel Richter	m.richter@ifw-dresden.de
	Dept. of Theoretical Solid State Physics Institute of Solid State and Materials Reserach (IFW) Dresden e.V. P.O. Box 270016 D-01171 Dresden, Germany	
Contact:	Manuel Richter (m.richter@ifw-dresden.de)	
Information:	http://www.ifw-dresden.de/events/fplo.htm	

This is a first information about the workshop 'Hands-on-FPLO' to be held in the first week of March 2002 at IFW Dresden. The intention is to provide the participants with an accurate, flexible, fast, and reliable tool to carry out density functional calculations on regular lattices. Please let me know your interest by sending back the following little form to

m.richter@ifw-dresden.de

Below you find more detailed information. A second information and registration form will be distributed in December.

```
-----------cut here---------------------------------------------------
Please remove the following address from the mailing list:

Please add the following address(es) to the mailing list:

I am interested and consider participation:

(please give your name, address, and probability of your participation)
-----------cut here---------------------------------------------------
```

The FPLO package is a full-potential minimum-basis local-orbitals code [1] to solve the Kohn-Sham equations in a regular lattice by using the local density approximation; the situation of a chemically disordered structure is covered by an implemented CPA (coherent potential approximation) solver [2]; relativistic effects can be treated in a related 4-component code that solves the Kohn-Sham-Dirac equations (RFPLO) [3]; the LSDA+U formalism is currently being implemented.

Much effort has been spent in the mentioned methods to achieve a level of numerical accuracy which is comparabel to advanced full-potential LAPW implementations, though the basis set is almost one order of magnitude smaller. In particular, the **absolute** values of the total energy were found to agree with the results of the FLAPW package WIEN-97 within about 1 mHartree per atom for non-relativistic calculations [1]. The agreement with respect to lattice parameters and bulk moduli is better than within 0.5 A comparison of the relativistic versions is currently being done. WIENxx and FPLO are to a certain extent complementary. While WIENxx in most cases still sets the accuracy standard, a major advantage of the FPLO package is its minimum basis concept. It makes highly accurate full-potential calculations for elementary cells of up to 100 transition metal atoms feasible and is a good starting point for approaches beyond the local density approximation.

References:

[1] K. Koepernik and H. Eschrig, Full-potential nonorthogonal local-orbital minimum-basis and-structure scheme, Phys. Rev. B 59, 1743 (1999); I. Opahle, K. Koepernik, and H. Eschrig, Full-potential band-structure calculation of iron pyrite, Phys. Rev. B 60, 14035 (1999).

[2] K. Koepernik, B. Velicky, R. Hayn, and H. Eschrig, Self-consistent LCAO-CPA method for disordered alloys, Phys. Rev. B 55, 5717 (1997).

[3] I. Opahle, PhD thesis, TU Dresden 2001 (publication in preparation).

Participants:	Those who are interested to get and use FPLO; for capacity reasons (available terminals and tutors in the practical sessions) we will have to restrict the number of participants to about 15. The workshop is meant to be a tutorial one. It should enable the participants to use FPLO, to interprete its output quantities, and to cope with simple problems that may arise when using the code.
place:	IFW Dresden e.V., Helmholtzstr. 20, Dresden, Germany http://www.ifw-dresden.de
time:	March 3-7, 2002

Preliminary schedule (status: November 20)

Place: IFW, room D2E.27

Sunday, March 3

Arrival and get-together at IFW

Monday, March 4

9:00 Opening (H. Eschrig)

9:10 DFT and the FPLO idea (H. Eschrig)

10:40 *Coffee*

11:00 The FPLO concept (K. Koepernik)

12:30 *Lunch*

14:00 Exercise: How can I run FPLO (simple systems)

15:40 *Coffee*

16:00 Performance and parallelization (U. Nitzsche)

17:30 Private discussion and exercises on request

Tuesday, March 5

9:00 Coherent Potential Approximation in FPLO (K. Koepernik)

10:30 *Coffee*

11:00 Fixed spin-moment calculations (M. Kuz'min)

11:30 Application to complex structures (H. Rosner)

12:00 Supercell approach for surfaces (M. Richter)

12:30 *Lunch*

14:00 Exercise: CPA, FSM, complex structures

15:40 *Coffee*

16:00 WIEN and FPLO: a comparison (M. Diviš)

16:30 Exercise (cont)

Wednesday, March 6

9:00 How to extract model parameters from FPLO (H. Rosner)

10:30 *Coffee*

11:00 LSDA+U in FPLO (I. Chaplyguine)

11:30 Relativistic FPLO (I. Opahle)

12:30 *Lunch*

14:00 Exercise: Model parameters, RFPLO

15:40 *Coffee*

16:00 lo-WIEN and RFPLO: a comparison (P. Novák/ J. Kunes)

16:30 Exercise (cont)

Thursday, March 7

Private discussion, exercises on request, departure

4.2.4 EMRS 2002 Spring Meeting: Atomic Scale Materials Design Symposium

EMRS 2002 Spring Meeting
Strasbourg, France
June 18-21, 2002
Symposium A
Atomic Scale Materials Design

Deadline for Abstract Submission: January 14, 2002
Details for registration and abstract submission can be found at:
http://www-emrs.c-strasbourg.fr
(go to the end of Announcement and description of symposia)

Symposium A provides a forum for researchers applying atomic scale computations to industrial problems, and allows experimentalists to address the computational materials science community on their requirements for atomic scale modelling and simulation. Although the areas of application for atomic scale computation are diverse, the underlying principles, algorithms and techniques are similar. Computational materials science has matured to the point where technological problems related to materials design, processing, and chemical synthesis, are being investigated directly by atomic scale calculation. We seek submissions with application of atomic scale materials design to:

- Microelectronics and Optoelectronic,
- Nanotechnology and Biotechnology
- Fine Chemicals and Drug Design
- Polymers

New computer aided design tools springing from computational materials science, physics and chemistry are being applied to reduce design cycle times and to eliminate costly design by trial and error within material oriented industries. Thus, Symposium A will explore the means by which **quantum Monte Carlo, ab initio quantum chemistry, density-functional theories and beyond, tight binding techniques, forcefield-based molecular dynamics and Monte Carlo simulations, molecular modelling, and mesoscale modelling** are being **applied to technology problems** related to materials design and characterisation. We seek applications of atomic scale computation to:

- Solids, liquids, gases
- Surfaces and interfaces
- Molecules and clusters

- Catalysis
- Biological molecules, macromolecules, polymers
- Plasmas, chemical vapor deposition, atomic layer deposition, and materials processing
- Nanostructures

We also seek submissions discussing advances in electronic structure theory, which enable new problems to be investigated.

Supported by the Ψ_k Network and the European Science Foundation.

Scientific Committee:
G.Gilmer, Bell Labs, USA
H.Goronkin, Motorola, USA
M.Jaraiz, University of Valladolid, Spain
J.Labanowski, Ohio Supercomputer Center, USA
J.-L. Leray, Commissariat a l'Energie Atomique CEA/DAM, France
P.Lindan, University of Kent, UK
D.Pettifor, Oxford University, UK
M.Scheffler, Fritz Haber Institute, Germany
T.Vrotsos, Texas Instruments, USA
G.Wachutka, Technische Universitaet Muenchen, Germany

Syposium Organizers:
Jim Greer
NMRC
University College
Lee Maltings, Prospect Row
Cork, Ireland
Tel: +353 21 4904345
Fax: +353 21 4270271
e-mail: Jim.Greer@nmrc.ie

Jrgen Hafner
Computational Materials
University of Vienna
Sensengasse 8
A-1090 Vienna, Austria
Tel: +43 1 4277 51401
Fax: +43 1 4277 9514
e-mail: Juergen.Hafner@univie.ac.at

Mehdi Djafari-Rouhani
Centre National de la
Recherche Scientifique (CNRS),
Laboratoire d'Analyse et
d'Architecture des Systmes (LAAS),
Toulouse , France
Tel: +5 61 33 64 96
Fax : +5 61 33 62 08
e-mail: djafari@laas.fr

Anatoli Korkin
Advanced Modeling & Simulation
Semiconductor Products Sector
Motorola Inc., MD M360
2200 W. Broadway Road
Mesa AZ, 85202 USA
Tel: +1 480 655-3171
Fax: +1 480 655-5013
e-mail: r40757@email.mot.com

Mike Finnis
Atomistic Simulation Group
School of Mathematics and Physics
The Queen's University of Belfast
Belfast BT7 1NN, Northern Ireland
Queen's University Belfast, UK
Tel.: +44 (0) 2890 335330
Fax: +44 (0) 2890 241958
e-mail: m.finnis@qub.ac.uk

4.2.5 The European Conference on PHYSICS OF MAGNETISM'02

July 1-5, 2002
Poznań, POLAND

Chairmen:

Andrzej Jezierski, *Institute of Molecular Physics, Polish Acadmy of Sciences, Poznań*
Roman Micnas, *Institute of Physics, Adam Mickiewicz University, Poznań*

The Conference **PHYSICS OF MAGNETISM'02** will be the tenth of the series organized, every three years since 1975, jointly by the Institute of Physics of the Adam Mickiewicz University and the Institute of Molecular Physics of the Polish Academy of Sciences in Poznań. The Conference is meant as an international forum for the presentation and discussion of novel scientific ideas, in a field of broadly understood magnetic phenomena (including experimental results and new materials) with special emphasis on the following subjects: **novel metallic oxides and anomalous magnetoresistive materials; low dimensional quantum magnets; heavy fermions, fluctuating valence and Kondo systems; magnetic multilayers, surfaces, and nanostructures; high temperature superconductors; electronic structure**.

The main objective of the Conference is to bring together scientists and technologists from the Western, Central and Eastern European countries involved in research and application of new magnetic materials and high temperature superconductors. The scope of the Conference is quite wide and covers: high-T_C superconductors, heavy fermions, mixed valence, rare-earth and actinides, quasi-1D and -2D magnets, disordered and amorphous magnetic alloys, magnetic semiconductors etc.

The plenary talks will be presented by the invited distinguished scientists from all over the world. The programme of 5-days Conference is planned to consist of 21 plenary talks and about 300 oral and poster contributed papers.

Information ⟶ http://www.ifmpan.poznan.pl/zp2/pm02.html

Secretaries:

A. Szajek

Institute of Molecular Physics
Polish Academy of Sciences

Smoluchowskiego 17, 60-179 Poznań, Poland
Phone: +48-61-8695 121
Fax: +48-61-8684 524

Email: pm02@ifmpan.poznan.pl

or

R.J. Wojciechowski

Institute of Physics
Adam Mickiewicz University

Solid State Theory Division
Umultowska 85, 61-614 Poznań, Poland
Phone: (+48-61)-8273041, 8273050, 8273043
Fax: +48-61-8257 758
Email: rom@alpha.amu.edu.pl

4.2.6 Brighton Conference: Mini-colloquium on Magnetoelectronics

19th General Conference of the Condensed Matter Division of the European Physical Society held jointly with CMMP 2002

April 7-11, 2002, Brighton, UK

Announcement and Call for Papers

We would like to draw your attention to the mini-colloquium on

Magnetoelectronics

to be held at the CMD19/CMMP2002 meeting.

There will be four invited talks: **P.M. Levy**, *"Magnetic Switching by Spin Injection"*; **P.J. Kelly**, *"Theory of Spin Transport"*; **J. Fontcuberta**, *"Colossal Magnetoresistance of Half-metallic Oxides"*; **D. Ferrand**, *"Ferromagnetism in Doped Semiconductors"*.

Poster contributions to this mini-colloquium are most welcome. There are many other colloquia on electronic structure and magnetism. Here we refer to the closely related mini-colloquium "Semiconductor spintronics and hybrid semiconductor/ferromagnet devices".

The deadline for submission of abstracts is 10 December 2001.

Further information concerning abstract submission as well as the conference can be found on the web at

http://physics.iop.org/IOP/Confs/CMD19/

Mini-Colloquium Organisers:

Peter H. Dederichs
Albert Fert
Laurens Molenkamp

4.2.7 Brighton Conference: Mini-colloquium on Non-Collinear Spin Structures

19th General Conference of the Condensed Matter Division of the European Physical Society held jointly with CMMP 2002

April 7-11, 2002, Brighton, UK

Announcement and Call for Papers

We would like to draw your attention to the mini-colloquium on

Non-Collinear Spin Structures

to be held at the CMD19/CMMP2002 meeting.

The deadline for submission of abstracts is 10 December 2001.

This mini-colloquium will cover methodological and conceptional advances on the (first-principles) description and in applications of non-collinear and spiral spin structures in bulk magnets, intermetallic compounds, disordered crystalline and amorphous alloys, multilayers, thin films, and nano-magnets. Specific topics may include:

- magnets with topological and geometrical frustration
- exchange bias
- 4f and 5f systems
- ab-initio treatment of spin-dynamics, spin-waves and magnon dispersion
- bridging the gap from ab-initio to micromagnetism
- finite temperature effects

This mini-colloquium is also supported by the Psi-k network (http://psi-k.dl.ac.uk) and a limited amount of financial support is available for young researchers.

Gustav Bihlmayer (Forschungszentrum Juelich, Germany) and **Martijn Marsman** (Universitaet Wien, Austria) will present invited talks. Contributions to this mini-colloquium are most welcome and encouraged. Some of the contributions will be chosen for 20 minute talks, while the others will be given as posters.

Further information concerning abstract submission as well as the conference can be found on the web at

http://physics.iop.org/IOP/Confs/CMD19/

Mini-Colloquium Organisers:

Stefan Bluegel (s.bluegel@fz-juelich.de)
Lars Nordstrom (larsn@fysik.uu.se)
Juergen Hafner (tina.branis@univie.ac.at -or- juergen.hafner@univie.ac.at)

4.2.8 Brighton Conference: Mini-colloquium on Electronic Structure of Correlated Systems

19th General Conference of the Condensed Matter Division of the European Physical Society held jointly with CMMP 2002

April 7-11, 2002, Brighton, UK

Announcement and Call for Papers

We would like to draw your attention to the mini-colloquium on

Electronic Structure of Correlated Systems

to be held at the CMD19/CMMP2002 meeting. This mini-colloquim is also supported by the Psi-k network (http://psi-k.dl.ac.uk) and limited amount of financial support is available for young researchers.

Prof Sasha Liechtenstein (University of Nijmegen, the Netherlands) will give an invited talk. Contributions to this mini-colloquium are most welcome. Some of the contributions will be chosen for 20 minute talks, while the others will be given as posters.

The deadline for submission of abstracts is 10 December 2001.

Further information concerning abstract submission as well as the conference can be found on the web at

http://physics.iop.org/IOP/Confs/CMD19/

Mini-Colloquium Organisers:

Antoine Georges
Thomas Pruschke
Walter Temmerman

4.2.9 Brighton Conference: Mini-colloquium on Wide Bandgap Semiconductors

19th General Conference of the Condensed Matter Division of the European Physical Society held jointly with CMMP 2002

April 7-11, 2002, Brighton, UK

Announcement and Call for Papers

We would like to draw your attention to the mini-colloquium on

Wide Bandgap Semiconductors

to be held at the CMD19/CMMP2002 meeting.

This colloquium will cover advances in basic science issues as well as in applications of wide bandgap semiconductors such as SiC, group-III nitrides, II/VI semiconductors including oxides. Specific topics include, but are not limited to:

Defects and doping in wide bandgap semiconductors
Optical and transport properties
Interfaces, extended defects and surfaces
Growth methods and simulations
- application of surfactants/antisurfactants
- formation of quantum dots
Applications
- electronic and optoelectronic devices
- sensors (chemical, optical)

This mini-colloquium is also supported by the Psi-k network (http://psi-k.dl.ac.uk) and limited amount of financial support is available for young researchers.

Martin Stutzmann (University of Munich, Germany) and **Chris Van de Walle** (Xerox Palo Alto Research Center, CA, USA) will give invited talks. Contributions to this mini-colloquium are most welcome. Some of the contributions will be chosen for 20 minute talks, while the others will be given as posters.

The deadline for submission of abstracts is 10 December 2001.

Further information concerning abstract submission as well as the conference can be found on the web at

http://physics.iop.org/IOP/Confs/CMD19/

Mini-Colloquium Organizers:

Joerg Neugebauer (neugebauer@fhi-berlin.mpg.de)
Wolfgang Richter (wolfgang.richter@tu-berlin.de)

4.2.10 Brighton Conference: Mini-colloquium on Mineralogy and Geophysics

19th General Conference of the Condensed Matter Division of the European Physical Society held jointly with CMMP 2002

April 7-11, 2002, Brighton, UK

Announcement and Call for Papers

We would like to draw your attention to the mini-colloquium on

Mineralogy and Geophysics

to be held at the CMD19/CMMP2002 meeting.

More than 60 mini-symposia organized during the meeting are aimed to cover a wide range of topics in the condensed matter area.

A mini-symposium "Mineralogy and Geophysics" is organized by Dr. Benco (Vienna University, Austria) and Prof. Winkler (Kiel/Frankfurt University, Germany). We would like to gather geophysicists and electronic-structure scientists to support interdisciplinary links and the establishment of a common language for mineralogy oriented researchers.

Invited speakers are **Martin Dove** (Cambridge, England) and **Dario Alfe** (University College London). Additional contributions are appreciated for both oral and poster presentation. Abstracts can be submitted through and more details can be found at the conference website

http://physics.iop.org/IOP/Confs/CMF19/

Dr. Lubomir Benco
Institute for Materials Physics
Vienna University
Sensengasse 8
A-1090 Vienna, Austria

5 General Workshop/Conference Announcements

5.1 Euro Winter School on Quantum Simulations

Euro Winter School

”Quantum Simulations of Complex Many-Body Systems: From Theory to Algorithms”

25 February - 1 March 2002 Rolduc/Kerkrade (NL)

http://www.fz-juelich.de/wsqs/

Call for Registration

Scope of the Winter School

This Winter School continues a recently lauched series of schools and conferences in Computational Science organized by the John von Neumann Institute for Computing (NIC). It will cover modern quantum simulation techniques and their implementation on high-performance computers, in particular on parallel systems. The focus clearly is on numerical methods which are tailored to treat large quantum systems with many coupled degrees of freedom ranging from superfluid Helium to chemical reactions. Among others, the following topics will be covered:

- Diffusion and Green’s function Monte Carlo
- Path integral Monte Carlo and molecular dynamics
- Car-Parrinello / ab initio molecular dynamics
- Real-time quantum dynamics for large systems
- Lattice and continuum algorithms
- Exchange statistics for Bosons and Fermions / sign problem
- Parallel numerical techniques and tools
- Numerical integration and random numbers

This strongly interdisciplinary School aims at bridging three ”gaps” in the vast field of large-scale quantum simulations: The first one between chemistry and physics, the second one between typical graduate courses in these fields and state-of-the-art research, and finally the one between the Monte Carlo and molecular dynamics communities. The participants - being mostly graduate students, postdocs as well as young researchers in the area of theoretical/computational physics and chemistry - are expected to have basic knowledge of quantum, classical, and statistical mechanics. They will benefit from this School by learning about recent methodological advances within and outside their field of specialization. In addition, they will get insights into recent software development and implementation issues involved, in particular in the context of high-performance computing.

For further details and registration:

http://www.fz-juelich.de/wsqs

Organization

This Euro Winter School is organized by the John von Neumann Institute for Computing (Forschungszentrum Juelich) Lehrstuhl fuer Theoretische Chemie (Ruhr-Universitaet Bochum) Institut fuer Theoretische Physik III (Universitaet Stuttgart). It is supported by European Commission as a "High-Level Scientific Conference"
Forschungszentrum Juelich
Ruhr-Universitaet Bochum
Universitaet Stuttgart.

We look forward to seeing you in Rolduc.

Johannes Grotendorst (Forschungszentrum Juelich)
Dominik Marx (Ruhr-Universitaet Bochum)
Alejandro Muramatsu (Universitaet Stuttgart)

5.2 9th International Conference on Theoretical Aspects of Catalysis

Zakopane, Poland, 25-30 June 2002

The conference is organized by the Institute of Catalysis and Surface Chemistry, Polish Academy of Sciences, Krakow, Poland and the Polish Catalysis Club.

The conference will consist of invited lectures, oral presentations and posters. In order to meet the requirements of modern catalysis we have decided to include in the conference topics all kinds of catalysis (heterogenous, homogenous, enzymatic) and different theoretical approaches (quantum chemistry, solid state physics, molecular dynamics). We have chosen keynote speakers according to the suggestions of participants. It is our pleasure to inform you that the following persons have been selected and agreed to deliver a lecture at our symposium: Jan Andzelm, Richard Catlow, Pierre Carlo Fantucci, Hans-Joachim Freund, Alexander Glushkov, Annick Goursot, Bjorg Hammer, Jozef Korecki, Matthew Neurock, Konstantin Neyman, Jens Norskov, John Neurig Thomas, Israel Wachs.

Keynote lectures will cover the modeling of:

- systems based on transition metal oxides
- metallic catalysts
- zeolites
- metalocenes
- bio-catalytic systems
- catalytic reactions

Further information about the conference are available on the conference web page:

http://www.ictac.ik-pan.krakow.pl

Prof. dr M. Witko
Institute of Catalysis and Surface Chemistry
Polish Academy of Sciences
Cracow, Poland

5.3 Brighton Conference: Mini-colloquium on Electronic Structure

19th General Conference of the Condensed Matter Division of the European Physical Society held jointly with CMMP 2002

April 7-11, 2002, Brighton, UK

Announcement and Call for Papers

We would like to draw your attention to the mini-colloquium on

Electronic Structure

to be held at the CMD19/CMMP2002 meeting.

Prof Francesco Mauri (*Universite Pierre et Marie Curie, France*) will give an invited talk. Contributions to this mini-colloquium are most welcome. Some of the contributions will be chosen for 20 minute talks, while the others will be given as posters.

The deadline for submission of abstracts is 10 December 2001.

Further information concerning abstract submission as well as the conference can be found on the web at

http://physics.iop.org/IOP/Confs/CMD19/

Mini-Colloquium Organisers:

Richard Needs
Michele Parrinello

5.4 Brighton Conference: Mini-colloquium on Magnetism in Reduced Dimensions

19th General Conference of the Condensed Matter Division of the European Physical Society held jointly with CMMP 2002

April 7-11, 2002, Brighton, UK

Announcement and Call for Papers

We would like to draw your attention to the mini-colloquium on

Magnetism in Reduced Dimensions

to be held at the CMD19/CMMP2002 meeting.

W. Hergert (*Martin Luther University, Germany*) and **S.S. Dhesi** (*ESRF, France*) will give invited talks. Contributions to this mini-colloquium are most welcome. Some of the contributions will be chosen for short talks, while the others will be given as posters.

This mini-colloquium will focuss on recent developments in the growth, electronic and magnetic behaviour of nanostructures, including clusters, 2D islands and atomic wires, on various substrates. XMCD measurements as well as Fano resonance in STM tunneling densities of states and Kondo resonances on such systems will be welcome. Considerations concerning the renormalisation group algorithm for quantum Hamiltonians in order to calculate energies and wave functions of small numbers of atoms are relevant also.

The deadline for submission of abstracts is 10 December 2001.

Further information concerning abstract submission as well as the conference can be found on the web at

http://physics.iop.org/IOP/Confs/CMD19/

Mini-Colloquium Organisers:

Chris Binns
L.P. Regnault
Jean-Claude Parlebas
Claude Demangeat

5.5 Brighton Conference: Mini-colloquium on Nanostructured Materials

19th General Conference of the Condensed Matter Division of the European Physical Society held jointly with CMMP 2002

April 7-11, 2002, Brighton, UK

Announcement and Call for Papers

We would like to draw your attention to the mini-colloquium on

Nanostructured Materials

to be held at the CMD19/CMMP2002 meeting.

The abstract submission deadline is 10 December 2001. Information concerning the abstract submission can be found on the conference website

http://physics.iop.org/IOP/Confs/CMD19/

The colloquium will be of special interest to researchers conducting theoretical and experimental studies in relation to:

Nanostructured Materials and Mesoscopic Physics
- electronic properties
- structural properties
- transport properties

Applications
- molecular electronics
- biophysics
- gas storage
- composite materials
- field-emission
- electro-mechanical devices (MENS)

New Theoretical Concepts related to Low Dimensionality and Experimental Characterisation (and Self Assembling) Techniques

The conference registration fees have not been finalised, but they will be about 30 GBP for students and about 130 GBP for EPS members and members of national physical societies affiliated to EPS. Please contact the organisers if you have any questions, and we look forward to welcoming you to Brighton.

Mini-Colloquium Organisers:

Siegmar Roth (s.roth@fkf.mpg.de)
Angel Rubio (arubio@sc.ehu.es)

6 General Job Announcements

One or more Postdoctoral Positions

Computational Materials Theory Group

Physics and Astronomy, Rutgers University

One or more postdoc positions may become available beginning summer or fall 2002, associated with Profs. David Langreth, Karin Rabe, and David Vanderbilt in the Computational Materials Theory Group, Department of Physics and Astronomy, Rutgers University. Experience with density-functional-based methods is strongly advantageous.

Interested applicants should send a CV, including names and contact information for three references, to Prof. Rabe by 1 February 2002. Email submission in the form of a postscript or pdf file is preferred.

rabe@physics.rutgers.edu

Prof. Karin Rabe
Dept. of Physics and Astronomy
Rutgers University
136 Frelinghuysen Road
Piscataway, NJ 08854-8019
USA

fax: 1-732-445-4343

Postdoctoral/Research Associate Positions in Electronic Structure Theory with Alex Zunger

National Renewable Energy Laboratory (NREL)
http://www.sst.nrel.gov

NREL's Solid State Theory Group is looking to fill postdoctoral or research associate positions in the areas of Electronic Structure Theory of (1) nanostructures (2),alloys, as well as(3) method development. These positions are with Dr. Alex Zunger and extend for 2-3 years starting January-August 2002 Applicants are expected to have a background in solid-state theory. Depending on experience and qualifications, the position could be at the rank of postdoctoral fellow ($40,000-53$,000 per year) or Research Associate ($52,000-65$,000 per year). More details about ongoing work in the group, computer facilities, personnel, publications are included in http://www.sst.nrel.gov. Clarification or further details can be obtained via e-mail to azunger@nrel.gov.

Interested candidates should send immediately a curriculum vitae, list of publications (including preprints of unpublished papers if possible), and arrange for two references addressed to:

Dr. Alex Zunger
National Renewable Energy Laboratory
1617 Cole Boulevard
Golden, Colorado 80401

NREL is an equal opportunity employer and proud of its commitment to diversity. Women and minorities are encouraged to apply.

Postdoctoral Position

First-Principles Calculations and Statistical Thermodynamics of Alloys

Penn State University

A postdoctoral position is immediately available to work on an exciting new multidisciplinary project involving universities (Penn State and University of Florida), industries (Ford, GE, and UES Inc.) and NASA-GRC. The objective is to develop computational tools for predicting the relationships among chemistry, microstructure, and mechanical properties in Ni-base superalloys. The main responsibility for the researcher will be to perform first-principles calculations of thermodynamic and kinetic properties that will be used to subsequently predict phase stability and microstructure. Although the official hire will be at Penn State, the researcher will have the opportunity to spend an extended period of time at Ford or at the Air Force Research Laboratory. Initial appointment will be for one year, and may be renewed annually, upon mutual agreement. For application, please send a copy of resume and names of three references to any one of the followings:

Professor Long-Qing Chen, 101 Department of Materials Science and Engineering and Materials Research Institute, Penn State University, University Park, PA 16802, phone: (814) 863-8101, fax: (814) 865-0016 (fax), email: lqc3@psu.edu.

Dr. Christopher Woodward, Materials Research Division, UES Inc., 4401 Dayton-Xenia Rd., Dayton, OH 45432, phone: (937)255-981, fax: (937) 656-7292,
e-mail: christopher.woodward@afrl.af.mil.

Dr. Christopher Wolverton, Ford Motor Company, MD3028/SRL, P. O. Box 2053 Dearborn, Michigan, 48121-2053, phone: (313) 390-9552, fax: (313) 322-7044, email: cwolvert@ford.com.

Penn State University is an equal opportunity employer.

Long-Qing Chen
Associate Professor
Department of Materials Science Engineering
Penn State University
University Park, PA 16802
814-863-8101 (phone)
814-865-0016 (fax)
lqc3@psu.edu or chen@ems.psu.edu
`http://www.ems.psu.edu/~chen`

Postdoctoral Position in Computational Matetrials Theory
Carnegie Institution of Washington, Washington D.C.

A postdoctoral associateship is available for a creative independent researcher at the Carnegie Institution of Washington, Washington D.C. to study ferroelectrics using first-principles methods. This research is to understand high electromechanical coupling piezoelectrics such as PMN-PT and PZN-PT. A second goal is to develop and test more accurate density functionals for these systems.

Applicants must be familiar with ab-initio density-functional methods, and should be adept at independent and collaborative research. Also important is the ability and inclination to write up research for publication in a timely way and to present results at scientific meetings. Facility with FORTRAN is essential and with MPI is highly desirable. Applicants should send a vita, bibliography, and 3 letters of reference to cohen@gl.ciw.edu . Please send applications by email (cohen@gl.ciw.edu) or fax to (253)322-2539, or to the following address:

Ronald Cohen
Geophysical Laboratory, Carnegie Institution of Washington
5251 Broad Branch Rd., N.W.
Washington, D.C. 20015

`http://www.gl.ciw.edu/~cohen/`

THEORY POSTDOC AT NRC OTTAWA, CANADA

Our group works mainly on structuring and functionalizing molecule-silicon interfaces. Through a detailed understanding of adsorbate/surface structures we aim to gain the control necessary to incorporate organic function into existing technologies and, eventually, to make new molecule scale devices. A parallel effort explores methods for determining transport properties of very small hybrid molecule/surface systems.

Experimental facilities include three UHV STMs (room temperature and variable temperature, one is combined AFM/STM) as well as FTIR, Auger, LEED, high resolution EELS. We also have two combination AFM/STM systems for operation under ambient or wet conditions.

To gain a detailed understanding of the physical processes involved we are collaborating with a number of theory groups in North America and Europe. We are looking for a theoretical physicist/chemist, to continue this work and to support the development of new methods for the description of electron transport and electron-phonon interactions.

The ideal candidate will have a PhD degree (required) in condensed matter theory/physical chemistry, as well as a strong background in theoretical modeling with state-of-the-art numerical methods. He will be expected to work with a range of existing codes based on density functional theory. After proper training he should be able to work independently with experimentalists in developing suitable models for experimental and numerical tests.

The position is paid on an internationally competitive level, appointments ordinarily run for two years and may be extended for a third year.

The research group includes people with backgrounds in chemistry, chemical physics and physics. We enjoy a pleasant and dynamic atmosphere where one can become immersed in exciting science. Ottawa, Canada's capital, offers the advantages of a big city, while the scenic beauty of its environment is ideal for a wide range of outdoor activities ranging from bicycling (dedicated bike paths run across the city) as well as skating (along the canal), ice-skating and skiing.

If you are interested please apply in writing to:

Robert A. Wolkow
National Research Council
100 Sussex Drive
Ottawa, Ontario K1A 0R6
Canada

bob.wolkow@nrc.ca

Position in Nuclear Solid State Physics group

University of Leuven, Belgium

A position is available for a Ph.D. student (4 years) and/or a post-doc (2 years, extension possible) in the Nuclear Solid State Physics group at the University of Leuven (Belgium). The goal of the project is the application of ab initio electronic structure methods to condensed matter problems, in tight collaboration with the experimentalists in the group. A large majority of the research group consists of experimentalists, using hyperfine interaction and ion beam techniques to study low-dimensional solids. The existence of accurate ab initio codes has lead to an increasing input of theoretical results in our research. The successful candidate will divide his/her time between a theoretical research project that is loosely connected to the running experimental work, and smaller theoretical projects that are raised by the needs of the experimentalists. For a Ph.D. student, a good knowledge of the fundamentals of condensed matter is required. Additionally, for a postdoc familiarity with the concepts and use of ab initio electronic structure codes is required. Knowledge of hyperfine interactions and Unix skills are useful but not fundamental. In principle, no theory development or programming tasks are contained in this project. Applications are considered until the position(s) are filled. A starting date can be agreed on (immediately is possible).

An overview of our activities can be found at:

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

For questions and details about how to apply, contact:

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

tel: + 32 16 32 72 59
fax: + 32 16 32 79 85
e-mail: Stefaan.Cottenier@fys.kuleuven.ac.be
http://www.fys.kuleuven.ac.be/iks/nvsf/nvsf.htm

POSTDOCTORAL POSITION IN COMPUTATIONAL MATERIALS SCIENCE
LAWRENCE BERKELEY NATIONAL LABORATORY

Lawrence Berkeley National Laboratory has one immediate postdoctoral opening in electronic structure calculations. The position is funded by a joint project between the scientific computing group at the National Energy Research Scientific Computing Center (NERSC), the Advanced Light Source (ALS) and the Materials Sciences Division (MSD) at LBNL. The hired person will work with Lin-Wang Wang and Andrew Canning at NERSC and Michel Van Hove in the ALS and MSD. The hired person will be working on first principles electronic structure calculations for systems of relevance to experiments carried out at the Advanced Light Source. It is also expected that he or she will be involved in methodology and code development, as well as apply simulation codes to interpret data measured by photoelectron diffraction and x-ray absorption fine structure. This project will involve close collaboration with experimentalists at the ALS and MSD at LBNL.

A Ph.D degree in physics or a related field is required and experience in electronic structure calculations is preferred. The position is initially for one year with the possibility of renewal for up to three years. A highly competitive salary will be offered. NERSC (http://www.nersc.gov) is the largest civilian research computer center in the United States with its recently installed 3328 processor IBM SP computer being the second fastest in the world (http://www.top500.org). The scientific computing group (http://www.nersc.gov/research/SCG) is a diverse group working on various aspects of scientific computation. More information about our research activities can be found at http://www.nersc.gov/. The Advanced Light Source is the world's brightest source of ultraviolet and soft x-ray beams–and the world's first third-generation synchrotron light source in its energy range–the ALS makes previously impossible studies possible. To learn more, please visit http://www-als.lbl.gov/. A strong and diverse experimental research program in nanoscience is associated with the ALS: the hired person would be able to interact closely with several of the relevant efforts.

Interested persons should send their curriculum vitae by email to canning@nersc.gov or by regular mail to

Andrew Canning
LBNL MS-50F
One Cyclotron Road
Berkeley CA94720
USA

Research Associate Position in Many–Body Quantum Simulations

Theoretical Chemistry, Ruhr-Universitaet Bochum

Applications are invited for an anticipated postdoctoral research associate position (German nomenclature: promovierter wiss. Mitarbeiter, BAT IIa), which includes full health, dental, and social benefits. The appointment will be for two years in the first instance, but an extension for two more years is very likely. Starting date is expected to be spring or summer 2002.

Applicants should hold a doctorate in theoretical/computational physics or a related discipline. In addition to excellent programming and computational skills the ideal candidate would have significant experience in *path integral* techniques and quantum simulations. She or he would work primarily on the development of novel *path integral* simulation techniques. In addition, he/she can be involved in other challenging research projects including both method development and large-scale applications. The Theoretical Chemistry Group at RUB offers an exciting interdisciplinary environment with excellent working conditions. The general interests of the group are covered in

`http://www.theochem.ruhr-uni-bochum.de/go/cprev.html`

and additional information can be obtained from the home page given below.

Related to the research topic(s) is also the upcoming Euro Winter School on "Quantum Simulations of Complex Many–Body Systems"

`http://www.fz-juelich.de/wsqs/`

Candidates should send a detailed resume including an outline of their research achievements and interests as well as the names and email addresses of academic references 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.

Graduate Positions

New Jersey Institute of Technology
Computational Condensed Matter Physics

Several graduate positions (for Ph. D candidates) are available immediately for students to work with Prof. Sergej Savrasov in Department of Physics, New Jersey Institute of Technology, on electronic structure calculations of strongly correlated electronic systems. The project involves extensive development of methods, algorithms and computer programs for integrating the dynamical-mean-field based many-body methods into the electronic structure framework as well as their applications to materials with strong correlations. Financial support will be provided via teaching assistants (TA) for the students with good GRE scores. The New Jersey Institute of Technology is located in downtown Newark with access to the Manhattan area. We have strong collaborations with Bell Laboratories, Rutgers University, Princeton University and Columbia University. To secure TA positions and to allow for student visa paperwork, interested candidates should contact S. Savrasov at savrasov@oak.njit.edu as soon as possible. Please also supply the names and addresses (e-mails) of two references. For additional information, please visit our web site http://www.njit.edu.

7 Abstracts

Spin currents and spin dynamics in time-dependent density-functional theory

K. Capelle[1], G. Vignale[2], B. L. Györffy[3]
[1] *Instituto de Química de São Carlos, Departamento de Química e Física Molecular, Universidade de São Paulo, Caixa Postal 780, São Carlos, 13560-970 SP, Brazil*
[2] *Department of Physics and Astronomy, University of Missouri-Columbia, Columbia, Missouri 65211, USA*
[3] *H.H. Wills Physics Laboratory, University of Bristol, Bristol BS8 1TL, United Kingdom*

Abstract

We derive and analyse the equation of motion for the spin degrees of freedom within time-dependent spin-density-functional theory (TD-SDFT). Results are (i) a prescription for obtaining many-body corrections to the single-particle spin currents from the Kohn-Sham equation of TD-SDFT, (ii) the existence of an exchange-correlation (xc) torque within TD-SDFT, (iii) a prescription for calculating, from TD-SDFT, the torque exerted by spin currents on the spin magnetization, (iv) a novel exact constraint on approximate xc functionals, and (v) the discovery of serious deficiencies of popular approximations to TD-SDFT when applied to spin dynamics.

(Accepted by Phys. Rev. Lett.)
Contact person: Klaus Capelle (capelle@iqsc.sc.usp.br)

Nonuniqueness and derivative discontinuities in density-functional theories for current-carrying and superconducting systems

K. Capelle[1], G. Vignale[2]

[1] *Instituto de Química de São Carlos, Departamento de Química e Física Molecular, Universidade de São Paulo, Caixa Postal 780, São Carlos, 13560-970 SP, Brazil*

[2] *Department of Physics and Astronomy, University of Missouri-Columbia, Columbia, Missouri 65211, USA*

Abstract

Current-carrying and superconducting systems can be treated within density-functional theory if suitable additional density variables (the current density and the superconducting order parameter, respectively) are included in the density-functional formalism. Here we show that the corresponding conjugate potentials (vector and pair potentials, respectively) are *not* uniquely determined by the densities. The Hohenberg-Kohn theorem of these generalized density-functional theories is thus weaker than the original one. We give explicit examples and explore some consequences.

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

Exchange-correlation effects in magnetic-field-induced superconductivity

K. Capelle

Instituto de Química de São Carlos, Departamento de Química e Física Molecular,
Universidade de São Paulo, Caixa Postal 780, São Carlos, 13560-970 SP, Brazil

Abstract

Motivated by recent experiments on the organic superconductor $\lambda - (BETS)_2FeCl_4$ we study the Jaccarino-Peter effect (JPE), the earliest example of magnetic-field-induced superconductivity, from the point of view of current-density-functional theory. It is found that both Meissner (diamagnetic) and Pauli (paramagnetic) pair breaking are suppressed by an exchange-correlation contribution to the vector potential, arising at the sites of the magnetic ions. This explains a number of otherwise puzzling experimental observations, and sheds new light on earlier theories of the JPE.

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

Magnetic coupling in Co/Pt multilayers studied by soft X-ray Resonant Magnetic Scattering

Chesnel K.[a], Belakhovsky M.[a], Landis S.[a], Rodmacq B.[a],
Dudzik E.[c], Collins S.P.[b], Dhesi S.S.[d], van der Laan G.[b]
[a]*CEA, DRFMC, SP2M, F-38054 Grenoble, France*
[b]*Daresbury Lab, Magnet Spectroscopy Group, Warrington WA4 4AD, Cheshire, UK*
[c]*Hahn Meitner Inst Kernforsch Berlin GmbH, D-14109 Berlin, Germany*
[d]*ESRF, F-38054 Grenoble, France*

Abstract

Arrays of silicon lines covered by a [Co(5)Angstrom /Pt-18 Angstrom] multilayer have been studied by soft X-ray Resonant Magnetic Scattering (XRMS). The magnetic peaks, which appear at the Co L-3 resonance, reveal the magnetic periodicity in the array, resulting from the magnetic coupling between the top of the lines, with a varying degree of influence from the trenches. In agreement with MFM images, the evolution of the magnetic peak intensities shows that small interline spacings and deep trenches favor antiferromagnetic order, which can be further reinforced by a specific demagnetization process.

(IEEE TRANSACTIONS ON MAGNETICS **37** (4), 1661-1663 (2001))
Contact person: G. van der Laan (G.vanderLaan@dl.ac.uk)

Resonant photoemission investigation of the electronic structure of Pu

Tobin J.G.[a], Terry J.[b], Schulze R.K.[c], Farr J.D.[c], Zocco T.[c],
Heinzelman K.[c], Rotenberg E.[c], Shuh D.K.[c], van der Laan G.[d],
Arena D.A.[a]
[a]*Lawrence Livermore Natl Lab, Livermore, CA 94550 USA*
[b]*Los Alamos Natl Lab, Los Alamos, NM 87545 USA*
[c]*Lawrence Berkeley Natl Lab, Berkeley, CA USA*
[d]*Daresbury Lab, Warrington, Cheshire, England*

Abstract

ABSTRACTS OF PAPERS OF THE AMERICAN CHEMICAL SOCIETY 222: 93-NUCL, 2001

Contact person: G. van der Laan (G.vanderLaan@dl.ac.uk)

Spin and orbital magnetic moments of ultrathin Fe films on GaAs(100)

Xu Y.B.[a], Tselepi M.[a], Dudzik E.[b], Guertler C.M.[a],
Vaz C.A.F.[a], Wastlbauer G.[a], Freeland D.J.[a], Bland J.A.C.[a],
van der Laan G.[b]
[a] *Univ Cambridge, Cavendish Lab, Cambridge CB3 0HE, England*
[b] *Daresbury Lab, Warrington WA4 4AD, Cheshire, England*

Abstract

The spin and orbital magnetic moments of 33 and 8 ML epitaxial BCC Fe films grown on GaAs(1 0 0)-4 x 6 have been measured using X-ray magnetic circular dichroism. Both samples have approximately the same spin moments of about 2.0 mu (B) close to that of the bulk value, which confirms that there are no magnetic dead layers at the interface. A giant orbital moment enhancement of about 300partially due to an increased degree of localization of electronic states at the Fe/GaAs interface.

(JOURNAL OF MAGNETISM AND MAGNETIC MATERIALS **226**, 1643-1645 (2001))
Contact person: G. van der Laan (G.vanderLaan@dl.ac.uk)

Magnetocrystalline anisotropy in FePd alloys studied using transverse X-ray magnetic circular dichroism

Dhesi S.S.[c], van der Laan G.[a], Durr H.A.[a], Belakhovsky M.[b],
Marchesini S.[b], Kamp P.[b], Marty A.[b], Gilles B.[b], Rogalev A.[c]
[a]*Daresbury Lab, Magnet Spect Grp, Warrington WA4 4AD, Cheshire, England*
[b]*CEA, SP2M, Dept Rech Fondamentale Matiere Condensee, Grenoble, France*
[c]*European Synchrotron Radiat Facil, F-38043 Grenoble, France*

Abstract

The structural and magnetic properties of Fe0.5Pd0.5 alloys have been correlated using X-ray diffraction (XD), vibrating sample magnetometry (VSM) and transverse X-ray magnetic circular dichroism. (TXMCD) at the Pd L-2,L-3 edges. XD indicates that codeposition of Fe and Pd, at elevated temperatures (350 degreesC), results in a well-ordered L1(0) phase which exhibits perpendicular magnetic anisotropy (PMA). On the other hand, codeposition at room temperature results in a disordered phase with in-plane easy-axis of magnetization. By codepositing at intermediate temperatures, a series of alloys has been produced with varying degree of compositional order. The TXMCD results show that increased compositional ordering leads to an increased orbital moment anisotropy favouring PMA. The magnetocrystalline anisotropy energy resulting from the orbital anisotropy is compared to VSM results.

(JOURNAL OF MAGNETISM AND MAGNETIC MATERIALS **226**, 1580-1582 (2001))
Contact person: G. van der Laan (G.vanderLaan@dl.ac.uk)

Ab initio calculations of theoretical tensile strength in metals and intermetallics

M. Šob[1], L. G. Wang[1,4], M. Friák[1,2], V. Vitek[3]
[1] *Institute of Physics of Materials, Academy of Sciences of the Czech Republic,*
Žižkova 22, CZ-616 62 Brno, Czech Republic
[2] *Institute of Condensed Matter Physics, Faculty of Science, Masaryk University,*
Kotlářská 2, CZ-611 37 Brno, Czech Republic
[3] *Department of Materials Science nad Engineering, University of Pennsylvania,*
3231 Walnut St., Philadelphia, PA 19104-6272, U.S.A.
[4] *Solid State Theory Group, National Renewable Energy laboratory,*
1617 Cole Blvd., Golden, CO 80401, U.S.A.

Abstract

The paper gives an account of applications of quantum-mechanical (first-principles) electronic structure calculations to the problem of theoretical tensile strength in metals and intermetallics. First, we briefly describe the way of simulating the tensile test and the electronic structure calculational method. Our approach is then illustrated on calculations of theoretical tensile strength in W, NiAl and transition metal disilicides $MoSi_2$ and WSi_2 with $C11_b$ structure. In W and NiAl, we consider uniaxial tension along [001] and [111] directions. Although tungsten is elastically nearly isotropic ($C_{44} \approx C'$), theoretical tensile strength exhibits a marked anisotropy ($\sigma^{th}_{001} = 29$ GPa, $\sigma^{th}_{111} = 40$ GPa). Calculated results compare favorably with experimental value of 24.7±3.6 GPa obtained for tungsten whiskers grown along the [110] direction. Similarly, in NiAl, the 'hard' orientation [001] differs very significantly from the [111] orientation ($\sigma^{th}_{001} = 46$ GPa, $\sigma^{th}_{111} = 25$ GPa). This anisotropy is explained in terms of higher-symmetry structures present or absent on the calculated deformation paths. In disilicides, the theoretical strength is calculated for [001] loading ($\sigma^{th}_{001} =$ 37 GPa and 38 GPa for $MoSi_2$ and WSi_2, respectively). The role of relaxation of internal structure parameter is discussed and changes in bonding conditions during the tensile test are analyzed.

(Published in Computational Modeling of Materials, Minerals, and Metals Processing, eds. M. Cross, J.W. Evans, and C. Bailey, The Minerals, Metals & Materials Society, Warrendale, PA, 2001, pp. 715-724.)

Contact person: Mojmír Šob (mojmir@ipm.cz)

The role of the ab initio electronic structure calculations in contemporary materials science

M. Šob[1], M. Friák[1,2], L. G. Wang[1,4], V. Vitek[3]
[1] *Institute of Physics of Materials, Academy of Sciences of the Czech Republic,*
Žižkova 22, CZ-616 62 Brno, Czech Republic
[2] *Institute of Condensed Matter Physics, Faculty of Science, Masaryk University,*
Kotlářská 2, CZ-611 37 Brno, Czech Republic
[3] *Department of Materials Science nad Engineering, University of Pennsylvania,*
3231 Walnut St., Philadelphia, PA 19104-6272, U.S.A.
[4] *Solid State Theory Group, National Renewable Energy laboratory,*
1617 Cole Blvd., Golden, CO 80401, U.S.A.

Abstract

Ab initio electronic structure theory has achieved considerable reliability concerning predictions of physical and chemical properties and phenomena. It provides understanding of matter at the atomic and electronic scale with an unprecendented level of detail and accuracy. In the present contribution, the state-of-the-art *ab initio* electronic structure calculation methods in solids are briefly reviewed and their applications are illustrated on the following problems: (i) magnetism of iron and its changes during phase transformations, (ii) theoretical tensile strength of metals and intermetallics, (iii) generation of interatomic potentials for large-scale computer simulations of defect configurations.

(To be published in Modeling Materials and Its Applications in Advanced Technologies, Symp. L of the Int. Conf. on Materials for Advanced Technologies (ICMAT 2001, Singapore, July 1-6, 2001), eds. C.H. Chiu, Z. Chen,H. Gao,K.Y. Lam, and A. Tay,Key Engineering Materials, ©2001 Trans Tech Publications, Zürich, Switzerland 2001.)

Contact person: Mojmír Šob (mojmir@ipm.cz)

Ab initio study of iron magnetism along Bain's path

M. Šob[1], M. Friák[1,2], V. Vitek[3]

[1] *Institute of Physics of Materials, Academy of Sciences of the Czech Republic,*
Žižkova 22, CZ-616 62 Brno, Czech Republic
[2] *Institute of Condensed Matter Physics, Faculty of Science, Masaryk University,*
Kotlářská 2, CZ-611 37 Brno, Czech Republic
[3] *Department of Materials Science nad Engineering, University of Pennsylvania,*
3231 Walnut St., Philadelphia, PA 19104-6272, U.S.A.

Abstract

A detailed theoretical study of magnetic behavior of iron along the bcc-fcc (Bain's) transformation paths at various atomic volumes is presented. The total energies and magnetic moments are calculated by spin-polarized full-potential LAPW method and are displayed in contour plots as functions of tetragonal distortion c/a and volume; borderlines between various magnetic phases are shown. Stability of tetragonal magnetic phases of γ-Fe is discussed. The calculated phase boundaries are used to predict the lattice parameters and magnetic states of iron overlayers on various (001) substrates. Detailed comparison of the LDA and GGA results is performed.

(To be published in Electron Correlations and Materials Properties 2, edited by A. Gonis et al., Kluwer Academic Publishers, Boston-London-Dordrecht, 2001 or 2002.)
Contact person: Mojmír Šob (mojmir@ipm.cz)

An *ab initio* Green-function formulation of the transfer matrix: Application to complex bandstructures

D. Wortmann[1], H. Ishida[2], and S. Blügel[3]
[1] *Institut für Festkörperforschung, Forschungszentrum Jülich,*
D-52425 Jülich, Germany
[2] *College of Humanities and Sciences, Nihon University,*
Sakura-josui, Tokyo 156, Japan,
[3] *Fachbereich Physik, Universität Osnabrück,*
D-49069 Osnabrück, Germany

Abstract

A new method for the first-principles calculation of the transfer matrix is presented. The method is based on a Green-function formulation and allows to relate the wavefunctions and their derivatives on boundaries at opposite sides of a film or junction of finite thickness. Both the underlying theory and an actual implementation in the full-potential linearized augmented planewave (FLAPW) method are described. Currently the embedding method is used to evaluate the Green-function matrix-elements and in turn we show that the transfer matrix can be used to construct the embedding potential. Some possible applications of the transfer-matrix method such as the calculations of the complex bandstructure or the calculation of the transmission and reflection coefficients for ballistic transport are discussed. As a first example, complex bandstructures of Cu, Fe, and Si are presented.

(submitted to Phys. Rev. B)
Contact person: d.wortmann@fz-juelich.de

Understanding electron-positron momentum densities in paramagnetic chromium

A. Rubaszek
W. Trzebiatowski Institute of Low Temperature and Structure Research,
Polish Academy of Sciences, P.O.Box 1410, 50-950 Wrocław 2, Poland
Z. Szotek and W.M. Temmerman
Daresbury Laboratory, Daresbury, Warrington, WA4 4AD, Cheshire, U.K.

Abstract

We focus on discrepancies between calculated and three-dimensional reconstructed electron-positron momentum densities in paramagnetic chromium, and consider various effects that can lead to such differences. In this context, the usefulness of the theoretical electron-positron momentum densities for interpreting experimental data, and gaining insight into underlying electronic structure, is also discussed.

(Submitted to Phys. Rev. B)
Contact person: Anna Rubaszek (ania@int.pan.wroc.pl)

Quantum theory of dissociative chemisorption on metal surfaces

Geert-Jan Kroes
Leiden Institute of Chemistry, Gorlaeus Laboratories, P.O. Box 9502,
2300 RA Leiden, The Netherlands
Axel Groß
Physik-Department T30, Technische Universität München, 85747 Garching, Germany
Evert-Jan Baerends
Theoretical Chemistry, Free University, De Boelelaan 1083, 1081 HV Amsterdam,
The Netherlands
Matthias Scheffler
Fritz-Haber-Institut der Max-Planck-Gesellschaft, Faradayweg 4–6,
14195 Berlin-Dahlem, Germany
Drew A. McCormack
Leiden Institute of Chemistry, Gorlaeus Laboratories, P.O. Box 9502,
2300 RA Leiden, The Netherlands

Abstract

Recent theoretical progress in molecule-surface reaction dynamics, a field relevant to heterogeneous catalysis, is described. One of the most fundamental reactions, the dissociative chemisorption of H_2 on metal surfaces, can now be treated accurately using quantum mechanics. Density functional theory is used to compute the molecule-surface interaction, and the motion of the hydrogen atoms is simulated using quantum dynamics, modeling the motion in all six molecular degrees of freedom. Theory is in good quantitative agreement with molecular beam experiments, offering useful interpretations, and allowing reliable predictions. The success of this approach calls for extension to larger systems, such as dissociative chemisorption of polyatomic molecules.

(submitted to: Accounts of Chemical Research)
Contact person: Axel Groß (agross@ph.tum.de)

Metastable precursors during the oxidation of the Ru(0001) surface

Karsten Reuter[1], M. Verónica Ganduglia-Pirovano[1], Catherine Stampfl[1,2],
and Matthias Scheffler[1]
[1]*Fritz-Haber-Institut der Max-Planck-Gesellschaft, Faradayweg 4–6,*
14195 Berlin-Dahlem, Germany
[2]*Northwestern University, 2145 Sheridan Road, Evanston IL60208, USA*

Abstract

Using density-functional theory, we predict that the oxidation of the Ru(0001) surface proceeds via the accumulation of sub-surface oxygen in two-dimensional islands between the first and second substrate layer. This leads locally to a decoupling of an O-Ru-O trilayer from the underlying metal. Continued oxidation results in the formation and stacking of more of these trilayers, which unfold into the $RuO_2(110)$ rutile structure once a critical film thickness is exceeded. Along this oxidation pathway, we identify various metastable configurations. These are found to be rather close in energy, indicating a likely lively dynamics between them at elevated temperatures, which will affect the surface chemical and mechanical properties of the material.

(submitted to: Phys. Rev. B)
Contact person: Karsten Reuter (reuter@fhi-berlin.mpg.de)

Energy barriers and chemical properties in the coadsorption of carbon monoxide and oxygen on Ru(0001)

Catherine Stampfl[1,2] and Matthias Scheffler[2]
[1]*Department of Physics and Astronomy, Northwestern University,*
Evanston 60208-3112, Illinois, USA
[2]*Fritz-Haber-Institut der Max-Planck-Gesellschaft, Faradayweg 4–6,*
14195 Berlin-Dahlem, Germany

Abstract

Using density-functional theory we investigate the interactions and chemical properties of the coadsorption of carbon monoxide and oxygen on ruthenium (0001). For the adsorption phases that occur in nature, where CO occupies the top site, we find that with increasing oxygen coverage, the adsorption energy of CO can remain practically unchanged or even exhibit a slight *increase*. We attribute the increase to an O-induced lateral weakening of Ru-Ru bonds of non-O-bonded surface Ru atoms. Thus, these non-O-bonded Ru atoms can form stronger bonds to an on-top CO adsorbate. In contrast, a more expected behavior of a notable decrease in CO adsorption energy with increasing O coverage is observed only if the O atoms bond to the *same* Ru atoms as CO as, for example, is the case when CO occupies hollow sites. Furthermore, for some of the structures, we find that there is a manifestation of small activation energy barriers for CO adsorption well above the surface.

(submitted to: Phys. Rev. B)

Contact person: Catherine Stampfl (stampflc@fhi-berlin.mpg.de)

First-principles surface phase diagram for hydrogen on GaN surfaces

C. G. Van de Walle
Xerox Palo Alto Research Center, 3333 Coyote Hill Road, Palo Alto, CA 94304, USA
J. Neugebauer
Fritz-Haber-Institut der Max-Planck-Gesellschaft, Faradayweg 4–6,
14195 Berlin-Dahlem, Germany

Abstract

We discuss the derivation and interpretation of a generalized surface phase diagram, based on first-principles density-functional calculations. Applying the approach to hydrogenated GaN surfaces, we find that the Gibbs free energies of relevant reconstructions strongly depend on temperature and pressure. Choosing chemical potentials as variables results in a phase diagram that provides immediate insight in the relative stability of different structures. A comparison with recent experiments illustrates the power of the approach for interpreting and predicting energetic and structural properties of surfaces under realistic growth conditions.

(submitted to: Phys. Rev. Lett.)
Contact person: Jörg Neugebauer (neugebauer@fhi-berlin.mpg.de)

Electronic Structure and Stability of the Ferrimagnetic Ordering in Double Perovskites

I. V. Solovyev
JRCAT-Angstrom Technology Partnership, c/o AIST, Central 4,
1-1-1 Higashi, Tsukuba, Ibaraki 305-0046, Japan
and
Institute of Metal Physics, Russian Academy of Sciences,
Ekaterinburg GSP-170, Russia

Abstract

Using results of first-principles band structure calculations and a model tight-binding approach we investigate the local stability of the half-metallic ferrimagnetic (FiM) states in double perovskites Sr_2FeMO_6 ($M=$ Mo, Re, and W). In ordered compounds, a generalized double exchange (DE) mechanism operating in the metallic minority-spin channel, in a hybrid Fe-M derived t_{2g} band, always competes with the strong antiferromagnetic superexchange (SE) interactions in the Fe-sublattice mediated by virtual electron hoppings into the unoccupied $M(d)$ states. In the local-spin-density approximation (LSDA), the SE mechanism largely prevails and the FiM phase is unstable with respect to a non-collinear spin-spiral alignment. The situation appears to be more generic. So, the on-site Coulomb repulsion between the Fe($3d$) electrons (ΔU) on the top of the LSDA picture suppress the SE interactions but may also modify some of the DE interactions through the change of the Fe-M hybridization. The total change of the electronic structure, caused by ΔU alone, does not explain the local stability of the FiM state. Therefore, we conclude that the FiM phase cannot be stabilized by purely electronic mechanisms. According to our scenario, that is exactly the situation realised in Sr_2FeWO_6. The experimental FiM ordering observed in Sr_2FeMoO_6 and Sr_2FeReO_6 should invoke to an additional mechanism, which destroys the half-metallic character of the electronic structure and decreases the saturation moment. We consider two possibilities: the alternating breathing distortions of the FeO_6 and MO_6 octahedra, and the anti-site (Fe-M interchange) disorder. In the former case, the oxygen displacement towards the Fe-sites leads to the partial depopulation of the majority-spin Fe(e_g) band and thereby activates an effective channel for the ferromagnetic DE interactions, similar to colossal-magnetoresistive manganites. In the latter case, the FiM ordering can be stabilized by SE interactions of a small (less than 10%) amount of Fe impurities with the host atoms. We discuss possible implications of these scenarios to different compounds with the emphasis on their magnetic and optical properties.

(Submitted to Phys. Rev. B)
Manuscripts available from: igor@jrcat.or.jp

Surfactant mediated heteroepitaxy versus homoepitaxy: Kinetics for group-IV adatoms on As-passivated Si(111)

K. Schroeder, A. Antons, R. Berger, and S. Blügel[1]
Institut für Festkörperforschung, Forschungszentrum Jülich,
D-52425 Jülich, Germany
[1] *Fachbereich Physik, Universität Osnabrück,*
D-49069 Osnabrück, Germany

Abstract

Using *ab initio* calculations we have determined the paths and activation energies for diffusion of group-IV atoms (Si, Ge, Sn) on top of the As layer on As-passivated Si(111), and for exchange with an As atom. The kinetics of Si, Ge, and Sn adatoms is substantially different: Si adatoms are readily incorporated under the As-layer. Ge adatoms diffuse on top of the As layer very far and can reach existing steps. The ratio between diffusion and exchange barrier strongly depends on the strain of the growing Ge film. Sn atoms remain on top of the As layer.

(Accepted at Phys. Rev. Lett.)
Availlable from: k.schroeder@fz-juelich.de

The electronic structure of the Sodium and Potassium Electro Sodalites, (Na/K)$_8$(AlSiO$_4$)$_6$

Georg K. H. Madsen[1], Bo B. Iversen[2], Peter Blaha[1], Karlheinz Schwarz[1]
[1] *Technische Universität Wien, Getreidemarkt 9/156,*
A-1060 Vienna, Austria
[2] *Department of Chemistry, University of Aarhus, DK-8000 Århus C, Denmark*

Abstract

The alkali doped electro sodalites form a unique class of magnetic materials where the magnetism comes from non-atom centered unpaired F-center electrons found inside body-centered cubic arrangements of alkali ion clusters supported by sodalite host-lattices. In the present work the crystal structure of Potassium-Electro-Sodalite (PES) has been determined at 20 K using synchrotron powder diffraction. Using the linearized augmented plane wave method the electronic structure of Sodium-Electro-Sodalite (SES) and PES is calculated. While non-magnetic and ferro-magnetic phases of SES and PES are found to be metallic, DFT in both the LSDA and the GGA version correctly predicts the non-metallic AFM phase to be the electronic ground state. Despite PES having a larger unit cell than SES the temperature of magnetic ordering is higher. This is found to be due to both a broadening of the bands belonging to the F-center states and to lower on-site correlations. Calculated optical properties are reported and the formation of F-centers inside sodalite cages causes the materials to absorb light with energies around 1 eV and above, depending on structure. Non-nuclear maxima are found in the total electron density of both SES and PES and the spin density is found mainly in the center of the sodalite cage.

(Phys Rev. B **64**, 195102 (2001))

Efficient linearization of the augmented plane-wave method

Georg K. H. Madsen[1], Peter Blaha[1], Karlheinz Schwarz[1],
Elisabeth Sjöstedt[2], Lars Nordström[2]
[1] *Technische Universität Wien, Getreidemarkt 9/156,*
A-1060 Vienna, Austria
[2] *Condensed Matter Theory Group, Physics Department, Uppsala University,*
S-75121 Uppsala, Sweden

Abstract

We present a detailed analysis of the newly developed APW+lo basis set for band structure calculations. This basis set consists of energy independent Augmented Plane-Wave (APW) functions. The linearization is introduced through local orbitals evaluated at the same linearization energy as the APW functions. It is shown that results obtained with the APW+lo basis set converge much faster and often more systematically towards the final value. The APW+lo thereby allows accurate treatment of systems that were previously unaccessible to LAPW. Furthermore it is shown that APW+lo converges to the same total energy as LAPW provided the higher angular momenta l are linearized, either by adding extra local orbitals or treating them by LAPW. It is illustrated that the APW basis functions are much closer to the true form of the eigen-functions than the LAPW basis functions. This is especially true for basis functions that have a strong energy dependence inside the sphere.

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Layer–resolved optical conductivity of Co | Pt multilayers

A. Vernes[a)], L. Szunyogh[a,b)], L. Udvardi[a,b)] and P. Weinberger[a)]
[a)] *Center for Computational Materials Science,*
Technical University Vienna,
Gumpendorferstr. 1a, 1060 Vienna, Austria
[b)] *Department of Theoretical Physics ,*
Budapest University of Technology and Economics
Budafoki út 8, 1521 Budapest, Hungary

Abstract

The complex optical conductivity tensor is calculated for the Co | Pt multilayer systems by applying a contour integration technique within the framework of the spin–polarized relativistic screened Korringa–Kohn–Rostoker method. It is shown that the optical conductivity of the Co | Pt multilayer systems is dominated by contributions arising from the Pt cap and/or substrate layers.

(J. Magn. Magn. Materials, in press)
Postscript preprints are available from A. Vernes (`av@cms.tuwien.ac.at`)

Magneto-optical properties of Co | Pt multilayer systems

A. Vernes[a)], L. Szunyogh[a,b)] and P. Weinberger[a)]
[a)] *Center for Computational Materials Science,*
Technical University Vienna,
Gumpendorferstr. 1a, 1060 Vienna, Austria
[b)] *Department of Theoretical Physics ,*
Budapest University of Technology and Economics
Budafoki út 8, 1521 Budapest, Hungary

Abstract

We are reporting, for the first time in the literature, theoretical Kerr spectra of Co | Pt multilayer systems as obtained on a first principles basis including multiple reflections and interferences from all the boundaries in–between the layers.

(J. Appl. Physics, in press)

Postscript preprints are available from A. Vernes (`av@cms.tuwien.ac.at`)

Ab–initio calculation of Kerr spectra for semi–infinite systems including multiple reflections and optical interferences

A. Vernes [a)], L. Szunyogh [a,b)] and P. Weinberger [a)]
[a)] *Center for Computational Materials Science,*
Technical University Vienna,
Gumpendorferstr. 1a, 1060 Vienna, Austria
[b)] *Department of Theoretical Physics ,*
Budapest University of Technology and Economics
Budafoki út 8, 1521 Budapest, Hungary

Abstract

Based on Luttinger's formulation the complex optical conductivity tensor is calculated within the framework of the spin–polarized relativistic screened Korringa–Kohn–Rostoker method for layered systems by means of a contour integration technique. For polar geometry and normal incidence ab–initio Kerr spectra of multilayer systems are then obtained by including via a 2 × 2 matrix technique all multiple reflections between layers and optical interferences in the layers. Applications to $\mathrm{Co|Pt_5}$ and $\mathrm{Pt_3\ |Co|Pt_5}$ on the top of a semi–infinite fcc–Pt(111) bulk substrate show good qualitative agreement with the experimental spectra, but differ from those obtained by applying the commonly used two–media approach.

(Submitted to Phys. Rev. B)
Postscript preprints are available from A. Vernes (`av@cms.tuwien.ac.at`)

Symmetry properties of the scattering path operator for arbitrary translationally invariant systems

T. Huhne and H. Ebert
Department Chemie, Physikalische Chemie, Universität München,
Butenandtstr. 5-13, D-81377 München, Germany

Abstract

In order to optimize the efficiency of relativistic band structure calculations for complex systems, one should take full advantage of the magnetic space group symmetry. Most important for the description of systems with reduced symmetry using the Korringa-Kohn-Rostoker (KKR) method of band structure calculation, a general derivation of magnetic symmetry properties of the scattering path operator both in real and reciprocal space is presented. In a straightforward way, this approach can be used to minimize the section of $\vec{k}$-space to be sampled for two and three dimensional numerical Brillouin zone integration. Practical aspects of an implementation of the very general scheme presented are discussed in detail.

(Submitted to Phys. Rev. B)
Manuscript available as ps-file on request from:
H. Ebert (he@gaia.cup.uni-muenchen.de)

All-electron *GW* approximation with the mixed basis expansion based on the full-potential LMTO method

Takao Kotani [1] and Mark van Schilfgaarde [2]

Department of Physics, Osaka University, Toyonaka 560-0043, Japan[1]

Sandia National Laboratory, Livermore, CA U.S.A.[2]

Abstract

We present a new all-electron, augmented-wave implementation of the *GW* approximation using eigenfunctions generated by a recent variant of the full-potential LMTO method. The dynamically screened Coulomb interaction W is expanded in a mixed basis set which consists of two contributions, local atom-centered functions confined to muffin-tin spheres, and plane waves with the overlap to the local functions projected out. The former can include any of the core states; thus the core and valence states can be treated on an equal footing. Systematic studies of semiconductors and insulators show that the GW fundamental bandgaps consistently fall low in comparison to experiment, and also the quasi-particle levels differ significantly from other, approximate methods, in particular those that approximate the core with a pseudopotential.

(Submitted to PRL)

Contact person: Takao Kotani (kotani@phys.sci.osaka-u.ac.jp), The copy is available from cond-mat/0111019. See http://al1.phys.sci.osaka-u.ac.jp for further informations.

Determination of the element-specific magnetic anisotropy in thin films and surfaces

Gerrit van der Laan
Magnetic Spectroscopy Group, Daresbury Laboratory,
Daresbury, Warrington WA4 4AD, UK

Abstract

We discuss the various element-specific methods to obtain the magnetocrystalline anisotropy energy (MAE) of thin films, multilayers and surfaces. X-ray magnetic circular dichroism (XMCD) has recently emerged as a routine method, where the orbital magnetic moment of $3d$ transition metals can be determined using the sum rule for the $L_{2,3}$ absorption spectra. The obtained orbital moment can be related to the MAE using Bruno's model, which is only valid under the assumption that the majority-spin subband is completely filled. This limitation can be avoided by employing x-ray magnetic linear dichroism (XMLD). The XMLD branching ratio is proportional to the anisotropy in the spin-orbit interaction, which, in second-order perturbation, can be related to the MAE. We present an expression for the angular dependence of the sum rules, which can be used to determine the magnetic anisotropy from the linear dichroism for a system with arbitrary point-group symmetry.

(J. Phys. Cond. Matter 13, 11149 - 11162 (2001), 10 December issue)
Contact person: g.vanderlaan@dl.ac.uk

8 SCIENTIFIC HIGHLIGHT OF THE MONTH

The SIESTA method for linear scaling ab initio simulations

J. M. Soler,[1] E. Artacho,[2] J. D. Gale,[3] A. García,[4]
J. Junquera,[1,5] D. Sánchez-Portal[6] and P. Ordejón[7]

[1] Depto. de Física de Materia Condensada (C-III), Univ. Autónoma de Madrid, 28049 Madrid, Spain
[2] Dept. of Earth Sciences, University of Cambridge, Downing St., Cambridge CB2 3EQ, U. K.
[3] Dept. of Chemistry, Imperial College, South Kensington SW7 2AY, U. K.
[4] Depto. de Física de la Materia Condensada, Univ. del País Vasco, Apt. 644, 48080 Bilbao, Spain
[5] Institut de Physique, Bâtiment B5, Université de Liège, B-4000 Sart-Tilman, Belgium
[6] Dept. de Física de Materiales and DIPC, Univ. del País Vasco, Apt. 1072, 20080 Donostia, Spain
[7] Institut de Ciència de Materials de Barcelona, CSIC, Campus de la UAB, 08193 Bellaterra, Spain

Abstract

We present SIESTA, a self-consistent density functional method using standard norm-conserving pseudopotentials and a flexible, numerical LCAO basis set, which includes multiple-zeta and polarization orbitals. Exchange and correlation are treated with the local spin density or generalized gradient approximations. The basis functions and the electron density are projected on a real-space grid, where the Hartree and exchange-correlation potentials and matrix elements are calculatd with a number of operations that scales linearly with the size of the system. We use a modified energy functional, whose minimization produces orthogonal wavefunctions and the same energy and density as the Kohn-Sham energy functional, without the need of an explicit orthogonalization. Additionally, using localized Wannier-like electron wavefunctions allows the computation time and memory, required to minimize the energy, to also scale linearly with the size of the system. Forces and stresses are also calculated efficiently and accurately, thus allowing structural relaxation and molecular dynamics simulations.

1. Introduction

The improvements in computer hardware and software is allowing the simulation of molecules and materials with an increasing number of atoms N, thus making the use of so-called order-N algorithms (in which the computer time and memory scales linearly with the simulated system size) increasingly important. Although these $\mathcal{O}(N)$ methods were available for classical potentials (including long range interactions) since the 1970's and 80's [1, 2], only in the last 5-10 years have they been developed for the much more complex quantum-mechanical methods. In these, linear scaling algorithms were first implemented in the most simple context of empirical or semiempirical tight-binding methods [3, 4] and in 'ab-initio' nonorthogonal-tight-binding and nonself-consistent Harris-functional methods [5, 6]. However, fully self-consistent density functional theory (DFT) methods [7], more reliable but also considerably more complex, pose the additional problem of the determination of the self-consistent Hamiltonian in $\mathcal{O}(N)$ iterations [8]. While this is difficult using plane waves, a localized basis set appears to be the natural choice. One proposed approach are the 'blips' of Hernandez and Gillan [9], regularly-spaced Gaussian-like splines that can be systematically increased, in the spirit of finite-element methods, although at a considerable computational cost.

We have developed a fully self-consistent DFT scheme, based on flexible linear combination of atomic orbitals (LCAO) basis sets, with essentially perfect $\mathcal{O}(N)$ scaling. It allows extremely fast simulations using minimal basis sets and very accurate calculations with complete multiple-ζ and polarized bases, depending on the required accuracy and available computational power. Apart from that of Born and Oppenheimer, the most basic approximations concern the treatment of exchange and correlation, and the use of pseudopotentials. Exchange and correlation (XC) are treated within Kohn-Sham DFT [10], with either the local (spin) density approximation [11] (LDA/LSD) or the generalized gradient approximation [12] (GGA). We use standard norm-conserving pseudopotentials [13, 14] in their fully non-local form [15], including scalar-relativistic effects and nonlinear partial-core-corrections for XC in the core region [16].

In previous papers [17, 18] we have described preliminary versions of this method, that we call SIESTA (Spanish Initiative for Electronic Simulations with Thousands of Atoms). There is also a review [19] of the tens of studies in a wide variety of systems, like metallic surfaces, nanotubes, and biomolecules, and for a large number of properties. Here we present a more complete description of the method, and illustrate the convergence of a few characteristic magnitudes with respect to the main precision parameters that characterize our method: basis size (number of atomic basis orbitals); basis range (radius of the basis orbitals); fineness of the real-space integration grid; and confinement radius of the Wannier-like electron states. We also show comparisons of results obtained with SIESTA with those of other *ab-initio* approaches to show the quality of the method. In particular, we will focus on the structure of molecular systems, including H-bonding in DNA base-pairs, and on the ferroelectric distortion in cubic $BaTiO_3$.

2. Pseudopotentials

We use first principles norm-conserving pseudopotentials [13] to elliminate the core electrons and, more importantly, to allow for the expansion of a smooth (pseudo)charge density on a uniform spatial grid. SIESTA reads them in semilocal form (a different radial potential $V_l(r)$ for each angular momentum l, optionally generated scalar-relativistically [20, 21]) from a data file that users can fill with their preferred choice. We generally use the Troullier-Martins parameterization [22]. We transform this semilocal form into the fully non-local form proposed by Kleinman and Bylander (KB) [15]:

$$\hat{V}^{PS} = V_{local}(r) + \hat{V}^{KB} \tag{3}$$

$$\hat{V}^{KB} = \sum_{l=0}^{l_{max}^{KB}} \sum_{m=-l}^{l} \sum_{n=1}^{N_l^{KB}} |\chi_{lmn}^{KB}\rangle v_{ln}^{KB} \langle\chi_{lmn}^{KB}| \tag{4}$$

$$v_{ln}^{KB} = < \varphi_{ln}|\delta V_l(r)|\varphi_{ln} > \tag{5}$$

where $\delta V_l(r) = V_l(r) - V_{local}(r)$. $\chi_{lmn}^{KB}(\mathbf{r}) = \chi_{ln}^{KB}(r) Y_{lm}(\hat{\mathbf{r}})$ (with $Y_{lm}(\hat{\mathbf{r}})$ a spherical harmonic) are the KB projection functions

$$\chi_{ln}^{KB}(r) = \delta V_l(r) \varphi_{ln}(r). \tag{6}$$

The functions φ_{ln} are obtained from the eigenstates ψ_{ln} of the semilocal pseudopotential (screened by the pseudo-valence charge density) at energy ϵ_{ln} using the orthogonalization scheme proposed by Blöchl [23]:

$$\varphi_{ln}(r) = \psi_{ln}(r) - \sum_{n'=1}^{n-1} \varphi_{ln'}(r) \frac{< \varphi_{ln'}|\delta V_l(r)|\psi_{ln} >}{< \varphi_{ln'}|\delta V_l(r)|\varphi_{ln'} >} \tag{7}$$

$$\left[-\frac{1}{2r}\frac{d^2}{dr^2} r + \frac{l(l+1)}{2r^2} + V_l(r) + +V^H(r) + V^{xc}(r) \right] \psi_{ln}(r) = \epsilon_{ln}\psi_{ln}(r) \tag{8}$$

V^H and V^{xc} are the Hartree and XC potentials for the pseudo-valence charge density, and we are using atomic units ($e = \hbar = m_e = 1$) throughout this work.

The local part of the pseudopotential $V_{local}(r)$ is in principle arbitrary, but it must join the semilocal potentials $V_l(r)$ which, by construction, all become equal to the (unscreened) all-electron potential beyond the pseudopotential core radius r_{core}. Thus, $\delta V_l(r) = 0$ for $r > r_{core}$. Ramer and Rappe have proposed that $V_{local}(r)$ be optimized for transferability [24], but most plane wave schemes make it equal to one of the $V_l(r)$'s for reasons of efficiency. Our case is different because $V_{local}(r)$ is the only pseudopotential part that needs to be represented in the real space grid, while the matrix elements of the non-local part $\hat{V}_{KB}$ are cheaply and accurately calculated by two-center integrals. Therefore, we optimize $V_{local}(r)$ for smoothness, making it equal to the potential created by a positive charge distribution of the form [25]

$$\rho^{local}(r) \propto \exp[-(\sinh(abr)/\sinh(b))^2], \tag{9}$$

where a and b are chosen to provide simultaneously optimal real-space localization and reciprocal-space convergence [26]. After some numerical tests we have taken b =1 and a =1.82/r_{core}. Figure 2 shows $V_{local}(r)$ for silicon.

Since $V_l(r) = V_{local}(r)$ outside r_{core}, $\chi_{ln}^{KB}(r)$ is strictly zero beyond that radius, irrespective of the value of ϵ_{ln}. Generally it is sufficient to have a single projector χ_{lm}^{KB} for each angular momentum (i.e. a single term in the sum on n). In this case we follow the normal practice of making ϵ_{ln} equal to the valence atomic eigenvalue ϵ_l, and the function $\varphi_l(r)$ in Eq. 6 is identical to the corresponding eigenstate $\psi_l(r)$. In some cases, particularly for alkaline metals, alkaline earths, and transition metals of the first few columns, we have sometimes found it necessary to include the semicore states together with the valence states [27]. In these cases, we also include two independent KB projectors, one for the semicore and one for the valence states. Also, since the non-local part of the pseudopotential is a relatively cheap operator within SIESTA, we generally (but not necessarily) use a larger than usual value of l_{max}^{KB} in Eq. (4), making it one unit larger than the l_{max} of the basis functions.

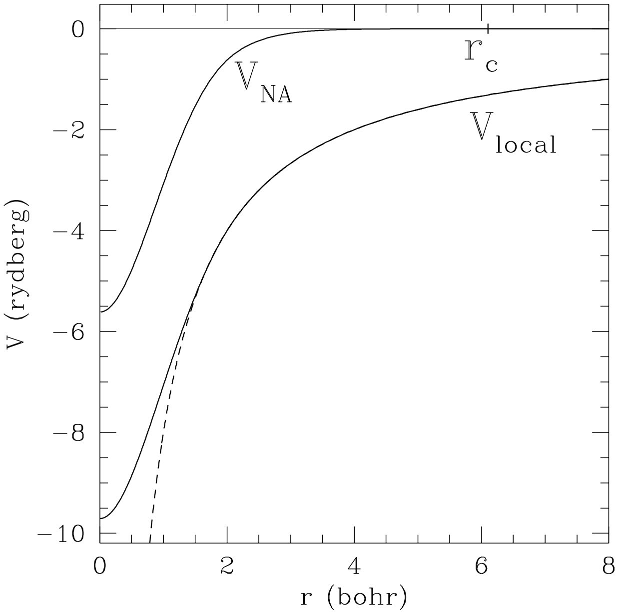

Figure 2: Local pseudopotential for silicon. V_{local} is the unscreened local part of the pseudopotential, generated as the electrostatic potential produced by a localized distribution of positive charge, Eq. (9), whose integral is equal to the valence ion charge ($Z = 4$ for Si). The dashed line is $-Z/r$. V_{NA} is the local pseudopotential screened by an electron charge distribution, generated by filling the first-ζ basis orbitals with the free-atom valence occupations. Since these basis orbitals are strictly confined to a radius r_{max}^c, V_{NA} is also strictly zero beyond that radius.

3. Basis set

Order-N methods rely heavily on the sparsity of the Hamiltonian and overlap matrices. This sparsity requires either the neglect of matrix elements that are small enough or the use of strictly confined basis orbitals, *i.e.*, orbitals that are zero beyond a certain radius [6]. We have adopted this latter approach because it keeps the energy strictly variational, thus facilitating the test of the convergence with respect to the radius of confinement. Within this radius, our atomic basis orbitals are products of a numerical radial function times a spherical harmonic. For atom I, located at $\mathbf{R}_I$,

$$\phi_{Ilmn}(\mathbf{r}) = \phi_{Iln}(r_I)Y_{lm}(\hat{\mathbf{r}}_I) \tag{10}$$

where $\mathbf{r}_I = \mathbf{r} - \mathbf{R}_I$, $r = |\mathbf{r}|$ and $\hat{\mathbf{r}} = \mathbf{r}/r$. The angular momentum (labelled by l, m) may be arbitrarily large and, in general, there will be several orbitals (labelled by index n) with the same angular dependence, but different radial dependence, which is conventionally called a 'multiple-ζ' basis. The radial functions are defined by a cubic spline interpolation [28] from the values given on a fine radial mesh. Each radial function may have a different cutoff radius and, up to that radius, its shape is completely free and can be introduced by the user in an input file. In practice, it is also convenient to have an automatic procedure to generate sufficiently good basis sets. We have developed several such automatic procedures, and we will describe here one of them for completeness, even though we stress that the generation of the basis set, like that of the pseudopotential is to a large extent up to the user and independent of the SIESTA method itself.

In the case of a minimal (single-ζ) basis set, we have found convenient and efficient the method of Sankey and Niklewski [6, 29]. Their basis orbitals are the eigenfunctions of the (pseudo)atom within a spherical box (although the radius of the box may be different for each orbital, see below). In other words, they are the (angular-momentum-dependent) numerical eigenfunctions $\phi_l(r)$ of the atomic pseudopotential $V_l(r)$, for an energy $\epsilon_l + \delta\epsilon_l$ chosen so that the first node occurs at the desired cutoff radius r_l^c:

$$\left(-\frac{1}{2r}\frac{d^2}{dr^2}r + \frac{l(l+1)}{2r^2} + V_l(r)\right)\phi_l(r) = (\epsilon_l + \delta\epsilon_l)\phi_l(r) \tag{11}$$

with $\phi_l(r_l^c) = 0$ (we omit indices I and n here for simplicity). In order to obtain a well balanced basis, in which the effect of the confinement is similar for all the orbitals, it is usually better to fix a common 'energy shift' $\delta\epsilon$, rather than a common radius r^c, for all the atoms and angular momenta. This means that the orbital radii depend on the atomic species and angular momentum.

One obvious possibility for multiple-ζ bases is to use pseudopotential eigenfunctions with an increasing number of nodes [29]. They have the virtue of being orthogonal and asymptotically complete. However, the efficiency of this kind of basis depends on the radii of confinement of the different orbitals, since the excited states of the pseudopotential are usually unbound. Thus, in practice we have found this procedure rather inefficient. Another possibility is to use the atomic eigenstates for different ionization states [30]. We have implemented a different scheme [31], based on the 'split-valence' method which is standard in quantum chemistry [32]. In that method, the first-ζ basis orbitals are 'contracted' (i.e. fixed) linear combinations of Gaussians, determined either variationally or by fitting numerical atomic eigenfunctions. The second-ζ orbital is then one of the Gaussians (generally the slowest-decaying one) which is 'released' or 'split' from the contracted combination. Higher-ζ orbitals are generated in a similar way by releasing more Gaussians. Our scheme adapts this split-valence method to our numerical orbitals. Following the same spirit, our second-ζ functions $\phi_l^{2\zeta}(r)$ have the same tail as the first-ζ orbitals $\phi_l^{1\zeta}(r)$ but change to a simple polynomial behaviour inside a 'split radius' r_l^s:

$$\phi_l^{2\zeta}(r) = \begin{cases} r^l(a_l - b_l r^2) & \text{if } r < r_l^s \\ \phi_l^{1\zeta}(r) & \text{if } r \geq r_l^s \end{cases} \tag{12}$$

where a_l and b_l are determined by imposing the continuity of value and slope at r_l^s. These orbitals therefore combine the decay of the atomic eigenfunctions with a smooth and featureless behaviour inside r_l^s. We have found it convenient to set the radius r_l^s by fixing the norm of $\phi_l^{1\zeta}$ in $r > r_l^s$; in practice, a reasonable value for this 'split-norm' is ~ 0.15. Actually, instead of $\phi_l^{2\zeta}$ thus defined, we use $\phi_l^{1\zeta} - \phi_l^{2\zeta}$, which is zero beyond r_l^s, to reduce the number of nonzero matrix elements, without any loss of variational freedom.

To achieve well converged results, in addition to the atomic valence orbitals, it is generally necessary to also include polarization orbitals, to account for the deformation induced by bond formation. Again, using pseudoatomic orbitals of higher angular momentum is frequently unsatisfactory, because they tend to be too extended, or even unbound. Instead, consider a valence pseudoatomic orbital $\phi_{lm}(\mathbf{r}) = \phi_l(r)Y_{lm}(\hat{\mathbf{r}})$, such that there are no valence orbitals with angular momentum $l+1$. To polarize it, we apply a small electric field $\mathcal{E}$ in the z-direction, and use first-order perturbation theory. Selection rules imply that the resulting perturbed orbital will only have components with $l' = l \pm 1, m' = m$. Since in general there will already be orbitals with angular momentum $l-1$ in the basis set, we select only the $l+1$ component. Thus we obtain the equation

$$\left[-\frac{1}{2r}\frac{d^2}{dr^2}r + \frac{(l+1)(l+2)}{2r^2} + V_l(r) - E_l\right]\varphi_{l+1}(r) = -r\phi_l(r) \tag{13}$$

which defines the polarization orbitals that are then added to the basis set: $\phi_{l+1,m}(\mathbf{r}) = C\varphi_{l+1}(r)Y_{l+1,m}(\hat{\mathbf{r}})$, where C is a normalization constant.

We have found that the previously described procedures generate reasonable minimal single-ζ (SZ) basis sets, appropriate for semiquantitative simulations, and double-ζ plus polarization (DZP) basis sets that yield high quality results for most of the systems studied. We thus refer to DZP as the 'standard' basis, because it usually represents a good balance between well converged results and a reasonable computational cost. In some cases (typically alkali and some transition metals), semicore states also need to be included for good quality results. More recently [33], we have obtained extremely efficient basis sets optimized variationally in molecules or solids. Figure 3 shows the performance of these atomic basis sets compared to plane waves, using the same pseudopotentials and geometries. It may be seen that the SZ bases are comparable to planewave cutoffs typically used in Car-Parrinello molecular dynamics simulations, while DZP sets are comparable to the cutoffs used in geometry relaxations and energy comparisons. As expected, the LCAO is far more efficient, tipically by a factor of 10 to 20, in terms of number of basis orbitals. This efficiency must be balanced against the faster algorithms available for plane waves, and our main motivation for using an LCAO basis is its suitability for $\mathcal{O}(N)$ methods. Still, we have generally found that, even without using the $\mathcal{O}(N)$ functional, SIESTA is considerably faster than a plane wave calculation of similar quality.

Table 2 shows the convergence of the lattice constant, bulk modulus and cohesive energy for silicon for different basis sets, and the correponding values for plane waves and LAPW calculations and the experiment. It can be seen that the 'standard' DZP basis offers already quite well converged results, comparable to those used in practice in most plane wave calculations.

Figure 4 shows the dependence of the lattice constant, bulk modulus, and cohesive energy of bulk silicon with the range of the basis orbitals, showing that a cutoff radius of 3 Å for both s and p orbitals yields very well converged results, specially when using a 'standard' DZP basis.

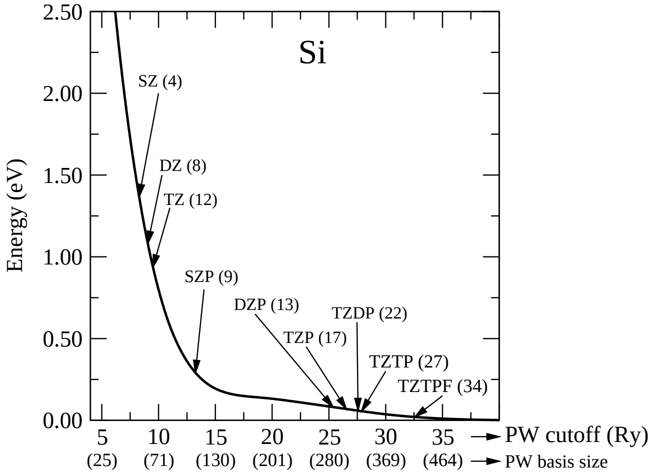

Figure 3: Comparison of convergence of the total energy with respect to the sizes of a plane wave basis set and of the LCAO basis set used by SIESTA. The curve shows the total energy per atom of silicon versus the cutoff of a plane wave basis, calculated with a program independent of SIESTA, which uses the same pseudopotential. The arrows indicate the energies obtained with different LCAO basis sets, calculated with SIESTA, and the plane wave cutoffs that yield the same energies. The numbers in parentheses indicate the basis sizes, i.e. the number of atomic orbitals or plane waves of each basis set. SZ: single-ζ (valence s and p orbitals); DZ: double-ζ; TZ: triple-ζ; DZP: double-ζ valence orbitals plus single-ζ polarization d orbitals; TZP: triple-ζ valence plus single-ζ polarization; TZDP: triple-ζ valence plus double-ζ polarization; TZTP: triple-ζ valence plus triple-ζ polarization; TZTPF: same as TZTP plus extra single-ζ polarization f orbitals.

Table 2: Comparisons of the lattice constant a, bulk modulus B, and cohesive energy E_c for bulk Si, obtained with different basis sets. The basis notation is as in Fig. 3. PW refers to a 50 Ry-cutoff plane wave calculation. The LAPW results were taken from ref. [34], and the experimental values from ref. [35].

Basis	a (Å)	B (GPa)	E_c (eV)
SZ	5.521	88.7	4.722
DZ	5.465	96.0	4.841
TZ	5.453	98.4	4.908
SZP	5.424	97.8	5.227
DZP	5.389	96.6	5.329
TZP	5.387	97.5	5.335
TZDP	5.389	96.0	5.340
TZTP	5.387	96.0	5.342
TZTPF	5.385	95.4	5.359
PW	5.384	95.9	5.369
LAPW	5.41	96	5.28
Expt.	5.43	98.8	4.63

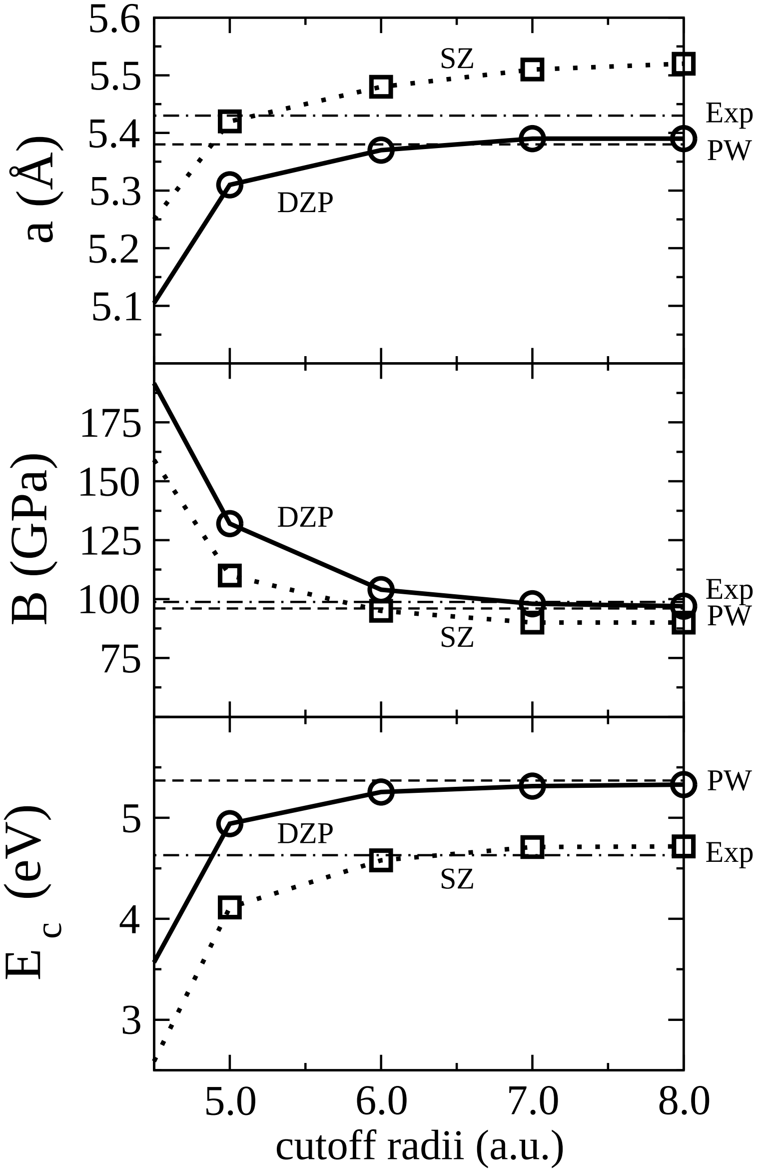

Figure 4: Dependence of the lattice constant, bulk modulus, and cohesive energy of bulk silicon with the cutoff radius of the basis orbitals. The *s* and *p* orbital radii have been made equal in this case, to simplify the plot. PW refers to a well converged plane wave calculation with the same pseudopotential.

4. Electron Hamiltonian

Within the non-local-pseudopotential approximation, the standard Kohn-Sham one-electron Hamiltonian may be written as

$$\hat{H} = \hat{T} + \sum_I V_I^{local}(\mathbf{r}) + \sum_I \hat{V}_I^{KB} + V^H(\mathbf{r}) + V^{xc}(\mathbf{r}) \tag{14}$$

where $\hat{T} = -\frac{1}{2}\nabla^2$ is the kinetic energy operator, I is an atom index, $V^H(\mathbf{r})$ and $V^{xc}(\mathbf{r})$ are the total Hartree and XC potentials, and $V_I^{local}(\mathbf{r})$ and $\hat{V}_I^{KB}$ are the local and non-local (Kleinman-Bylander) parts of the pseudopotential of atom I.

In order to eliminate the long range of V_I^{local}, we screen it with the potential V_I^{atom}, created by an atomic electron density ρ_I^{atom}, constructed by populating the basis functions with appropriate valence atomic charges. Notice that, since the atomic basis orbitals are zero beyond the cutoff radius $r_I^c = \max_l(r_{Il}^c)$, the screened 'neutral-atom' (NA) potential $V_I^{NA} \equiv V_I^{local} + V_I^{atom}$ is also zero beyond this radius [6] (see Fig. 2). Now let $\delta\rho(\mathbf{r})$ be the difference between the self-consistent electron density $\rho(\mathbf{r})$ and the sum of atomic densities $\rho^{atom} = \sum_I \rho_I^{atom}$, and let $\delta V^H(\mathbf{r})$ be the electrostatic potential generated by $\delta\rho(\mathbf{r})$, which integrates to zero and is usually much smaller than $\rho(\mathbf{r})$. Then the total Hamiltonian may be rewritten as

$$\hat{H} = \hat{T} + \sum_I \hat{V}_I^{KB} + \sum_I V_I^{NA}(\mathbf{r}) + \delta V^H(\mathbf{r}) + V^{xc}(\mathbf{r}) \tag{15}$$

The matrix elements of the first two terms involve only two-center integrals which are calculated in reciprocal space and tabulated as a function of interatomic distance. The remaining terms involve potentials which are calculated on a three-dimensional real-space grid. We consider these two approaches in detail in the following sections.

5. Two-center integrals

The overlap matrix and the largest part of the Hamiltonian matrix elements are given by two-center integrals [36]. We calculate these integrals in Fourier space, as proposed by Sankey and Niklewski [6], but we use some implementation details explained in this section. Let us consider first overlap integrals of the form

$$S(\mathbf{R}) \equiv \langle \psi_1 | \psi_2 \rangle = \int \psi_1^*(\mathbf{r}) \psi_2(\mathbf{r} - \mathbf{R}) d\mathbf{r}, \tag{16}$$

where the integral is over all space and ψ_1, ψ_2 may be basis functions ϕ_{lmn}, KB pseudopotential projectors χ_{lmn}, or more complicated functions centered on the atoms. The function $S(\mathbf{R})$ can be seen as a convolution: we take the Fourier transform

$$\psi(\mathbf{k}) = \frac{1}{(2\pi)^{3/2}} \int \psi(\mathbf{r}) e^{-i\mathbf{k}\mathbf{r}} d\mathbf{r} \tag{17}$$

Using the planewave expression of Dirac's delta function, $\int e^{i(\mathbf{k}'-\mathbf{k})\mathbf{r}} d\mathbf{r} = (2\pi)^3 \delta(\mathbf{k}' - \mathbf{k})$, we find the usual result that the Fourier transform of a convolution in real space is a simple product in reciprocal space:

$$S(\mathbf{R}) = \int \psi_1^*(\mathbf{k}) \psi_2(\mathbf{k}) e^{-i\mathbf{k}\mathbf{R}} d\mathbf{k} \tag{18}$$

Let us assume now that the functions $\psi(\mathbf{r})$ can be expanded exactly with a finite number of spherical harmonics:

$$\psi(\mathbf{r}) = \sum_{l=0}^{l_{max}} \sum_{m=-l}^{l} \psi_{lm}(r) Y_{lm}(\hat{\mathbf{r}}), \tag{19}$$

$$\psi_{lm}(r) = \int_0^{\pi} \sin\theta d\theta \int_0^{2\pi} d\varphi Y_{lm}^*(\theta,\varphi)\psi(r,\theta,\varphi). \tag{20}$$

This is clearly true for basis functions and KB projectors, which contain a single spherical harmonic, and also for functions like $x\psi(\mathbf{r})$, which appear in dipole matrix elements. We now substitute in (17) the expansion of a plane wave in spherical harmonics [37]

$$e^{i\mathbf{kr}} = \sum_{l=0}^{\infty} \sum_{m=-l}^{l} 4\pi i^l j_l(kr) Y_{lm}^*(\hat{\mathbf{k}}) Y_{lm}(\hat{\mathbf{r}}), \tag{21}$$

to obtain

$$\psi(\mathbf{k}) = \sum_{l=0}^{l_{max}} \sum_{m=-l}^{l} \psi_{lm}(k) Y_{lm}(\hat{\mathbf{k}}), \tag{22}$$

$$\psi_{lm}(k) = \sqrt{\frac{2}{\pi}}(-i)^l \int_0^{\infty} r^2 dr j_l(kr)\psi_{lm}(r). \tag{23}$$

Substituting now (22) and (21) into (18) we obtain

$$S(\mathbf{R}) = \sum_{l=0}^{2l_{max}} \sum_{m=-l}^{l} S_{lm}(R) Y_{lm}(\hat{\mathbf{R}}) \tag{24}$$

where

$$S_{lm}(R) = \sum_{l_1 m_1} \sum_{l_2 m_2} G_{l_1m_1,l_2m_2,lm} S_{l_1m_1,l_2m_2,l}(R), \tag{25}$$

$$G_{l_1m_1,l_2m_2,lm} = \int_0^{\pi} \sin\theta d\theta \int_0^{2\pi} d\varphi Y_{l_1m_1}^*(\theta,\varphi) Y_{l_2m_2}(\theta,\varphi) Y_{lm}^*(\theta,\varphi), \tag{26}$$

$$S_{l_1m_1,l_2m_2,l}(R) = 4\pi i^{l_1-l_2-l} \int_0^{\infty} k^2 dk j_l(kR) i^{-l_1}\psi_{1,l_1m_1}^*(k) i^{l_2}\psi_{2,l_2m_2}(k), \tag{27}$$

Notice that $i^{-l_1}\psi_1(k), i^{l_2}\psi_2(k)$, and $i^{l_1-l_2-l}$ are all real, since $l_1 - l_2 - l$ is even for all l's for which $G_{l_1m_1,l_2m_2,lm} \neq 0$. The Gaunt coefficients $G_{l_1m_1,l_2m_2,lm}$ can be obtained by recursion from Clebsch-Gordan coefficients [6]. However, we use real spherical harmonics for computational efficiency:

$$Y_{lm}(\theta,\varphi) = C_{lm} P_l^m(\cos\theta) \times \begin{cases} \sin(m\varphi) & \text{if } m < 0 \\ \cos(m\varphi) & \text{if } m \geq 0 \end{cases} \tag{28}$$

where $P_l^m(z)$ are the associated Legendre polynomials and C_{lm} normalization constants [28]. This does not affect the validity of any of previous equations, but it modifies the value of the Gaunt coefficients. Therefore, we find it is simpler and more general to calculate $G_{l_1m_1,l_2m_2,lm}$ directly from Eq. (26). To do this, we use a Gaussian quadrature [28]

$$\int_0^{\pi} \sin\theta d\theta \int_0^{2\pi} d\varphi \to 4\pi \frac{1}{N_\theta} \sum_{i=1}^{N_\theta} w_i \sin\theta_i \frac{1}{N_\varphi} \sum_{j=1}^{N_\varphi} \tag{29}$$

with $N_\varphi = 1 + 3l_{max}, N_\theta = 1 + \text{int}(3l_{max}/2)$, and the points $\cos\theta_i$ and weights w_i are calculated as described in ref. [28]. This quadrature is exact in equation (26) for spherical harmonics Y_{lm}

(real or complex) of $l \leq l_{max}$, and it can be used also to find the expansion of $\psi(\mathbf{r})$ in spherical harmonics (eq. (20)).

The coefficients $G_{l_1m_1,l_2m_2,lm}$ are universal and they can be calculated and stored once and for all. The functions $S_{l_1m_1,l_2m_2,l}(R)$ depend, of course, on the functions $\psi_{1,2}(\mathbf{r})$ being integrated. For each pair of functions, they can be calculated and stored in a fine radial grid R_i, up to the maximum distance $R_{max} = r_1^c + r_2^c$ at which ψ_1 and ψ_2 overlap. Their value at an arbitrary distance R can then be obtained very accurately using a spline interpolation.

Kinetic matrix elements $T(\mathbf{R}) \equiv \langle\psi_1^*|-\frac{1}{2}\nabla^2|\psi_2\rangle$ can be obtained in exactly the same way, except for an extra factor k^2 in Eq. (27):

$$T_{l_1m,l_2m_2,l}(R) = 4\pi i^{l_1-l_2-l}\int_0^\infty \frac{1}{2}k^4 dk j_l(kR) i^{-l_1}\psi_{1,l_1m_1}^*(k) i^{l_2}\psi_{2,l_2m_2}(k). \tag{30}$$

Since we frequently use basis orbitals with a kink [6], we need rather fine radial grids to obtain accurate kinetic matrix elements, and we typically use grid cutoffs of more than 2000 Ry for this purpose. Once obtained, the fine grid does not penalize the execution time, because the interpolation effort is independent of the number of grid points. It also affects very marginally the storage requirements, because of the one-dimensional character of the tables. However, even though it needs to be done only once, the calculation of the radial integrals (23), (27), and (30) is not negligible if performed unwisely. We have developed a special fast radial Fourier transform for this purpose, as explained elsewhere [38]

Dipole matrix elements, such as $\langle\psi_1|x|\psi_2\rangle$, can also be obtained easily by defining a new function $\chi_1(\mathbf{r}) \equiv x\psi_1(\mathbf{r})$, expanding it using (20), and computing $\langle\chi_1|\psi_2\rangle$ as explained above (with the precaution of using $l_{max}+1$ instead of l_{max}).

6. Grid integrals

The matrix elements of the last three terms of Eq. (15) involve potentials which are calculated on a real-space grid. The fineness of this grid is controlled by a 'grid cutoff' E_{cut}: the maximum kinetic energy of the planewaves that can be represented in the grid without aliasing [39]. The short-range screened pseudopotentials $V_I^{NA}(\mathbf{r})$ in (15) are tabulated as a function of the distance to atoms I and easily interpolated at any desired grid point. The last two terms require the calculation of the electron density on the grid. Let $\psi_i(\mathbf{r})$ be the Hamiltonian eigenstates, expanded in the atomic basis set

$$\psi_i(\mathbf{r}) = \sum_\mu \phi_\mu(\mathbf{r})c_{\mu i}, \tag{31}$$

where $c_{\mu i} = \langle\tilde{\phi}_\mu|\psi_i\rangle$ and $\tilde{\phi}_\mu$ is the dual orbital of ϕ_μ: $\langle\tilde{\phi}_\mu|\phi_\nu\rangle = \delta_{\mu\nu}$. We use the compact index notation $\mu \equiv \{Ilmn\}$ for the basis orbitals, Eq. (10). The electron density is then

$$\rho(\mathbf{r}) = \sum_i n_i|\psi_i(\mathbf{r})|^2 \tag{32}$$

where n_i is the occupation of state ψ_i. If we substitute (31) into (32) and define a density matrix

$$\rho_{\mu\nu} = \sum_i c_{\mu i}n_i c_{i\nu}, \tag{33}$$

where $c_{i\nu} \equiv c^*_{\nu i}$, the electron density can be rewritten as

$$\rho(\mathbf{r}) = \sum_{\mu\nu} \rho_{\mu\nu} \phi^*_\nu(\mathbf{r}) \phi_\mu(\mathbf{r}) \tag{34}$$

To calculate the density at a given grid point, we first find all the atomic basis orbitals, Eq. (10), at that point, interpolating the radial part from numerical tables, and then use (34) to calculate the density. Notice that only a small number of basis orbitals are non-zero at a given grid point, so that the calculation of the density can be performed in $\mathcal{O}(N)$ operations, once $\rho_{\mu\nu}$ is known. The calculation of $\rho_{\mu\nu}$ itself with Eq. (33) does not scale linearly with the system size, requiring instead the use of special $\mathcal{O}(N)$ techniques to be described below. However, notice that in order to calculate the density, only the matrix elements $\rho_{\mu\nu}$ for which ϕ_μ and ϕ_ν overlap are required, and they can therefore be stored as a sparse matrix of $\mathcal{O}(N)$ size. Once the valence density is available in the grid, we add to it, if necessary, the non-local core correction [16], a spherical charge density intended to simulate the atomic cores, which is also interpolated from a radial grid. With it, we find the exchange and correlation potential $V^{xc}(\mathbf{r})$, trivially in the LDA and using the method described in ref. [40] for the GGA. To calculate $\delta V^H(\mathbf{r})$, we first find $\rho^{atom}(\mathbf{r})$ at the grid points, as a sum of spherical atomic densities (also interpolated from a radial grid) and subtract it from $\rho(\mathbf{r})$ to find $\delta\rho(\mathbf{r})$. We then solve Poisson's equation to obtain $\delta V^H(\mathbf{r})$ and find the total grid potential $V(\mathbf{r}) = V^{NA}(\mathbf{r}) + \delta V^H(\mathbf{r}) + V^{xc}(\mathbf{r})$. Finally, at every grid point, we calculate $V(\mathbf{r})\phi^*_\mu(\mathbf{r})\phi_\nu(\mathbf{r})\Delta\mathbf{r}^3$ for all pairs ϕ_μ, ϕ_ν which are not zero at that point ($\Delta\mathbf{r}^3$ is the volume per grid point) and add it to the Hamiltonian matrix element $H_{\mu\nu}$.

To solve Poisson's equation and find $\delta V^H(\mathbf{r})$ we normally use fast Fourier transforms in a unit cell that is either naturally periodic or made artificially periodic by a supercell construction. For neutral isolated molecules, our use of strictly confined basis orbitals makes it trivial to avoid any direct overlap between the repeated molecules, and the electric multipole interactions decrease rapidly with cell size. For charged molecules we supress the $\mathbf{G} = 0$ Fourier component (an infinite constant) of the potential created by the excess of charge. This amounts to compensating this excess with a uniform charge background. We then use the method of Makov and Payne [41] to correct the total energy for the interaction between the repeated cells. Alternatively, we can solve Poisson's equation by the multigrid method, using finite differences and fixed boundary conditions, obtained from the multipole expansion of the molecular charge density. This can be done in strictly $\mathcal{O}(N)$ operations, unlike the FFT's, which scale as $N \log N$. However, the cost of this operation is typically negligible and therefore has no influence on the overall scaling properties of the calculation.

We have found it convenient for the efficiency of the calculations to use a given grid (defined by E_{cut}) during the self-consistency, and then to refine the integrals using a finer grid in the final calculation of the energy and forces (using the density obtained self-consistently with the original grid). This provides a significant improvement in accuracy with very little computational overhead. The grid refinement is done defining a grid-cell-sampling of several points per each original grid point.

Figure 5 shows the convergence of different magnitudes with respect to the energy cutoff of the integration grid. For orthogonal unit cell vectors this is simply, in atomic units, $E_{cut} = (\pi/\Delta x)^2/2$ with Δx the grid interval.

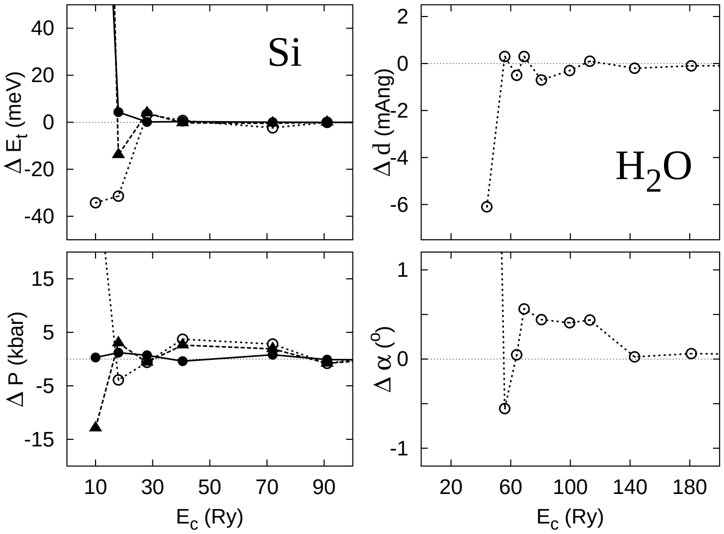

Figure 5: (a) Convergence of the total energy and pressure in bulk silicon as a function of the energy cutoff E_{cut} of the real space integration mesh. Circles and continuous line: using a grid-cell-sampling of eight refinement points per original grid point. The refinement points are used only in the final calculation, not during the self-consistency iteration (see text). Triangles: two refinement points per original grid point. White circles: no grid-cell-sampling. (b) Bond length and angle of the water molecule as a function of E_{cut}

7. Brillouin zone sampling

Integration of all magnitudes over the Brillouin zone (BZ) is essential for small and moderately large unit cells, especially of metals. Although SIESTA is designed for large unit cells, in practice it is very useful, especially for comparisons and checks, to be able to also perform calculations efficiently on smaller systems without using expensive superlattices. On the other hand, an efficient k-sampling implementation should not penalize, because of the required complex arithmetic, the Γ-point calculations used in large cells. A solution used in some programs is to have two different versions of all or part of the code, but this poses extra maintenance requirements. We have dealt with this problem in the following way: around the unit cell (and comprising itself) we define an auxiliary supercell large enough to contain all the atoms whose basis orbitals are non-zero at any of the grid points of the unit cell, or which overlap with any of the basis orbitals in it. We calculate all the non-zero two-center integrals between the unit cell basis orbitals and the supercell orbitals, without any complex phase factors. We also calculate the grid integrals between *all* the supercell basis orbitals $\phi_{\mu'}$ and $\phi_{\nu''}$ (primed indices run over all the supercell), but *within the unit cell only.* We accumulate these integrals in the corresponding matrix elements, thus making use of the relation

$$< \phi_\mu|V(\mathbf{r})|\phi_{\nu'} > = \sum_{(\mu'\nu'')\equiv(\mu\nu')} < \phi_{\mu'}|V(\mathbf{r})f(\mathbf{r})|\phi_{\nu''} > . \tag{35}$$

$f(\mathbf{r}) = 1$ for $\mathbf{r}$ within the unit cell and is zero otherwise. ϕ_μ is within the unit cell. The notation $\mu' \equiv \mu$ indicates that $\phi_{\mu'}$ and ϕ_μ are equivalent orbitals, related by a lattice vector translation.

$(\mu'\nu'') \equiv (\mu\nu')$ means that the sum extends over all pairs of supercell orbitals $\phi_{\mu'}$ and $\phi_{\nu''}$ such that $\mu' \equiv \mu$, $\nu'' \equiv \nu'$, and $\mathbf{R}_\mu - \mathbf{R}_{\nu'} = \mathbf{R}_{\mu'} - \mathbf{R}_{\nu''}$. Once all the real overlap and Hamiltonian matrix elements are calculated, we multiply them, at every k-point by the corresponding phase factors and accumulate them by folding the supercell orbital to its unit-cell counterpart. Thus

$$H_{\mu\nu}(\mathbf{k}) = \sum_{\nu' \equiv \nu} H_{\mu\nu'} e^{i\mathbf{k}(\mathbf{R}_{\nu'} - \mathbf{R}_\mu)} \tag{36}$$

where ϕ_μ and ϕ_ν are within the unit cell. The resulting $N \times N$ complex eigenvalue problem, with N the number of orbitals in the unit cell, is then solved at every sampled k point, finding the Bloch-state expansion coefficients $c_{\mu i}(\mathbf{k})$:

$$\psi_i(\mathbf{k}, \mathbf{r}) = \sum_{\mu'} e^{i\mathbf{k}\mathbf{R}_{\mu'}} \phi_{\mu'}(\mathbf{r}) c_{\mu' i}(\mathbf{k}) \tag{37}$$

where the sum in μ' extends to all basis orbitals in space, i labels the different bands, $c_{\mu' i} = c_{\mu i}$ if $\mu' \equiv \mu$, and $\psi_i(\mathbf{k}, \mathbf{r})$ is normalized in the unit cell.

The electron density is then

$$\rho(\mathbf{r}) = \sum_i \int_{BZ} n_i(\mathbf{k}) |\psi_i(\mathbf{k}, \mathbf{r})|^2 d\mathbf{k} = \sum_{\mu'\nu'} \rho_{\mu'\nu'} \phi^*_{\nu'}(\mathbf{r}) \phi_{\mu'}(\mathbf{r}) \tag{38}$$

where the sum is again over all basis orbitals in space, and the density matrix

$$\rho_{\mu\nu} = \sum_i \int_{BZ} c_{\mu i}(\mathbf{k}) n_i(\mathbf{k}) c_{i\nu}(\mathbf{k}) e^{i\mathbf{k}(\mathbf{R}_\nu - \mathbf{R}_\mu)} d\mathbf{k} \tag{39}$$

is real (for real ϕ_μ's) and periodic, i.e. $\rho_{\mu\nu} = \rho_{\mu'\nu'}$ if $(\nu, \mu) \equiv (\nu', \mu')$ (with '$\equiv$' meaning again 'equivalent by translation'). Thus, to calculate the density at a grid point of the unit cell, we simply find the sum (38) over all the pairs of orbitals ϕ_μ, ϕ_ν in the supercell that are non-zero at that point.

In practice, the integral in (39) is performed in a finite, uniform grid of the Brillouin zone. The fineness of this grid is controlled by a k-grid cutoff l_{cut}, a real-space radius which plays a role equivalent to the planewave cutoff of the real-space grid [42]. The origin of the k-grid may be displaced from $\mathbf{k} = 0$ in order to decrease the number of inequivalent k-points [43].

If the unit cell is large enough to allow a Γ-point-only calculation, the multiplication by phase factors is skipped and a single real-matrix eigenvalue problem is solved (in this case, the real matrix elements are accumulated directly in the first stage, if multiple overlaps occur). In this way, no complex arithmetic penalty occurs, and the differences between Γ-point and k-sampling are limited to a very small section of the code, while all the two-center and grid integrals use always the same real-arithmetic code.

8. Total energy

The Kohn-Sham [10] total energy can be written as a sum of a band-structure (BS) energy plus some correction terms, sometimes called 'double count' corrections. The BS term is the sum of the energies of the occupied states ψ_i:

$$E^{BS} = \sum_i n_i \langle \psi_i | \hat{H} | \psi_i \rangle = \sum_{\mu\nu} H_{\mu\nu} \rho_{\nu\mu} = \mathrm{Tr}(H\rho) \tag{40}$$

where spin and k-sampling notations are omitted here for simplicity. At convergence, the ψ_i's are simply the eigenvectors of the Hamiltonian, but it is important to realize that the Kohn-Sham functional is also perfectly well defined outside this so-called 'Born-Oppenheimer surface', i.e. it is defined for any set of orthonormal ψ_i's. The correction terms are simple functionals of the electron density, which can be obtained from equation (34), and the atomic positions. The Kohn-Sham total energy can then be written as

$$E^{KS} = \sum_{\mu\nu} H_{\mu\nu}\rho_{\nu\mu} - \frac{1}{2}\int V^H(\mathbf{r})\rho(\mathbf{r})d^3\mathbf{r} + \int(\epsilon^{xc}(\mathbf{r}) - V^{xc}(\mathbf{r}))\rho(\mathbf{r})d^3\mathbf{r} + \sum_{I<J}\frac{Z_I Z_J}{R_{IJ}} \tag{41}$$

where I, J are atomic indices, $R_{IJ} \equiv |\mathbf{R}_J - \mathbf{R}_I|$, Z_I, Z_J are the valence ion pseudoatom charges, and $\epsilon^{xc}(\mathbf{r})\rho(\mathbf{r})$ is the exchange-correlation energy density. In order to avoid the long range interactions of the last term, we construct from the local-pseudopotential V_I^{local}, which has an asymptotic behavior of $-Z_I/r$, a diffuse ion charge, $\rho_I^{local}(r)$, whose electrostatic potential is equal to $V_I^{local}(r)$:

$$\rho_I^{local}(\mathbf{r}) = -\frac{1}{4\pi}\nabla^2 V_I^{local}(\mathbf{r}). \tag{42}$$

Notice that we define the electron density as positive, and therefore $\rho_I^{local} \leq 0$. Then, we write the last term in (41) as

$$\sum_{I<J}\frac{Z_I Z_J}{R_{IJ}} = \frac{1}{2}\sum_{IJ} U_{IJ}^{local}(R_{IJ}) + \sum_{I<J}\delta U_{IJ}^{local}(R_{IJ}) - \sum_I U_I^{local} \tag{43}$$

where U_{IJ}^{local} is the electrostatic interaction between the diffuse ion charges in atoms I and J:

$$U_{IJ}^{local}(|\mathbf{R}|) = \int V_I^{local}(\mathbf{r})\rho_J^{local}(\mathbf{r}-\mathbf{R})d^3\mathbf{r}, \tag{44}$$

δU_{IJ}^{local} is a small short-range interaction term to correct for a possible overlap between the soft ion charges, which appears when the core densities are very extended:

$$\delta U_{IJ}^{local}(R) = \frac{Z_I Z_J}{R} - U_{IJ}^{local}(R), \tag{45}$$

and U_I^{local} is the fictitious self interaction of an ion charge (notice that the first right-hand sum in (43) includes the $I = J$ terms):

$$U_I^{local} = \frac{1}{2}U_{II}^{local}(0) = \frac{1}{2}\int V_I^{local}(r)\rho_I^{local}(r)4\pi r^2 dr. \tag{46}$$

Defining ρ_I^{NA} from V_I^{NA}, analogously to ρ_I^{local}, we have that $\rho_I^{NA} = \rho_I^{local} + \rho_I^{atom}$, and equation (41) can be transformed, after some rearrangement of terms, into

$$\begin{aligned} E^{KS} &= \sum_{\mu\nu}(T_{\mu\nu} + V_{\mu\nu}^{KB})\rho_{\nu\mu} + \frac{1}{2}\sum_{IJ} U_{IJ}^{NA}(R_{IJ}) + \sum_{I<J}\delta U_{IJ}^{local}(R_{IJ}) - \sum_I U_I^{local} \\ &+ \int V^{NA}(\mathbf{r})\delta\rho(\mathbf{r})d^3\mathbf{r} + \frac{1}{2}\int \delta V^H(\mathbf{r})\delta\rho(\mathbf{r})d^3\mathbf{r} + \int \epsilon^{xc}(\mathbf{r})\rho(\mathbf{r})d^3\mathbf{r} \end{aligned}$$

where $V^{NA} = \sum_I V_I^{NA}$ and $\delta\rho = \rho - \sum_I \rho_I^{NA}$.

$$U_{IJ}^{NA}(R) = \int V_I^{NA}(\mathbf{r})\rho_J^{NA}(\mathbf{r}-\mathbf{R})d^3\mathbf{r} = -\frac{1}{4\pi}\int V_I^{NA}(\mathbf{r})\nabla^2 V_J^{NA}(\mathbf{r}-\mathbf{R})d^3\mathbf{r} \tag{47}$$

is a radial pairwise potential that can be obtained from $V_I^{NA}(r)$ as a two-center integral, by the same method described previously for the kinetic matrix elements:

$$T_{\mu\nu} = \langle\phi_\mu| - \frac{1}{2}\nabla^2|\phi_\nu\rangle = -\frac{1}{2}\int \phi_\mu^*(\mathbf{r})\nabla^2\phi_\nu(\mathbf{r} - \mathbf{R}_{\mu\nu})d^3\mathbf{r} \tag{48}$$

$V_{\mu\nu}^{KB}$ is also obtained by two-center integrals:

$$V_{\mu\nu}^{KB} = \sum_\alpha \langle\phi_\mu|\chi_\alpha\rangle v_\alpha^{KB}\langle\chi_\alpha|\phi_\nu\rangle \tag{49}$$

where the sum is over all the KB projectors χ_α that overlap simultaneously with ϕ_μ and ϕ_ν.

The last three terms in Eq. (47) are calculated using the real space grid. In addition to getting rid of all long-range potentials (except that implicit in $\delta V^H(\mathbf{r})$), the advantage of (47) is that, apart from the relatively slowly-varying exchange-correlation energy density, the grid integrals involve $\delta\rho(\mathbf{r})$, which is generally much smaller than $\rho(\mathbf{r})$. Thus, the errors associated with the finite grid spacing are drastically reduced. Critically, the kinetic energy matrix elements can be calculated almost exactly, without any grid integrations.

It is frequently desirable to introduce a finite electronic temperature T and/or a fixed chemical potential μ, either because of true physical conditions or to accelerate the self-consistency iteration. Then, the functional that must be minimized is the free energy [44]

$$\begin{aligned} F(\mathbf{R}_I, \psi_i(\mathbf{r}), n_i) = E^{KS}(\mathbf{R}_I, \psi_i(\mathbf{r}), n_i) - \mu\sum_i n_i \\ -k_BT\sum_i(n_i\log n_i + (1 - n_i)\log(1 - n_i)). \end{aligned} \tag{50}$$

The functional is built in such a way that minimization with respect to n_i yields the usual Fermi-Dirac distribution $n_i = 1/(1 + e^{(\epsilon_i - \mu)/k_BT})$.

9. Atomic forces and stress

Atomic forces and stresses are obtained by direct differentiation of (47) with respect to atomic positions (at finite temperture, really corresponding to the derivatives of the free energy). They are obtained simultaneously with the total energy, mostly in the same places of the code, under the general paradigm “a piece of energy ⇒ a piece of force/stress” (except that some pieces are calculated only in the last self-consistency step). This ensures that all contributions, including Pulay corrections, are automatically included.

The force contribution from the first term in (47) is

$$\begin{aligned} \frac{\partial}{\partial\mathbf{R}_I} \quad \sum_{\mu\nu}(T_{\mu\nu} + V_{\mu\nu}^{KB})\rho_{\nu\mu} = \sum_{\mu\nu}(T_{\mu\nu} + V_{\mu\nu}^{KB})\frac{\partial\rho_{\nu\mu}}{\partial\mathbf{R}_I} + 2\sum_\mu\sum_{\nu\in I}\frac{dT_{\mu\nu}}{d\mathbf{R}_{\mu\nu}}\rho_{\nu\mu} \\ +2\sum_\mu\sum_{\nu\in I}\sum_\alpha S_{\mu\alpha}v_\alpha^{KB}\frac{dS_{\alpha\nu}}{d\mathbf{R}_{\alpha\nu}}\rho_{\nu\mu} - 2\sum_{\mu\nu}\sum_{\alpha\in I}S_{\mu\alpha}v_\alpha^{KB}\frac{dS_{\alpha\nu}}{d\mathbf{R}_{\alpha\nu}}\rho_{\nu\mu} \end{aligned}$$

where α are KB projector indices, $\in I$ indicates orbitals or KB projectors belonging to atom I, and we have considered that

$$\frac{\partial S_{\mu\nu}}{\partial\mathbf{R}_{I_\nu}} = -\frac{\partial S_{\mu\nu}}{\partial\mathbf{R}_{I_\mu}} = \frac{dS_{\mu\nu}}{d\mathbf{R}_{\mu\nu}}, \tag{51}$$

where $\mathbf{R}_{I_\mu}$ is the position of atom I_μ, to which orbital ϕ_μ belongs and $\mathbf{R}_{\mu\nu} = \mathbf{R}_{I_\nu} - \mathbf{R}_{I_\mu}$.

Leaving aside for the moment the terms containing $\partial\rho_{\nu\mu}/\partial\mathbf{R}_I$, the other derivatives can be obtained by straightforward differentiation of their expansion in spherical harmonics (Eq. (24)). However, instead of using the spherical harmonics $Y_{lm}(\hat{\mathbf{r}})$ themselves, it is convenient to multiply them by r^l, in order to make them analytic at the origin. Thus

$$\begin{aligned}\frac{dS_{\mu\nu}(\mathbf{R})}{d\mathbf{R}} &= \sum_{lm} \nabla \left(\frac{S^{\mu\nu}_{lm}(R)}{R^l} R^l Y_{lm}(\hat{\mathbf{R}}) \right) \\ &= \sum_{lm} \frac{d}{dR} \left(\frac{S^{\mu\nu}_{lm}(R)}{R^l} \right) R^l Y_{lm}(\hat{\mathbf{R}}) \hat{\mathbf{R}} + \sum_{lm} \frac{S^{\mu\nu}_{lm}(R)}{R^l} \nabla (R^l Y_{lm}(\hat{\mathbf{R}})) \end{aligned} \tag{52}$$

In fact, it is $S^{\mu\nu}_{lm}(R)/R^l$, rather than $S^{\mu\nu}_{lm}(R)$, that is stored as a function of R on a radial grid. Its derivative, $d(S^{\mu\nu}_{lm}(R)/R^l)/dR$, is then obtained from the same cubic spline interpolation used for the value itself. The value and gradient of $R^l Y_{lm}(\hat{\mathbf{R}})$ are calculated analytically from explicit formulae (up to $l = 2$) or recurrence relations [28]. Entirely analogous equations apply to $dT_{\mu\nu}/d\mathbf{R}_{\mu\nu}$.

The second and third terms in Eq. (47) are simple interatomic pair potentials whose force contributions are calculated trivially from their radial spline interpolations. The fourth term is a constant which does not depend on the atomic positions. Taking into account that $V^{NA}(\mathbf{r}) = \sum_I V_I^{NA}(\mathbf{r} - \mathbf{R}_I)$, and therefore $\partial V^{NA}(\mathbf{r})/\partial\mathbf{R}_I = -\nabla V_I^{NA}(\mathbf{r} - \mathbf{R}_I)$, the force contribution from the fifth term is

$$\frac{\partial}{\partial\mathbf{R}_I} \int V^{NA}(\mathbf{r}) \delta\rho(\mathbf{r}) d^3\mathbf{r} = -\int \nabla V_I^{NA}(\mathbf{r}) \delta\rho(\mathbf{r}) d^3\mathbf{r} + \int V^{NA}(\mathbf{r}) \frac{\partial \delta\rho(\mathbf{r})}{\partial\mathbf{R}_I} d^3\mathbf{r} \tag{53}$$

The sixth term is the electrostatic self-energy of the charge distribution $\delta\rho(\mathbf{r})$:

$$\frac{\partial}{\partial\mathbf{R}_I} \frac{1}{2} \int \delta V^H(\mathbf{r}) \delta\rho(\mathbf{r}) d^3\mathbf{r} = \int \delta V^H(\mathbf{r}) \frac{\partial \delta\rho(\mathbf{r})}{\partial\mathbf{R}_I} d^3\mathbf{r} \tag{54}$$

In the last term, we take into account that $d(\rho\epsilon^{xc})/d\rho = v^{xc}$ to obtain

$$\frac{\partial}{\partial\mathbf{R}_I} \int \epsilon^{xc}(\mathbf{r}) \rho(\mathbf{r}) d^3\mathbf{r} = \int V^{xc}(\mathbf{r}) \frac{\partial \rho(\mathbf{r})}{\partial\mathbf{R}_I} d^3\mathbf{r} \tag{55}$$

Now, using Eq. (34) and that, for $\nu \in I$, $\partial\phi_\nu(\mathbf{r})/\partial\mathbf{R}_I = -\nabla\phi_\nu$, the change of the self-consistent and atomic densities are

$$\frac{\partial\rho(\mathbf{r})}{\partial\mathbf{R}_I} = \mathrm{Re} \sum_{\mu\nu} \frac{\partial\rho_{\nu\mu}}{\partial\mathbf{R}_I} \phi^*_\mu(\mathbf{r}) \phi_\nu(\mathbf{r}) - 2\mathrm{Re} \sum_{\mu} \sum_{\nu\in I} \rho_{\nu\mu} \phi^*_\mu(\mathbf{r}) \nabla\phi_\nu(\mathbf{r}) \tag{56}$$

$$\frac{\partial\rho^{atom}(\mathbf{r})}{\partial\mathbf{R}_I} = -2\mathrm{Re} \sum_{\mu\in I} \rho^{atom}_{\mu\mu} \phi^*_\mu(\mathbf{r}) \nabla\phi_\mu(\mathbf{r}) \tag{57}$$

where we have taken into account that the density matrix of the separated atoms is diagonal. Thus, leaving still aside the terms with $\partial\rho_{\nu\mu}/\partial\mathbf{R}_I$, the last term in Eq. (53), as well as those in (54) and (55), have the general form

$$\mathrm{Re} \sum_{\mu} \sum_{\nu\in I} \rho_{\nu\mu} \int V(\mathbf{r}) \phi^*_\mu(\mathbf{r}) \nabla\phi_\nu(\mathbf{r}) d^3\mathbf{r} = \mathrm{Re} \sum_{\mu} \sum_{\nu\in I} \rho_{\nu\mu} \langle \phi_\mu | V(\mathbf{r}) | \nabla\phi_\nu \rangle. \tag{58}$$

These integrals are calculated on the grid, in the same way as those for the total energy (i. e. $\langle\phi_\mu|V(\mathbf{r})|\phi_\nu\rangle$). The gradients $\nabla\phi_\nu(\mathbf{r})$ at the grid points are obtained analytically, like those of $\phi_\nu(\mathbf{r})$ from their radial grid interpolations of $\phi(r)/r^l$:

$$\nabla\phi_{Ilmn}(\mathbf{r}) = \frac{d}{dr}\left(\frac{\phi_{Iln}(r)}{r^l}\right) r^l Y_{lm}(\hat{\mathbf{r}})\hat{\mathbf{r}} + \frac{\phi_{Iln}(r)}{r^l}\nabla(r^l Y_{lm}(\hat{\mathbf{r}})). \tag{59}$$

In some special cases, with elements that require hard partial core corrections or explicit inclusion of the semicore, the grid integrals may pose a problem for geometry relaxations, because they make the energy dependent on the position of the atoms relative to the grid. This 'eggbox effect' is small for the energy itself, and it decreases fast with the grid spacing. But the effect is larger and the convergence slower for the forces, as they are proportional to the amplitude of the energy oscillation, but inversely proportional to its period. These force oscillations complicate the force landscape, especially when the true atomic forces become small, making the convergence of the geometry optimization more difficult. Of course, the problem can be avoided by decreasing the grid spacing but this has an additional cost in computer time and memory. We have found it useful to minimize this problem by recalculating the forces using the grid-cell sampling described in section 6. This is equivalent to computing the forces averaging over a set of positions, determined by translating the whole system by a set of points in a finer mesh, and thus minimizing the error associated with the translational symmetry breaking.

We now turn to the force terms containing $\partial\rho_{\mu\nu}/\partial\mathbf{R}_I$. Substituting the first term of Eq. (56) into Eqs. (53-55) and adding the first term of Eq. (51) we obtain a simple expression that contains all those terms: $\sum_{\mu\nu} H_{\nu\mu}\partial\rho_{\mu\nu}/\partial\mathbf{R}_I$. The derivative of $\rho_{\mu\nu}$ with respect to the atomic positions is non-zero for atomic orbitals bases, since the orbitals move with the atoms, and the orthogonalization of the wave-functions must be imposed upon atomic displacements. It can be shown [6, 45] that this term can be expressed as:

$$\mathbf{F}_I^{orthog} = 2\sum_\mu\sum_{\nu\in I} E_{\nu\mu}\frac{\partial S_{\mu\nu}}{\partial\mathbf{R}_{\mu\nu}} \tag{60}$$

where $E_{\mu\nu}$ is the so-called energy-density matrix:

$$E_{\mu\nu} = \frac{1}{2}\sum_{\eta\zeta}\left(S^{-1}_{\mu\eta}H_{\eta\zeta}\rho_{\zeta\nu} + \rho_{\mu\eta}H_{\eta\zeta}S^{-1}_{\zeta\nu}\right) = \sum_i c_{\mu i}n_i\epsilon_i c_{i\nu} \tag{61}$$

where ϵ_i are the eigenstate energies. This equation has been derived in different ways, and Ordejón et al [45] found it also for the $\mathcal{O}(N)$ functional, even though it does not require the occupied states to be orthogonal. In this case, Eq. (61) must be substituted by a more complicated expression [45].

The derivation of the stress formulas follows the same lines. We define the stress tensor as the positive derivative of the total energy with respect to the strain tensor

$$\sigma_{\alpha\beta} = \frac{\partial E^{KS}}{\partial\epsilon_{\alpha\beta}} \tag{62}$$

where α, β are Cartesian coordinate indices. To translate to standard units of pressure, we must simply divide by the unit-cell volume and change sign. During the deformation, all vector positions, including those of atoms and grid points (and of course lattice vectors), change according to

$$r'_\alpha = \sum_{\beta=1}^{3} (\delta_{\alpha\beta} + \epsilon_{\alpha\beta}) r_\beta \tag{63}$$

The shape of the basis functions, KB projectors, and atomic densities and potentials do not change, but their origin gets displaced according to (63). From this equation, we find that

$$\frac{\partial r_\gamma}{\partial \epsilon_{\alpha\beta}} = \delta_{\gamma\alpha} r_\beta \tag{64}$$

The change in E^{KS} is essentially due to these position displacements, and therefore the calculation of the stress is almost perfectly parallel to that of the atomic forces, thus being performed in the same sections of the code. For example:

$$\frac{\partial T_{\mu\nu}}{\partial \epsilon_{\alpha\beta}} = \sum_{\gamma=1}^{3} \frac{\partial T_{\mu\nu}}{\partial r^\gamma_{\mu\nu}} \frac{\partial r^\gamma_{\mu\nu}}{\partial \epsilon_{\alpha\beta}} = \frac{\partial T_{\mu\nu}}{\partial r^\alpha_{\mu\nu}} r^\beta_{\mu\nu} \tag{65}$$

Since $\partial T_{\mu\nu}/\partial r^\alpha_{\mu\nu}$ is evaluated to calculate the forces, it takes very little extra effort to multiply it also by $r^\beta_{\mu\nu}$ for the stress. Equally, force contributions like (58) have their obvious stress counterpart

$$\sum_{\mu\nu} \rho_{\nu\mu} \langle \phi_\mu | V(\mathbf{r}) | (\nabla_\alpha \phi_\nu) r_\beta \rangle \tag{66}$$

However, there are three exceptions to this parallelism. The first concerns the change of the volume per grid point or, in other words, the Jacobian of the transformation (63) in the integrals over the unit cell. This Jacobian is simply $\delta_{\alpha\beta}$, and it leads to a stress contribution

$$\left[\int \left(V^{NA}(\mathbf{r}) + \frac{1}{2} \delta V^H(\mathbf{r}) \right) \delta\rho(\mathbf{r}) d^3\mathbf{r} + E^{xc} \right] \delta_{\alpha\beta} \tag{67}$$

Notice that the the renormalization of the density, required to conserve the charge when the volume changes, enters through the orthonormality constraints, and yields to a contribution to the stress:

$$\sigma^{orthog}_{\alpha\beta} = -\sum_{\mu\nu} E_{\nu\mu} \frac{\partial S_{\mu\nu}}{\partial R^\alpha_{\mu\nu}} R^\beta_{\mu\nu} \tag{68}$$

The second special contribution to the stress lies in the fact that, as we deform the lattice, there is a change in the factor $1/|\mathbf{r} - \mathbf{r}'|$ of the electrostatic energy integrals. We deal with this contribution in reciprocal space, when we calculate the Hartree potential by FFTs, by evaluating the derivative of the reciprocal-space vectors with respect to $\epsilon_{\alpha\beta}$. Since $G'_\alpha = \sum_\beta G_\beta (\delta_{\beta\alpha} - \epsilon_{\beta\alpha})$:

$$\frac{\partial}{\partial \epsilon_{\alpha\beta}} \frac{1}{G^2} = \frac{2 G_\alpha G_\beta}{G^4} \tag{69}$$

The third special stress contribution arises in GGA exchange and correlation, from the change of the gradient of the deformed density $\rho(\mathbf{r}) \to \rho(\mathbf{r}')$. The treatment of this contribution is explained in detail in reference [40].

10. Order-N functional

The basic problem for solving the Kohn-Sham equations in $\mathcal{O}(N)$ operations is that the solutions (the Hamiltonian eigenvectors) are extended over the whole system and overlap with each other.

Just to check the orthogonality of N trial solutions, by performing integrals over the whole system, involves $\sim N^3$ operations. Among the different methods proposed to solve this problem [4, 8], we have chosen the localized-orbital approach [46, 5, 47] because of its superior efficiency for non-orthogonal basis sets. The initially proposed functional [46, 5] used a fixed number of occupied states, equal to the number of electron pairs, and it was found to have numerous local minima in which the electron configuration was easily trapped. A revised functional form [47] which uses a larger number of states than electron pairs, with variable occupations, has been found empirically to avoid the local minima problem. This is the functional that we use and recommend.

Each of the localized, Wannier-like states, is constrained to its own localization region. Each atom I is assigned a number of states equal to $\mathrm{int}(Z_I^{val}/2+1)$ so that, if doubly occupied, they can contain at least one excess electron (they can also become empty during the minimization of the energy functional). These states are confined to a sphere of radius R_c (common to all states) centered at $\mathbf{R}_I$. More precisely, the expansion (Eq. (31)) of a state ψ_i centered at $\mathbf{R}_I$ may contain only basis orbitals ϕ_μ centered on atoms J such that $|\mathbf{R}_{IJ}| < R_c$. This implies that $\psi_i(\mathbf{r})$ may extend to a maximum range $R_c + r_c^{max}$, where r_c^{max} is the maximun range of the basis orbitals. For covalent systems, a localization region centered on bonds rather than atoms is more efficient [48] (it leads to a lower energy for the same R_c), but it is less suitable to a general algorithm, especially in case of ambiguous bonds. Therefore, we generally use the atom-centered localization regions.

In the method of Kim, Mauri, and Galli (KMG) [47], the band-structure energy is rewritten as:

$$\begin{aligned} E^{KMG} &= 2\sum_{ij}(2\delta_{ji} - S_{ji})(H_{ij} - \eta S_{ij}) \\ &= 4\sum_i \sum_{\mu\nu} c_{i\mu}\delta H_{\mu\nu} c_{\nu i} - 2\sum_{ij}\sum_{\alpha\beta\mu\nu} c_{i\alpha} S_{\alpha\beta} c_{\beta j} c_{j\mu} \delta H_{\mu\nu} c_{\nu i} \end{aligned} \tag{70}$$

Where $S_{ij} = \langle\psi_i|\psi_j\rangle$, $H_{ij} = \langle\psi_i|H|\psi_j\rangle$, $\delta H_{\mu\nu} = H_{\mu\nu} - \eta S_{\mu\nu}$, and we have assumed a non-magnetic solution with doubly occupied states. The 'double count' correction terms of Eq. (41) remain unchanged and the electron density is still defined by (34), but the density matrix is re-defined as

$$\rho_{\mu\nu} = 2\sum_{ij} c_{\mu i}(2\delta_{ij} - S_{ij})c_{j\nu} = 4\sum_i c_{\mu i}c_{i\nu} - 2\sum_{ij}\sum_{\alpha\beta} c_{\mu i}c_{i\alpha}S_{\alpha\beta}c_{\beta j}c_{j\nu} \tag{71}$$

The parameter η in Eq. (70) plays the role of a chemical potential, and must be chosen to lie within the band gap between the occupied and empty states. This may be tricky sometimes, since the electron bands can shift during the self-consistency process or when the atoms move. In general, the number of electrons will not be exactly the desired one, even if η is within the band gap, because the minimization of (70) implies a trade-off in which the localized states become fractionally occupied. To avoid an infinite Hartree energy in periodic systems, we simply renormalize the density matrix so that the total electron charge $\sum_{\mu\nu} S_{\mu\nu}\rho_{\nu\mu}$ equals the required value.

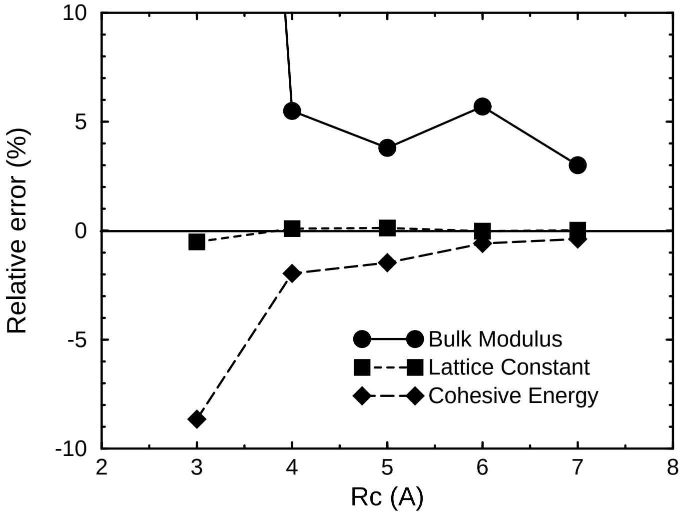

Figure 6: Convergence of the lattice constant, bulk modulus, and cohesive energy as a function of the localization radius R_c of the Wannier-like electron states in silicon. We used a supercell of 512 atoms and a minimal basis set with a cutoff radius $r_c = 5$ a.u. for both s and p orbitals.

For a given potential, the functional (70) is minimized by the conjugate-gradients method, using its derivatives with respect to the expansion coefficients

$$\frac{\partial E^{KMG}}{\partial c_{i\mu}} = 4\sum_{\nu} \delta H_{\mu\nu} c_{\nu i} - 2\sum_{j}\sum_{\alpha\beta\nu} \left(S_{\mu\nu} c_{\nu j} c_{j\alpha} \delta H_{\alpha\beta} c_{\beta i} + \delta H_{\mu\nu} c_{\nu j} c_{j\alpha} S_{\alpha\beta} c_{\beta i}\right) \tag{72}$$

The minimization proceeds without need to orthonormalize the electron states ψ_i. Instead, the orthogonality, as well as the correct normalization (one below η and zero above it) result as a consequence of the minimization of E^{KMG}. This is because, in contrast to the KS functional, E^{KMG} is designed to penalize any nonorthogonality [47]. The KS ground state, with all the occupied ψ_i's orthonormal, is also the minimum of (70), at which $E^{KMG} = E^{KS}$. If the variational freedom is constrained by the localization of the ψ_i's, the orthogonality cannot be exact, and the resulting energy is slightly larger than for unconstrained wavefunctions. In insulators and semiconductors, the Wannier functions are exponentially localized [49], and the energy excess due to their strict localization decreases rapidly as a function of the localization radius R_c, as can be seen in Fig. 6.

If the system is metallic, or if the chemical potential is not within the band gap (for example because of the presence of defects), the KMG functional cannot be used in practice. In fact, although some $\mathcal{O}(N)$ methods can handle metallic systems in principle [8], we are not aware of any practical calculations at a DFT level. In such cases we copy the Hamiltonian and overlap matrices to standard expanded arrays and solve the generalized eigenvalue problem by conventional order-N^3 diagonalization techniques [50]. However, even in this case, most of the operations, and particularly those to find the density and potential, and to set up the Hamiltonian, are still performed in $\mathcal{O}(N)$ operations.

Table 3: Average number of selfconsistency (SCF) iterations (per molecular dynamics step) and average number of conjugate-gradient (CG) iterations (per SCF iteration) required to minimize the $\mathcal{O}(N)$ functional, during a simulation of bulk silicon at $\sim$ 300 K. We used the Verlet method [53] at constant energy, with a time step of 1.5 fs, and a minimal basis set with a cutoff radius $r_c = 5$ a.u. R_c is the localization radius of the Wannier-like wavefunctions used in the $\mathcal{O}(N)$ functional (see text). N is the number of atoms in the system.

	$R_c = 4$Å		$R_c = 5$Å	
N	CG	SCF	CG	SCF
64	5.8	9.3	8.4	8.4
512	4.9	11.4	8.8	10.1
1000	4.3	11.5	9.9	11.5

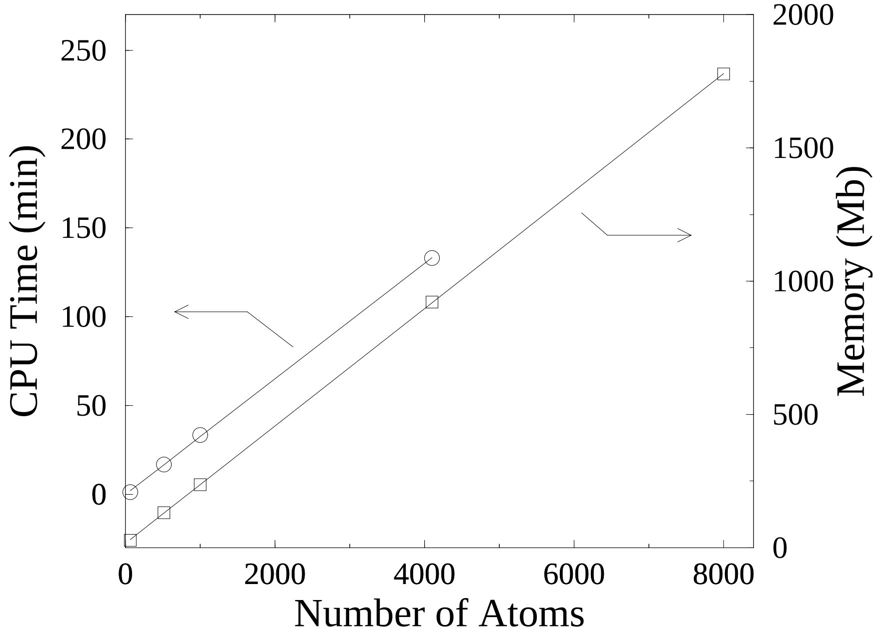

Figure 7: CPU time and memory for silicon supercells of 64, 512, 1000, 4096, and 8000 atoms. Times are for one average molecular dynamics step at 300 K. This includes 10 SCF steps, each with 10 conjugate gradient minimization steps of the $\mathcal{O}(N)$ energy functional. Memories are peak ones. Although the memory requierement for 8000 atoms was determined accurately, the run could not be performed because of insufficient memory in the PC used.

Irrespective of whether the $\mathcal{O}(N)$ functional or the standard diagonalization is used, an outer selfconsistency iteration is required, in which the density matrix is updated using Pulay's Residual Metric Minimization by Direct Inversion of the Iterative Subspace (RMM-DIIS) method [51, 52]. Even when the code is strictly $\mathcal{O}(N)$, the CPU time may increase faster if the number of iterations required to achieve the solution increases with N. In fact, it is a common experience that the required number of selfconsistency iterations increases with the size of the system. This is mainly because of the 'charge sloshing' effect, in which small displacements of charge from one side of the system to another give rise to larger changes of the potential, as the size increases. Fortunately, the localized character of the Wannier-like wavefunctions used in the $\mathcal{O}(N)$ method help to solve also this problem, by limiting the charge sloshing. Table 3 presents the average number of iterations required to minimize the $\mathcal{O}(N)$ functional and the average number of selfconsistency iterations, during a molecular dynamics simulation of bulk silicon at room temperature. It can be seen that these numbers are quite small and that they increase very moderately with system size. As might be expected, the number of minimization iterations increase with the localization radius, i.e. with the number of degrees of freedom ($c_{\mu i}$ coefficients) of the wavefunctions. But this increase is also rather moderate.

Figure 7 shows the essentially perfect $\mathcal{O}(N)$ behaviour of the overall CPU time and memory. This is not surprising in view of the completely strict enforcement of $\mathcal{O}(N)$ algorithms everywhere in the code (except the marginal $N \log N$ factor in the FFT used to solve Poisson's equation, which represents a very small fraction of CPU time even for 4000 atoms).

11. Other features

Here we will simply mention some of the possibilities and features of the SIESTA implementation of DFT:

- The most recent version of SIESTA is partially writen in Fortran-90, and implements dynamical memory allocation, so that the same executable can be used for any system under study. Also, parallelization has been achieved using MPI. In benchmark calculations performed on an SGI Origin computer, using the Kim *et al.* Order-N functional, a system with 131,072 silicon atoms was solved using 64 processors.

- A general-purpose package [54], the flexible data format (fdf), initially developped for the SIESTA project, allows the introduction of all the data and precision parameters in a simple tag-oriented, order-independent format which accepts different physical units. The data can then be accessed from anywhere in the program, using simple subroutine calls in which a default value is specified for the case in which the data are not present. A simple call also allows the read pointer to be positioned in order to read complex data 'blocks' also marked with tags.

- Non-collinear spin polarized systems [55, 56, 57] can be studied with SIESTA [58]. The spin direction is defined in the real space grid points, and therefore no atomic sphere approximation is used.

- The systematic calculation of atomic forces and stress tensor allows the simultaneous relaxation of atomic coordinates and cell shape and size, using a conjugate gradients minimization or several other minimization/annealing algorithms.

- It is possible to perform a variety of molecular dynamics simulations, at constant energy or temperature, and at constant volume or pressure, also including Parrinello-Rahman dynamics with variable cell shape [53]. The geometry relaxation may be restricted, to impose certain positions or coordinates, or more complex constraints.

- The auxiliary program VIBRA processes systematically the atomic forces for sets of displaced atomic positions, and from them computes the Hessian matrix and the phonon spectrum. An interface to the PHONON program [59] is also provided within SIESTA.

- A linear response program (LINRES) to calculate phonon frequencies has also been developed [60]. The code reads the SCF solution obtained by Siesta, and calculates the linear response to the atomic displacements, using first order perturbation theory. It then calculates the dynamical matrix, from which the phonon frequencies are obtained.

- The calculation of the electric polarization, as an integral in the grid across the unit cell, is standard and almost free for molecules, chains and slabs (in the directions perpendicular to the chain axis, or to the surface). For bulk systems, the electric polarization cannot be found from the charge distribution in the unit cell alone. In this case, we use the so-called Berry-phase theory of polarization [61, 62], which we have implemented in SIESTA [63]. This allows us to compute quantities like the dynamical charges [61] and piezoeletric constants [64, 65].

- A number of auxiliary programs allows various representations of the total density, the total and local density of states, and the electrostatic or total potentials. The representations include both two-dimensional cuts and three-dimensional views, which may be colored to simultaneously represent the density and potential.

- Thanks to an interface with the TRANSIESTA program, it is posible to calculate transport properties across a nanocontact, finding self-consistently the effective potential across a finite voltage drop, at a DFT level, using the Keldish Green's function formalism [66].

- The optical response can be studied with SIESTA using different approaches. An approximate dielectric function can be calculated from the dipolar transition matrix elements between occupied and unoccupied single-electron eigenstates using first order time-dependent pertubation theory [67]. For finite systems, these are easily calculated from the matrix elements of the position operator between the basis orbitals. For infinite periodic systems, we use the matrix elements of the momentum operator. It is important to notice, however, that the use of non-local pseudopotentials requires some correction terms [68]. We have also implemented a more sophisticated approach to compute the optical response of finite systems, using the adiabatic approximation to time-dependent DFT [69, 70]. The idea is to integrate the time-dependent Schrödinger equation when a time depedent perturbation is applied to the system [71]. From the time evolution, it is then possible to extract the optical adsorption and dipole strength functions, including some genuinely many-body effects, like plasmons. Using this approach we have succesfully calculated the electronic response of systems such as fullerenes and small metallic clusters [72].

12. Some applications to benchmark systems

12.1 Ferroelectric perovskites

DFT calculations are making a big impact is the study of ferroelectric materials, and in particular, ferroelectric perovskite oxides. The combination of accurate DFT calculations with Monte Carlo approaches are allowing to advance very significantly in understanding the basic physics of the ferroelectric transition in these systems. However, the advance in this field has been limited by the fact that the relevant energies involved in the ferroelectric distortions are very small, and therefore very accurate calculations are required to produce reasonable results [73, 74]. This poses a problem even for standard methods like pseudopotential-plane-waves, because of the important role played by the semicore states, which must be included explicitly in the calculation and makes it very costly, since very large plane-waves cutoff are needed to describe these states.

Due to these difficulties and the high computational cost, only the simplest ferroelectric perovskites have been studied so far by means of first principles methods. More complex and technologically more important materials, or complex combinations of these (heterostructures, thin films, etc) are therefore quite out of reach so far. It seems obvious that a method which would produce the accuracy necessary while keeping a low computational cost would be of great importance in this field. Here we present results for $BaTiO_3$ that show that SIESTA is able to provide such accuracy for a variety of properties such as lattice constant, energy surfaces, phonon frequencies and effective Born charges.

The calculations presented here were done as follows. We have used the LDA functional of Perdew and Zunger. Due to the importance of semi-core states, the $3s$ and $3p$ electrons of Ti and the $5s$ and $5p$ of Ba were included explicitly in the calculation. The Troullier-Martins [22] pseudopotentials were generated with those states in the valence, and with the following reference configurations: $3s^2 3p^6 3d^2$ for Ti^{+2}, $5s^2 5p^6$ for Ba^{+2} and $2s^2 2p^4$ for O. The radii used were: for Ti, 1.3 a.u for the s, p and d states, and 2.0 for the f states; for Ba, 1.75, 2.0, 2.5 and 2.5 a.u. for the s, p, d and f states, respectively; and for O, 1.15 a.u. for the s, p and d states and 1.5 a.u. for the f states. The basis set used here was single-ζ for the semicore states of Ti and Ba, and double-ζ plus a single shell of polarization functions for the valence states of all atoms. For Ba, an extra single shell of $5d$ orbitals was added. This amounts to a total of 19 orbitals for Ti, 14 orbitals for Ba and 13 orbitals for O.

To obtain the integrals of the Hamiltonian that are computed on a real space grid, we have used an equivalent cutoff of 200 Ry to represent the charge density. Once self-consistency was achieved, the grid was refined (reducing the spacing between grid points by half) to compute the total energy, atomic forces and stress. The sampling of reciprocal space was done using a $(6 \times 6 \times 6)$ Monkhorst-Pack mesh. Although $BaTiO_3$ is an insulator, it has been shown that this large sampling is necessary to reproduce properly the energetics of the system [73, 74].

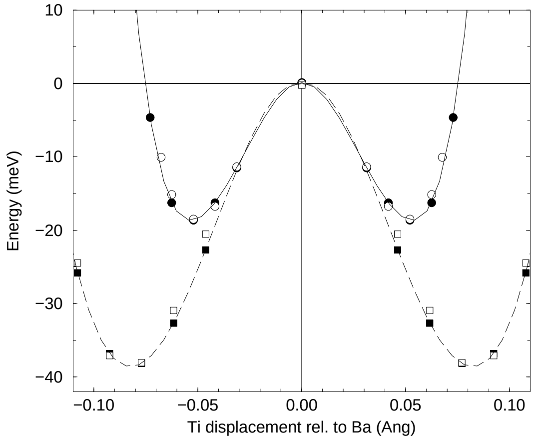

Figure 8: Energy versus distortion for cubic $BaTiO_3$, for tetragonal (circles) and rhombohedral (squares) distortions. The full symbols are the results of SIESTA, whereas the open symbols are the FPLAPW results. The patterns of the distortions were taken from the experiment. The calculations were done at the experimental lattice constant. The lines are fit to the results of SIESTA, to guide the eye. Energies are referred to that of the cubic phase at the experimental lattice constant.

We have first considered the undistorted cubic phase. We obtain an equilibrium lattice constant of 7.46 a.u., very close to previous LDA results from LAPW (7.45 a.u.) [75] or with plane-waves (7.456 a.u.) [73] calculations. The LDA results underestimate significantly the lattice constant of the cubic phase, which experimentally is found to be 7.57 a.u.

We have next considered the energy gain for a ferroelectric distortion. At high temperature, $BaTiO_3$ shows a cubic symmetry with no net polarization. Upon lowering the temperature, three ferroelectric transitions appear: first, to a tetragonal, then an orthorombic and finally a rhombohedral phase. We have calculated the energy as a function of ferroelectric displacement for two different distortions: the rhombohedral and the tetragonal. In the calculation, we have used a cubic cell with a lattice constant at the experimental value, although experimentally the unit cell is found to deform slightly according to the symmetry of the ferroelectric distortion. We will neglect this deformation, since our goal is to validate the results of SIESTA by comparing them with benchmark DFT calculations. To that end, we use the FPLAPW method [76, 77], which is the most accurate DFT approach which can be used to study these systems. The comparison is presented in Figure 8, which shows the energy as a function of the displacement of the Ti atom (the distortion vector is taken from the experiment [78]). We can observe that the agreement between both methods is excellent. Both calculations are able to reproduce the minimum of the energy for a value of the distortion parameter very close to the experimental one. The energy gain in the rhombohedral phase is more than twice as much as that of the tetragonal phase. This is consistent with the experiment, where the tetragonal phase occurs at higher temperature than the rhombohedral one, which is the low temperature stable phase.

Many of the features of the ferroelectric behavior of $BaTiO_3$ can be explained by looking at the phonon structure of the undistorted cubic phase. The appearance of unstable modes (with

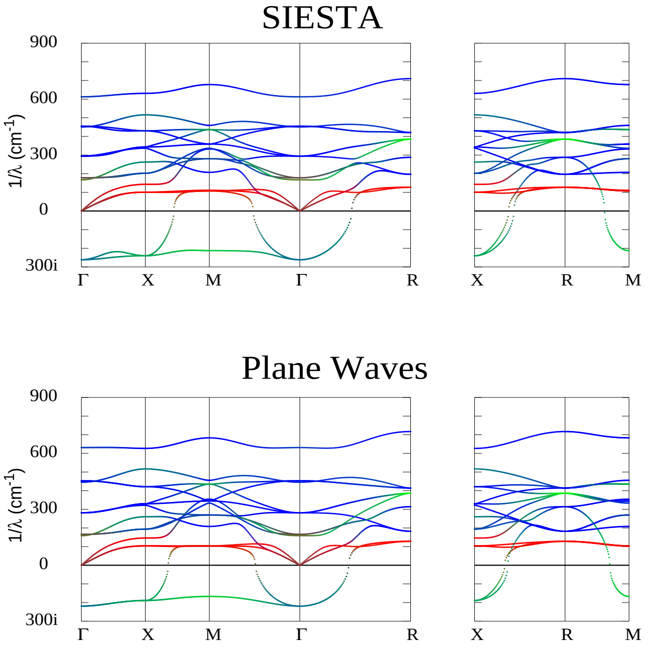

Figure 9: Phonon dispersion relations for cubil $BaTiO_3$, calculated with Siesta (top panel) and with plane waves (taken from [79]). The colors indicate the main atoms that participate in each vibration: blue, green and red correspond to O, Ti and Ba, respectively. Unstable modes are indicated by imaginary frequencies.

imaginary frequency) indicate the presence of instabilities which cause the ferroelectric transitions. Figure 9 shows a plot of the phonon spectra of cubic $BaTiO_3$, computed with Siesta (upper panel) and with plane-waves (lower panel) [79]. We see that the agreement is very good. In particular, Siesta is able to reproduce all the unstable branches throughout the Brillouin zone. The colors represent the character of each mode: blue, green and red correspond to O, Ti and Ba displacements, respectively. Both the frequencies and the character of all modes are well described with Siesta.

We have also computed the Born effective charges of the cubic phase. These are important because they determine the value of the polarization for a ferroelectric distortion, as well as other properties such as the IR response, or the LO-TO splitting. The symmetry of the cubic $BaTiO_3$ phase reduces the number of nonzero elements of the dynamical charge tensor to four: Z*(Ti) and Z*(Ba) for the two metal atoms (their effective charge tensor is isotropic), and $Z^*(O_I)$ and $Z^*(O_{II})$ for the oxygen, corresponding to displacements parallel or normal to BaO planes. We have calculated the Born charges by finite differences, using the Berry phase method [61, 62] implemented in Siesta [63], to compute the net polarization of the system for finite values of the atomic displacements. These were taken as about 0.3% of the value of the lattice constant. We used a $(4 \times 4 \times 20)$ k-point grid, to allow for a larger number of k-points in the direction of the atomic displacement. We summarize our results in table 4, together with those obtained with plane-waves calculations by other authors [80, 81]. Again, we find good agreement, although the differences between our results and those of plane waves are larger (but comparable) to those between different plane-waves calculations. As with plane-waves, we find

Table 4: Born charges for cubic $BaTiO_3$ computed with SIESTA and with plane waves [80, 81].

	SIESTA	PW [80]	PW [81]
Ba	2.72	2.77	2.75
Ti	7.60	7.25	7.16
O_{II}	-2.18	-2.15	-2.11
O_I	-5.96	-5.71	-5.69

values quite larger than the nominal valences of the atoms in the compound, pointing out the importance of covalency in this material.

12.2 Molecular systems

Here, we show some results of a thorough study of the ability of SIESTA to tackle complex organic and inorganic molecules [82]. In these calculations, we used a double-ζ basis set plus a single shell of polarization orbitals on all the atoms. The radii of the orbitals were obtained using an energy shift parameter of 0.005 Ry, resulting in relatively long orbitals. Troullier-Martins pseudopotentials [22], and the GGA functional of Perdew, Burke and Erzenhof [12] were used. The real space integrals grid cutoff was set to 150 Ry.

In a first study, we focus on the structure of a set of 103 molecules. For details, the complete list of molecules is available (http://uqbar.ncifcrf.gov/˜rcachau/Siesta). The set was selected to include some of the most difficult cases reported in the evaluation of semiempirical methods as well as highly stressed (e.g. very polar bonds) and very similar (e.g. alcohol series) geometries for sensitivity analysis. They also include several H-bonded complexes. We compare our results with those obtained from calculations using gaussian basis sets, with the B3LYP functional [83], and with semiempirical methods like AM1 and PM3 [84]. B3LYP, AM1 and PM3 calculations were performed using Gaussian 98 A.7 [85] with 6311G(2d,2p) atomic basis sets and standard cutoffs for SCF, and geometry optimization. All semiempirical (AM1 and PM3) calculations were performed using the amide molecular mechanics correction where required.

Figure 10 shows a comparison of the geometries obtained with the different methods. The bond angles and bond distances were selected to exclude symmetry related redundancy. Note the extremely good correlation between SIESTA and B3LYP calculations. The correlation of B3LYP geometries with experimental values is well known, and also translates to the SIESTA geometries. The bond distances were presented as squared values to expand the scale. This helps observe the clustered aspect of the semiempirical plots (not observed in the SIESTA vs. B3LYP correlations), which is a direct result of the parametrization procedure. More details of these results can be found in Ref. [82] and http://uqbar.ncifcrf.gov/˜rcachau/Siesta).

In a second test case [86], we will discuss the description of H-bonds and the comparison with the results of accurate quantum-chemical second-order Moller-Plesset (MP2) calculations . In particular, we will focus on the study of DNA base pairs due to their biological relevance and the availability of extensive MP2 calculations [87]. H-bonding interactions are of paramount

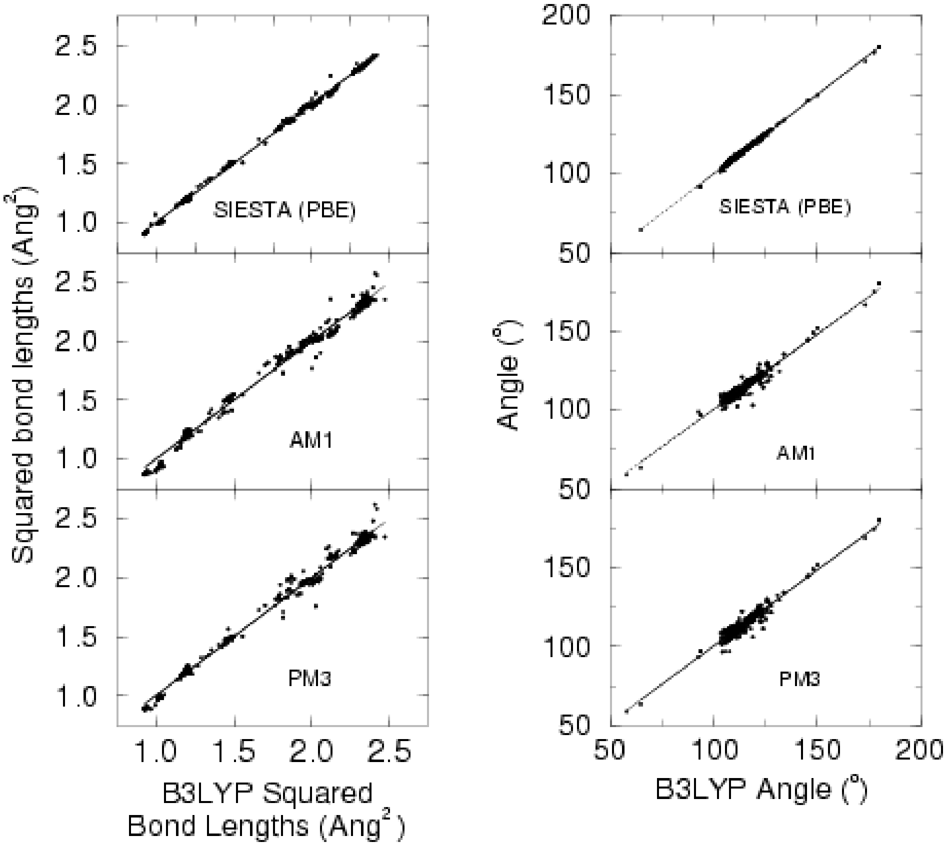

Figure 10: Comparison of the squared bond distances (left) and bond angles (right) between the B3LYP results and those of SIESTA and the semiempirical AM1 and PM3 methods, for the database of 103 organic and inorganic molecules.

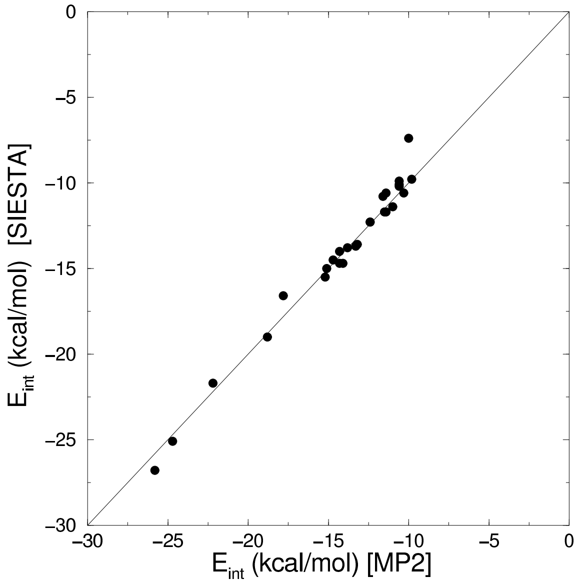

Figure 11: Binding energies of a set of 30 DNA base-pairs, comparing the results obtained with SIESTA with those of MP2 calculations (by Sponer et al. [87])

importance in the description of DNA systems, among the many factors that stabilize the double helix. In order to validate the capability of SIESTA to describe DNA, we considered first the interactions between nitrogenated base pairs (adenine, guanine, thymine and cytosine). A thorough study of 30 nucleic acid pairs was performed, addressing the precision of the approximations (basis sets, grids, etc) and the accuracy of the GGA functional. Our calculations, presented in detail elsewhere [86], show that the PBE functional [12] provides excellent results. In figure 11 we show a comparison of the binding energies (difference between the energy of the H-bonded pair and the free bases) for 30 different base pairs, with those obtained by Sponer et al. [87], by means MP2 calculations. In both cases, the coordinates were the same: those obtained by Sponer and co-workers at the Hartree-Fock level (due to the numerical workload, it was not possible to optimize the structures at the MP2 level). The results of figure 11 show that the correlation of the energies obtained with SIESTA and those of MP2 are excellent, with an average deviation of only 0.73 kcal/mol. This is considerably better than the accuracy that can be expected from total energies in DFT, showing the very nice performance of the PBE functional for these systems, and validating SIESTA as an accurate method for the study of hydrogen bonds in DNA complexes. We have also performed structural optimizations with SIESTA to obtain the first geometries for many of the base-pairs under study. Former DFT works had only considered the structures of the most common Watson-Crick base-pairs. For these, our result agree closely (always within 2% for the bonding distances at the H-bonds) with those of previous calculations. Further details can be found on [86].

13. Conclusions

The SIESTA approach for DFT calculations has been thoroughly described, with illustrations of the convergence with respect to the main precision parameters that characterize the method. We have shown that the method is able to produce very fast calculations with small basis sets, allowing to compute systems a thousand of atoms in single processor workstations (and many more in parallel platforms). At the same time, the use of more complete and accurate bases allows to achieve accuracies comparable to those of standard plane waves calculations, still at an advantageous computational cost. We have shown some examples of the accuracy of the method, in the context of ferroelectric materials and molecular systems, although many others have been studied so far (see http://www.uam.es/siesta/). The capabilities, performance and flexibility of the method make it a very useful tool for the study of large molecules and complex, and we hope it will serve an increasing number of groups in our community.

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